

**ALGORITHMIC CALCULATIONS,
SOLUTION THERMODYNAMICS AND
SPECTROSCOPIC INVESTIGATION OF
POLY(ETHYLENE GLYCOL)/SOLVENT SYSTEMS**

**POLİ(ETİLEN GLİKOL)/ÇÖZÜCÜ SİSTEMLERİNİN
ALGORİTMİK HESAPLARI, ÇÖZELTİ TERMODİNAMİĞİ VE
SPEKTROSKOPİK İNCELENMESİ**

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To my dear family

and

*to everyone who has touched my life and
helped me to keep learning along the way*

POLİ(ETİLEN GLİKOL)/ÇÖZÜCÜ SİSTEMLERİNİN ALGORİTMİK HESAPLARI, ÇÖZELTİ TERMODİNAMİĞİ VE SPEKTROSKOPİK İNCELENMESİ

Cemile Özdemir

ÖZ

Poli(etilen glikol) (PEG)'in dört farklı molekül ağırlığında tetrahidrofuran (THF), kloroform, dimetilsulfoksit (DMSO), metanol ve suda oluşturduğu sistemler; algoritmik, viskometrik ve spektral analiz yöntemleriyle incelenmiştir.

Çalışmanın ilk aşamasında PEG ve çözücülerin çözünürlük parametreleri van Krevelen-Hoftyzer, Hoy, Breitreutz, Askadskii ve Small yaklaşımlarına göre hesaplanmış ve 2-, 3-boyutlu grafikleri çizilmiştir. Algoritmik hesaplar sonucunda PEG için THF'nin en iyi, suyun en kötü çözücü olduğu belirlenmiştir.

İkinci bölümde PEG/çözücü sistemlerinin çözelti termodinamiğini incelemek amacıyla viskometrik çalışma gerçekleştirilmiştir. Ekstrapolasyon yöntemlerinden bozulmamış boyut parametresi (K_θ) ve uzun mesafeli etkileşim parametresi (B) hesaplanmıştır. Üç ayrı ekstrapolasyon ve iki ayrı interpolasyon yöntemiyle hesaplanan θ sıcaklıkları arasında PEG/THF sisteminin en yüksek θ sıcaklığına sahip olduğu bulunmuştur.

Üçüncü bölümde PEG/çözücü sistemleri katı halde X-ışını kırınımı (XRD), Fourier dönüşümlü kızılötesi spektroskopisi (FTIR) ve Raman spektroskopisi ile karakterize edilmiştir. Bu sistemlerin XRD'leri incelendiğinde, kristalinite yüzdelerinde en fazla düşmenin, THF'den hazırlanan örneklerde olduğu belirlenmiştir. FTIR ve Raman spektrumlarında ise çeşitli gerilme ve bükülme titreşimlerinin en büyük frekans kaymaları kloroform ve özellikle THF'den hazırlanan örneklerde olduğu gözlenmiştir.

Bu çalışmada PEG'in çözünürlük parametresi farklı algoritmik yaklaşımlar kullanılarak hesaplanmıştır. Polimerin seçilen çözücüler içindeki çözünürlük profilleri oluşturularak, bu çözücülerin PEG'i çözme yeteneği tartışılmıştır.

“Benzer benzeri çözer” ilkesinin matematiksel uygulaması olan algoritmik yöntemler, polimerin çözelti termodinamiği temelinde farklı termodinamik büyüklükler üzerinden ne tip benzerlikler/uyuşmalar göstereceği incelenmiştir.

Polimerin sırasıyla; Small, Hoy, VKH, Askadskii ve Breitzkreutz algoritmik hesaplamalarıyla bulunan δ_t değerleri, bazı çalışma grupları tarafından bulunan (Small, Hoy, VKH and Breitzkreutz) δ_t değerleriyle uyumludur. Benzer uyuşmalar katı halde XRD, FTIR ve Raman spektroskopik yöntemleriyle izlenerek de yorumlanmıştır.

Polimerin seçilen çözücülerdeki hidrodinamik ve termodinamik büyüklükleri kıyaslandığında da; suyun zayıf çözücü ve THF ile kloroformun ise iyi çözücü davranışı sergilediği görülmüştür.

Sonuç olarak, PEG için çözücülerin çözme gücü aşağıdaki sıraya göre azalır:

THF > kloroform > DMSO > metanol > su

Anahtar kelimeler: PEG, çözünürlük parametresi, viskometri, PEG çözeltileri, çözelti termodinamiği, FTIR, Raman, XRD.

Danışman: Prof. Dr. Ali GÜNER, Hacettepe Üniversitesi, Fen Fakültesi, Kimya Bölümü, Polimer Kimyası Anabilim Dalı.

ALGORITHMIC CALCULATIONS, SOLUTION THERMODYNAMICS AND SPECTROSCOPIC INVESTIGATION OF POLY(ETHYLENE GLYCOL)/SOLVENT SYSTEMS

Cemile Özdemir

ABSTRACT

The systems involving four different molecular weights of poly(ethylene glycol) (PEG) in tetrahydrofuran (THF), chloroform, dimethyl sulfoxide (DMSO), methanol and water have been investigated by algorithmic, viscometric and spectral analysis techniques.

At the initial stage of the research, the solubility parameters of PEG and solvents have been evaluated with respect to van Krevelen-Hoftyzer, Hoy, Breitskreutz, Askadskii and Small approaches and their 2-, 3-dimensional graphs have been drawn. As a consequence of algorithmic calculations, THF has been determined as the best solvent whereas water is found to be the weakest solvent.

In the second step, viscometric studies have been made in order to investigate the solution thermodynamics of PEG/solvent systems. Unperturbed dimension (K_θ) and long-range interaction parameter (B) have been calculated via extrapolation methods. Three different extrapolation and two different interpolation methods have been employed for the evaluation of θ temperatures among which PEG/THF system has been found to possess the highest θ temperature.

In the third stage, PEG/solvent systems have been characterized in the solid state by X-ray diffraction (XRD), Fourier transform infrared (FTIR) and Raman spectroscopy. When the XRD charts of these systems are analyzed, the highest decrease in crystallinity percent has been detected in the sample cast from THF. On the other hand, the largest frequency shifts of various stretching and bending vibrations have been observed for the samples cast from chloroform and especially THF in FTIR and Raman spectra.

In this study, the solubility parameter of PEG has been calculated by the use of several different algorithmic approaches. By creating the solubility profiles of the polymer in selected solvents, the dissolving capability of these solvents has been discussed.

Algorithmic methods, as the mathematical application of the principle “like dissolves like”, have been employed on the basis of the solution thermodynamics of the polymer, and the type of similarities/agreements displayed on the basis of various thermodynamic magnitudes to interpret the solvent power in PEG/solvent systems.

δ_t values of the polymer determined in this work from Small, Hoy, VKH, Askadskii and Breitzkreutz algorithmic calculations, respectively, are also in agreement with δ_t values found by some other working groups (Small, Hoy and VKH) as well. Similar agreements have been also interpreted by XRD, FTIR and Raman spectroscopic methods from the detections in the solid state.

When the hydrodynamic and thermodynamic magnitudes of the polymer in selected solvents are compared, water still displays its nature as the weakest solvent, THF and chloroform display good solvent behaviors.

Consequently, solvency power of solvents for PEG decreases below order:

THF > chloroform > DMSO > methanol > water

Key words: PEG, solubility parameter, viscometry, PEG solution, solution thermodynamics, FTIR, Raman, XRD.

Advisor: Prof. Dr. Ali GÜNER, Hacettepe University, Faculty of Science, Department of Chemistry, Polymer Chemistry Division.

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NOMENCLATURE INDEX

English letters

a	Exponent of the Mark-Houwink equation
a'	Parameter representing the ratio of interfacial tension/surface tension of solvent
$\text{\AA}$	Angstrom unit
A_a	Area of amorphous zone
A_c	Area of crystalline zone
A_j	Constant (0.0181)
A_2	Second virial coefficient
B	Long-range interaction (excluded volume) parameter
B_o	Constant independent of temperature
c	concentration
c^*	critical concentration
C_j	Constant (0.0751)
C_M	Coefficient lumps together numerical and molecular constants.
Δe_j	Energy of vaporization contribution of group j
E	Potential energy
E_{hi}	H-bonding energy
E_{coh}	Molar cohesive energy
E_d	Contribution of dispersion forces to the cohesive energy
E_h	Contribution of hydrogen bonding forces to the cohesive energy
E_p	Contribution of polar forces to the cohesive energy
ΔE_i^*	Cohesive energy density of the repeating unit of the polymer and solvents
ΔE_i^v	Energy of vaporization of species i ,
F	Additive function/molar attraction constant
F_d	Dispersion component of the molar attraction function

F_p	Polar component of molar attraction function
F_{pi}	Polar components of the molar attraction constant
F_{di}	Dispersion components of the molar attraction constant
F_t	Molar attraction function
g	Gravitational acceleration
ΔG_m	Gibbs free energy of fusion
ΔG_M	Gibbs free energy of mixing
Δh_M	Specific enthalpy of mixing (enthalpy of mixing per unit volume)
ΔH_m	Molar enthalpy of fusion (enthalpy change of mixing)
ΔH_M	Enthalpy of mixing
k_{avg}	Constant (0.681)
K	Mark-Houwink constant
K_θ	Unperturbed viscosity dimension
ℓ	Length of capillary tube
m	Number of atoms in the repeat unit of polymer
M_i	Polymer molecular weight
$\overline{M}_n$	Number-average molecular mass
$\overline{M}_w$	Weight-average molecular mass
$\overline{M}_z$	z-average molecular mass
M_p	Molecular weight of polymer
n	Number of monomer units
n_j	Number of groups of type j in the molecule
$\bar{n}$	Number of repeating units per effective chain segment of the polymer.
N_A	Avogadro number
$\langle r^2 \rangle^{1/2}$	Mean square average end-to-end distance (short-range interactions) (called the unperturbed dimensions)
$\langle r^2 \rangle_\theta^{1/2}$	Unperturbed root-mean-square end-to-end distance
R	Distance from center of gravity (radius of polymer solubility circle)
R	Gas constant

R_H	Stokes hydrodynamic radius
^jR	Interaction radius of polymer sphere
^{ij}R	Distance of the liquid @ at position $(^i\delta_d, ^i\delta_p, ^i\delta_h)$ from the center of the sphere of solubility (sphere radii of the polymer observed for the polymer-solvent couple)
$\langle s^2 \rangle^{1/2}$	Radius of gyration
ΔS_M	Entropy of mixing
ΔS_m	Specific entropy of fusion (entropy change of mixing)
t	Efflux time
$\bar{t}_B$	Average efflux time of benzene
$\bar{t}_T$	Average efflux time of toluene
T	Absolute temperature
T_b	Boiling point,
T_{cr}	Critical temperature
T_g	Glass-rubber transition temperature
T_m	Crystalline melting temperature
Δv	Hydrogen bonding number
$\bar{v}$	Specific volume of the polymer
V	Viscometer bulb volume
V	Volume
V_i	Molar volume of species @,
V_p	Molar volume of the polymer
V_s	Molar volume of solvent
^zV_g	Group molar volume constants of the repeat unit
^wV_i	van der Waals volume of molecule
Vr	Molecular electrostatic potential topology
X_C (%)	Percent crystallinity
z	Excluded volume parameter

Greek letters

α	Aggregation number
α^*	Chain aggregation number
α_η	Hydrodynamic expansion factor
γ_p	Surface tension of polymer
γ_s	Surface tension of solvent
γ_{s-p}	Interfacial tension
δ_a	Association-dependent solubility parameter
δ_d	Contribution of dispersion forces to the solubility parameter
δ_h	Contribution of hydrogen bonding to the solubility parameter
δ_i	Solubility parameter of a repeating unit
δ_p	Contribution of polar forces to the solubility parameter
δ_r	Residual solubility parameter
δ_t	Hildebrand parameter
δ_v	Volume-dependent solubility parameters
δ_P	Solubility parameter of polymer
δ_S	Solubility parameter of solvent
δ^*	Specific surface cohesive energies
$\overline{\Delta\delta}$	Solubility parameter difference of polymer-solvent pair
Δ_T	Lydersen constant for solvents
$\Delta_T^{(P)}$	Lydersen-Hoy constant for polymers
ν	Kinematic viscosity
ν_T	Kinematic viscosity of toluene
ν_B	Kinematic viscosity of benzene
η	Absolute viscosity (shear viscosity)
$[\eta]$	Limiting viscosity number (intrinsic viscosity)
$[\eta]_\theta$	Intrinsic viscosity of theta solution

θ	Theta temperature
ρ	Constant (0.687)
ρ_S	Density of solvent
ρ_P	Density of the polymer
ϕ	Askadskii parameter representing solubility criteria
ϕ'	Flory universal constant
ϕ_i	Volume fraction of <i>i</i> in the mixture
χ	Thermodynamic interaction parameter
χ_H	Individual values of enthalpy dilution parameters
χ_S	Individual values of entropy dilution parameters
μ	Askadskii parameter representing the ratio of surface tension of polymer and solvent.
π	Internal pressure

Acronyms

CED	Cohesive energy density
3-D	Three-dimensional
2-D	Two-dimensional
DMSO	Dimethyl sulfoxide
exp.	Experimental
FTIR	Fourier transform infrared
GPC	Gel permeation chromatography
H.I.	Heterogeneity index
IPGC	Inverse phase gas chromatography
ISK	Inagaki-Suzuki-Kurata
KSF	Kurata-Stockmayer-Fixman
LCST	Low critical solution temperature
MW	Molecular weight
NMR	Nuclear magnetic resonance
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
POE	Poly(oxyethylene)

RALS	Right Angle Light Scattering
calc.	Calculated
THF	Tetrahydrofuran
UCST	Upper critical solution temperature
VKH	van Krevelen –Hoftyzer method
XRD	X-ray diffraction
WAXD	Wide-angle X-ray diffraction

1. INTRODUCTION

As PEG has good water-solubility even in its solid state, it is used as a releasing agent for foam rubber, latex rubber, etc. PEG is also used as an airpack releasing agent, inner releasing agent, and lubricant in the tire industry. In addition PEG improves grinding effects by being added to the grinding powder and it is used as a raw material for anticorrosion and the cleaning of metals. By dipping wood in a PEG solution in advance, contraction and cracking of wood can be avoided. Furthermore it is used as the raw material of paints and resins, base materials of ointments, hand creams, lotions, shampoos, softener, antistatic agent, scouring agent, sizing agent, dyeing auxiliary in the textile industry (Cell Chemical Company, 2000).

PEG is compatible with most organic solvents and it is characterized by less toxicity and skin irritation and hygroscopic property is controllable.

Thus PEGs dissolution behavior in different solvents plays an important role. Solubility parameters can be determined by direct measurements, correlations with other physical parameters, or indirect calculations. Hildebrand parameter (δ_t) cannot be calculated for polymers from heat of vaporization data because of their nonvolatility. The solubility parameters of polymers can only be determined indirectly and may be affected by variations in their chemical constitutions, i.e., the number of crosslinks, crystallinity and the distribution of chain branches or substitutive groups along the polymer backbone.

At the initial stage of the study, group contribution methods (Small, VKH, Hoy, Breitzkreutz and Askadskii) from indirect methods are described and calculated for PEG and different solvents (molecules with H- donor, with H- acceptor and with both H-donor and H-acceptor groups) in Part 4. However, only the (δ_t) cannot accurately predict the solubility behavior of the polymer. Solubility can be affected by any specific interactions. Four solvency indexes-cohesive energy density, solubility parameter, H-bonding and dipole moment are important in controlling solubility for amorphous polymers and methods of estimating them are very

important. Therefore, individual contributions of δ_d , δ_p and δ_h (dispersion, polar and H-bond interactions respectively) to the δ_t values are also calculated and 2-D (Bagley, Henry, Hoernschemeyer-1 and -2) and 3-D (Hansen) graphing and modeling techniques have been developed for PEG. According to these diagrams, the majority of the solubility parameters of good solvents indeed fall in a single region. This region can approximately be delimited by a circle and its center. As a consequence of algorithmic calculations, THF has been determined as the best solvent whereas water is found to be the weakest solvent.

In the second step, viscometric studies have been made in order to investigate the solution thermodynamics of PEG/solvent systems. The unperturbed molecular dimensions of PEG samples (of different molecular weights) have been evaluated in aqueous and nonaqueous solutions from viscosity measurements at 25°, 30°, 35° and 40 °C. The unperturbed dimension, K_θ , has been determined from extrapolation methods, i.e, Kurata-Stockmayer-Fixman (KSF), Inagaki-Suzuki-Kurata (ISK) and Berry equations. The hydrodynamic expansion factor; α_η , as well as the unperturbed root-mean-square end-to-end distance; $\langle r^2 \rangle_\theta^{1/2}$ found for the system indicated that the polymer coils contract as the temperature is raised from 25°C to 40°C. The long-range interaction (excluded volume) parameter, B , was also evaluated and a significant decrease was found for the PEG/solvent systems between 25°C and 40°C. The theta temperatures, θ , were obtained from the temperature dependence of $(1/2 - \chi)$ and the second virial coefficient was detected in the temperature interval of 25° to 40°C for the systems and quite a good agreement with the calculated values evaluated via extrapolation and interpolation methods was observed. The thermodynamic interaction parameter χ was evaluated through the sum of the individual values of enthalpy and entropy dilution parameters, χ_H and χ_S , for PEG samples. Calculated unperturbed molecular dimensions were interpreted mainly on the basis of H-bond formation between polymer segments and PEG-solvent molecules in solution.

In the submitted thesis the thermodynamic aspects of poly(ethylene glycol) in dilute solutions are explained. The restrictions applying to the establishment of

concentration regimes, short-range interactions (theta condition, unperturbed dimensions, chain flexibility, the transition from theta to collapsed regime), and long-range interactions (excluded volume effect by intermolecular and intramolecular interactions, conformational characteristics and conformational transitions phenomena) are discussed.

In this study, investigation of the solubility of PEG is not aimed only the in the liquid state, but also in the solid state by FTIR, Raman and XRD spectroscopy. When the XRD charts of these systems are analyzed, the highest decrease in crystallinity percent has been detected in the sample cast from THF. On the other hand, the largest frequency shifts of various stretching and bending vibrations of PEG have been observed for the samples cast from chloroform and especially THF in FTIR and Raman spectra.

In the present study, solubility profiles of PEG/solvent systems are investigated algorithmically and the parallelism of algorithmic calculations and experimental work has been determined both in solution and in the solid state by XRD, FTIR and Raman studies.

2. GENERAL INFORMATION

2.1. Poly(ethylene oxide) and Poly(ethylene glycol)

In recent years, poly(ethylene oxide), (PEO) has gained fundamental academic interest in the advance of biophysics and biochemistry (Gonzalez and Pérez-Parajon, 2003).

The chemical structure, $\text{H}-(\text{O}-\text{CH}_2-\text{CH}_2-)_m-\text{OH}$, of this synthetic polymer includes two terminal groups, H and OH, which play an important role in short compounds. The hydrophobic ethylene units and the hydrophilic oxygens, which alternate along the chain, are responsible for its amphoteric character (Magazù, 1996).

PEO is a commercially available polymer with a simple chemical structure and specific properties. It is built from flexible, linear macrochains consisting of elements with different electronegativity carbon and oxygen atoms. In crystalline solid state PEO exists mainly in the form of a regular helix but in solution it can change its conformation to a random coil with statistically placed residual helix segments (Elias, 1997; Gray, 1991; Kaczmarek et al., 1999).

PEO is a well known and industrially important polymer much used in many commercially available high and low molecular weight grades in pharmaceutical and textile industries, as excipients in drug formulation, or as fiber-forming aids. It is also used in many other industries in the form of surface-active agents when combined with hydrocarbon moieties and in the manufacture of esters, polymers, polishes, lubricants, mold release agents and in water treatment (Graham et al., 1982).

PEO has been widely used in a variety of dosage forms (Stringer and Peppas, 1996; Zhang and McGinity, 1999) including transdermal and transmucosal dosage forms (Repka et al., 2002), PEO is semi-crystalline, bioadhesive and mucoadhesive due to its water solubility, hydrophilicity, high viscosity, ability to form H-bonds and biocompatibility (Dow Chemical Company, 2002). PEO has been previously studied for the production of hot-melt extruded tablets and as an

adjuvant in hot-melt extruded hydroxypropyl cellulose films (Repka and McGinity, 2000).

PEO possesses solid polymer-electrolyte properties upon mixing with an appropriate electrolyte salt (Visco et al., 1990). Later, this property has received much attention because it may lead to developing polymer-electrolyte batteries. Other applications range from adhesives, pharmaceuticals cosmetics packaging films, paper coatings, textile wraps and lubricant additives (Al-Saigh, 1999).

PEO is perceived as a “flexible” polymer, with a structure described as a random coil and can change conformation dynamically in solution (Bailey and Koleske, 1976). The size of the coil is dependent upon the solvent quality, which in turn is dependent on temperature, concentration, and molecular architecture of the polymer molecule.

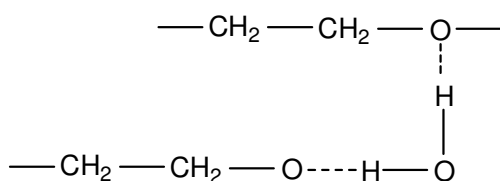
For about 40 years, PEO in solution has been the subject of many studies involving a lot of laboratories and techniques. These studies have led to somewhat contradictory results concerning the ability of PEO to be perfectly soluble in dispersed species in some solvents or to form aggregates in these same solvents. For example, one of the first works by Elias et al. (1966) on the couple PEO/water shows that PEO is completely soluble in aqueous solution. This result was confirmed by Devanand et al. (1991) and Kinugasa et al. (1994). However, the formation of aggregates on the same system has been reported in many other studies (Brown, 1985; Polik and Burchard, 1983). Formation of aggregates in the PEO solutions which is connected with some peculiar situations are investigated (Duval and Sarazin, 2000). It is the association of the temperature effect ($t > 30\text{ }^{\circ}\text{C}$) and the nature of the solvent (water) which is the main factor governing this formation. Once they are created these clusters are difficult to break and are still present when the sample is dissolved in the best solvent of the polymer. The molecular weight of the aggregates is very high whereas their concentration is very low. However, it seems obvious that subsequent dissolution in hot water (60° and $89\text{ }^{\circ}\text{C}$) of two PEO samples should increase either the molecular weight or the concentration of the aggregates. This should bring upward curvatures in the Zimm plot given by the PEO solutions as observed by other authors (Polik and Burchard,

1983; Kambe and Honda, 1984). The cluster formation originates from hydrophobic interactions that take place at high temperature in the vicinity of the θ point in aqueous solution (Duval and Sarazin, 2000).

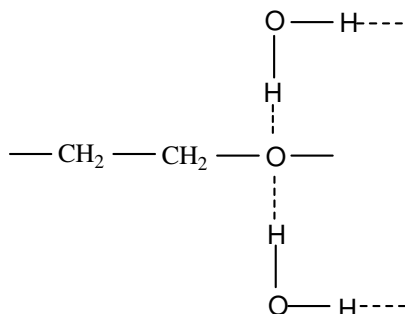
PEO is a simple and representative linear amphiphilic polymer with interesting behavior both in solution and in the solid state. It dissolves not only in a large number of organic solvents but also in water. The studies have been carried out both in the polymer and colloid field but the behavior of PEO in water has been less quantitatively understood, when compared with that of, say, polystyrene in organic solvents. Unusual phenomena observed in water have been exclusively ascribed to the specificity of water as a solvent. Studies on PEO solution properties are concerned with three subjects (Kawaguchi et al., 1997);

First, PEO exhibits in water both upper and lower critical solution temperature phenomena (UCST and LCST). Several models have been proposed, including an entropic model due to structured water, H-bond formation between polymer segments and solvent, and a conformation model. The first two models are the result of specific water structuring along a PEO backbone. There are data suggesting that two water molecules are associated with each ethylene oxide monomer unit and the diffusion coefficient of the water near a chain is substantially lower than in bulk water (Liu and Parsons, 1969; Glowinkowski et al., 1981).

The introduction of the first few (isolated) water molecules into the polymer matrix gives rise to no net heat effect; this is because for each water molecule two H-bonds are broken in removing it from the water lattice and then two of slightly greater strength (compensating for the polymer-polymer interactions overcome) are formed when it is introduced into the polymer, to bridge two separate ethylene oxide units



On the other hand, as more water molecules are introduced there is then a net (exothermic) heat effect, due to cooperative H-bonding of pairs of water molecules onto the same ethylene oxide unit (Molyneux, 1984):



The phase separation, however, also takes place in a non-H-bonding solvent such as *t*-butyl acetate. This shows that water specificity as a solvent is not necessarily a key factor in this behavior. Several spectroscopic studies using Raman and X-ray scattering, NMR and dielectric constant measurements have shown that the conformation around the central OC-CO bond varies depending on the polarity of the surroundings. Later, the local conformation of the PEO chain has caused controversy (Smith et al., 1993).

The second problem concerns the tendency of PEO to aggregate in solution. The aggregation in various solvents has been reported by several research groups. For example, Polik and Burchard (1983) reported that PEO chains aggregate significantly in water over a wide temperature range from 20° to 90 °C. Zhou and Brown (1990) also reported that the PEO molecules aggregate in methanol at room temperature. They observed a significant downturn in the angular dependence of the light scattering, indicating the presence of some aggregates in good solvents. However, Kato et al., (1981) reported that PEO does not aggregate in water from the measurements of dynamic and static light scattering and viscometry. Static and dynamic light scattering measurements by Devanand et al., (1991) and Kinugasa et al. (1994) found that PEO molecules do not aggregate in water, methanol, and acetonitrile at room temperature, when the solutions are meticulously prepared. All the solutions except for the θ -solvent were prepared by standing in the dark without shaking at room temperature at least for three days.

The third subject of interest is the complexation of PEO with small cations in organic solvents. Lunderberg et al. (1966) reported that PEO chains behave like a polyelectrolyte in methanol when potassium iodide is added. In water, however, the complexation may not take place but the solubility power of water for PEO chains may decrease with increasing salt concentration (Kawaguchi et al., 1996).

The polymer which has been most extensively investigated as a host matrix is PEO. This hard polybasic molecule is an open macromolecular structure composed of OCH_2CH_2 repeat units which act as polydentate ligands with a remarkable ability to coordinate cations through the ether oxygen atoms. In this sense PEO may be considered to be the polymer analog of crown ethers. It is therefore not surprising that the development of polymer electrolytes has closely accompanied that of host-guest chemistry (Bermudez et al., 2000).

PEOs are commercially available in extremely broad molecular weight (M_w) range and PEO with repeating units (<150) is generally called PEG (Crupi et al., 1995). However, PEG definition may still be employed in a wider range of molecular weight (200-20000 g/mol) as well (Ferreira et al., 1999). PEG is very water-soluble compared to polymers such as polyethylene owing to the hydrophilic heteroatoms enabling H-bonds with water (Ridell, 2003).

It exhibits several remarkable properties that have been reviewed by Harris (1992). Lusse and Arnold (1996) studied the interaction of PEG with water by NMR relaxation time measurement in PEG aqueous solution and found that water was bound to PEG by H-bond and that the structure of solution was related to the water content (Jiang and Han, 1999). The decreased solubility of PEG in water at elevated temperatures is also related to the H-bonding; higher temperatures result in decreased H-bonding and an increase of hydrophobic interactions between the macromolecular chains (Denes 2004).

PEGs comprehend a series of water soluble, nonirritating, linear chain polymers of oxyethylene units, with low toxicity. These properties enable their use for commercial and technological applications such as purification of biological

materials, pharmaceutical drugs, edible films for food coating and water treatment (Davidson, 1980; Da Silva et al. 1997).

IR, Raman and computer simulation studies (Crupi et al., 1995) reveal, also in the liquid phase, the existence of an intra-molecular H-bond which makes the gauche conformation the most energetically favored. In addition, the OH interacting groups promote links among adjacent chains, via H- bonding, giving rise to many transient species. The findings so far agree with the conformational assignment for the crystalline state to internal rotation about the O-CH₂, CH₂-CH₂ and CH₂-O bonds of *trans-gauche-trans* (*tgt*) respectively. Crystalline PEO is retained to present a helical conformation that contains seven structural units CH₂-CH₂-O with two helical turns per fiber identity period. It has become clear, however, that a strongly disordered conformation is stabilized, due to H-bonds between the ether-oxygen chain and water molecules (Bailey and Koleske, 1976; Koenig and Angood, 1970).

The presence of the electron-rich oxygen atoms in the backbone structure of the polymers offers a site for coordination and the ability of electron-poor groups to associate with these polymers is important for their use in many applications (Cellesi et al., 2002 and Seneci, 2001).

PEO has been proposed to be an important polymer in drug release systems (Apicela et al., 1994) and for dissolving salts in electrolyte complexes (Murata, 1995). The presence of an oxygen atom in every third position produces special physical-chemical properties, for example solubility, crystallinity and flexibility and complexation power, which are often very different from those of the parent compound (Ferreira et al., 1999).

The two-hydroxyl end groups of PEG have been suitably functionalized prior to coupling with ligands of biological relevance, although the hydroxyl groups themselves have been used as well. Because the number of terminal groups of PEGs (only two) to attach with drugs limits their drug loading capacity, extensive

work has been done to functionalize them by copolymerizing PEGs with various functional monomers (Danprasert et al., 2003).

A more biocompatible method can be found in the photolithographic patterning of PEG hydrogels, which generally involves three steps: spin coating of a PEG solution onto a substrate, exposing gel precursor through a photomask, and then developing using solvents such as water, toluene, or supercritical CO₂ (Beebe et al., 2000; Revzin et al., 2001). Using this process, PEG microstructures have been successfully applied to the fabrication of enzyme electrodes (Lesho and Sheppard, 1996), pH sensitive devices (Beebe et al., 2000) and optical sensors (Revzin et al., 2001). Suh et al. (2004) found that the substrate surface can be directly exposed during the molding process due to the ability to control the wetting properties of the PEG on the stamp, which is a key factor to patterning proteins and cells.

Chen et al. (2005) cover the interesting physical properties of PEG solutions in water, their unique solvent properties, and finally the metal cation coordination ability of PEG solutions. These properties are important in the use of PEG as an alternative phase-transfer catalyst; and in the application of aqueous biphasic reactive extraction in the development of alternative pulping processes, catalytic chemistry, and enzymatic catalysis.

Menna et al. (2003) prepared PEG grafted to shortened single-walled carbon nanotubes and reported a novel procedure for microwave-assisted synthesis of this polymer. Potential applications of these polymers were envisioned in the field of molecular electronics (Avouris, 2002), composite polymers (Andrews et al., 1999), nanowires (Wong, 1997), optical limiters (Chen et al., 1999; Vivien et al., 2002) or gase-storage devices (Ma et al., 2002).

PEGs are commonly applied in industry as superionic conductors, surfactants, thickening agents, stabilizers and wetters. PEGs have also enjoyed much interest in biotechnology and biomedicine as they can be used as simple models of biological systems, e.g. a diffusion cell for protein (Begum and Matsuura, 1997).

Mark (1986) widely used PEG in ceramics, cosmetics, lubricants, metalworking, pharmaceuticals, rubber chemicals, electronics and other applications. They play also an important role as basic components in production of polyesters and polyurethanes. A very important feature of PEGs is their solubility in water. The water solubility of these polymers is due to H-bonding between PEG and water. They also exhibit low toxicity, good stability, good lubricity and can be mixed with water or other solvents to give a wide range of viscosities. The lower molecular weight polymers are viscous liquids at room temperature. Higher viscosities are due to the influence of the hydroxyl end groups. With increasing molecular weight they change to soft solids and then to waxy solids at room temperature; their crystallinity increases with the molecular weight. Polymer structure and properties depend strongly on inter- and intramolecular interactions between molecules. As the chain length of the polymer increases, the intermolecular interactions also increase. However, elongation of the polymer chain reduces concentration of the OH groups, and, in this way, the number of H-bonds (important only for low molecular weight PEGs). Moreover, the dipole nature of the C-O bond causes conformational changes in the polymer chain, depending on the length of the chain. These effects may additionally influence the intermolecular interactions between polymer molecules. Thus, the physical properties will vary with changing molecular weight of PEGs.

Molecular dynamics of PEGs have been extensively studied by Drozdowski group (2002). Analysis of their results provides the information on the most probable description of the structure and intermolecular interactions in PEG samples. They indicated that the presence of molecular interactions in short chain PEGs ($M_w < 1000$) leads to formation of molecular aggregates composed of extended molecules of predominantly parallel configuration. The formation of aggregates is determined by the shape of the molecules and dipolar interactions between them. With the increase of molecular weight the influence of H-bonding between PEG molecules decreases and the molecules fold, this leads to formation of statistical coils. This conclusion is confirmed by the results reported in Heymann and Grubmülle (1999) proving that the solubility of a linear form of the molecules requires considerable energy.

In water, the PEG molecule forms a loose coil (Vennaman et al., 1987). There is some experimental evidence of short-range *ttg* sequences in PEG molecules in water (Matsuura and Fukuhara, 1985; Yang et al., 1997; Begum and Matsuura, 1997; Oesterhelt et al., 1999; Smith et al., 2000; Bedrov and Smith, 2003). The overall PEG conformation in deuterated water is that of a coil, but that at the lower molecular weights of 1.73×10^2 g/mol, only the polymer rods form (Alessi et al., 2005). PEO assumes an expanded random coil conformation in water at 25 °C when Mw is above $7 - 8 \times 10^3$ (Kawaguchi et al., 1997).

2.2. Introduction to Solubility Parameter Values

Solubility parameter is of technical importance in the fields of paints, spinning fibers and casting films, and the plasticization of polymers (Small, 1953). Applications of solubility parameters include selecting compatible solvents for coating resins, predicting the swelling of cured elastomers by solvents estimating solvent vapor pressure in polymer solutions for devolatilization and reaction systems (Blanks, 1977) and predicting phase equilibria for polymer-polymer (Shaw, 1974), polymer-binary (Piccarolo and Titomanlio, 1982), random copolymer (Schneier, 1972), and multicomponent solvents (Froehling and Hillegers, 1981; Ribgi, 1978) (Brandrup et al., 2003).

Cohesive energy density (CED) and solubility parameters are defined in this section on the basis of solubility of polymer. In addition, limitations, calculation and correlation of solubility parameters are discussed. This section also contains lists of three-component solubility parameters of solvents (chloroform, THF, DMSO, methanol and water) calculated by Hansen and Hoy. Furthermore, three-component solubility parameters of PEG calculated according to van Krevelen-Hoftyzer (VKH) (1976, 1997), Hoy (1985, 1989) and Breitzkreutz's (1998) atomic group contribution methods and total solubility parameters (Hildebrand parameters) of PEG are calculated according to Small's group contribution method and Askadskii's method (2003) about molar volumes in terms of van der Waals volumes of the constituent atoms or groups here. The group contribution methods were used in this thesis to calculate Hildebrand solubility parameters of PEG, since these data compare well with each other.

2.2.1. One-component Solubility Parameter (Hildebrand Parameter) and Cohesive Energy Density

The basic assumption in the solubility parameter concept is that there is a correlation between the cohesive energy density (potential energy per unit volume) and mutual solubility.

$$\delta_t = (-E/V)^{1/2} \quad (2.1)$$

The one-component solubility parameter defined by Eq. 2.1 has proved useful for regular solutions, i.e., solutions without molecular polarity or specific interactions, and good estimates of excess Gibbs energy (and consequently activity coefficients, etc.) have been obtained because of a fortuitous cancellation of errors. It is still used for various purposes in nonregular solutions, but to some extent has been superseded by multicomponent solubility parameters (Barton, 1975).

Cohesion parameter concept is directly applicable only to amorphous polymers, and when considering crystalline polymers it is in principle necessary to calculate the activity of the crystalline solid relative to the real or hypothetical amorphous material at the same temperature. In practice the distinction between amorphous and crystalline polymers is not so clear-cut, and non-thermodynamic empirical methods are used frequently in the estimation of cohesion parameters for polymers (Barton, 1991).

The process of dissolving an amorphous polymer in a solvent is governed by the free energy of mixing

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2.2)$$

where ΔG_m is the Gibbs free energy change of mixing, ΔH_m is the enthalpy change of mixing, T is the absolute temperature, and ΔS_m is the entropy change of mixing. A negative ΔG_m predicts that a process will occur spontaneously. Since the dissolution of a high-molecular-weight polymer is always connected with a

large increase in entropy, the enthalpy term (the sign and magnitude of ΔH_m) is the deciding factor in determining the sign of the Gibbs free energy change. Solubility parameters were developed to describe the enthalpy of mixing of simple liquids (nonpolar nonassociating solvents), but have been extended to polar solvents and polymers.

Hildebrand and Scott (1959) and Scatchard (1949) proposed that

$$\Delta H_m = V\phi_1\phi_2\left[\left(\frac{\Delta E_1^v}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^v}{V_2}\right)^{1/2}\right]^2 \quad (2.3)$$

where V is the volume of the mixture, ΔE_i^v is energy of vaporization of species i , V_i is the molar volume of species i , and ϕ_i is the volume fraction of i in the mixture. ΔE_i^v is the energy change upon isothermal vaporization of the saturated liquid to the ideal gas state at infinite volume (Mieczkowski, 1990).

Formally, the cohesive energy may be divided into three parts, corresponding with the three of interaction forces

$$\Delta E_{coh} = \Delta E_d + \Delta E_p + \Delta E_h \quad (2.4)$$

where ΔE_d is contribution of dispersion forces, ΔE_p is contribution of polar forces and ΔE_h is contribution of H-bonding (van Krevelen, 1997).

The corresponding equation for the total solubility parameter is

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2.5)$$

In Hansen's approach (1967), the Hildebrand solubility parameter of a compound is sub-divided into three partial parameters which represent the contribution of dispersion forces, polar interactions and H-bond formation to the total solubility parameter of the substance (Breitkreutz, 1998).

The corresponding equation for the enthalpy of mixing can be calculated by

$$\Delta h_M = \phi_1 \phi_2 (\delta_S - \delta_P)^2 \quad (2.6)$$

where Δh_M is enthalpy of mixing per unit volume, δ_S and δ_P are solubility parameters of solvent and polymer respectively (van Krevelen, 1997).

Eq. 2.6 predicts that $\Delta H_m = 0$ if $\delta_S = \delta_P$, so that two substances with equal solubility parameters should be mutually soluble due to the negative entropy factor. This is in accordance with the general rule that chemical and structural similarity favors solubility. As the difference between δ_S and δ_P increases, the tendency towards dissolution decreases (van Krevelen, 1997).

By using Eq. 2.5, Eq. 2.6 becomes

$$\Delta h_M = \phi_1 \phi_2 [(\delta_{dS} - \delta_{dP})^2 + (\delta_{pS} - \delta_{pP})^2 + (\delta_{hS} - \delta_{hP})^2] \quad (2.7)$$

The CED, ΔE_i^v , is the energy of vaporization per cm^3 . The solubility parameter has been defined as the square root of the CED and describes the attractive strength between molecules of the material. In addition, the solubility parameter, in the absence of specific polymer-solvent interaction, can be related to the cohesive energy density which gives information about the strength of intermolecular forces in polymer in the amorphous state (Mieczkowski, 1990).

$$\delta_i = \left(\frac{\Delta E_i^v}{V_1} \right)^{1/2} = (CED)^{1/2} \quad (2.8)$$

The solubility parameter can be considered as the internal pressure of the solvent. δ_i of Eq. 2.8 is often called the Hildebrand parameter (Brandrup and Immergut, 1989). Because polymers are more often encountered as crystalline or amorphous solid like materials than as liquids, and because polymers can act as “solvents” as well as “solutes”, the use of the more general term “cohesion parameter” is particularly appropriate in place of the rather restrictive “solubility parameter” (Barton, 1991). The term “cohesion parameter” correlates with a large number of

physical and chemical properties and is not just the miscibility of components. The solubility parameter of a mixture is often taken to be the sum of the products of the component solubility parameters with their volume fractions (Brandrup and Immergut, 1989).

Unfortunately, values of δ_d , δ_p and δ_h cannot be determined directly.

There are, in principle, two ways for a more intricate use of the solubility parameter concept (van Krevelen, 1997):

- a. the use of other measurable physical quantities besides the solubility parameter for expressing the solvent properties of a liquid;
- b. indirect determination of the solubility parameter components δ_d , δ_p and δ_h .

The first method was used by Beerbower et al. (1967), who expressed the amount of H-bonding energy by the H-bonding number, Δv . Beerbower et al. plotted the data for various solvents in a diagram with the solubility parameter δ_t along the horizontal axis and the H-bonding number Δv along the vertical axis. All the solvents in which a given polymer is soluble fall within a certain region.

Crowley et al. (1966, 1967) used an extension of this method by including the dipole moment of the solvent in the characterization. However, as this involves a comparison of a number of solvents in a three-dimensional (3-D) system, the method is impractical.

The second method was developed by Hansen (1967a, 1967b, 1969). Hansen presumed the applicability of Eqs. 2.5 and 2.7 and developed a method for the determination of δ_d , δ_p and δ_h for a number of solvents (van Krevelen, 1997).

Hildebrand parameters give the overall cohesive energy in the materials but less information on the relative strengths of the various types of forces present (dispersion, polar, and H-bonding). Consequently, improved predictive qualities can be obtained using the Hansen partial solubility parameters (δ_d , δ_p and δ_h).

One practical problem of calculating Hansen parameters using group contribution methods is the limited data available on structural groups, thus causing difficulties for complex molecules (Greenhalgh et al., 1999).

2.2.2. Two Component (Physical-Chemical) Solubility Parameter

Bagley et al. (1971) indicates that two component-solubility parameters based on physical (polar and nonpolar) and chemical effects may be superior to three-component systems. One term, δ_v , includes the volume-dependent terms in the liquid state energy expression and corresponds to the physical, polar and nonpolar effects. It is derived by experimental methods directly from internal pressure (π). The other term is the residual solubility parameter, δ_r , arising from chemical (notably H-bonding) effects (Barton, 1975).

Bagley et al. (1971) introduced combined solubility parameters δ_v and δ_a , defined as volume-dependent solubility parameter:

$$\delta_v^2 = \pi = \left(\frac{\partial U}{\partial V} \right)_T, \quad \delta_v = (\delta_d^2 + \delta_p^2)^{1/2} \quad (2.9)$$

and association-dependent solubility parameter:

$$\delta_a = (\delta_p^2 + \delta_h^2)^{1/2} \quad (2.10)$$

with these composed solubility parameter a projection of the 3-D solubility parameter space into a 2-D plot is achieved. A figure which demonstrates the relation of δ_v versus δ_h is called Bagley diagram (Breitkreutz, 1998).

Sometimes δ_p and δ_h (the association interactions) are collectively described as Eq. 2.10 where δ_a is the association-dependent solubility parameter. This is equivalent to the “polar solubility parameter” of Blanks and Prausnitz (1964) (Barton, 1975).

Thermodynamic considerations led Bagley et al. (1971) to the conclusion that the effects of δ_d and δ_p show close similarity, while the effect of δ_h is of a quite different nature. Accordingly, they introduced the parameter Eq. 2.9. This leads to a diagram in which δ_v and δ_h are plotted on the axes (van Krevelen, 1997). δ_v includes the volume-dependent terms in the liquid energy expression and corresponds to the physical polar and nonpolar effects. It is derived by experiment directly from the internal pressure. A figure which demonstrates the relation of δ_v versus δ_h is called Bagley diagram (Barton, 1975).

The other term is residual solubility parameter, δ_r , arising from chemical (notably H-bonding) effects. Considerable agreement would be expected between the values of δ_v^2 and $\delta_d^2 + \delta_p^2$ and between the values of δ_r and δ_h , but because both types of parameter are based on simplified concepts, there is no combination of polar and H-bonding terms (Barton, 1975).

The different combinations are all derived from the basic scheme:

$$\delta_t^2 = \overbrace{\delta_d^2 + \delta_p^2}^{\delta_v^2} + \underbrace{\delta_a^2}_{\delta_h^2} \quad (2.11)$$

At the moment the $\delta_v - \delta_h$ diagram seems to be the most efficient way to represent polymer-solvent interactions (van Krevelen, 1997).

Other 2-D methods for the representation of solubility data are the $\delta_p - \delta_h$ diagram proposed by Henry (Henry, 1974), the $\delta_h - \delta_t$ diagram proposed by Hoernschemeyer (1974) or the $\delta_p - \delta_t$ diagram.

The solubility parameter components δ_d , δ_p and δ_h (and their combinations: δ_v and δ_a) are known for a limited number of solvents only. Therefore a method for predicting these quantities is valuable.

It is to be expected that the polar component δ_p is correlated with the dipole moment μ and that the H-bonding component δ_h is correlated with the H-bonding number Δv . This is not of much use, however, as also μ and Δv are only known for a limited number of solvents. A useful prediction method must be based on the molecular structure of the solvent.

2.2.3. Hansen's Three-Component Solubility Parameters

Hansen (1967a, 1983) proposed a practical extension of the Hildebrand parameter method to polar and H-bonding systems, primarily for use in polymer-liquid interactions. Hansen's total cohesion parameter, δ_t , should equal the Hildebrand parameter, although the quantities may differ for materials with specific interactions when they are determined by different methods (Barton, 1991). It was assumed that dispersion, polar and H-bonding parameters were valid simultaneously, with the values of each component being determined empirically on the basis of many experimental observations.

According to Hansen, the total change in the internal energy of vaporization, ΔE_v may be considered as the sum of three individual energy of vaporization: one due to H-bonds ΔE_h , another due to permanent dipole interactions ΔE_p , and a third from dispersion (van der Waals or London) forces ΔE_d :

$$\Delta E_{coh} = \Delta E_d + \Delta E_p + \Delta E_h \quad (2.12)$$

Dividing by the molar volume v gives

$$\frac{\Delta E_v}{v} = \frac{\Delta E_d}{v} + \frac{\Delta E_p}{v} + \frac{\Delta E_h}{v} \quad (2.13)$$

where $\delta_j = (\Delta E_j / \nu)^{1/2}$, $j = d, p, h$ (Rosen, 1993) and δ_d accounts for a variety of association bonds, including H-bonds and permanent dipole-induced dipole (Good, 1967). Thus, the solubility parameter δ_t may be thought of as a vector in a 3-D d, p, h space. Eq. 2.5 gives the magnitude of the vector in terms of its components (Rosen, 1993). These three components are not arithmetically additive but they lie as vectors along orthogonal axes. The end-point of the radius vector thus represents Hildebrand's solubility parameter (δ_t) in the 3-D space. The solubility of a polymer is represented in 3-D spaces as a spheroid. The location of the center of the spheroid determines the value of the solubility parameter for the polymer (Mieczkowski, 1990).

A solvent, therefore, with given values of $\delta_{p,S}$, $\delta_{d,S}$ and $\delta_{h,S}$ is represented as a point in space, with δ_t being the vector from the origin to this point. A polymer is also characterized by $\delta_{p,P}$, $\delta_{d,P}$ and $\delta_{h,P}$. Furthermore, it has been found on a purely empirical basis that if δ_d is plotted on a scale twice the size as that used for δ_p and δ_h , then all solvents that dissolve that polymer fall within a sphere of radius R surrounding the point ($\delta_{p,P}$, $\delta_{d,P}$ and $\delta_{h,P}$) (Rosen, 1993). The Hansen theory may, therefore, be considered a graphical quantification of the old "like dissolves like" concept of solubility.

Hansen determined experimentally the solubility of a number of polymers in a series of solvents. All the solvents were characterized by a point in a 3-D structure, in which δ_d , δ_p and δ_h could be plotted on three mutually perpendicular axes. The values of δ_p and δ_h for the various solvents were shifted until all the solvents in which a given polymer was soluble were close together in space. Hansen also determined δ_d , δ_p and δ_h of the polymers involved, being the coordinates of the center of the solvents region in his 3-D structure .

The method of Hansen has the disadvantage that 3-D structures are necessary for a graphical representation of the interaction between polymers and solvents. For

practical applications a 2-D method is to be preferred. For simplicity, the graphical representation of this “solubility space” is often reduced to a 2-D plot of δ_p versus δ_h . This graphics is generally an acceptable practice because the dispersive component parameters (δ_d) of many common solvents are quite similar (Dupont Nylon, 2005).

Using Hansen’s three components, which are calculable from the properties of the pure components, Hansen has constructed a 3-D solubility diagram in which a given liquid or polymer is represented by a point (Chen, 1971). A region of solubility has been characterized by the distance between solvent and solute coordinates (Beerbower and Dickey, 1969) (Brandrup et al., 2003). Each solute, j , was characterized by a set of Hansen parameters defining the center of the solubility sphere, coordinates which could be used in Eq. 2.14 and an interaction radius ${}^jR$. For solubility to be predicted, the distance ${}^{ij}R$ of the liquid i at position $({}^i\delta_d, {}^i\delta_p, {}^i\delta_h)$ from the center of the sphere of solubility $({}^j\delta_d, {}^j\delta_p, {}^j\delta_h)$,

$${}^{ij}R = [4(\delta_{d,S} - \delta_{d,P})^2 + (\delta_{p,S} - \delta_{p,P})^2 + (\delta_{h,S} - \delta_{h,P})^2]^{1/2} \quad (2.14)$$

must be less than the interaction radius ${}^jR$.

Occasional negative values of the component parameters have been attributed to the center of maximum interaction lying closer to the axis than the radius of the solubility sphere. The doubling of the δ_d scale, leading to the factor “4” in the first term, was intended to make the “volume of solubility” approximately spherical, although this may not be necessary (Figure 2.1) (Barton, 1991). This factor is theoretically predicted corresponding states theory of polymer solutions by the Prigogine (1957) when the geometric mean is used to estimate the interaction in mixtures of dissimilar molecules.

This may be expressed as

$${}^{ij}A = ({}^i\delta_d - {}^j\delta_d)^2 + 0.25 [({}^i\delta_p - {}^j\delta_p)^2 + ({}^i\delta_h - {}^j\delta_h)^2] \quad (2.15)$$

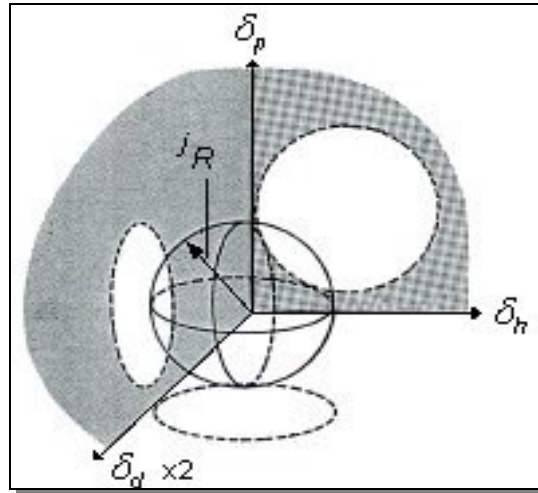


Figure 2.1. Representation of a Hansen parameter solubility sphere and its projections on three axial planes (Adopted from Beerbower and Dickey, 1969).

A more general definition of the region of solubility is

$${}^{ij}R = \delta_S - \delta_P = [a(\delta_{d,S} - \delta_{d,P})^2 + b(\delta_{p,S} - \delta_{p,P})^2 + b(\delta_{h,S} - \delta_{h,P})^2]^{1/2} \quad (2.16)$$

where a and b are empirical weighing factors (Barton, 1991).

If the distance between the solvent and the solute Hansen coordinate position exceeds ${}^{ij}R$, the two components are not soluble, or swelling is less than expected. ${}^{ij}R$ reduces the need for 3-D plots. Some investigators have used 2-D plots for polar and H-bonding terms, but the technique may be misleading for materials with large dispersion contributions. Barton (1983) gives a number of models and contour map examples (Brandrup et al., 2003). The distance ${}^{ij}R$ in Eq. 2.15 can be compared with the radius ${}^jR$ of a solute sphere of solubility, and if ${}^{ij}R < {}^jR$ there is a high likelihood of the liquid i dissolving j . The “sphere” can be projected onto the three planes passing through two axes and the origin, to provide circles in 2-D graphs, as illustrated in Fig. 2.1 (Barton, 1991).

The incorporation of the numerical factor 4 in Eq. 2.14 does not appear necessary to provide spherical interaction volumes; the apparent non-spherical representations which were observed were the result of the restricted range of δ_d

values compared with the δ_p and δ_h ranges, and an equation based on Eq. 2.14 is just as satisfactory:

$${}^{ij}R = {}^{ij}A^{1/2} = [({}^i\delta_d - {}^j\delta_d)^2 + ({}^i\delta_p - {}^j\delta_p)^2 + ({}^i\delta_h - {}^j\delta_h)^2]^{1/2} \quad (2.17)$$

Hansen and Andersen (1988) have also defined the relative energy-difference as the ratio ${}^{ij}R / {}^jR$, so if this number is less than 1.0, liquid i is predicted to be a solvent for j , with values greater than unity indicating progressively poorer solvents (Eq. 2.18). There are applications to several materials of biological interest (Hansen and Andersen, 1988).

$$\text{Relative energy-difference} = {}^{ij}R / {}^jR \quad (2.18)$$

An relative energy-difference number of 0 is found for no energy difference. These numbers less than 1.0 indicate high affinity; It equal to or close to 1.0 is boundary condition; and progressively lower affinities (Hansen, 2000; Miller-Chou, 2003).

The range of δ_d 's spanned by typical polymers and solvents is rather small. In practice, therefore, the 3-D scheme is often reduced to 2-D, with polymers and solvents represented on $\delta_h - \delta_p$ coordinates with a polymer solubility circle of radius R (Rosen, 1993).

Despite its semiempirical nature, the 3-D solubility parameter has proved of great practical utility, particularly in the paint industry, where the choice of solvents to meet economic, ecological and safety constraints is of critical importance. It is capable of explaining those cases in which solvent and polymer δ 's are almost perfectly matched, yet the polymer will not dissolve (the δ vectors have the same magnitudes, but different directions), or where two nonsolvents can be mixed to form a solvent (the solvent components lie on opposite sides outside the sphere, the mixture within) (Rosen, 1993).

2.3. Methods for Determination of Solubility Parameter

Hildebrand parameters cannot be calculated for polymers from heat of vaporization data because of their nonvolatility. Literatures about indirect methods are described below (Brandrup et al., 2003):

2.3.1. Indirect methods

The techniques of determination of solubility parameter for polymers have been widely described in literature, solvency testing (screening procedure) (Gee, 1943), osmotic pressure (Fedors, 1974), swelling values (Gee, 1943; Huglin and Pass, 1968; Errede, 1986, Hamurcu and Baysal, 1994 and Şen and Güven, 1997), turbidimetric titration (Suh and Clarke, 1967; Marco et al., 1986), specific volume (Liron and Cohen, 1983), intrinsic viscosity (Flory, 1953; Stockmayer and Fixman, 1963; Errede, 1986), inverse gas chromatography (Dipaola-Baranayi, 1982; Ashworth and Price, 1986) and Matrix Assisted Laser Desorption Ionization, MALDI (Sperling, 2001).

2.3.2. Correlation methods

Refractive index (Koenhen and Smolders, 1975; Mandel et al., 1982; dipole moment (Koenhen and Smolders, 1975), H-bonding parameter (Hansen and Beerbower, 1971), surface tension (Thomos, 1975), dielectric constant (Darbye et al., 1967), Flory-Huggins interaction parameter (Shultz and Glory, 1955), are some of these techniques. The other and simplest technique for the determination of solubility parameter of polymers is the group contribution method. This technique is based on the assumption that the contribution of different functional groups to a thermodynamic property is additive (Ravindra et al., 1998).

2.3.3. Atomic Group Contribution Methods

These methods have been used to estimate the solubility parameter (Dunkel, 1928; Bowden and Jones, 1948; Hoftyzer and van Krevelen, 1970; Hoy, 1970; Small, 1953; Fedors, 1974). VKH (1972), Fedors (1974) and Barton (1983) have

reviewed these techniques and given tables of group values. The molar volume of solvents and polymers can also be estimated by group contribution techniques.

The sets of group constants of Small (1953), Hoy (1970), van Krevelen (1965) and VKH (1967) seem to be most comprehensive. Small's values were derived from measurements of the heat of vaporization. Hoy's values were derived from vapor pressure measurements. The group contribution values of VKH are based on cohesive energy data of polymers (Brandrup et al., 2003).

The group contribution techniques are based on the assumption that the contributions of different functional groups to the thermodynamic property are additive. The energy of vaporization of a solvent or polymer is

$$\Delta E_i^v = \sum_j n_j \Delta e_j \quad (2.19)$$

where Δe_j is the energy of vaporization contribution of group j , and n_j the number of groups of type j in the molecule. The solubility parameter is obtained by combining Eqs. 2.8 and 2.19:

$$\delta_i = \left(\frac{\Delta E_i^v}{V_i} \right)^{1/2} = \left(\frac{\sum_j n_j \Delta e_j}{V_i} \right)^{1/2} \quad (2.20)$$

Small (1953) defined the molar attraction constant as

$$F_j = (\Delta E_{i,j}^v V_{i,j})^{1/2} \quad (2.21)$$

That can be used to calculate the solubility parameter by

$$\delta_i = \left(\frac{\Delta E_i^v V_i}{V_i^2} \right)^{1/2} = \frac{\sum_j F_j}{V_i} = \frac{\rho_p \sum_j F_j}{M_i} \quad (2.22)$$

where ρ_p is the polymer density and M_i is the molecular weight of polymer, δ_i can be evaluated for polymer repeating group by using group contribution calculations for the molar volume and the cohesive energy density or molar

attraction constant. Table 2.1 gives sets of molar attraction constants and the energy of vaporization provided by several different authors. It is preferable to use parameters from only one set when determining the solubility parameter of a repeating unit (Brandrup, et al., 2003).

a) Fedors' group contributions

Fedors (1974) has developed a system of additive atomic and group increments which permit the estimation of both the solubility parameter and the molar volume for both liquids and high molecular weight amorphous polymers and requires only knowledge of the chemical structure.

The system of group contributions published by Fedors (1974) gives a less accurate prediction of E_{coh} . Table 2.1 gives sets of molar attraction constants and the energy of vaporization of PEG provided by several different authors. Fedors's cohesive energy densities and group molar volumes may give less accurate estimates than from others. But it has still value because it is more comprehensive and can be applied to more systems (Brandrup et al., 2003).

Table 2.1. Group contributions to cohesive energy density for PEG

Group	$F [MPa^{1/2}cm^3 / mol]$			$\Delta E_i^v (J / mol)$	
	Small (1953)*	van Krevelen (1965)*	Hoy (1970)*	Fedors (1974)	van Krevelen and Hoftyzer (1990)
>CH_2	272	280	269	4940	4190
-O-	143	255	235	3350	6290

*Brandrup et al., 2003.

b) Barton's group contributions

Barton (1985) recommended that cohesion parameters provide one of the simplest methods of correlating and predicting the cohesive and adhesive properties of polymers and solvents from knowledge of the properties of the individual components alone. The most important situation where caution is required in using Hildebrand parameters or Hansen parameters is where extent of donor-acceptor

(Lewis acid-Lewis base) interactions (particularly H-bonding) within a component is very different from that between components. Common examples are systems involving H-bonding: alcohols (particularly methanol), carboxylic acids, water, primary and secondary amines, and glycol ethers.

In the case of water, for example, it is necessary to distinguish between systems of water with low permittivity organic liquids (i.e. associated water, with limited interaction between water and organic molecules) and systems of water with H-bonding organic liquids where there is more intermolecular association at the expense of intramolecular association. In terms of Hansen parameters, the properties of water are described in Table 2.2.

Table 2.2. Hansen parameters for water (Barton, 1985).

	δ -components (Jcm^{-3}) ^{1/2}			
	δ_d	δ_p	δ_h	δ_t
self-associated water (water-with low permittivity organic liquids)	20	18	18	32
water with H-bonding organic liquids	12-16	16-31	34-42	48

It is worth emphasizing:

- i) that the δ_t value of pure water is a definite, experimental figure, $[(\Delta H - RT)/V]^{1/2}$, but the way it is subdivided into Hansen parameters is less clear;
- ii) that because $\delta_t^2 = \delta_h^2 + \delta_d^2 + \delta_p^2$, δ_h for “H-bonding water” dominates;
- iii) that although a max. cohesion capability of $48 \text{ MPa}^{1/2}$ exists in water, much of this is unavailable for interaction with low permittivity, non-associating organic liquids which “see” a much lower value.

In this situation, it is clear that one cannot use a single Hildebrand parameter or even a single set of Hansen parameters to describe the behavior of either water or the long chain alcohols (Barton, 1985).

2.3.3.1. Method of Small (1953)

Small (1953) has started with pioneer studies in order to determine the solubility parameter of polymers. In his calculations, he uses cohesive energy density values, molar volumes and molar attraction constants of the repeating unit so as to find the solubility parameter of the polymer and finally he is capable of determining the total solubility parameter. Later, as can be viewed more in detail, by the employment of improved algorithmic calculations the solubility parameter components may also be readily evaluated.

Small has proposed three different equations for the total solubility parameter:

$$\delta_t = \left(\frac{\Delta E_i^v V_i}{V_i^2} \right)^{1/2} \quad (2.23)$$

$$\delta_t = \frac{\sum F_j}{V_i} \quad (2.24)$$

$$\delta_t = \frac{\rho_i \sum F_j}{M_i} \quad (2.25)$$

where δ_t is total solubility parameter of polymer, E_i^v is cohesive energy of repeating unit, V_i is molar volume of repeating unit, ρ_i is density of polymer, F_j is molar attraction constant of repeating unit, M_i is molecular weight of repeating unit.

The available experimental data prove, however, that it is impossible to derive a simple system for an accurate prediction of solubility parameter components from the chemical structure. Especially the interaction of different structural groups in producing overall polar and H-bonding properties is so complicated that it does not obey simple rules.

Three approaches have been published, viz. that of Hoftyzer and van Krevelen (1976, 1997); that of Hoy (1985) and Breitzkreutz (1998); in three of these methods the same basic assumption is made, that of Hansen.

2.3.3.2. Method of Hoftyzer and van Krevelen (VKH) (1976, 1997)

The solubility parameter components may be predicted from group contributions, using the following equations:

$$\delta_d = \frac{\sum F_{di}}{V} \quad (2.26)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad (2.27)$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V} \quad (2.28)$$

This means that for the prediction of δ_d , the same type of formula is used as Small proposed for the prediction of the total solubility parameter δ_t . The group contributions F_{di} to the dispersion component F_d of the molar attraction constant can simply be added (van Krevelen, 1997).

The same method holds for δ_p as long as only one polar group is present. To correct for the interaction of polar groups, the form of Eq. 2.27 has been chosen.

The dispersive Hansen parameter treats the molar attraction constants as additive. The polar Hansen parameters also are additive, unless more than one polar group is present. The group contributions F_{di} , F_{pi} and E_{hi} for a number of structural groups of PEG are given in Part 4.2: additional polar groups do not add linearly to the polar Hansen term. The molar attraction constant is not applied to the H-bonding Hansen parameter. Rather, a H-bonding energy, E_{hi} , is used (Brandrup et al., 2003).

2.3.3.3. Method of Hoy (1985, 1989)

Hoy (1970) also expanded Small's method and in addition introduced the concept of "chameleonic" materials which adopt the character of the surrounding environment, for example, by dimerization (e.g. carboxylic acids) or intramolecular H-bonding (e.g. glycol ethers). In polar or H-bonding solvents these materials act in the appropriate fashion respectively, but in other solvents the polar or H-bonding interactions are intramolecular.

Hoy (1985) determined nonpolar, polar and H-bonding parameters by semi-empirical methods which involved (Barton, 1991):

a) Separation of the total cohesion parameter by calculation of the aggregation number (α) from a regression analysis of molar volumes as a function of ratio of boiling point to critical temperature as well as molecular weight, and density

$$\log \alpha = 3.39066 T_b / T_{cr} - 0.15848 - \log(M / \rho) \quad (2.29)$$

The ratio T_b / T_{cr} may be estimated from Lyderson's equation,

$$T_b / T_{cr} = 0.567 + \sum z \Delta_T - (\sum z \Delta_T)^2 \quad (2.30)$$

and the Δ_T values (critical temperature Lyderson group constants) were provided by Hoy, so it is possible to estimate the component cohesion parameters knowing only the density and structure, although the accuracy is limited by the approximation made.

b) Calculation of the H-bonding parameter from

$$\delta_h = \delta_t [(\alpha - 1) / \alpha]^{1/2} \quad (2.31)$$

c) Evaluation of the polar parameter by a group molar attraction method from

$$\delta_p = \delta_t [\sum z {}^z F_p / (\alpha \sum z {}^z F)]^{1/2} \quad (2.32)$$

d) Calculation of the nonpolar parameter δ_d by difference (Eq. 2.5).

e) The number of monomer units was estimated for a segment of the polymer chain from

$$n = 1 / \left(2 \sum_z \Delta_T^P \right) \quad (2.33)$$

where Δ_T^P is the sum of the aggregation constants for the repeat unit of the segment in the polymer chain. The Hildebrand parameter for the polymer was then evaluated from

$$\delta_t = (n \sum_z {}^zF + 276.3) / n \sum_z {}^zV_g \quad (2.34)$$

where $\sum {}^zV_g$ is the sum of the group molar volume constants for the repeat unit.

The chain aggregation number α^* was estimated from

$$\alpha^* = 777.4 \sum_z \Delta_T^P / \sum_z {}^zV_g \quad (2.35)$$

Hoy's method is in many respects different from that of Hoftyzer and van Krevelen. Hoy (1985, 1989) has an alternative group contribution method. Table 2.3 gives a survey of the system of equations to be used. It contains four additive molar functions, a number of auxiliary equations and the final expressions and the final expressions for δ_t and for the components of δ_t (van Krevelen, 1997).

F_t is the molar attraction function, F_p its polar component (both as discussed earlier); V is the molar volume of the solvent molecule or the structural unit of the polymer. Δ_T is the Lyderson correction for non-ideality, used in the auxiliary equations. The values for low-molecular liquids were derived by Lydersen (1995); the corresponding values for polymers, which are slightly different, have been derived by Hoy ($\Delta T_T^{(P)}$) (van Krevelen, 1997).

Of the other quantities in the auxiliary equations, the significance is the following: α is the molecular aggregation number, describing the association of the

molecules: $\bar{n}$ is the number of repeating units per effective chain segment of the polymer.

Table 2.3. Equations to be used for Hoy's system (1985) for estimation of the solubility parameter and its components*.

Formula	Solvents	Amorphous Polymers
Additive molar functions	$F_t = \sum n_i F_{t,i}$ $F_p = \sum n_i F_{p,i}$ $V = \sum n_i V_i$ $\Delta_T = \sum N_i \Delta_{T,i}$	$F_t = \sum n_i F_{t,i}$ $F_p = \sum n_i F_{p,i}$ $V = \sum n_i V_i$ $\Delta_T^{(P)} = \sum n_i \Delta_{T,i}^{(P)}$
Auxiliary equations	$\text{Log } \alpha = 3.39 \left(\frac{T_b}{T_{cr}} \right) - 0.1585 - \log V$ T_b : boiling point, T_{cr} : critical temp. $\left(\frac{T_b}{T_{cr}} \right) = 0.567 + \Delta_T - (\Delta_T)^2$ (Lydersen equation)	$\alpha^{(P)} = \frac{777 \Delta_T^{(P)}}{V}$ $\bar{n} = \frac{0.5}{\Delta_T^{(P)}}$
Expressions for δ And δ -compounds	$\delta_t = \frac{F_t + B}{V}, B = 277$ $\delta_p = \delta_t \left(\frac{1}{\alpha} \frac{F_p}{F_t + B} \right)^{1/2}$ $\delta_h = \delta_t \left(\frac{\alpha - 1}{\alpha} \right)^{1/2}$ $\delta_d = (\delta_t^2 - \delta_p^2 - \delta_h^2)^{1/2}$	$\delta_t = \frac{F_t + B/\bar{n}}{V}, B = 277$ $\delta_p = \delta_t \left(\frac{1}{\alpha^{(P)}} \frac{F_p}{F_t + B/\bar{n}} \right)^{1/2}$ $\delta_h = \delta_t \left(\frac{\alpha^{(P)} - 1}{\alpha^{(P)}} \right)^{1/2}$ $\delta_d = (\delta_t^2 - \delta_p^2 - \delta_h^2)^{1/2}$

*In the equations given here, F_t is always combined with a Base value; α is the molecular aggregation number, and $\bar{n}$ the number of repeating units per polymer chain segment.

It must be emphasized that Hoy is the only author who uses a “base value” in the calculation of F_t , whereas he neglects a base value in V : it was mentioned earlier that Traube (1895) already proved that for the additive calculation of the molar volume of liquids a base value has to be used (van Krevelen, 1997).

2.3.3.4. Method of Breitzkreutz (1998)

The partial solubility parameters describe the ability of a molecule to interact with another one of the same or a different type via intermolecular forces. The molecular forces and the molar volume are composed by the sum of the contributions of all structural fragments which are present in the molecule. Fedors (1974) supposed group contributions to the molar volume of molecules and van Krevelen/Hoftyzer (1976) group contributions to the molecular forces. By combining both methods, partial solubility parameters can be calculated as follows (Gröning and Braun, 1996):

$$\delta_d = \frac{\sum_i F_{di}}{\sum_i V_i} \quad (2.36)$$

$$\delta_p = \frac{\sum_i F_{pi}^2}{\sum_i V_i} \quad (2.37)$$

$$\delta_h = \frac{\sqrt{\sum_i E_{hi}}}{\sqrt{\sum_i V_i}} \quad (2.38)$$

where i is the structural group within the molecule, F_{di} is the group contributions to dispersion forces, F_p is the group contributions to polar forces and E_h is group contributions to H-bond energy and V_i is group contributions to molar volume.

The parameter set is based on the group contribution methods of Fedors and VKH. The contributions are fitted to an experimental based training data set

(Barton, 1975). Variations from the original contributions have been added (Breitkreutz, 1998), (see Part 4.2.5).

2.3.3.5. Method of Askadskii (2003)

Askadskii (2003) before entering the solubility parameter components, explained the approach used in detail in his published book in order to evaluate the total solubility parameter of the polymer. Askadskii gives the total solubility parameter as shown below:

$$\delta_t^2 = \frac{\Delta E^*}{N_A \sum_i \Delta^W V_i} = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta^W V_i^*} \quad (2.39)$$

Here, ΔE_i^* may be taken as the cohesive energy density for the repeating unit of the polymer and solvents. However, Askadskii uses the van der Waals volume ($^W V_i$) in the selected molecule or repeating unit of the polymer instead of the molar volume which is used in both Small's and later observed algorithmic calculations. N_A is the Avogadro number. One other distinction of Askadskii from other algorithmic calculations is that he has taken the cohesive energy values of the atoms present in the repeating unit instead of groups during cohesive energy calculations.

Askadskii (2003) expresses that the surface tensions of the polymer and solvent systems may well be explained. The calculation steps proposed for this is given below:

$$\delta^* = \frac{\sum_i \Delta E_i^*}{\left(\sum_i \Delta V_i \right)^{2/3}} \quad (2.40)$$

where δ^* is the specific surface cohesive energy or cohesive energy per specific surface.

$$V_m = \frac{N_A \sum_i \Delta V_i}{k_{avg}} \quad (2.41)$$

where V_m is molar volume of the polymer and solvent, k_{avg} is a constant (0.681).

$$\phi = \frac{4(V_s V_p)^{1/3}}{(V_s^{1/3} + V_p^{1/3})^2} \quad (2.42)$$

where ϕ is a parameter, V_s and V_p are molar volumes of the solvent and polymer, respectively.

$$\gamma_p = C_j \frac{\sum_i \Delta E_i^*}{\left(\sum_i \Delta V_i \right)^{2/3} m^{1/3}} \quad (2.43)$$

where γ_p is a surface tension of polymer, C_j is a parameter which depends on the affiliation of the polymer to the given group (polar group) ($C_j = 0.0751$) and m is the number of atoms in the repeat unit of polymer ($m=7$ for PEG).

$$\gamma_s = A_j \frac{\sum_i \Delta E_i^*}{\left(\sum_i \Delta V_i^* \right)^{2/3}} \quad (2.44)$$

where γ_s is the surface tension of solvent, A_j is a parameter (for second group components; alcohols, amides, acids...; $A_j=0.0181$).

$$\mu = \gamma_p^2 / \gamma_s^2 \text{ or } \mu = \delta_p^2 / \delta_s^2 \quad (2.45)$$

where μ is a parameter and it presents the ratio of surface tension of polymer and solvent.

$$\gamma_{s-p} = \gamma_s + \gamma_p - 2\phi(\gamma_s \gamma_p)^{1/2} \quad (2.46)$$

where γ_{s-p} is interfacial tension.

$$a' = \gamma_{s-p} / \gamma_s \quad (2.47)$$

where a' is a parameter and it presents the ratio of interfacial tension/surface tension of solvent.

and finally,

$$\mu < 2\rho\phi\left(\phi - \sqrt{\phi^2 - 1 + a'}\right) \quad (2.48)$$

where ρ is a constant (0.687).

As a consequence of all these calculations, Askadskii defends that in case the right hand side of the inequality is greater or equal to μ value, solubility is most probable.

2.4. Solubility Parameter Difference for PEG-Solvent Pair Systems

A solubility plot for a given polymer can be represented by a point around which a sphere can be constructed. This sphere defines the zone of solubility for a given polymer.

The general rule is that

- (i) any liquid lying within the sphere is a true solvent for the polymer;
- (ii) any liquid lying outside the sphere is a non-solvent;
- (iii) any liquid lying close to the boundary of the sphere may be partially miscible with the polymer.

3-D solubility analysis is useful in solving several engineering problems, especially in the paint and coating industries (Rabek 1980).

In the 2-D graphics the degree of solubility (volume of polymer per volume of solvent) can be indicated by a number. The solubility region can approximately be

delimited by a circle with a radius of about 5δ -units. Solubility increases approximately as the distance from the centre of the circle decreases.

$$\overline{\Delta\delta} = [(\delta_{d,p} - \delta_{d,s})^2 + (\delta_{p,p} - \delta_{p,s})^2 + (\delta_{h,p} - \delta_{h,s})^2]^{1/2} \quad (2.49)$$

For a good solubility $\overline{\Delta\delta}$ must be small (≤ 5) (van Krevelen, 1997).

2.5. Criteria for Polymer Solubility

2.5.1. Solution Process

Polymer dissolution in solvents is an important area of interest in polymer science and engineering because of its many applications in industry such as microlithography, membrane science, plastics recycling, and drug delivery. Unlike non-polymeric materials, polymers do not dissolve instantaneously, and the dissolution is controlled by either the disentanglement of the polymer chains or by the diffusion of the chains through a boundary layer adjacent to the polymer-solvent interface (Miller-Chou, 2003). Dissolving a polymer is a slow process that occurs in two stages. First, solvent molecules slowly diffuse into the polymer to produce a swollen gel. Subsequently, the polymer-polymer intermolecular forces are high because of crosslinking, crystallinity, or strong H-bonding. But if these forces can be overcome by the introduction of strong polymer-solvent interactions, the second stage of solution can take place. Here, the gel gradually disintegrates into a true solution. Only this stage can be materially speeded by agitation. Even so, the solution process can be quite slow (days or weeks) for materials of very high molecular weight (Billmeyer, 1971).

2.5.2. Polymer Texture and Solubility

Solubility relations in polymer systems are more complex than those among low-molecular weight compounds, because of the size difference between polymer and solvent molecules, the viscosity of the system, and the effects of the texture and molecular weight of the polymer. In turn, the presence or absence of solubility as conditions (such as the nature of the solvent or the temperature) are varied can give much information about the polymer. From what has already been said, it is

clear that the topology of the polymer is highly important in determining its solubility. The theory of solubility, based on the thermodynamics of polymer solutions, is highly developed.

2.5.3. Solution Viscosity

The viscosity of a dilute solution of a polymer is a maximum in the “best” solvent, that is, in one where the cohesion parameters of solvent and polymer are comparable. Equilibrium configuration of molecular chains, both in swelling situations and in polymer solution viscosity studies, depends on the balance between the Gibbs free energy change due to mixing and that due to elastic deformation. The extent of deformation depends on the relative strengths of intramolecular (segment-segment) and intermolecular (segment-solvent) interactions. In a “good” solvent the polymer is unfolded, retaining to the maximum extent the more favorable polymer-solvent interactions (and therefore the greatest viscosity), while in a “poor” solvent the polymer molecules remain folded because of more favorable intramolecular interactions.

The viscosities of dilute polymer solutions show minima in poor solvents because the polymer molecules remain coiled as the polymer concentration is increased, there is a “changeover” in behavior: the viscosity exhibits a maximum in poor solvents at higher concentration. There is an aggregation or clustering of polymer molecules, a preliminary to phase separation, when solvents are used that have cohesion parameters near the limits of the miscibility range for the polymer. It is probable that the clusters are not completely broken down to individual molecules even in good solvents with cohesion parameters in the middle of the miscibility range.

This rather complex behavior can be described in terms of entropy and free volume effects which are not present in liquid-liquid systems, and it should not be expected that it can be fully correlated by means of cohesion parameters providing direct information only on the enthalpy aspect of the interactions. Attempts are being made to relate concentrated polymer solution behavior to dilute solution parameters such as the Mark-Houwink K and a (Barton, 1990).

2.5.4. Theta Temperature (Flory Temperature) and Theta Solvents

Flory θ – temperature is defined by several different criteria:

1. It is the temperature where A_2 is zero for dilute solutions, and $\chi = 0.5$.
2. It is the temperature where the radius of gyration approximates that of the bulk polymer.
3. It is the temperature at which an infinite molecular weight fraction would just precipitate (Sperling, 2001).

In a poor solvent, where both χ_H and χ_S are usually positive, at the theta temperature $\chi = 0.5$, and the partial molar Gibbs free energy of polymer-liquid interaction is zero. This means that the molecular dimensions of the polymer are unperturbed by interactions and the molecules can mutually interpenetrate freely: this is described as *pseudo-ideal* solution behavior. Flory theta temperatures are associated with both the upper and lower critical solution temperatures exhibited by all polymer solutions. At temperatures just below the UCST ($T < \theta$) the molecules attract one another, and if the temperature falls much below θ , precipitation of polymer occurs. It has been shown that the critical temperature for phase separation is

$$T_{cr} \approx \theta / (1 + CM^{-1/2}) \quad (2.50)$$

where M is the molar mass of the polymer and C is a constant related to χ_S for the polymer-liquid system. As M approaches infinity, T_{cr} approaches θ ; that is, the theta temperature is the lowest temperature at which a polymer molecule of infinite length would be completely miscible with the liquid. Below the theta temperature, the polymer exists as a ball or tight coil, with intramolecular interactions between groups in the same molecule. When the temperature is raised to the theta temperature, these interactions disappear and the polymer behaves as an ideal “*statistical*” coil, the liquid is called a *theta solvent*, and the polymer is said to be in the *theta condition*. At temperatures above θ in poor

solvents there is little change in polymer chain dimensions, but in “good” solvents the chains tend to uncoil (Barton, 1990).

2.5.5. Thermodynamics of Polymer Solutions

The size and conformations of dissolved polymer molecules require special theoretical treatment to explain their solution properties. Conversely, it is possible to obtain information about the size and shape of polymer molecules from studies of their solution properties. Polymer solutions invariably exhibit large deviations from Raoult’s law except at extreme dilutions, where ideal behavior is approached as an asymptotic limit. At concentrations above a few percent, deviations from ideality are so great that the ideal law is of little value for predicting or correlating the thermodynamic properties of polymer solutions. Deviations from ideality in polymer solutions arise largely from small entropies of mixing. These are not abnormal but are the natural result of the large difference in molecular size between the components. They can be interpreted in terms of a simple molecular model. It is assumed that the polymer molecules consist of a large number x of chain segments of equal length, flexibly joined together. Each link occupies one lattice site, giving the arrangement of Figure 2.2. It can now be seen qualitatively why the entropy of mixing of polymer solutions is small compared to that with normal solutes.

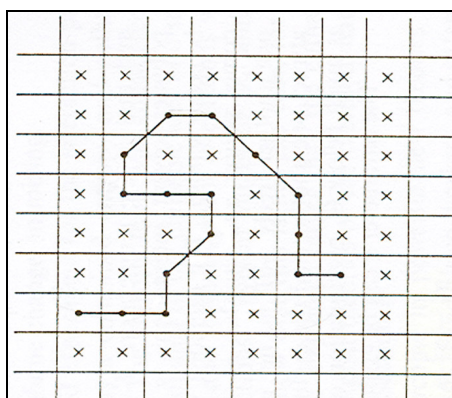


Figure 2. 2. Two dimensional representation of a polymer molecule located in the liquid lattice (Billmeyer, 1971).

The lattice model used in the Flory-Huggins treatment neglects the fact that a very-dilute polymer solution must be discontinuous in structure, consisting of domains or clusters of polymer chain segments separated on the average by

regions of polymer-free solvent. Flory and Krigbaum (1950) assume such a model, in which each cloud of segments is approximately spherical, with a density that is a maximum at the center and decreases in an approximately Gaussian function with distance from the center. Within the volume occupied by the segments of one molecule, all other molecules tend to be excluded. Within such an excluded volume occur long-range intramolecular interactions.

2.5.6. Flory-Huggins Interaction Parameter

The Flory interaction parameter (often called the Flory-Huggins interaction parameter) (χ) is a measure of the interaction between any given solvent and a given polymer. It is a free-energy parameter and contains both entropy and enthalpy terms:

a) The interaction parameter is the sum of χ_H and χ_S , which are the excess enthalpy and excess entropy of dilution parameters. For non-polar or slightly polar polymer-solvent systems, χ is given by

$$\chi = \chi_S + \chi_H \quad (2.51)$$

(dimensionless), where

χ_S is the entropy term, equal to the inverse of the lattice coordination number (z) (i.e. equal to the inverse of the number of nearest neighbors of a molecule or segment in solution) (χ is a temperature-dependent quantity),

χ_H is the enthalpy term given by

$$\chi_H = (V_S / RT)(\delta_P - \delta_S)^2 \quad (2.52)$$

V_S is the molar volume of the solvent, R is the universal gas constant, T is the thermodynamic temperature (in Kelvin), δ_S and δ_P are the solubility parameters of solvent and polymer, respectively;

b) For polar polymer-solvent systems, the solubility parameter of a polymer should be replaced by a three-dimensional solubility parameter.

The Flory-Huggins interaction parameter (χ) is a temperature-dependent quantity and is also concentration dependent over a wide range of polymer concentrations. The parameter, χ must be measured for every polymer-solvent pair.

χ can be calculated from measurements of the second virial coefficient (A_2) and also by other different methods (Rabek, 1980).

The Flory-Huggins theory is useful in considering the thermodynamics of dilute polymer solutions, but it has theoretical limitations and is not necessarily of great value in all solvent formulation problems. The shortcomings of the Flory interaction parameter include (Barton, 1990):

- It is not a constant, but depends on polymer concentration and molecular weight as well as temperature.
- It is not possible to evaluate simply for every polymer-liquid combination.
- It characterizes a polymer-liquid pair, and so is inconvenient for multicomponent systems.
- It is a composite term influenced by factors such as H-bonding.

2.5.7. Second Virial Coefficient

The second virial coefficient is a measure of the interaction between a solvent and a polymer and is expressed according to the complex Flory-Huggins-Krigbaum theory as

$$A_2 = (1/2 - \chi) \left(\frac{\bar{v}^2}{V_S} \right) J(X) = \Delta S_m \left(1 - \frac{\theta}{T} \right) \left(\frac{\bar{v}^2}{V_S} \right) J(X) \quad (2.53)$$

where χ is the Flory interaction parameter, $\bar{v}$ is the specific volume of the polymer, V_S is the molar volume of the solvent, ΔS_m is the entropy of mixing, θ is the theta temperature, T is the temperature at which interaction between solvent and polymer occurs, $J(X)$ is a quantity which depends on molecular weight, the nature of the solvent, and the temperature and becomes equal to unity at the theta temperature, where $\chi=0.5$.

The *second virial coefficient* A_2 can be evaluated from Flory interaction parameter.

$$A_2 = (1/2 - \chi) \frac{\bar{v}^2}{N_o V_S} \quad (2.54)$$

and

$$A_2 = (1/2 - \chi)(\rho_p^2 V_S)^{-1} \quad (2.55)$$

where ρ_p , $\bar{v}$ and V_S is density, specific volume of the polymer and molar volume of solvent, respectively (Yamakawa, 1971; Wakker, 1991).

A general rule is that

- a)** for “good solvents”, A_2 is high;
- b)** for “poor solvents”, A_2 is low;
- c)** at $A_2=0$ the polymer precipitates from solution.

The second virial coefficient is dependent on several factors:

- a)** temperature (A_2 decreases with increasing temperature);
- b)** polymer-solvent system;
- c)** molecular weight and molecular weight distribution of the polymer;
- d)** tacticity of the polymer;
- e)** molecular shape of macroions (Rabek, 1980).

2.5.8. Conformations of Dissolved Polymer Chains

In solution, a polymer molecule is a randomly coiling mass most of whose conformations occupy many times the volume of its segments alone. The average density of segments within a dissolved polymer molecule is of the order of $10^{-4} - 10^{-5} \text{ g/cm}^3$. The size of the molecular coil is very much influenced by the polymer-solvent interaction forces. In a thermodynamically “good” solvent, where

polymer-solvent contacts are highly favored, the coils are relatively extended. In a “poor” solvent, they are relatively contracted (Billmeyer, 1971).

The random coil arises from the relative freedom of rotation associated with the chain bonds of most polymers and formidably large number of conformations accessible to the molecule. One of conformations, the fully extended chain (often an all-*trans* planar zigzag carbon chain) has special interest because its length, the contour length of the chain, can be calculated in a straightforward way. In all other cases, the size of random coil must be expressed in terms of statistical parameters such as the root-mean-square distance between its ends, $\langle r^2 \rangle^{1/2}$, or its radius of gyration, the root-mean-square distance of the elements of the chain from its center of gravity, $\langle s^2 \rangle^{1/2}$. For linear polymers the mean-square end-to-end distance and the square of the radius of gyration are simply related: $\langle r^2 \rangle = 6 \langle s^2 \rangle$.

2.5.9. Unperturbed Dimensions of Linear Chain Macromolecules

The size of macromolecules (dimension) in solution cannot strictly be defined because a single molecular coil alters in shape with time and these conformational changes are due to Brownian motion. The molecular size varies from molecule to molecule of identical mass and structure, and it can only be described in terms of average properties.

2.5.9.1. Mean Square Average End-to-End Distance

Mean square average end-to-end distance ($\langle r^2 \rangle$) of linear chain molecule, given by

$$\langle r^2 \rangle = \langle r^2 \rangle_o \alpha^2 \quad (2.56)$$

(in square meters SI), where $\langle r^2 \rangle_o$ is the unperturbed mean-square average-end-to-end distance, α is the expansion factor.

2.5.9.2. Square Average Radius of Gyration

Square average radius of gyration ($\langle s^2 \rangle$), given by

$$\langle s^2 \rangle = \langle s^2 \rangle_o \alpha^2 \quad (2.57)$$

(in square meters SI), where $\langle s^2 \rangle_o$ is the unperturbed square average radius of gyration, α is the expansion factor;

For linear polymers

$$\langle r^2 \rangle = 6 \langle s^2 \rangle \quad (2.58)$$

Akcasu and Han (1979) have shown that the Stokes hydrodynamic radius R_H is not equal to the radius of gyration (Fig. 2.3). The relation between $\langle s^2 \rangle$ and R_H might be expressed by recent experimental data as

$$R_H = 0.77 \langle s^2 \rangle \quad (2.59)$$

where $\langle s^2 \rangle$ is radius of gyration, R_H is Stokes hydrodynamic radius.

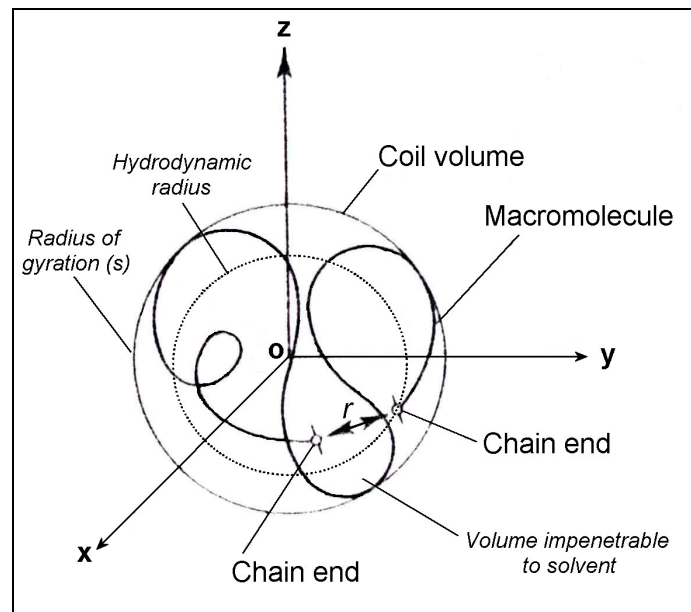


Figure 2.3. Schematic representation of a linear coil (Rabek, 1980 and Rangelov and Brown, 2000).

Qian et al. (2001) reported that the concentration dependence of the radius of gyration of a polymer molecule in solution can be written as

$$\langle s^2 \rangle^3 = \frac{3M[\eta]}{3\phi' \left\{ 1 + \frac{[\eta] - [\eta]_\theta}{[\eta]_\theta} \left[1 - \exp\left(-\frac{c}{c^*}\right) \right] \right\}} \quad (2.60)$$

where c^* is a critical concentration, at which the polymer coils begin to overlap each other, defined by

$$c^* = \frac{3M}{4\pi N_A \langle s^2 \rangle^3} = \frac{3\phi'}{4\pi N_A [\eta]} \quad (2.61)$$

where ϕ' is the Flory universal constant which equals 3.1×10^{23} when $[\eta]$ is expressed in mL/g, and the other symbols have common meaning.

$\langle s^2 \rangle$ allows determination of the Flory-Fox viscosity term, ϕ' , by

$$\phi' = \frac{[\eta]M}{6^{3/2} \langle s^2 \rangle^3} \quad (2.62)$$

In this regard, it should be noted that the limiting viscosity number has been expressed as

$$[\eta] \sim \langle s^2 \rangle^2 R_H / M \quad (2.63)$$

(Fetters et al., 1991).

Perturbed dimensions are the chain dimensionless in a given solvent, where intermolecular interactions between macromolecules and solvent occur.

Unperturbed dimensions are the chain dimensions in a given solvent, determined solely by bond lengths and angles.

The *theta temperature* (the *Flory temperature*) is that temperature of a given solvent $T = \theta$ where linear chain molecules have unperturbed dimensions.

The unperturbed dimensions of a linear polymer chain ($\langle r^2 \rangle_o$ or $\langle s^2 \rangle_o$) vary with molecular weight ($\bar{M}_n$). Values of the type $\langle r^2 \rangle_o / \bar{M}_n$ or $\langle s^2 \rangle_o / \bar{M}_n$ depend only on chain structure and not upon a solvent or a temperature.

Long-range interactions are defined as those between spatially proximate groups that are separated along the chain by many segments (Fig. 2.4). For single chains, both long-range and short-range interactions are intramolecular but the former is intersegmental and the latter intrasegmental (Elias, 1997)..

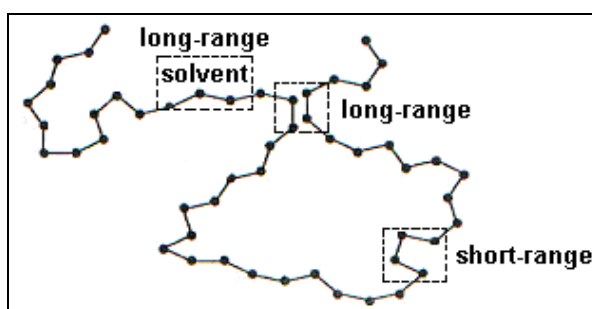


Figure 2.4. Long-range and short-range (local) interactions between chain segments (Elias, 1997).

The dimensions of polymer chains in diluted solutions determine by short- and long-range interactions:

2.5.9.3. Short-range Interactions

One of the triumphs of modern polymer chemistry is the extent to which Flory and his collaborates (Flory 1969), among others, have calculated completely and accurately the effect of short-range interactions on the dimensions of random-coil polymers. Conformations that would place two atoms close together along the chain too close to one another are not allowed, leading to further expansion. The most important of these is the so-called *pentane interference* (Taylor 1948) between the first and fifth chain atoms in a sequence. The net results of these short-range interactions can be expressed as a characteristic ratio of the square of the actual chain dimensions in the absence of long-range interactions (called the unperturbed dimensions and given the symbol $\langle r^2 \rangle_o$).

Short-range interactions such as bond angle restrictions and steric restrictions to internal rotation. These are determined by the unperturbed mean-square end-to-end distance $\langle r^2 \rangle_0$ or by the unperturbed square average radius of gyration $\langle s^2 \rangle_0$. A measure of the effect of short-range interactions is given by the quantity C_∞ , defined as

$$C_\infty = \lim_{n \rightarrow \infty} \langle r^2 \rangle_0 / \sum_i n_i l_i \quad (2.64)$$

where n_i is the number of the i th kind of bond of length l_i .

2.5.9.4. Long-range Interactions and Excluded Volume

Each segment of a real chain exists within a volume from which all other segments are excluded. The effect of the long-range interactions is to cause a further expansion of the chain over its unperturbed dimensions, since more of the compact conformations, with small values of $\langle r^2 \rangle$, must be excluded. The actual dimensions of the real chain can be expected to exceed its unperturbed dimensions by an expansion factor α , thus $\langle r^2 \rangle^{1/2} = \alpha \langle r^2 \rangle_0^{1/2}$. The value of α depends on the nature of the solvent: a solvent for which α is large is said to be a thermodynamically “good” solvent for that polymer, and vice versa. In a sufficiently poor solvent, or at a sufficiently low temperature (since solvent power and α vary with the temperature), it is possible to achieve the condition $\alpha = 1$, where the chain attains its unperturbed dimensions. This special point is called the *Flory temperature* θ ; a solvent used at $T = \theta$ is called a θ -solvent. $\langle r^2 \rangle = 6 \langle s^2 \rangle$.

Long-range interactions, which depend upon the polymer-solvent interactions are determined by the expansion factor (α) and the *excluded volume* parameter (z), which are correlated by

$$\lim_{z \rightarrow \infty} \alpha^x = \text{constant } xz \quad (2.65)$$

where x is a constant independent of z . Several values between 1 and 6.67 for x have been predicted, from different theories.

The excluded volume is the volume from which a given polymer molecule effectively excludes all others. The excluded volume is a result of the virtual repulsion between polymer molecules arising from their spatial requirements. Each molecule in a very dilute solution in a good solvent will tend to exclude all others from the volume which it occupies (Rabek, 1980).

The *expansion factor* (α) is the ratio of the chain dimension in a given solvent (perturbed dimensions) ($\langle r^2 \rangle$ or $\langle s^2 \rangle$) and in a theta solvent (unperturbed dimensions) ($\langle r^2 \rangle_o$ or $\langle s^2 \rangle_o$) at specific temperature:

$$\alpha = \frac{\langle r^2 \rangle^{1/2}}{\langle r^2 \rangle_o^{1/2}} = \frac{\langle s^2 \rangle^{1/2}}{\langle s^2 \rangle_o^{1/2}} \quad (2.66)$$

(dimensionless).

If the polymer is in a good solvent, the expansion factor (α) is greater than unity; this means that the actual perturbed dimensions ($\langle r^2 \rangle$ or $\langle s^2 \rangle$) exceed the unperturbed dimensions ($\langle r^2 \rangle_o$ or $\langle s^2 \rangle_o$). The expansion factor (α) also increases with molecular weight ($\bar{M}_n$), because the number of uncompensated interactions between chain segments increases with the number of segments when $T > \theta$. The expansion factor (α) is also related to the solvent power (Rabek, 1980).

2.5.9.5. Flory Expansion Factor

Flory expansion factor is defined as the usual dimensionless ratios with respect to θ solvent values, e.g.

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \quad (2.67)$$

where $[\eta]_\theta$ designates the θ solvent value of $[\eta]$ (Yamakawa 1971).

The parameter α can be evaluated in terms of thermodynamic quantities:

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi)M^{1/2} \quad (2.68)$$

and

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi_s)(1 - \theta/T)M^{1/2} \quad (2.69)$$

where C_M lumps together numerical and molecular constants. This equation, which involves the assumption of validity of theories involving intermolecular interactions as well as intramolecular interactions, must be accepted with some reservations. It predicts that α increases without limit with increasing molecular weight; since $\langle r_o^2 \rangle$ is proportional to M . It also leads to fact that, at $T = \theta$, $\alpha = 1$ and molecular dimensions are unperturbed by intramolecular interactions. Since α depends on the entropy parameter, χ_s , it is larger in better solvents.

The *expansion of the coil* in a dilute solution is given by the Flory-Krigbaum equation:

$$\alpha^5 - \alpha^3 = 2C_M \Delta S_m (1 - \theta/T) M^{1/2} \quad (2.70)$$

where ΔS_m is the entropy of mixing parameter, θ is the theta temperature, T is the temperature at which expansion of the coil occurs, M is the molecular weight of the polymer, C_M is a quantity defined by

$$C_M = \frac{9}{2^{5/2} \pi^{3/2}} \left(\frac{\bar{v}^2}{N_A V_S} \right) \left(\frac{M}{\langle r^2 \rangle_o} \right)^{3/2} \quad (2.71)$$

$\bar{v}$ is the specific volume of a polymer, N_A is the Avogadro number, V_S is the molar volume of solvent, $\langle r^2 \rangle_o$ is the unperturbed mean-square end-to-end distance.

The coefficient C_M presented above is also given by,

$$C_M = 27\bar{v}^2 M^{3/2} / [2NV_S(2\pi \langle r^2 \rangle_o)^{3/2}] \quad (2.72)$$

where $\bar{v}$ is the specific volume of the polymer, N is the Avogadro's number, and V_S is the molar volume of the solvent (Wakker, 1991).

The expansion of the coil in a dilute solution depends upon its molecular weight and upon the thermodynamic interactions with the solvent. At the temperatures above the theta temperature the expansion of the coil will be increased. As the temperature is lowered the expansion of the coil will be decreased, reaching zero at the theta temperature. At this temperature the molecular coil has its unperturbed dimensions (Rabek, 1980).

2.5.10. Methods for Determination of the Unperturbed Chain Dimensions from Viscosity Measurements

The unperturbed chain dimensions of linear polymers can be determined from the following equations:

- a) Flory-Fox Equation,
- b) Extrapolation methods (Kurata-Stockmayer-Fixman, Inagaki-Suzuki-Kurata and Berry Equations),
- c) Interpolation methods ($T - (1/2 - \chi)$ and $T-A_2$ behaviors).

2.5.10.1. Flory-Fox Equation

$$[\eta]\bar{M} = \phi' V_h = \phi' (\langle r^2 \rangle_o)^{3/2} \quad (2.73)$$

where $[\eta]$ is the limiting viscosity number, $\bar{M}$ is the average molecular weight of the polymer, ϕ is a function related to the hydrodynamic behavior of macromolecules in solution—for a narrow fraction and theta condition, $\phi = \phi_o = 2.8 \times 10^{21} \text{ mol}^{-1}$ (ϕ is also called the Flory constant), a theoretical value of

$3.6 \times 10^{21} \text{ dL/mol cm}^3$ can be calculated from a study of the chain fractional coefficients (Flory, 1953), V_h is the hydrodynamic volume (i.e. the volume occupied by the macromolecule) (cubic meters SI), $\langle r^2 \rangle$ is the mean-square end-to-end distance (Rabek, 1980).

Replacing $\langle r^2 \rangle$ in Eq. 2.73 by $\langle r^2 \rangle_o \alpha^2$ and isolating the term $\langle r^2 \rangle_o \bar{M}^{-1}$ an equation is obtained which allows to calculate the unperturbed chain dimensions ($\langle r^2 \rangle_o$):

$$[\eta] = \phi_o \left(\frac{\langle r^2 \rangle_o}{\bar{M}} \right)^{3/2} \bar{M}^{1/2} \alpha^3 \quad (2.74)$$

where α is the expansion factor, given by

$$\alpha^3 = [\eta]/[\eta]_\theta \quad (2.75)$$

$[\eta]_\theta$ is the value of $[\eta]$ at the theta temperature, K_θ is a constant for a given polymer, independent of solvent, temperature, and molecular weight (except in the range of low molecular weight) and given by

$$K_\theta = \phi_o (\langle r^2 \rangle_o \bar{M}^{-1})^{3/2} \quad (2.76)$$

K_θ can be obtained from measurement of the limiting viscosity number at the theta temperature,

$$[\eta]_\theta = K_\theta \bar{M}^{1/2} \quad (2.77)$$

The Flory-Fox equation has been replaced by the related semiempirical Mark-Houwink Equation in which the constants K and a must be obtained from absolute or relative molecular-weight measurement. These parameters are readily associated with polymer characterization (Eq. 2.78):

$$[\eta] = KM^a \quad (2.78)$$

contains parameters K and a which are complex functions of the polymer, solvent, co-solutes and temperature (Keary, 2001). This relationship is expressed by the Mark-Houwink equation in which the proportionality constant K is characteristic of the polymer and solvent and the exponential " a " is a function of the shape of the polymer coil in a solution. In a θ solvent, the value for the ideal statistical coil is 0.5. This value, which is actually a measure of the interaction of the solvent and polymer, increases as the coil expands in a good solvent, and the value is between 1.8-2.0 for a rigid polymer chain extended to its full contour length and zero for spheres. However, the value " a " is usually 0.5 to 0.8 in polymer solution. K generally has values in the range 10^{-2} - 10^{-4} mL/g (Carraher, 1996). Parameter " a " does not depend on the molecular weight of flexible-chain polymers but is reported (Lapasin and Prici, 1995) to become a decreasing function of M for semi-flexible chains above a critical molecular weight. Both parameters are related to stiffness of the polymer. K reflects the stereochemistry of the intra-molecular species (Keary, 2001).

2.5.10.2. Extrapolation Methods

Unperturbed dimensions were derived via six different extrapolation procedures, namely those of Stockmayer-Fixman (1963), Cowie (1966), Dondos-Benoit (1978), Kurata-Stockmayer (1963), Inagaki-Suzuki-Kurata (1966), Berry (1967) (Shaban 1993).

In this study; KSF, ISK and Berry equations have been employed among six methods mentioned above since they all yield the same B value. In extrapolation methods selected, M_n values of PEG samples were used.

2.5.10.2.1. Kurata-Stockmayer-Fixman (KSF) Equation

$$[\eta]\bar{M}^{-1/2} = K_{\theta} + 0.51B\phi_0\bar{M}^{1/2} \quad (2.79)$$

where

$$B = 2\bar{V}^2(1/2 - \chi) / N_A V_S \quad (2.80)$$

$\bar{v}$ is the specific volume of a polymer, V_S is the molar volume of a solvent, χ is the Flory interaction parameter, N_A is the Avogadro number (Fig. 2.5) (Rabek, 1980).

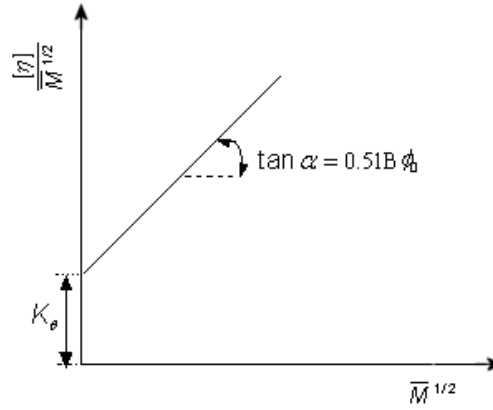


Figure 2.5. A typical KSF plot for a linear polymer in a given solvent at constant temperature.

2.5.10.2.2. Inagaki-Suzuki-Kurata (ISK) Equation

$$[\eta]^{4/5} \bar{M}^{-2/5} = 0.786 K_{\theta}^{4/5} + 0.454 K_{\theta}^{2/5} \phi_0^{2/3} B^{2/3} \bar{M}^{1/3} \quad (2.81)$$

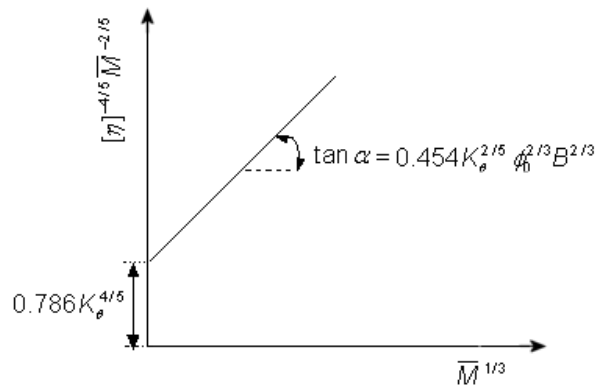


Figure 2.6. A typical ISK plot for a linear polymer in a given solvent at constant temperature.

2.5.10.2.3. Berry Equation

$$[\eta]^{1/2} \bar{M}^{-1/4} = K_{\theta}^{1/2} + 0.42 K_{\theta}^{1/2} \phi_0 B \bar{M} [\eta]^{-1} \quad (2.82)$$

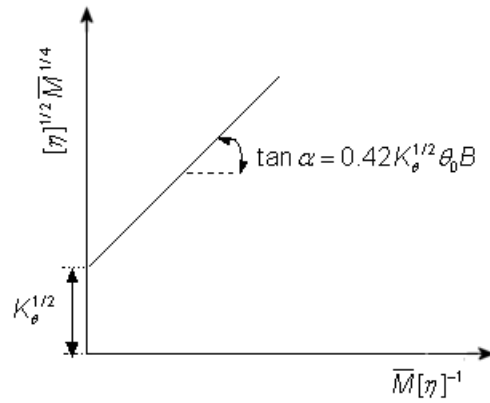


Figure 2. 7. A typical Berry plot for a linear polymer in a given solvent at constant temperature.

2.5.10.2.4. $1/T$ - B behavior

$$B = B_0 \left(1 - \frac{\theta}{T}\right) \quad (2.83)$$

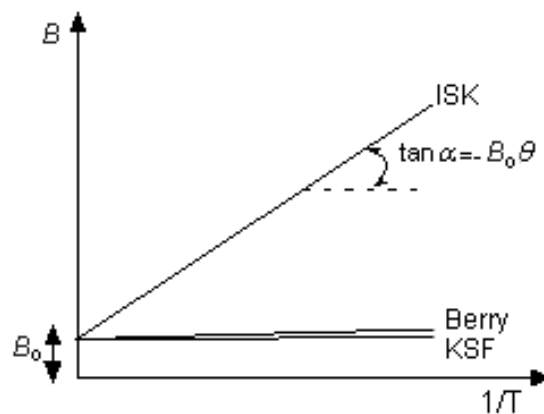


Figure 2. 8. A typical $1/T$ - B plot for a linear polymer in a given solvent at constant temperature.

2.5.10.3. Interpolation Methods

2.5.10.3.1. T - $(1/2 - \chi)$ behavior

The plot of $(1/2 - \chi)$ against temperature yields straight lines from which interpolated values were determined.

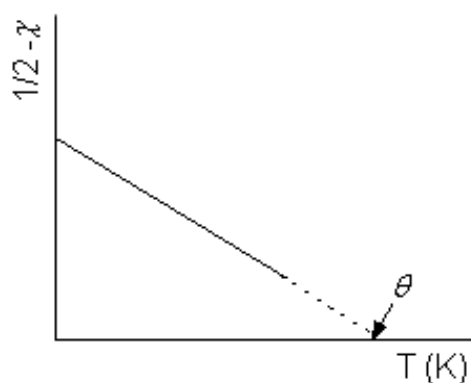


Figure 2. 9. A typical interpolation plot $T-(1/2 - \chi)$.

2.5.10.3.2. $T - A_2$ behavior

The plot of A_2 versus temperature also yields straight lines from which interpolated values were determined.

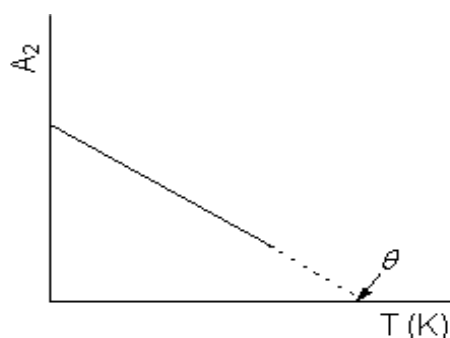


Figure 2.10. A typical interpolation plot $T-A_2$.

2.5.11. Properties of PEGs in Aqueous Solutions

Studies on PEG solution properties are concerned with three subjects. First, PEG exhibits in water both UCST and LCST phenomena (Kawaguchi et al., 1997). Several models have been proposed, including an entropic model due to structured water, H-bond formation between polymer segments and solvent, and a conformation model (Friberg and Lindman, 1992). The first two models are the result of specific water structuring along a PEO backbone. There are data suggesting that two water molecules are associated with each ethylene oxide monomer unit and the diffusion coefficient of water near a chain is substantially

lower than in bulk water. The second problem concerns the tendency of PEO to aggregate in solution. Polik and Burchard (1983) reported that PEG chains aggregate significantly in water over a wide temperature range from 20° to 90 °C. Zhou and Brown (1990) also reported that the PEG molecules aggregate in methanol at room temperature. However, Kato et al. (1981) reported that PEG does not aggregate in water from the measurements of dynamic and static light scattering, and viscometry. Kinugasa et al. (1994) found that PEG molecules do not aggregate in water, methanol, and acetonitrile at room temperature, when the solutions are meticulously prepared.

PEO is one of the most important synthetic polymer from both theoretical and application points view. The solubility in water and the simple structure make it a good model system for the study of the interaction mechanisms of water with hydrophilic surfaces and biopolymers (e.g. in water, PEO assumes a helix conformation as DNA does). On the other hand, it is widely employed in a series of applications for example those connected with its drag-reducing properties in the flow of water through ducts and channels, when high molecular weight (M_w) polymer is present at concentrations even less than 10 ppm. These effects could be due to an interfacial layer of PEO between the water flow and the tube, or to the capacity of PEO to form long filaments in water flow which reduce local turbulences. The first hypothesis would be supported by evidence of aggregation whereas the good solvent behavior of water would support the second one. For this, aggregation behavior of PEO in water, starting from very dilute concentrations and from oligomers up to high M_w s, is both controversial and important (Magazù and Maisano, 2001).

A coil of water molecules around the PEO chain H-bonded to two sites of ether oxygen was found. Water spirals are formed in such a way that more water molecules accumulate on the cavities surrounding the PEOs oxygen atoms (Ary et., 2004). Figure 2.11 shows topology predicts a coil of water molecules H-bonded around PEO.

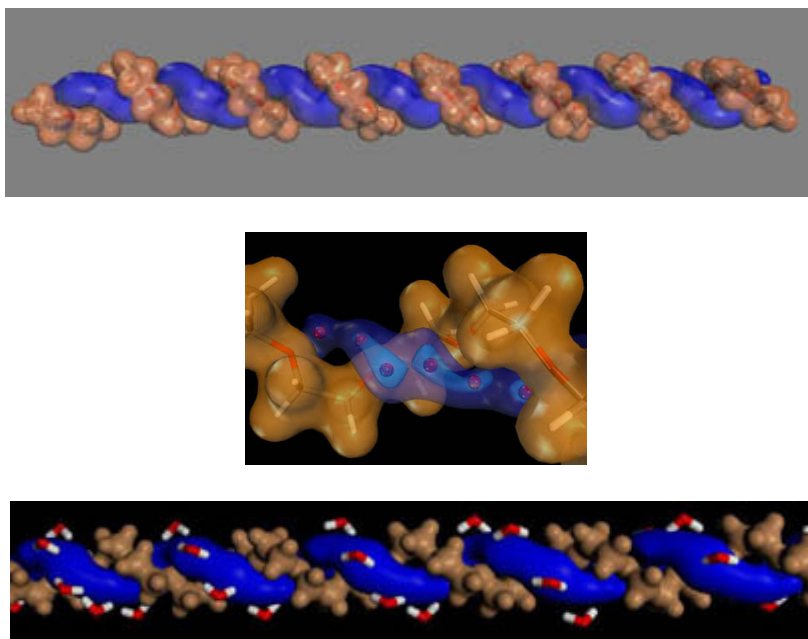


Figure 2.11. $V(r)$ topology predicted a coil of H-bonded water molecules around PEO (Array et., 2004).

In Fig. 2.11, blue and brown contours denote the negative and positive valued zones of the potential (Top), details of a section of the polymer showing the characteristic network of blue contours around the minima (red spheres) (middle), critical points of the oxygen atoms (Bottom).

Bonding of the first solvation shell facilitates the formation of a second water shell bound through cooperative electrostatic interactions between the water O-H bonds and the PEO lone pairs. Using Amorphous Cell, two solvation shells of water (118 molecules) were accommodated around a PEO₂₀ polymer model. It was observed that the water molecules concentrate inside the O-C-C-O core interstitial region neighboring the PEO oxygen atoms, and are depleted around the carbon atoms. Inside the solvation shell, water is H-bonded to PEO as well as to other water molecules. Array's calculations are confirmed the preference for the hydrophilic *trans-gauche-trans* conformation of O-C-C-O dihedral sequences of PEO monomers in water at low temperatures and concentrations, as predicted by previous experimental and theoretical studies (Array et al., 2004).

Water is known to be highly structured and its thermodynamic characteristics are strongly associated with its tetragonal structure. The importance of the reorientation and the restructuring of water molecules upon dissolution of a solute have been stressed (Tasaki, 1999).

In the case of PEG the alternate structure along the polymer chain of ether oxygen and ethylene units provide different associations with water molecules. The association of ether oxygen units of PEG with water has been observed both by viscometric measurements and thermodynamic studies. Recently a structural model has been proposed for PEG/water system. PEG in aqueous solution is surrounded by an extended region with enhanced water structure i.e. a hydration sheath (Ataman, 1987a, 1987b).

2.6. Crystalline Polymers

2.6.1. Dissolution of Crystalline Polymers

A polymer below its second-order transition point is in a thermodynamically unstable state, like a glass or supercooled liquid. When a solvent is absorbed, the transition temperature is lowered, which liberates the excess free energy of the unstable state. Polymers below their transition points should be more readily soluble than their cohesive energy densities would indicate; the thermodynamic equilibria will not be changed, but the release of this excess free energy during the solution process should increase the rate of solution or rate of swelling (Small, 1953).

Partially crystalline polymers have a lower free energy than the corresponding liquid polymers. In order to dissolve them, the free energy necessary to melt the crystals must be supplied. If the polymer is much below its melting point, this free energy will be considerable and the entropy of mixing will not suffice; crystalline polymers are thus, as a rule, appreciably soluble (much below their melting points) only in solvents that have some specific interaction with them, other than dispersion forces, which can only give a positive ΔH of mixing. Such interactions

are usually H-bonding. Evolution of heat on mixing is always evidence of specific interactions (Small, 1953).

The free energy of mixing for crystalline polymers contains terms for the free energy of fusion which may contain terms that account for the loss of crystalline volume fraction of the material. The free energy of fusion may contain terms that account for the loss of crystallite surface area and the mixing of amorphous material with oriented material. These terms would be added to Eq 2.2. The enthalpy of mixing could still be modeled using Eqs. 2.3 or 2.6 (Brandrup et al., 2003). Influence of crystallinity was pointed out from the beginning that the concept of the solubility parameter was applicable only to amorphous (van Krevelen, 1997) or partially crystalline polymers (Barton, 1991).

In order to adapt the method to highly crystalline polymers some way must be found to deal with the heat of fusion (ΔH_m) in the free enthalpy equation:

$$\Delta G_M = \left\{ \Delta H_M + \Delta H_m \right\} - T \left\{ \Delta S_M + \Delta S_m \right\} \quad (2.84)$$

Highly crystalline polymers such as polyethylene and poly(tetrafluoroethylene) are insoluble in all solvents at room temperature. These polymers, however, obey the solubility parameter at temperatures near their melting point, $T \geq 0.9 T_m$ (van Krevelen, 1997). Solvent swelling experiments with crystalline polymers may fit Eq. 2.2, particularly if the solvent is a poor one for the polymer and does not significantly dissolve crystalline regions (Brandrup et al., 2003).

For instance, polyethylene becomes soluble above 80 °C. Furthermore, crystalline polymers do obey the rules even at room temperature in so far as swelling behavior is concerned. This again is a demonstration that crystalline regions serve as apparent (physical) cross-links (van Krevelen, 1997). Some crystalline polymers with strong H-bonding groups can be made to dissolve at room temperature. But in these cases a very specific interaction between polymer and solvent must occur. For example, cellulose is soluble in 70% sulphuric acid and in

aqueous ammonium thiocyanate; nylon 6,6 is soluble in phenol and in a 15% calcium chloride solution in methanol (van Krevelen, 1997).

For completely amorphous polymers there is no enthalpy change of fusion, but when crystalline polymers dissolve, the overall enthalpy change must also provide energy to melt the crystalline polymers. Highly crystalline polymers (e.g. polyethylene, polytetrafluoroethylene) well below their melting points are insoluble in all solvents. While the solubility parameter is extremely useful for predicting the solubility behavior of amorphous polymers, crystalline polymers pose one of the challenges for the solubility parameter method (Burrell, 1968) (Barton, 1975).

Crystallinity can also have an effect on solubility parameters, as was shown by Egawa et al. (1992) where amorphous cefalexin was shown to have higher partial solubility parameters compared to crystalline sample (Greenhalgh et al., 1999).

However, despite the limitations of the approach, solubility parameters may provide a simple and generic capability for rotational selection of carriers in the preparation of solid dispersions (Greenhalgh et al., 1999).

The cohesive pressures of polymers can be evaluated directly by thermodynamic means only for vaporizable materials, although some of the indirect thermodynamic methods can be applied in correlations and estimations. Also, the cohesion parameter concept is directly applicable only to amorphous polymers, and when considering crystalline polymers it is in principle necessary to calculate the activity of the crystalline solid relative to the real or hypothetical amorphous material at the same temperature. In practice the distinction between amorphous and crystalline polymers is not so clear-cut, and non-thermodynamic empirical methods are used frequently in the estimation of cohesion parameters for polymers (Barton, 1990).

The internal pressure of a glassy polymer (a polymer below T_g) is about half the value of that just above T_g , even when considered at constant volume, so cohesive energy and cohesion parameters are likely to play a significant role in the

description of the transition, and have received considerable attention. The general observation is that there is a broad linear dependence of T_g on cohesive pressure, so that polymers with high Hildebrand parameter values tend to have high values of T_g (Barton, 1991).

2.6.2. Percentage Crystallinity Determination by X-Ray Diffraction

The determination of the percentage crystallinity has always been of great importance for the understanding of the material properties of polymeric and fibrous materials. In the study of these type of materials many methods for the determination of the crystalline to amorphous ratio have been developed. One method that is unique in its ability to study the microstructure of materials is x-ray diffraction. X-ray diffraction can be used in a number of different ways to determine the amorphous to crystalline ratio. With the recent increase in the speed of development of new drugs and biotechnologies, the determination of the amorphous to crystalline ratio of an organic material has become increasingly important. The degree of crystallinity, not only affects the long-term stability of the pharmaceutical but also its bio-activity, which could mean the difference between toxic doses and ineffective doses. Clearly, potentially toxic or unstable drug formulations are to be avoided at all costs, making percentage crystallinity determination a critical analysis for the pharmaceutical industry. With these new organic materials, the degree of crystallinity is usually at the two extremes of close to 100% or close to 0%. The challenge is to determine whether the techniques developed for the polymeric materials, which usually lie close to 50% crystallinity, can be applied to the new pharmaceutical materials (Kratos, 1999).

2.6.3. Analytical Strategy Characterization of Solid State Parameters

X-ray diffraction will give very distinct patterns for crystalline and amorphous materials. The diffracting x-rays interact with the variation of electron density inside the sample. For the crystalline material, the periodic repeating electron density will give rise to well defined diffraction peaks whose widths are determined by the crystalline "quality" (Kratos, 1999). "High quality" crystalline material will give rise

to sharp peaks (high frequency) whose widths are limited by the instrumental resolution, while "poor quality" crystalline material will give rise to broader more diffuse diffraction peaks (low frequency). By "quality" is meant the length scale over which the crystal order exists and also the reproducibility of crystalline spacing. Amorphous materials may come in different forms depending on their formation. If it is a glassy amorphous phase, which could be produced from spray drying, then the diffraction signal is the radial distribution of nearest neighbor molecular interactions. On the other hand, if the amorphous phase is derived from the crystalline phase then usually it corresponds to "poor quality" para-crystalline material (Kratos, 1999). Para-crystalline material will either generate extremely broad peaks corresponding to the crystalline peaks or it will diffract intensity corresponding to the diffraction from a single unit cell (Unit Cell Structure Factor). Whether glassy or para-crystalline, the amorphous diffraction is usually a broad very low frequency halo with the occasional harmonic. While we are discussing the different types of diffraction from crystalline and amorphous materials, one source of error to be aware of is the use of spiked material as calibration standards. Spiked material is made by adding pure 100% crystalline material to a 100% amorphous material. The crystalline material used is usually high "quality" giving very sharp well-defined peaks. However, in the real world the crystalline contamination could be nucleated out of the amorphous phase. As such the crystalline component is more like para-crystalline material in nature with very broad peaks. Calibration curves made out of the spiked material cannot be effectively applied to the nucleated material (Kratos, 1999).

3. EXPERIMENTAL

3.1. Materials

The PEG (of different molecular weights) samples used in this thesis were supplied from Aldrich (Tables 3.1-3.2).

Table 3.1. PEG samples used in this study.

Polymer $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$	Firm, Catalog number	Specific gravity at 25 °C (g / ml)
PEG 2000	Aldrich, 29,590-6	1.127
PEG 4600	Aldrich, 37,300-1	1.127
PEG 8000	Aldrich, 20,245-2	1.270
PEG 10000	Aldrich, 30,902-8	1.070

The molecular weight characteristics and distribution of polymer samples are determined by the manufacturer and are given as:

Table 3.2. The molecular weight characteristics of PEGs*.

Molecular Weight	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	H.I.
PEG 2000	1880	2030	2666	1.080
PEG 4600	3940	4040	4099	1.025
PEG 8000	7330	7550	7659	1.030
PEG 10000	10850	10950	11069	1.009

*GPC-RALS study conditions (Solvent: NaH_2PO_4 , NaCl, Column set: 2xG2500PWXL aqueous column, Triple detector: refractive index, right angle light scattering, viscometer, Detector temperature: 35 °C).

Experiments for semi dilute solutions with various degrees of solvent quality, such as θ -, good or marginal solvents have been made. Solvents (H-donor solvent: chloroform; H-acceptor solvents: THF and DMSO; both H-acceptor and -donor solvents: methanol and water) were analytical grade (Table 3.3). The water used as solvent was deionized and bidistilled.

Table 3.3. Solvents used in this study.

Solvents	Firm, Catalog number
chloroform	Merck, 1.02431
THF	Merck, 1.08114
DMSO	Merck, 1.16743
methanol	Merck, 1.06008
water	-

3.2. Experimental Methods

3.2.1. Calculations of Solubility Parameters

The calculated total solubility parameter and solubility parameter components of polymers and solvents were obtained from their chemical structures of repeating units by using group contribution methods of VKH, Hoy, Breitzkreutz, Small and by using van-der Waals volumes of atoms by Askadskii. Using calculated solubility parameter components for polymer and solvents, the 2-D and 3-D plots of polymer were drawn. These modeling was performed by using 3ds Max and OriginPro 7.5 softwares.

3.2.2. Viscosity Measurements

The PEG samples used in this thesis were supplied from Aldrich. The commercial molecular weights of polymer samples were given as, 2000, 4600, 8000 and 10000 g/mol. All the polymer samples were dried and stored *in vacuo* at least for 24 h at room temperature just before preparation of the solution and were used without further purification. All the solutions were prepared by standing in the dark without shaking at room temperature for 24 hours to minimize degradation of the polymer samples.

The viscometric measurements were carried out at 25°, 30°, 35° and 40 °C, using an Ubbelohde type of capillary viscometer. The temperature of thermostat was controlled within a range of ± 0.1 °C, and the flow times were measured with a digital accuracy of ± 0.01 s. The concentration dependence of the viscosity results

of dilute polymer solutions (in a 2.5-0.2 gDL⁻¹ concentration range) was followed by the well-known Huggins equation. For intrinsic viscosity studies, a stock solution was prepared from which dilutions were made such that the maximum concentration was approximately 1/5 $[\eta]$, where $[\eta]$ is in dL/g (Keary, 2001). Duplicate measurements, made on fresh portions of the solutions, agreed within 0.1 second. The average elution times of solutions were determined after several measurements.

Gennes et al. (1979) determined a regime as shown below for the formulation of concentration regimes in a good solvent,

$$\begin{aligned} 1 < c[\eta] < 10 & \quad \text{in semidilute (coil overlap)} \\ c[\eta] \geq 10 & \quad \text{in concentrated (entanglement)} \end{aligned}$$

This regime appears in this work as follows

$$0.2 < c[\eta] < 0.6$$

Thus, neither coil overlap nor entanglements will be observed.

3.2.3. Kinetic Energy Correction

Poiseuille Equation,

$$\eta = \frac{\pi(h\rho_S g)R^4}{8v\ell} t - \frac{mv\rho_S}{8\pi\ell} \frac{1}{t} \quad (3.1)$$

where η is the absolute viscosity, h is the height of solvent in capillary, ρ_S is the liquid density, g is the gravitational acceleration, R is the radius of capillary tube, v is the viscometer bulb volume, ℓ is the length of capillary tube, t is the efflux time, m is a number which characterizes the kinetic energy contribution.

Kinematic viscosity (ν) is given by the equation below:

$$\nu = \frac{\eta}{\rho_S} \quad (3.2)$$

According to this, the above equation is rearranged as:

$$\nu = \underbrace{\frac{\pi h g R^4}{8 \nu \ell}}_A t - \underbrace{\frac{m \nu}{8 \pi \ell}}_B \frac{1}{t} \quad (3.3)$$

and simplifying it more, ν maybe written as $\nu = At - B\frac{1}{t}$. With the neglect of the term $B\frac{1}{t}$, $\nu = At$ equation is obtained. Due to the numerical closeness of $\frac{t_A}{t_B} = \frac{\nu_A}{\nu_B}$ ratios of two different solvents (A and B), one can decide for requirement of a kinetic energy correction. If the ratios were distinct from each other, the neglect of term $B\frac{1}{t}$ can not be done.

The kinetic energy control of the Ubbelohde type capillary viscometer has been achieved in two different solvents (benzene and toluene) and at two different temperatures.

At 25 °C, $\nu_B/\nu_T = 1.0766$ $\bar{t}_B/\bar{t}_T = 1.0770$

At 30 °C, $\nu_B/\nu_T = 0.0600$ $\bar{t}_B/\bar{t}_T = 0.0603$.

The ratio values have been found to be very close to each other, thus, no requirement is needed for kinetic energy correction (In both solvents, kinematic viscosity values have been taken from International Critical Tables (Washburn, E.W., 2003)).

3.2.4. Statistical Analysis

Statistical analysis has been applied to linear behaviors such as $y = a + bx$ (KSF, ISK, Berry and B vs $1/T$) and $y = a - bx$ ($(1/2-\chi)$ vs T and A_2 vs T); subsequently, the results have been evaluated employing Origin 7.5 computer program.

The evaluation of intercept and slope values together with their standard error values have been followed by the calculation of t -values (Fleming and Nellis, 1994).

Four different molecular weights and four different temperatures are employed to be substituted in the equation used. Degrees of freedom has been taken as; $n-1=4-1=3$. At this degree of freedom, the probability of right hand side values have been obtained from the t -table as $t_{0.05} = 2.3534$ for $P = 0.05$. This value indicates the reliability of these equations up to 95%. The calculated t -values being larger than 2.3534 strongly exhibit the validity of the employed model (equations, in this study). Another criteria is that, near is the $\text{Prob} > |t|$ to zero, much more valid will the employed model be assumed. In the equations we use, the high correlation coefficient ($r^2 > 0.96$), low standard deviation, t value > 2.3534 and $\text{Prob} > |t|$ values being closer to zero have been considered and thus the reliability of the parameters obtained from the intercept and slope values has been determined whilst those values not complying with these criteria are quitted.

3.2.5 Determination of Density and Specific Volume

The densities of solutions of PEG with molecular weights of 2000, 4600, 8000 and 10000 g/mol were measured. The density measurements were carried out using a 10 mL glass pycnometer. Densities of the polymer samples were determined in water, THF, DMSO, chloroform and methanol using a pycnometer at 25°, 30°, 35°, and 40 °C. A constant temperature water bath was used to control the temperature at an accuracy of ± 0.1 K. The reproducibility of density measurements was estimated to be ± 0.02 gcm⁻³.

The volume of the pycnometer was calibrated as a function of temperature using double-distilled water. The densities of water at 25°, 30°, 35°, and 40 °C were taken from Perry's Chemical Engineering Handbook (Perry and Green, 1984). For measurement of density, the pycnometer was filled with the solution and immersed in the water bath. After thermal equilibrium was achieved, the pycnometer was

removed from the bath and then cleaned, dried and weighed quickly. Densities were determined from measurements of the mass of the samples and the pycnometer volume. Specific volume was determined from the reciprocal of density.

3.2.6. Preparation of Solid Samples

The concentration of PEG in water, chloroform, DMSO, THF and methanol solutions was changed between 1.0 - 0.2 g/dL according to molecular weight of polymer. The polymer samples for FTIR, Raman and XRD spectra were prepared by solvent evaporation at room temperature and dried at 25°C under vacuum for 1-10 days depending on the nature of solvent.

3.2.7. X-ray Diffraction Measurements (XRD)

X-ray diffraction patterns were taken at Hacettepe University, in Physics Engineering Department by using a Rigaku DMAX 2200 X-ray Powder Diffractometer in the $2\theta = 5^\circ - 60^\circ$ range with CuK_α radiation. This diffractometer consists of a RINT2000 wide angle goniometer with a $1/2^\circ$ dispersion slit, a 0.73 mm scatter slit and a 0.3 mm receiving slit. The Cu anode X-ray tube was operated at 40kV and 36mA in combination with a Ni filter to give monochromatic CuK_α X-rays. Measurements were taken from 5° to 60° in the Bragg's angle 2θ scale at a step size of 4° per min for qualitative analysis. Diffractograms were taken at room temperature consecutively.

Crystalline and amorphous regions have been found by Polynomial Regression method through Microsoft Office Excel 2003 program and subsequently, percentage crystallinities were evaluated.

3.2.8. FTIR Measurements

The Fourier transform infrared (FTIR) spectra were recorded on a ATI UNICAM Mattson 1000 FTIR spectrometer at room temperature. The spectra were collected

over the range 4000-400 cm^{-1} by averaging 40 scan at a maximum resolution of 16 cm^{-1} .

Solid PEG samples (0.01 g) were finely ground and analyzed by dispersing them in 0.09 g of dried spectroscopic grade KBr (Merck) by pressed-disc technique.

3.2.9. Raman Measurements

Raman spectra of samples were recorded using Labram 800 HR Raman spectrometer (Jobin Yvon) with a He-Ne Laser source emitting at 633 nm, 600-1200 grooves/mm holographic grating and a charge coupled device (CCD) detector. Raman spectra were obtained in 250 s integrations with an average of three scans. Spectra were recorded with reproducibility within 1 cm^{-1} . Hole: 400 μm , Slit: 150 μm . Resolution: 0.1 μm .

4. RESULTS AND DISCUSSION

4.1. Comparison of Hansen's and Hoy's Solubility Parameter Components for Solvents

The values of Hansen's components for solvents were calculated from a large number of solubility data sets (Brandrup et al., 2003). Hansen's parameters for solvents used in this thesis are listed in Table 4.1.

Table 4.1. Hansen solubility parameters of studied solvents at 25 °C*.

Solvent	Molar volume (cm ³ /mol)	Solubility parameters (MPa ^{1/2})			
		δ_d	δ_p	δ_h	δ_t
THF	81.7	16.8	5.70	8.0	19.4
chloroform	80.7	17.8	3.10	5.70	19.0
DMSO	71.3	18.4	16.4	10.2	26.6
methanol	40.7	15.1	12.3	22.3	29.7
water	18.0	15.5**	16.0**	42.4**	47.9

* Brandrup et al., 2003.

** values uncertain.

The Hansen parameters give improved agreement with the data but are still not completely accurate in predicting solution thermodynamics for every system. Peiffer (1980) has related dispersion, polar and induced solubility parameters to intermolecular forces and molecular size. The dispersive component increases with molecular size, while the polar component decreases with molecular size (Brandrup et al., 2003).

Hoy's values of δ_t , δ_d , δ_p and δ_h for solvents used in this study are included in Table 4.2 (Barton, 1991).

Table 4.2. Hoy's solubility parameters for studied solvents at 25 °C.

Solvent	Solubility parameters (MPa ^{1/2})			
	δ_d	δ_p	δ_h	δ_t
THF	11.0	13.7	6.3	18.7
chloroform	13.3	11.0	6.7	18.5
DMSO	-	-	-	-
methanol	11.6	13.0	24.0	29.7
water	12.2	22.8	40.4	48.0

Hoy's dispersion components, δ_d , being evaluated by difference, may be considered less reliable than those of Hansen, which were evaluated directly by homomorph methods; the homomorph of a polar molecule is a nonpolar molecule having very nearly the same size and shape. On the other hand, Hansen's method introduces small H-bonding components to the aromatic liquids. The H-bonding components in Hansen's values for aromatic liquids are not supported (Barton, 1991). Currently two approaches, the Hoy and the Hansen approaches for solvents evoked considerable interest for predicting the solubility.

4.2. Determination of Solubility Parameter of PEG by Atomic Group Contribution Methods

4.2.1. Calculation of total solubility parameter of PEG by Small's method

Small has proposed that the solubility parameter of the polymer can be evaluated by three different ways (Eqs. 2.23, 2.24 and 2.25) and that the solubility parameters calculated by each method will yield the same numerical number.

$$1) \delta_t = \left(\frac{\Delta E_i^v V_i}{V_i^2} \right)^{1/2}$$

$$2) \delta_t = \frac{\sum F_j}{V_i}$$

The value of the solubility parameter of the polymer evaluated by the first and second approaches nearly appear to be the same (19.1 and 19.2 $(Jcm^{-3})^{1/2}$) (Table 4.3).

Table 4.3 Calculated total solubility parameters of PEG by Small's methods (Eqs. 2.23, 2.24).

Methods	Structural Groups	E_i^v J/mol*	V_i^* cm^3 / mol	F_i^{**} $J^{1/2} cm^{3/2} mol^{-1}$	δ_t $(Jcm^{-3})^{1/2}$
1)	-CH ₂ (2)	2 x 4940.7	2 x 16.1	-	-
	- O	3349.6	3.8	-	-
	Total	13231.0	36.0	-	19.2
2)	-CH ₂ (2)	-	2 x 16.1	2 x 272	-
	- O	-	3.8	143	-
	Total	-	36.0	687	19.1

* Small, 1953.

** Brandrup et al., 2003.

In the third approach, Small has also considered the density and molecular weight of the polymer for determining the solubility parameter of the polymer.

$$3) \delta_t = \frac{\rho_i \Sigma F_j}{M_i}$$

Here, M_i is molecular weight of polymer, δ_t is the solubility parameter of the repeating unit in the polymer (Brandrup, et al., 2003). According to this equation, the value determined by considering the polymer molecular weight is expected to give the solubility parameter of the repeating unit. These magnitudes, when multiplied by the number of repeating units of the polymer ($\bar{M}_w / 44.1$) will yield the solubility parameter of the polymer. These values are presented in Table 4.4. The solubility parameter thus evaluated ($\sim 18 (Jcm^{-3})^{1/2}$) with this method is found to be very similar to those determined by the other two methods.

Table 4.4. Calculated total solubility parameters of PEG by Small's method (Eq. 2.25).

Method	Polymer	$\bar{M}_w$	$\bar{n}$ $(\bar{M}_w / 44.1)$	ρ at 25 °C (g / ml)	δ_t $(Jcm^{-3})^{1/2}$
3)	PEG 2000	2030	46	1.127	17.6
	PEG 4600	4040	92	1.127	17.7
	PEG 8000	7550	171	1.270	19.8
	PEG 10000	10950	248	1.070	16.6
average					18.00

These equations (Eqs. 2.23, 2.24 and 2.25) remind one the number of repeating units of a polymer may well be determined by algorithmic calculations. If the numerical value obtained from the first and second equations is found to be reliable than this value showed also be equal to the solubility parameter of the third equation. If the denominator value in the third equation is considered as the product of the molecular weight of the repeating unit with the number of repeating units, the latter may be very easily evaluated. In this respect, the number of repeating units, have been calculated as 50, 99, 165 and 285 for four polymer samples (PEG 2000, 4600, 8000 and 10000), respectively (Table 4.4). These values are found to be very similar to those obtained when the weight average molecular weight of the polymer is divided into the molecular weight of the repeating unit.

The total solubility parameters of PEG evaluated agree quite well with literature values, While Otozai ve Tohyama (1976) have found this value as $18.8 (Jcm^{-3})^{1/2}$ for PEG 6000 by using Small approach, Kawakami et al. (1976) have evaluated these values as 18, 19.1 and 18.9 for PEG 600, 1000 and 4000, respectively. The values found for lower molecular weight PEGs (200 and 400 g/mol) are 19.1 and 18.4 (Takamiya et al., 1959; Vaughan, 1985).

In this study, the solubility profiles of PEG have been investigated by five different solvents. Taking the numerical resemblance of δ_t values of the polymer and the solvent as the basic criteria, necessary evaluations will be made. In the coming sections, the comparison of δ_t values determined by different methods will be discussed in detail.

4.2.2. Calculation of Total Solubility Parameter of PEG by Askadskii's Method

The total cohesive energy, van der Waals volumes and total solubility parameters are determined through Eq. 2.39 are given in Tables 4.5 and 4.6 for PEG and selected five different solvents.

Table 4.5. Cohesive energy and van der Waals volume values of atoms and intermolecular interactions in PEG calculated according to Askadskii.

Atoms and type of intermolecular interaction	$\sum_i E_i^*$ (J / mol)	$\sum V_i^W$ ($\text{\AA}^3$)
2 x C	2 x 2304.15	2 x 16.2
4 x H	4 x 199.6	4 x 2
1 x O	1 x 596.6	1 x 3.4
Dipol-dipol interaction	6790.6	-
Total	12793.8	43.8

Table 4.6. Total cohesive energy, total van der Waals volume and solubility parameter values calculated according to Askadskii of PEG and studied solvents.

	$\sum_i \Delta E_i^*$ (J / mol)	$\sum_i \Delta V_i^W$ ($\text{\AA}^3$)	δ_t (Jcm^{-3}) ^{1/2}
PEG	12793.8	43.8	22.0
H ₂ O	24225	17	48.2
methanol	20138	37	30.2
DMSO	30042	70	26.7
chloroform	20080	66	22.5
THF	23488	87	21.2

If a simple comparison is to be constructed with respect to the solubility parameters of polymer-solvent systems, it is clearly observed that the difference between water and methanol is great whereas in THF and chloroform this gap relatively decreases.

The specific surface cohesive energies, molar volumes, surface tensions of the PEG and solvents and interfacial tensions for PEG/solvent systems displayed in Table 4.7.

Table 4.7. Calculated physical characteristics of related solvents and PEG according to Askadskii.

	δ^*	V_m cm^3 / mol	γ_{s-p} (dyn / cm)	γ (dyn / cm)	
				In this work (calc.)	Reference (exp.)
PEG	1028.7	38.7	-	40.4	42.9 ^a , 42.9 ^b , 42.5 ^c
H ₂ O	3621.7	18.0*	5.42	65.4	
methanol	1826.8	40.7*	0.43	33.1	
DMSO	1767.1	71.3*	1.14	50.7	
THF	1196.3	81.7*	1.22	34.3	
chloroform	1229.5	80.7*	0.94	32.8	

* Brandrup et al., 2003 (Hansen's values for solvents are used).

^a Rastogi, 1971, ^b Wu, 1974 and Roe, 1969, ^c Kasemura and Hata, 1976.

The calculations achieved with regard to surface tensions yield the results for the solubility behavior of PEG/solvent systems displayed in Table 4.8.

Table 4.8. The results of the application of Askadskii's solubility criterion for PEG/solvent pair systems.

Solvent	ϕ	a'	Left side of formula μ	Right hand side of formula	Solubility of PEG
	(dimensionless)				
H ₂ O	0.98	0.08	0.21	1.03	Soluble
methanol	1.00	0.01	0.53	1.20	Soluble
DMSO	0.99	0.02	0.68	1.19	Soluble
chloroform	0.99	0.03	1.07	1.18	Soluble
THF	0.99	0.04	1.08	1.17	Soluble

The evaluations display that PEG may dissolve in these selected five different solvents. However, an interesting point is that μ values evaluated from THF and chloroform calculations are very similar to those found from the right hand side of the equation.

According to Askadskii (2003), solubility must be observed if calculated values $\mu < 2\rho\phi\left(\phi - \sqrt{\phi^2 - 1 + a'}\right)$ are greater or equal to the value of $\mu = \delta_p^2 / \delta_s^2$. It is clearly observed that this condition is provided in THF and chloroform.

4.2.3. Calculation of δ_t from Molar Attraction Constants by VKH's Method

The dispersion and polar components of the molar attraction constant (F_{di} and F_{pi}) and contribution of the H-bonding forces to the cohesive energy (E_{hi}) calculated from the VKH method for the structural groups of PEG are given in Table 4.9.

Table 4.9. Solubility parameter component s of group contributions for PEG*.

Structural Groups	F_{di} ($J^{1/2}cm^{3/2}mol^{-1}$)	F_{pi} ($J^{1/2}cm^{3/2}mol^{-1}$)	E_{hi} (J/mol)	V (cm^3mol^{-1})
-CH ₂	270 (x2)	0	0	15.55 (x2)
-O-	100	400	3000	6.45
Total	640	400	3000	37.55

* van Krevelen, 1997.

The calculated values of δ_d , δ_p and δ_h along with δ_t are given in Table 4.12 and compared with the values obtained by the Hoy's and Breitskreutz's system together.

4.2.4. Calculation of δ_t from Molar Attraction Constants by Hoy's Method

As mentioned in Part 2.3.3.3, Hoy's method is an alternative method to determine individual values of δ_d , δ_p and δ_h which is somewhat different from that of VKH.

The values of various groups are given in Table 4.10.

Table 4.10. Solubility parameter component group contributions and Lydersen correction calculated by Hoy's system for PEG.

Structural Group	$F_{t,i}$ ($J^{1/2}cm^{3/2}/mol$)	$F_{p,i}$ ($J^{1/2}cm^{3/2}/mol$)	V_i (cm^3mol^{-1})	$\Delta_{T,i}^{(P)}$ -
-CH ₂	269 (x2)	0	15.55 (x2)	0.020 (x2)
-O-	235	216	6.45	0.018
Total	773	216	37.55	0.058

Hoy, 1985, 1989.

Substituting the values from Table 2.3 and Table 4.10, $\alpha^{(P)}$ is obtained as 1.2 for PEG. The number of repeating units per effective chain segment of the polymer ($\bar{n}$) is obtained as 8.7 for PEG. The contributions of δ_d , δ_p and δ_h are calculated from "Expressions for δ_t and δ -compounds" (Table 2.3).

The calculated values of δ -components and δ_t are given in Table 4.12.

4.2.5. Calculation of δ_t from Molar Attraction Constants by Breitzkreutz's Method

Variations from the original contributions have been added to Table 4.11 (Breitzkreutz, 1998).

Table 4.11. Contributions to molecular forces and molar volume from molecular structural groups of PEG*.

Structural Group	$F_{d,i}$	$F_{p,i}$	E_{hi}	V_i
	($J^{1/2}cm^{3/2}/mol$)	($J^{1/2}cm^{3/2}/mol$)	(J/mol)	(cm^3mol^{-1})
-CH ₂	270 (x2)	0	0	15.55 (x2)
-O-, (at adjacent C-atoms) ^a	120	530	3500	4.5
Total	660	530	3500	35.6

* Breitzkreutz, 1998.

^a Deviating contributions from Fedors' and van Krevelen/Hofter's values.

It appears from Table 4.12 that Hoy's and VKH methods give similar δ_t values in this particular case, whereas the value by Breitzkreutz's system is not very close.

4.3. Comparison of Solubility Parameter Components Calculated for PEG According to VKH, Hoy and Breitzkreutz's Methods

Solubility parameter components have been calculated by three different algorithmic methods. δ_d , δ_p , δ_h and δ_t values evaluated with respect to VKH, Hoy and Breitzkreutz approaches, respectively, are given in Table 4.12.

Table 4.12. Solubility parameter components calculated for PEG according to different methods.

	Solubility parameter components (Jcm^{-3}) ^{1/2}					
	δ_d	δ_p	δ_h	δ_t	δ_v	δ_a
VKH	17.0	10.7	8.9	22.0	20.1	13.9
Hoy	16.8	10.2	8.6	21.4	19.7	13.3
Breitzkreutz	18.5	14.9	9.9	25.8	23.8	17.9

According to VKH approach (Eqs. 2.26, 2.27 and 2.28), total solubility parameter determined with regard to the solubility parameter components of PEG has been found as $22 (Jcm^{-3})^{1/2}$. The total solubility parameter and solubility parameter components calculated with regard to Hoy have been found very close to those obtained from VKH approach. The magnitudes of solubility parameter components have also been observed to be very similar to each other in VKH and Hoy approaches. The solubility parameter components and δ_t value (Eqs. 2.36-2.38) proposed by Breitskreutz have been found greater when compared to other methods (Table 4.12).

The purpose of the present investigation was to test the current approaches (Small, VKH, Hoy, Breitskreutz and Askadskii) for estimating the solubility parameter of PEG and solvents. These approaches are largely empirical, employing statistical analysis of the experimental results to estimate the solubility behavior.

4.4. Calculation of Solubility Parameter Difference for PEG-Solvent Pair Systems

The difference of polymer-solvent solubility parameters are taken as a measure of mixing (Eq. 2.49). In case this difference is small the idea of mixing probability is widely accepted.

The condition of solubility parameter difference being less than 5 is assumed to be the limit of solubility (van Krevelen, 1997). $\overline{\Delta\delta}$ values calculated by considering Hansen's values as the solubility parameter of solvents have been presented in Table 4.13. According to VKH and Hoy, THF appears to be a good solvent whilst DMSO is a good solvent with respect to Breitskreutz.

Table 4.13. $\overline{\Delta\delta}$ values for different PEG/related solvent system.

		$\overline{\Delta\delta}, (Jcm^{-3})^{1/2}$		
		VKH	Hoy	Breitkreutz
Hansen's Parameters * ($Jcm^{-3})^{1/2}$)	THF	5.00	4.50	9.50
	DMSO	6.00	6.60	1.50
	chloroform	8.30	7.70	12.5
	methanol	13.6	14.0	13.1
	water	33.9	34.4	32.6

* Hansen solubility parameters for solvents are taken from Brandrup and Immergut, 1989.

If one has to give an order for the solvents with respect to their $\overline{\Delta\delta}$ differences evaluated by three different methods;

According to VKH method,

$\overline{\Delta\delta}$; THF > DMSO > chloroform > methanol > water.

According to Hoy method,

$\overline{\Delta\delta}$; THF > DMSO > chloroform > methanol > water.

According to Breitzkreutz method,

$\overline{\Delta\delta}$; DMSO > THF > chloroform > methanol > water.

The order of this sequence clearly reveals that water is placed as the last solvent whereas DMSO and THF are placed in the first two rows due to their H-acceptor natures.

Table 4.14 summarizes the calculated differences ($\overline{\Delta\delta}$) between Hoy's solubility parameter components for solvents and those of VKH, Hoy and Breitzkreutz for PEG.

Table 4.14. The difference between the polymer and solvent solubility parameters ($\overline{\Delta\delta}$).

		$\overline{\Delta\delta}, (Jcm^{-3})^{1/2}$		
		VKH	Hoy	Breitkreutz
Hoy's Parameters* (Jcm^{-3}) ^{1/2}	THF	4.40	4.10	7.20
	DMSO**	6.00	6.60	1.50
	chloroform	7.30	7.20	8.40
	Methanol	16.2	16.5	15.8
	water	34.1	34.6	32.1

* Hoy's solubility parameters of solvents except DMSO is taken from CRC Handbook, 1991.

** Hansen's solubility parameter of DMSO is taken from Brandrup and Immergut, 1989.

According to Table 4.14, THF appears to be the best solvent with respect to VKH and Hoy and water seems to be the worst solvent and the following sequences have been found due to decreasing the order of solvents.

According to VKH method,

$\overline{\Delta\delta}$; THF > DMSO > chloroform > methanol > water.

According to Hoy method,

$\overline{\Delta\delta}$; THF > DMSO > chloroform > methanol > water.

According to Breitkreutz method,

$\overline{\Delta\delta}$; DMSO > THF > chloroform > methanol > water.

In general, the graphical method (Eqs. 2.14 and 2.16) does not account for the known influence of molar volume and cohesive energy density of solubility, and incorrectly assumes a linear relationship between the solubility parameter difference and solubility (Brandrup et al., 2003).

4.5. Comparison of Solubility Parameter Values of PEG

δ_t values determined by various research groups for PEG are displayed in Table 4.15.

Table 4.15. Solubility parameters together with calculated and experimental data taken from different references for the PEG.

$\delta_t, (Jcm^{-3})^{1/2}$		References
Calculated	Experimental	
Small; 18.0-19.1	18.0-23.7 (Mw:200-6000g/mol)	Sakellariou et al., 1986*.
Hoy; 19.7-21.5	-	Sakellariou et al., 1986*.
VKH; 22.4-26.1	-	Sakellariou et al., 1986*.
17.8	19.9 $\pm$ 2 (IPGC)	Mieczkowski, 1991.
	20.2 $\pm$ 2 (IPGC)	DiPalaBaranayi, 1982.
	19.64 (IPGC)	Galin, 1983.
	20.1-20.9 (GC)	Fernández-Berridi et al., 1982.

*For detailed information; Vaughan, 1985; Takamiya et al., 1959; Kawakami et al., 1976; Otozai and Tohyama, 1976.

In this work the total solubility parameter values for PEG evaluated by different methods are given in Table 4.16.

Table 4.16. Solubility parameters calculated in this work for PEG.

Method	$\delta_t, (Jcm^{-3})^{1/2}$
Small (method 1, Eq. 2.23)	19.1
Small (method 2, Eq. 2.24)	19.2
Small (method 3, Eq. 2.25)	18.0
Askadskii	22.0
VKH	22.0
Hoy	21.4
Breitkreutz	25.8

When δ_t of PEG is determined by calculations with regard to different approaches the magnitudes are found in a wide range (18-26 $(Jcm^{-3})^{1/2}$). It is reported that this magnitude is $\sim 20 \pm 2 (Jcm^{-3})^{1/2}$ when experimentally determined. According to results of calculations, the total solubility parameters determined with regard to other two approaches apart from Breitkreutz have been found as

$20 \pm 2 (Jcm^{-3})^{1/2}$. This result is in quite good agreement with those previously calculated and experimentally determined values.

4.6. Three- and Two-dimensional Approaches to PEG Solubility

4.6.1. 3-D Hansen Graphics

For the construction of 3-D solubility profile, only the δ_d , δ_p and δ_h values of 17.0, 10.7 and 8.9 with regard to VKH have been employed since the solubility parameter components of PEG obtained from both VKH and Hoy methods are very close to each other ($\delta_d=16.8$, $\delta_p= 10.2$ and $\delta_h= 8.6$ for Hoy).

The sphere radii of the polymer observed for the polymer-solvent couple using the solubility parameter components of the polymer calculated by VKH method and Hansen solubility parameters of the solvent (Table 4.17) have been subsequently calculated from the following equation (Eq. 2.17).

$$R_{polymer-solvent} = [(\delta_{d,S} - \delta_{d,P})^2 + (\delta_{p,S} - \delta_{p,P})^2 + (\delta_{h,S} - \delta_{h,P})^2]^{1/2}$$

Table 4.17. Solubility parameter components needed for plotting Hansen solubility sphere.

		δ -components, $(Jcm^{-3})^{1/2}$		
		δ_d	δ_p	δ_h
PEG (according to VKH)		17.0	10.7	8.9
Hansen's Parameters $(Jcm^{-3})^{1/2}$	DMSO	18.4	16.4	10.2
	MeOH	15.1	12.3	22.3
	water	15.5	16.0	42.4
	THF	16.8	5.70	8.00
	chloroform	17.8	3.10	5.70

According to the calculations employing the above equation the radius of PEG sphere is found as

$$R_{polymer} = R_{d,p,h} = \delta_t = 22 (Jcm^{-3})^{1/2}$$

Table 4.18. Interaction radius and Hansen's solubility criterion for PEG/solvent pair.

solvents	$R_{polymer/solvent}$		$R_{polymer}$	$R_{polymer/solvent} < R_{polymer} \Rightarrow$ soluble
water	33.9	>	22.0	nonsoluble
methanol	13.6	<	22.0	soluble
DMSO	6.01	<	22.0	soluble
chloroform	8.30	<	22.0	soluble
THF	5.10	<	22.0	soluble

The distance $R_{polymer-solvent}$ is compared with the interaction radius of PEG ($R_{polymer}$) sphere for the solubility criterion. If $^iR < ^jR$, there is a high likelihood of the solvent dissolving the polymer.

When the interaction radius of the polymer is compared with those of polymer-solvent, solubility profiles appear to be quite lightening. Here, if one compares $R_{polymer-solvent}$ and $R_{polymer}$ radii, the four other solvents apart from water seem to remain within the radius of the sphere with $R_{polymer}$ and thus dissolve the polymer. However, the same argument is not true for water.

The "sphere" is projected onto the three planes passing through two axes and the origin, to provide circles in 2-D graphs, as illustrated in Figure 4.1. It shows the solubility sphere for PEG ($\delta_d = 17.0$; $\delta_p = 10.7$; $\delta_h = 8.9$; $R = 22$, all in Hildebrands).

As a consequence of the observation of this 3-D profile, THF and DMSO occupy the first two rows in the order of solubility of the polymer (Fig. 4.1).

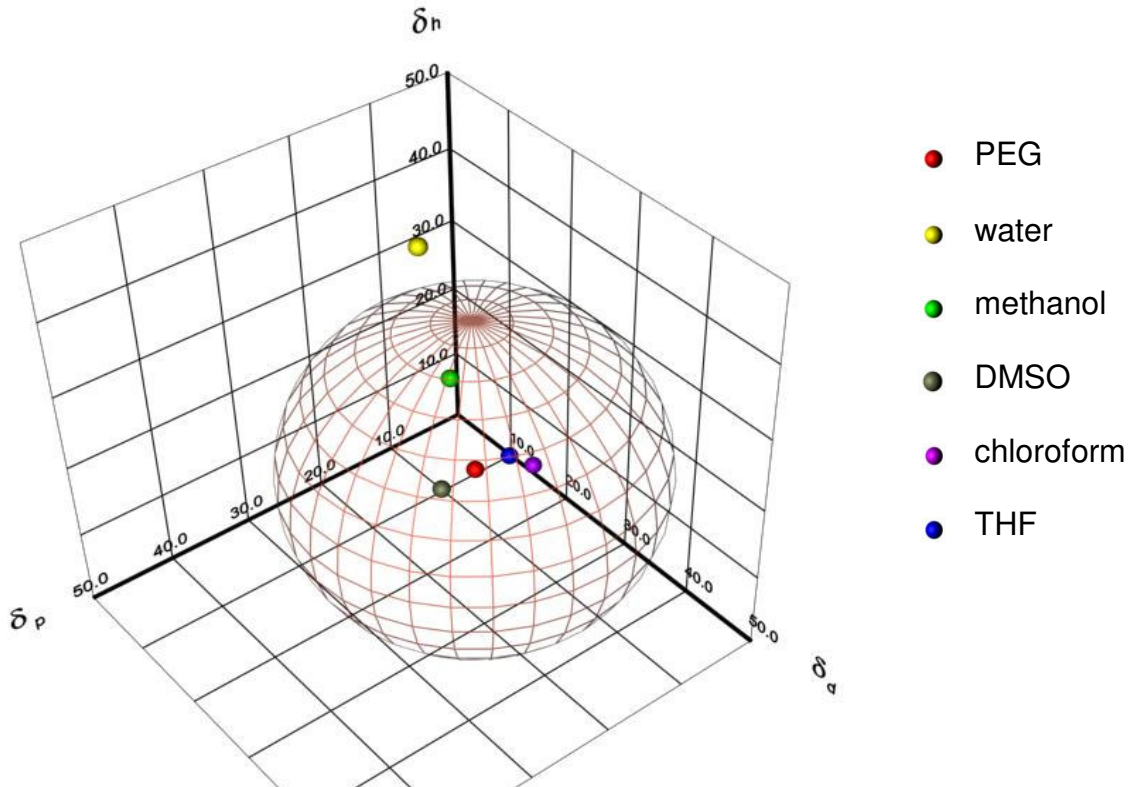


Figure 4.1. The Hansen parameter solubility sphere for PEG and studied five solvents ($\delta_d = 17.0$; $\delta_p = 10.7$; $\delta_h = 8.9$; $R = 22$ for PEG).

When 3-D profile is reduced to 2-D graphs (Fig 4.2) the solubility parameter components are employed as couples forming $\delta_h - \delta_p$, $\delta_h - \delta_d$, $\delta_p - \delta_d$ planes. In fact, each plane is a mirror image of the sphere in 3-D profile. Again, the order of the sequence with respect to the solubility of the polymer has been determined to be the same as that of previously determined. The solubility parameter of water and the solubility parameter component of the polymer lie in the $\delta_h - \delta_p$ plane. The polymer solubility sphere seems to be more likely being involved within $\delta_h - \delta_p$ plane, however, δ_d values of polymer and solvent are somewhat very close to each other ($\delta_{d,PEG} = 17$ and $\delta_{d,water} = 15.5$) (Rosen, 1993) when $\delta_p - \delta_d$ plane is considered which creates a wrong opinion about the solubility of PEG in water.

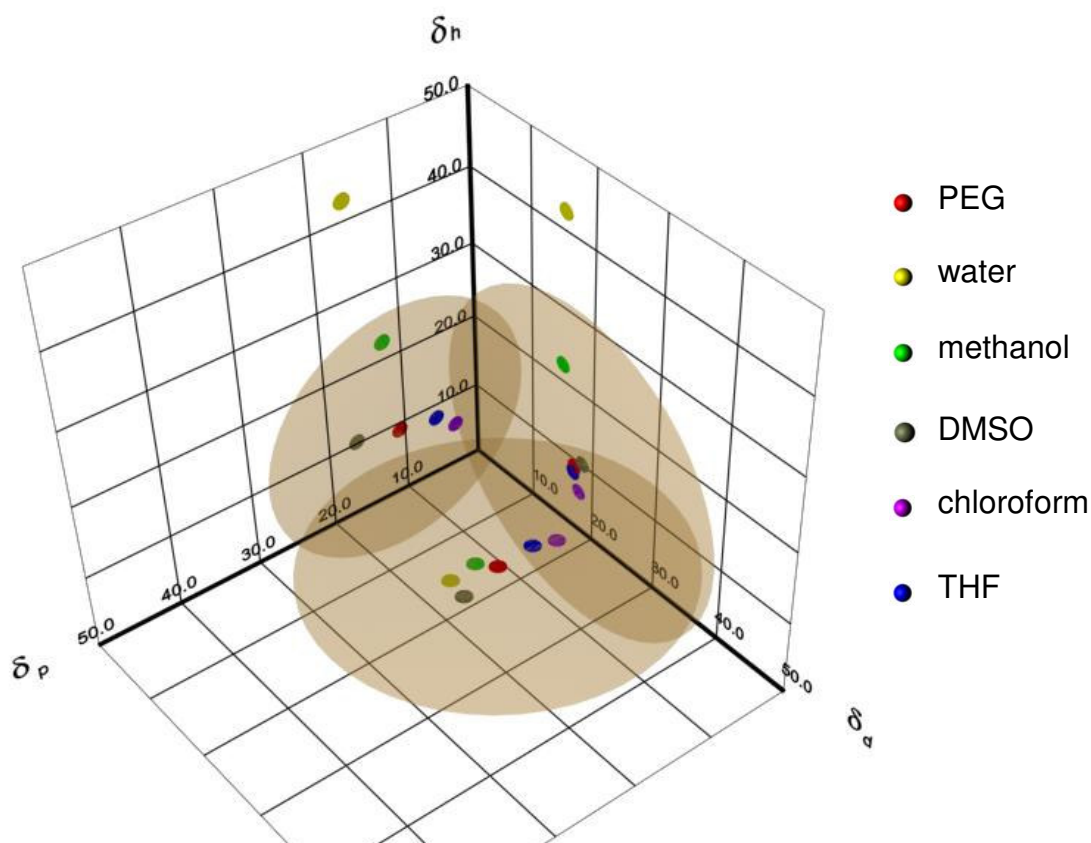


Figure 4. 2. The Hansen parameter solubility sphere's projections on three axial planes for PEG and studied five solvents.

According to Eq. 25, if ${}^i j R / {}^j j R < 1$, solvent i is a good solvent for polymer j . Thus, this ratio expressed as relative energy difference is less than one for all other PEG/solvent systems except for PEG/water couple.

The comparison of 3-D and 2-D profiles will be given in the later sections after the investigation of 2-D graphs (Table 4.24).

The three-component solubility parameter is theoretically more correct, but the practical results are no better than those given by two-component parameters. In all discussions so far, solvents have been specified as points and solutes as volumes or areas in multicomponent parameter space. It would probably be preferable to treat the solvents also as volumes, even in liquid-liquid interactions, accepting that the solubility parameter does depend on the system used to measure it.

4.6.2. Two-Dimensional Approaches to PEG Solubility

When deriving Eq. 2.6, Hildebrand had only considered dispersion forces between structural units. However, for most liquids and amorphous polymers the cohesive energy density also depends on the interaction of polar groups and H-bonding and the total is given as Eq. 2.4 contributing as dispersion forces, polar forces and H-bonding which may be replaced by the corresponding Eq. 2.5 for the solubility parameter.

An extension of this method in a “3-D” system (dispersion, polar interactions and H-bonds) may well be achieved; however, the method is rather impractical since it involves the dipole moments of a number of solvents in addition during comparison of solute-solvent systems. Thus, for a practical comparison a “2-D” ($\delta_v - \delta_h$, $\delta_p - \delta_h$, $\delta_t - \delta_h$, $\delta_t - \delta_a$ individual pairs) method is preferred. Bagley et al. (1971), Henry (1974) and Hoernschemeyer (1974) have employed different diagrams where different solubility parameter components have been employed for the axes of these diagrams as tabulated in Table 4.19. Types of 2-D graphs are shown which are plotted according to van Krevelen-Hoftyzer (VKH) and Hoy approaches below:

Table 4.19. The coordinates of 2-D solubility parameter components

Methods	Graphic Parameters
Bagley et al. (1971)	$\delta_v - \delta_h$, $[\delta_v = (\delta_d^2 + \delta_p^2)^{1/2}]$.
Henry (1974)	$\delta_p - \delta_h$.
Hoernschemeyer -1 (1974)	$\delta_t - \delta_h$, $[\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}]$.
Hoernschemeyer-2 (1974)	$\delta_t - \delta_a$, $[\delta_a = (\delta_h^2 + \delta_p^2)^{1/2}]$.

All these diagrams have a common feature such that the solubility parameter component of the polymer is placed as the center of the circle. The solubility parameter components of all the other solvents remaining within the circle and closer to the solubility parameter component of the polymer are all considered as good solvents whereas the one remaining outside the circle may be assumed as either slightly swelling the polymer or having no effect at all (Güner, 2004).

Regarding the solubility parameter components variously chosen as the axes of these diagrams provide, an order with respect to the distance of the solubility parameter components of the solvent from the center of the circle.

Using estimated δ - component values for the polymer and solvents, the 2-D plots of PEG were constructed and are shown in

- a) Bagley (Figures 4.3 - 4.4),
- b) Henry (Figures 4.5 - 4.6),
- c) Hoernschemeyer -1 and (Figures 4.7 - 4.8)
- d) Hoernschemeyer -2 (Figures 4.9 - 4.10) diagrams.

4.6.2.1. 2-D Bagley diagrams

Polymer's H-bonding potential which is important for the solubility in solvents can be directly observed in Bagley diagram. The H-bonding potential is calculated by weighted group contributions fitted to a training set of molecules and therefore can describe more precisely rather than counting the number of potential H-bond locations within a molecule. Moreover, the H-bonding potential of the solubility parameter concept is related to the molar volume and hence to the molecular size. Substances with very low H-bonding potential are located outside the region of solubility (Breitkreutz, 1998).

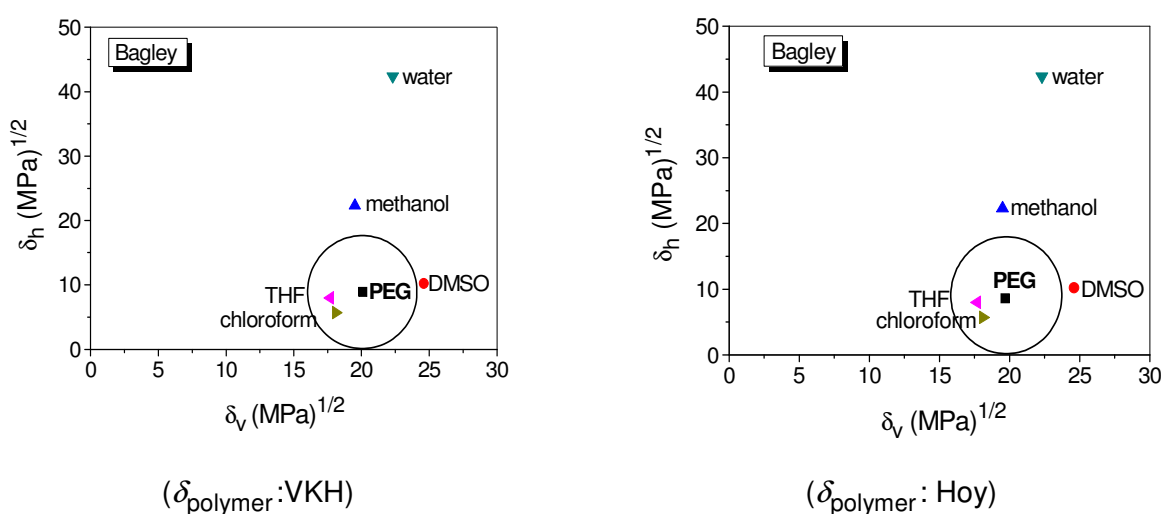


Figure 4.3. Solubility of PEG in various solvents, Bagley diagram ($\delta_{\text{solvent}}:\text{Hansen}$).

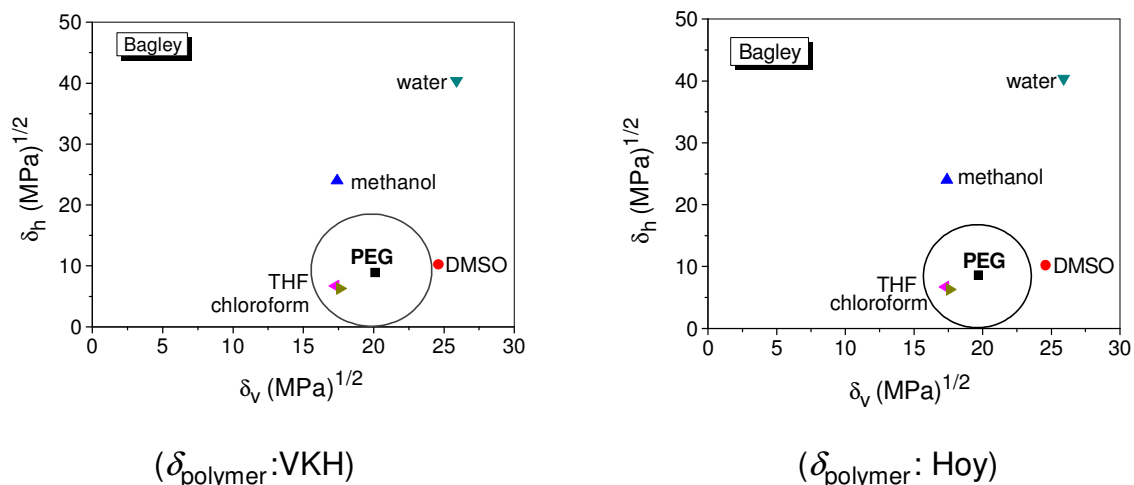


Figure 4.4. Solubility of PEG in various solvents, Bagley diagram, $(\delta_{\text{solvent}}: \text{Hoy})$.

Table 4.20. Sequences of solvents for PEG according to Bagley diagrams.

Sequence of solvents	Calculation method for δ
THF $\approx$ chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}: \text{VKH}$, $\delta_{\text{solvent}}: \text{Hansen}$.
THF $\approx$ chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}: \text{VKH}$, $\delta_{\text{solvent}}: \text{Hoy}$.
THF $\approx$ chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}: \text{Hoy}$, $\delta_{\text{solvent}}: \text{Hansen}$.
THF $\approx$ chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}: \text{Hoy}$, $\delta_{\text{solvent}}: \text{Hoy}$.

According to Bagley et al., the order is respectively given as:

THF $\approx$ chloroform > DMSO > methanol > water .

4.6.2.2. 2-D Henry diagrams

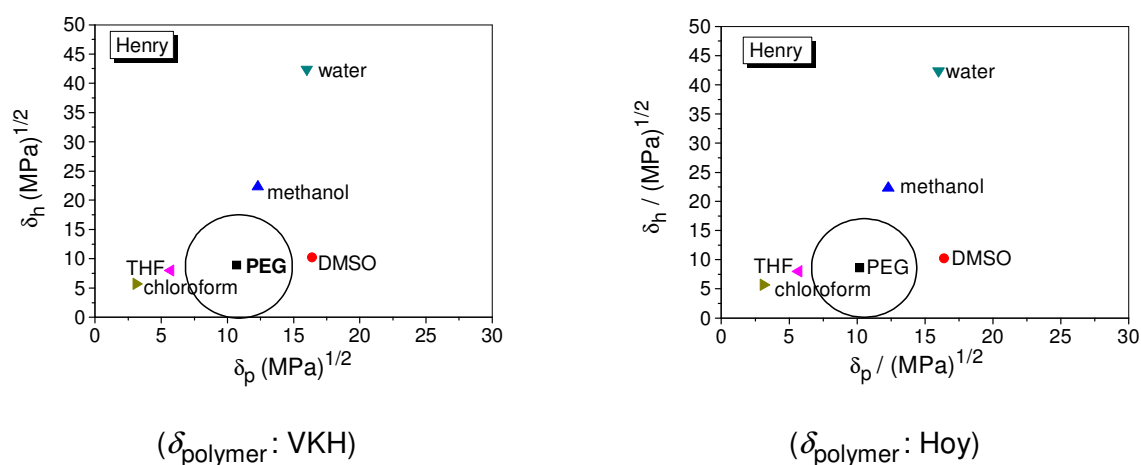


Figure 4.5. Solubility of PEG in various solvents, Henry diagram, $(\delta_{\text{solvent}}: \text{Hansen})$.

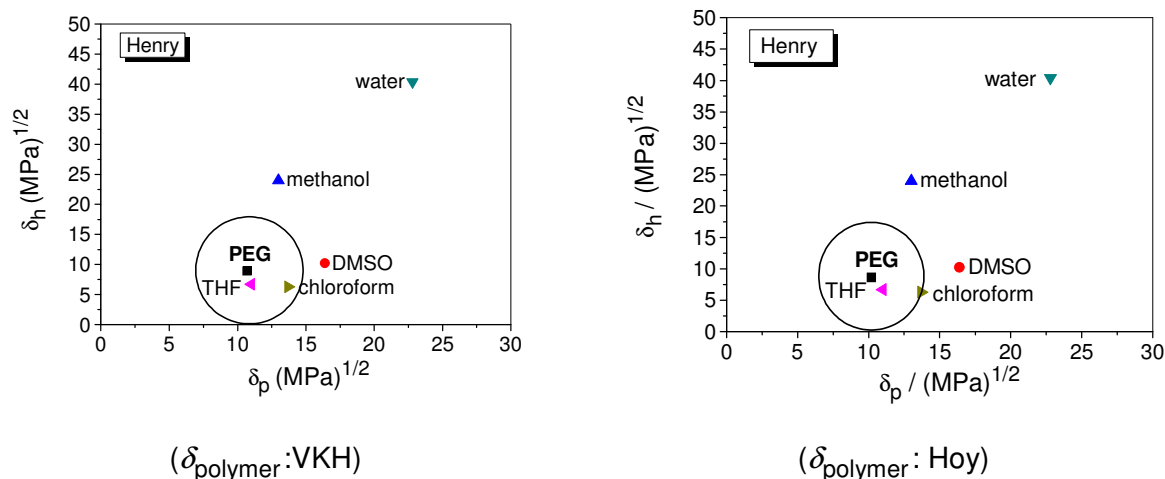


Figure 4.6. Solubility of PEG in various solvents, Henry diagram, ($\delta_{\text{solvent}}: \text{Hoy}$).

Table 4.21. Sequences of solvents for PEG according to Henry diagrams.

Sequence of solvents	Calculation method for δ
THF > DMSO > methanol > chloroform > water	$\delta_{\text{polymer}}: \text{VKH}$, $\delta_{\text{solvent}}: \text{Hansen}$.
THF $\approx$ chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}: \text{VKH}$, $\delta_{\text{solvent}}: \text{Hoy}$.
THF > chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}: \text{Hoy}$, $\delta_{\text{solvent}}: \text{Hansen}$.
THF > chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}: \text{Hoy}$, $\delta_{\text{solvent}}: \text{Hoy}$.

In view of Henry's diagram (1974) this order is changed slightly as:

THF $\approx$ chloroform > DMSO > methanol > water .

4.6.2.3. 2-D HOERNSCHEMEYER-1 diagrams

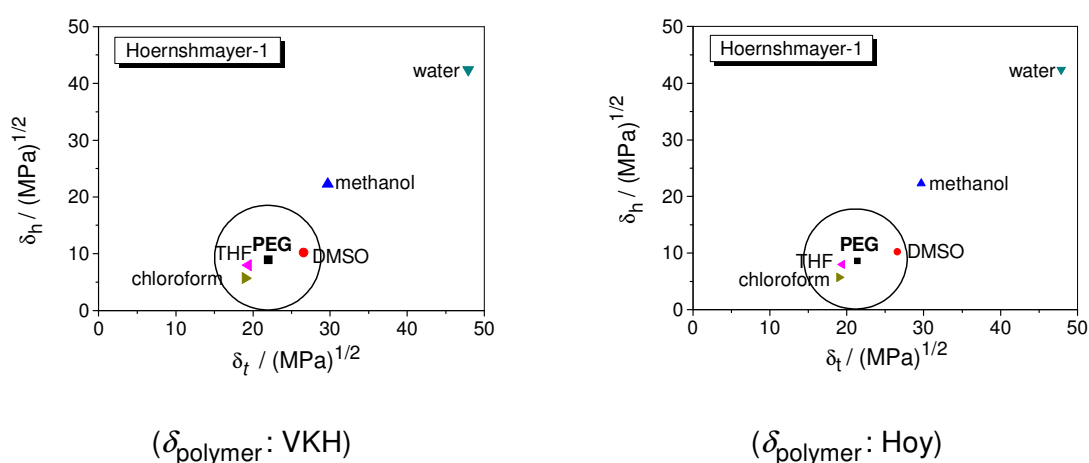


Figure 4.7. Solubility of PEG in various solvents, Hoernschemeyer -1 diagram ($\delta_{\text{solvent}}: \text{Hansen}$).

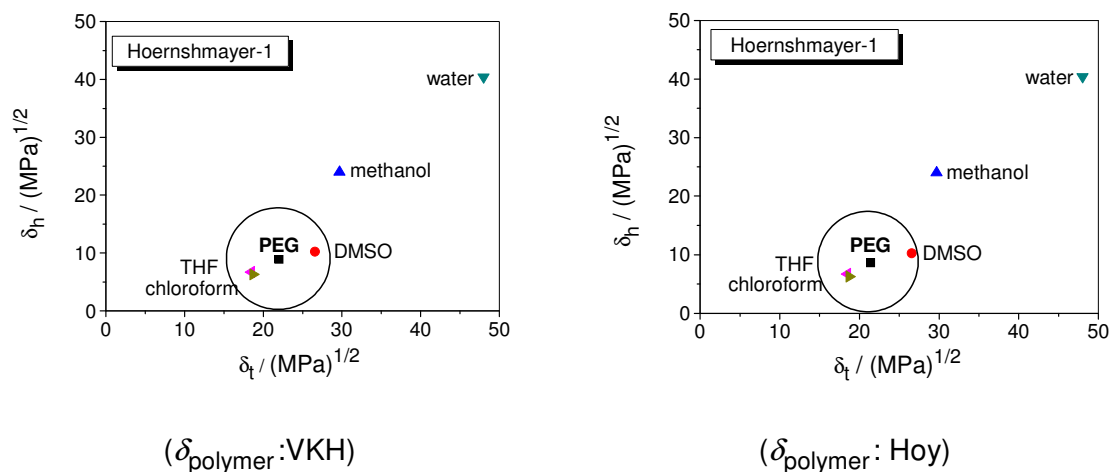


Figure 4.8. Solubility of PEG in various solvents, Hoernshemeyer-1 diagram ($\delta_{\text{solvent}}:\text{Hoy}$).

Table 4.22. Sequences of solvents for PEG according to Hoernshemeyer-1 diagrams.

Sequence of solvents	Calculation method for δ
THF > chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}:\text{VKH}$, $\delta_{\text{solvent}}:\text{Hansen}$.
THF > chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}:\text{VKH}$, $\delta_{\text{solvent}}:\text{Hoy}$.
THF $\approx$ chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}:\text{Hoy}$, $\delta_{\text{solvent}}:\text{Hansen}$.
THF $\approx$ chloroform > DMSO > methanol > water	$\delta_{\text{polymer}}:\text{Hoy}$, $\delta_{\text{solvent}}:\text{Hoy}$.

4.6.2.4. 2-D HOERNSCHEMEYER-2 diagrams

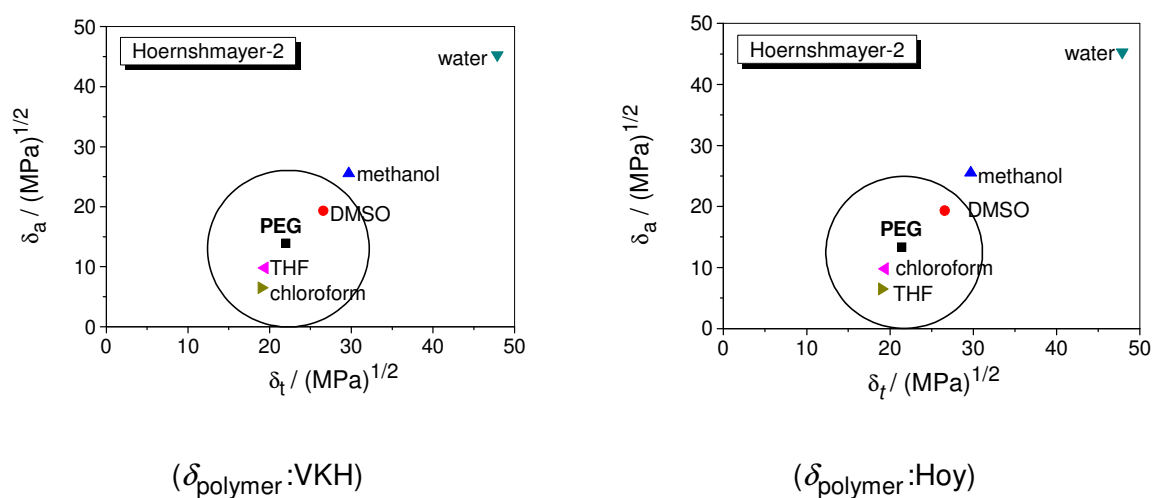


Figure 4.9. Solubility of PEG in various solvents, Hoernshemeyer -2 diagram ($\delta_{\text{solvent}}:\text{Hansen}$).

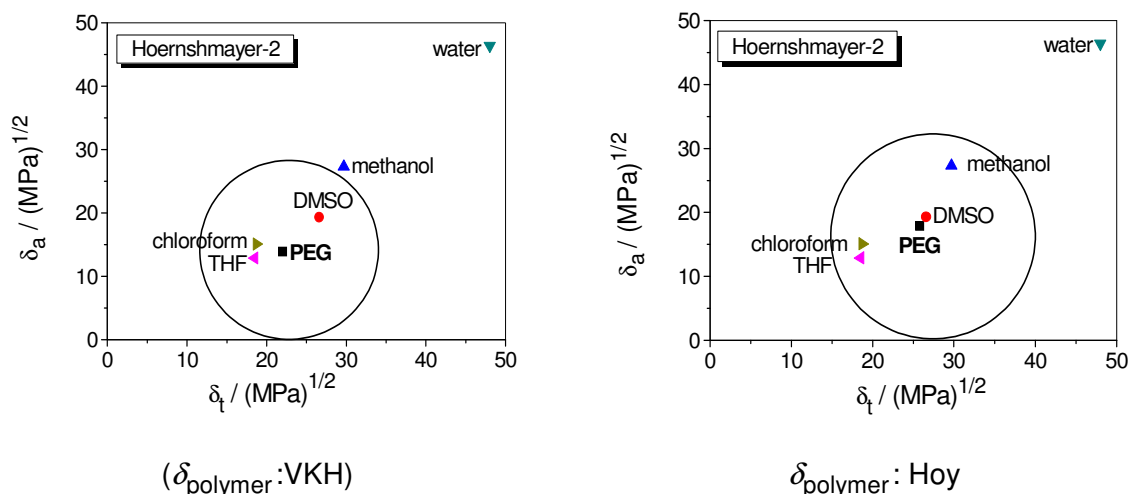


Figure 4.10. Solubility of PEG in various solvents, Hoernschemeyer -2 diagram (δ_{solvent} : Hoy) .

Table 4.23. Sequences of solvents for PEG according to Hoernschemeyer -2 diagrams.

Sequence of solvents	Calculation method for δ
THF > chloroform > DMSO > methanol > water	δ_{polymer} :VKH, δ_{solvent} : Hansen .
THF > chloroform > DMSO > methanol > water	δ_{polymer} :VKH, δ_{solvent} : Hoy .
THF $\approx$ chloroform > DMSO > methanol > water	δ_{polymer} :Hoy , δ_{solvent} : Hansen .
THF $\approx$ chloroform > DMSO > methanol > water	δ_{polymer} :Hoy , δ_{solvent} : Hoy .

Finally, in view of Hoernschemeyer's diagram (1974) the decreasing of solubility power is found as:

$$\text{THF} > \text{chloroform} > \text{DMSO} > \text{methanol} > \text{water} .$$

for both of the two different diagrams.

Hoernschemeyer (1974) proposed that a solubility map for a polymer can be constructed by plotting δ_t , δ_h and δ_a loci for liquids and noting the region of solubility. Fortunately, in many cases the solubility behavior of a polymer can be adequately represented by a 2-D graph of δ_h versus δ_t or δ_a versus δ_t . It was found that the best solvents would be located near the center of the solubility diagram, and this idea is confirmed by two facts. The primary one is that, solvents near the center requires the largest amount of nonsolvent to cause precipitation

(Crowley et al., 1966). And second, solutions from solvents with loci near the center of the solubility envelope exhibit the lowest specific viscosities.

The solubility circles for PEG can be determined by first locating the polymer and all available liquids in the 2-D plane and then determining the solvent power for solvents located at different distances from the polymer.

The solubility parameter of polymer obtained from VKH and Hoy approaches or the solubility of solvent calculated by Hoy and Hansen do not change much the sequence of solvent power.

The accuracy of the 2-D approach was also compared to that of Hansen's 3-D approach in Table 4.24. Liquids lying within the circle are good solvents, and those lying near and outside the circle are poor solvents and nonsolvents, respectively. Hansen's polymer solubility sphere can be expressed as a circle in the 2-D plane. It was found that water is a weakest solvent for PEG.

For the PEG solution, in which both mutual and self-associations occur; solubility or nonsolubility may mainly depend on the relative importance of mutual association between the polymer and the solvent or self-association in the polymer or in the solvent. Since 2-D approach can be used to characterize and predict the solvent power of solvents for PEG, the H-bonding contribution to Gibbs free energy of dissolving can be separated from the physical contribution (a sum of dispersion and polar contributions), at least in a practical sense; and the dispersion and polar contributions have a similar nature (Chen, 1971).

The characteristics of solvent power are displayed in Table 4.24 for the selected five different solvents obtained from both 3-D and 2-D graphs presenting generally the good and poor solvents for PEG where water is a weakest solvent in both cases.

Table 4.24. Comparison of solvency power of solvents for PEG between the 2-D approach and Hansen's 3-D approach.

solvents	2-D graphics			3-D graphics
	Bagley	Henry	Hoernschemeyer-1 and -2	Hansen
water	weakest	weakest	weakest	weakest
methanol	moderate	moderate	moderate	good
DMSO	moderate	moderate	good	good
chloroform	good	moderate	good	good
THF	good	moderate	good	good

Any approach to the theory of solutions should have one of two clear aims:

- (i) the development of a fundamental method of studying the thermodynamics and other properties of solutions, with great accuracy, and with the acceptance of complex and cumbersome mathematical descriptions; or
- (ii) the construction of a practical tool which a solvent formulator can use in laboratory to the simplified task (Barton, 1975).

The solubility parameter concept should be associated primarily with aim *ii*, and should not sacrifice simplicity for accuracy. There is a good thermodynamic reason for this: the Gibbs energy of mixing is made up of two quantities only one of which is described by the solubility parameter. Solubility parameters tell only half the story, even if it is usually the most important half (Barton, 1975).

4.7. Solution Thermodynamics

4.7.1. Calculation of Short-range and Long-range Parameter from Extrapolation Methods (KSF, ISK and Berry)

The unperturbed dimension parameter, K_θ , is independent of temperature, molecular weight of the polymer, and solvent. It measures only the short-range interactions of the polymer segments, and can be determined by various techniques. One of the basic techniques to receive information on unperturbed dimensions has been found from extrapolation methods starting from viscosity

measurements, namely, the KSF equation (Eqs. 2.79 and 2.76) employed in the present study,

$$[\eta]\bar{M}^{-1/2} = K_{\theta} + 0.51B\phi_o\bar{M}^{1/2}$$

and the relationship between K_{θ} and $\langle r^2 \rangle_o$ is given by

$$K_{\theta} = [\eta]_{\theta}M^{-1/2} = \phi_o(\langle r^2 \rangle_o \bar{M}^{-1})^{3/2}$$

where, $[\eta]$ is the intrinsic viscosity, M is the molecular weight of the polymer (number-average molecular weight), B is the parameter for long-range (polymer-solvent) interactions, ϕ_o is Flory's constant ($2.1 \times 10^{23} \text{ mol}^{-1}$), $[\eta]_{\theta}$ is the intrinsic viscosity at theta temperature, and finally, $\langle r^2 \rangle_o^{1/2}$ represents the root-mean-square end to end distance of unperturbed polymer chain.

The Berry equation (Eq. 2.82)

$$[\eta]^{1/2}\bar{M}^{-1/4} = K_{\theta}^{1/2} + 0.42K_{\theta}^{1/2}\phi_o B\bar{M}[\eta]^{-1}$$

and the ISK equation (Eq. 2.81)

$$[\eta]^{4/5}\bar{M}^{-2/5} = 0.786K_{\theta}^{4/5} + 0.454K_{\theta}^{2/5}\phi_o^{2/3}B^{2/3}\bar{M}^{1/3}$$

have been used for the determination of short- and long-range interaction parameters for the PEG /solvent systems.

By the use of these equations, the plots of $[\eta]\bar{M}_n^{-1/2}$ against $\bar{M}_n^{1/2}$, $[\eta]^{1/2}\bar{M}_n^{-1/4}$ against $\bar{M}_n[\eta]^{-1}$ and $[\eta]^{4/5}\bar{M}_n^{-2/5}$ against $\bar{M}_n^{1/3}$ yielded straight lines with high correlation, the intercept being K_{θ} and the slope characterizing the polymer-solvent interactions was determined by linear regression analysis as shown in Figures 4.11-4.15 for five different solvents according to KSF, Figures 4.16-4.20 for five different solvents according to ISK and finally Figures 4.21-4.25 for the same solvents according to Berry, respectively.

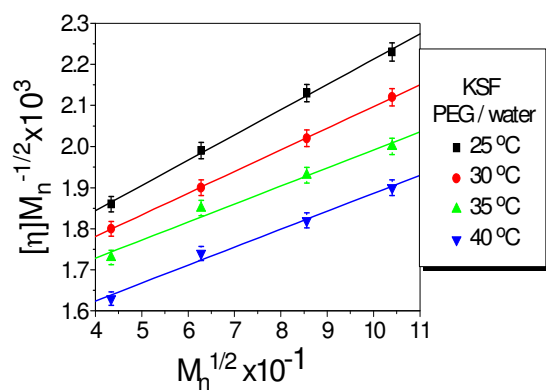


Figure 4.11. KSF plot for PEG/water system.

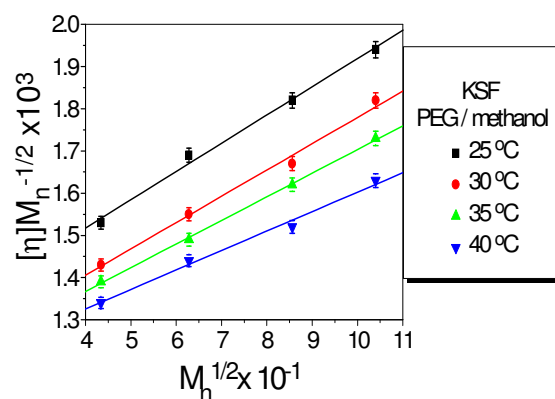


Figure 4.12. KSF plot for PEG/methanol system.

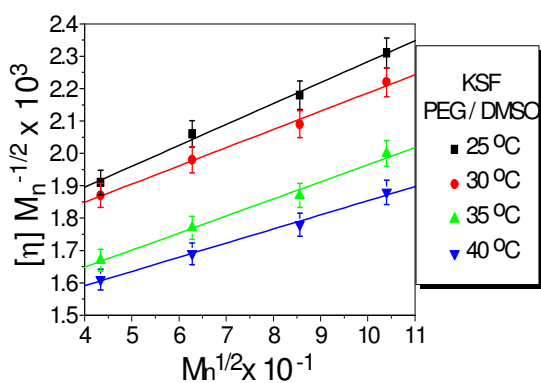


Figure 4.13. KSF plot for PEG/DMSO system.

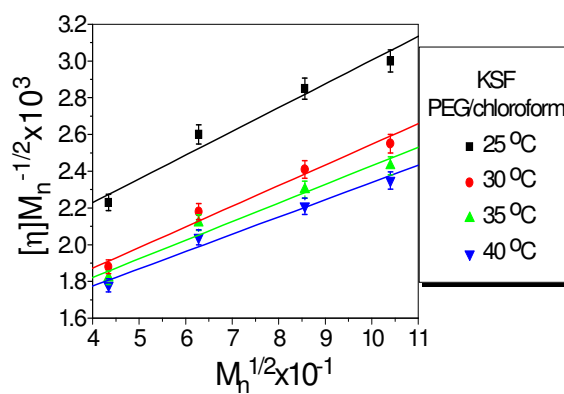


Figure 4.14. KSF plot for PEG/chloroform system.

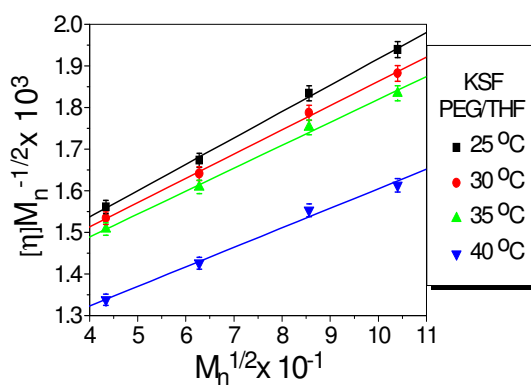


Figure 4.15. KSF plot for PEG/THF system.

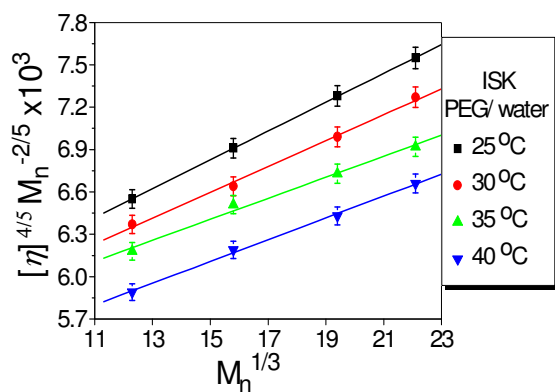


Figure 4.16. ISK plot for PEG/water system.

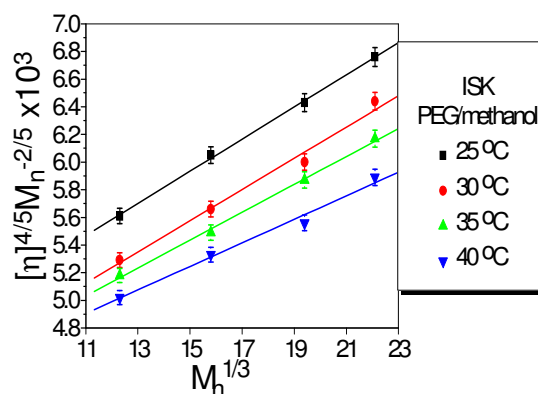


Figure 4.17. ISK plot for PEG/methanol system.

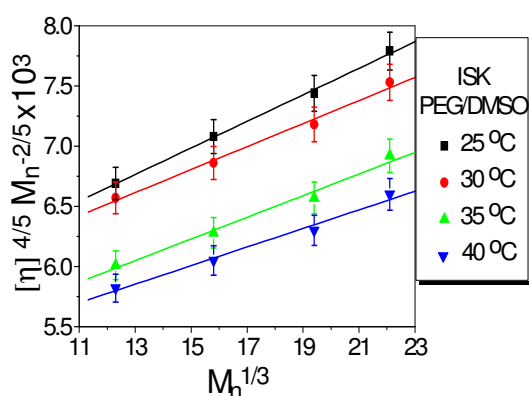


Figure 4.18. ISK plot for PEG/DMSO system.

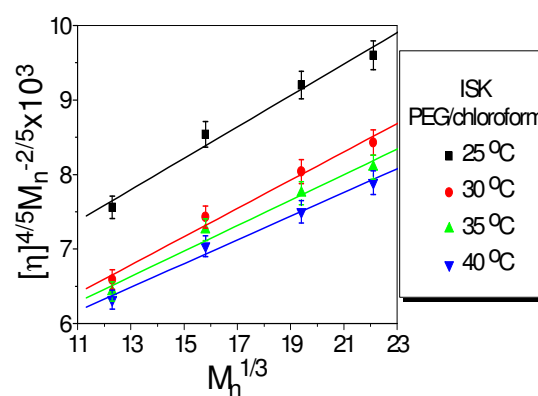


Figure 4.19. ISK plot for PEG/chloroform system.

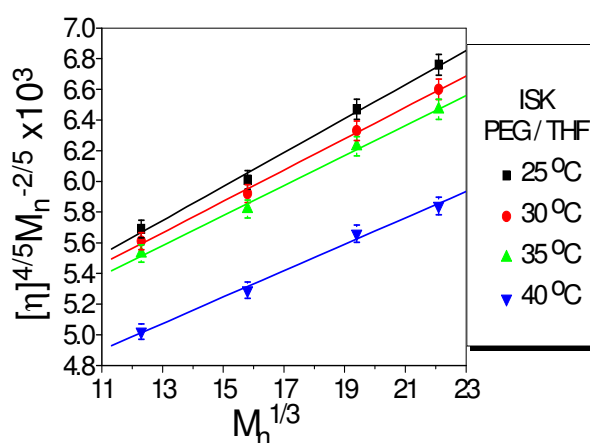


Figure 4.20. ISK plot for PEG/THF system.

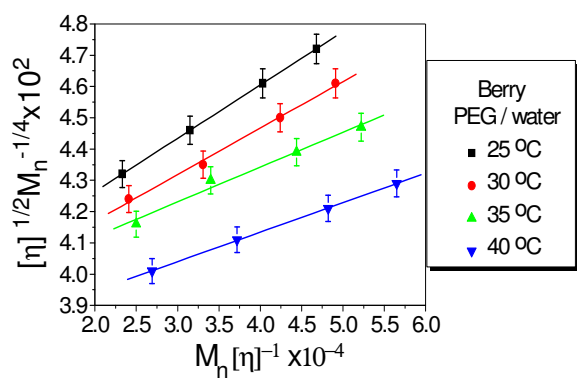


Figure 4.21. Berry plot for PEG/water system.

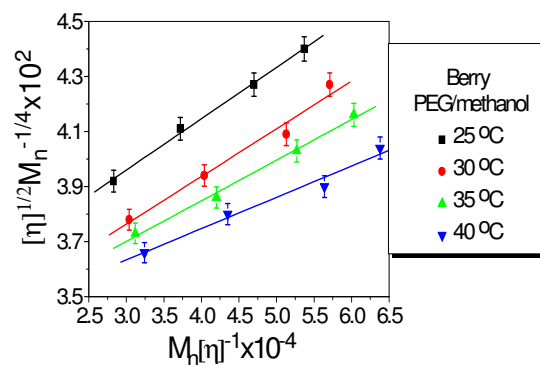


Figure 4.22. Berry plot for PEG/methanol system

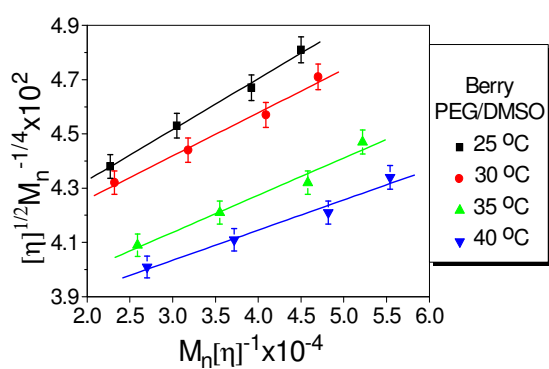


Figure 4.23. Berry plot for PEG/DMSO system.

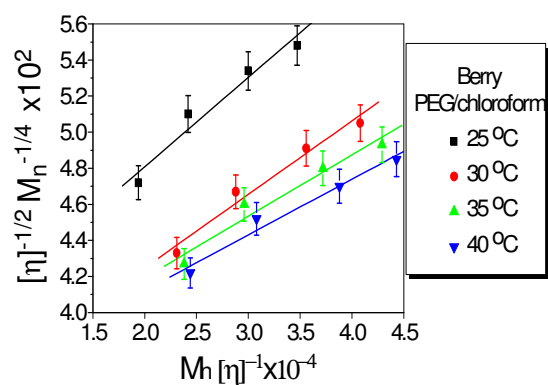


Figure 4.24. Berry plot for PEG/chloroform system.

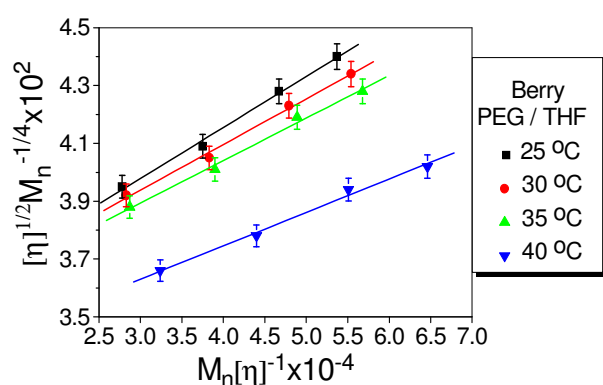


Figure 4.25. Berry plot for PEG/THF system.

The unperturbed dimension parameters (K_θ) and long-range interaction parameters (B) calculated from extrapolation methods are given in Tables 4.25-4.29 for PEG/water, PEG/methanol, PEG/DMSO, PEG/chloroform, PEG/THF, respectively.

Table 4.25. Calculated thermodynamic parameters for PEG/water solution.

t ($^{\circ}\text{C}$)	KSF		ISK		Berry	
	$K_\theta \times 10^4$ (dLg^{-1})	$B \times 10^{28}$ (cm^3)	$K_\theta \times 10^4$ (dLg^{-1})	$B \times 10^{28}$ (cm^3)	$K_\theta \times 10^4$ (dLg^{-1})	$B \times 10^{28}$ (cm^3)
25	16.0	0.573	19.3	6.84	15.4	0.492
30	15.7	0.492	19.0	5.88	15.0	0.435
35	15.5	0.410	19.3	4.26	15.2	0.324
40	14.5	0.408	17.7	4.73	14.1	0.284

Table 4.26. Calculated thermodynamic parameters for PEG/methanol solution.

t ($^{\circ}\text{C}$)	KSF		ISK		Berry	
	$K_\theta \times 10^4$ (dLg^{-1})	$B \times 10^{28}$ (cm^3)	$K_\theta \times 10^4$ (dLg^{-1})	$B \times 10^{28}$ (cm^3)	$K_\theta \times 10^4$ (dLg^{-1})	$B \times 10^{28}$ (cm^3)
25	12.5	0.625	14.4	9.88	11.6	0.621
30	11.6	0.582	13.1	10.0	10.5	0.605
35	11.4	0.523	13.3	8.39	10.6	0.514
40	11.4	0.430	13.5	6.44	10.8	0.391

Table 4.27. Calculated thermodynamic parameters for PEG/DMSO solution.

t ($^{\circ}\text{C}$)	KSF		ISK		Berry	
	$K_\theta \times 10^4$ (dLg^{-1})	$B \times 10^{28}$ (cm^3)	$K_\theta \times 10^4$ (dLg^{-1})	$B \times 10^{28}$ (cm^3)	$K_\theta \times 10^4$ (dLg^{-1})	$B \times 10^{28}$ (cm^3)
25	16.4	0.603	19.5	7.64	15.6	0.539
30	16.2	0.525	19.6	6.13	15.5	0.458
35	14.4	0.492	17.4	6.01	13.9	0.417
40	14.2	0.408	17.3	4.80	13.7	0.341

Table 4.28. Calculated thermodynamic parameters for PEG/chloroform solution.

t (°C)	KSF		ISK		Berry	
	$K_\theta \times 10^4$ (dLg ⁻¹)	$B \times 10^{28}$ (cm ³)	$K_\theta \times 10^4$ (dLg ⁻¹)	$B \times 10^{28}$ (cm ³)	$K_\theta \times 10^4$ (dLg ⁻¹)	$B \times 10^{28}$ (cm ³)
25	17.1	1.21	18.2	21.0	14.6	1.47
30	14.2	1.05	15.0	20.1	11.8	1.35
35	14.2	0.95	15.3	17.0	12.3	1.10
40	14.0	0.88	15.4	15.2	12.3	1.00

Table 4.29. Calculated thermodynamic parameters for PEG/THF solution.

t (°C)	KSF		ISK		Berry	
	$K_\theta \times 10^4$ (dLg ⁻¹)	$B \times 10^{28}$ (cm ³)	$K_\theta \times 10^4$ (dLg ⁻¹)	$B \times 10^{28}$ (cm ³)	$K_\theta \times 10^4$ (dLg ⁻¹)	$B \times 10^{28}$ (cm ³)
25	12.8	0.592	14.9	9.01	11.9	0.580
30	12.8	0.544	15.0	7.93	12.0	0.517
35	12.7	0.514	14.9	7.46	11.9	0.482
40	11.4	0.438	13.4	6.58	10.8	0.399

The unperturbed dimension parameters evaluated from KSF and Berry are in high accordance with each other, and a decrease in K_θ values at increasing temperatures is quite obvious with all these extrapolation techniques as well as the observation for the long-range interaction parameter-temperature behavior. At this point, it would be better to discuss the interactions between the polymer segments and polymer-solvent molecules. Corresponding the structure of PEG, it is strongly expected that molecular association/interaction will form between the polymer segments and solvent molecules through H-bonding. Of course, this decrement in terms of temperature increment results in the break of polymer-solvent associations, i.e., H-bonds between polymer and solvent molecules as well as in rupture of the interactions between the polymer segments.

4.7.2. Calculation of Theta Temperatures from Extrapolation and Interpolation Methods

The theta temperature dependence of the long-range interaction parameter is given by Flory (1953) (Eq.2.83):

$$B = B_o \left(1 - \frac{\theta}{T}\right)$$

where B_o is a constant (independent of temperature) and θ is the theta temperature of the polymer-solvent pair.

The plots of the B obtained from extrapolation methods (KSF, ISK and Berry) against the reciprocal of the temperature according to Eq. 2.83, resulted in straight lines, where the slope yielded the theta temperature of each studied polymer/solvent system. As an example to $1/T$ - B behavior, plot of PEG/water system is given in Fig. 4.26.

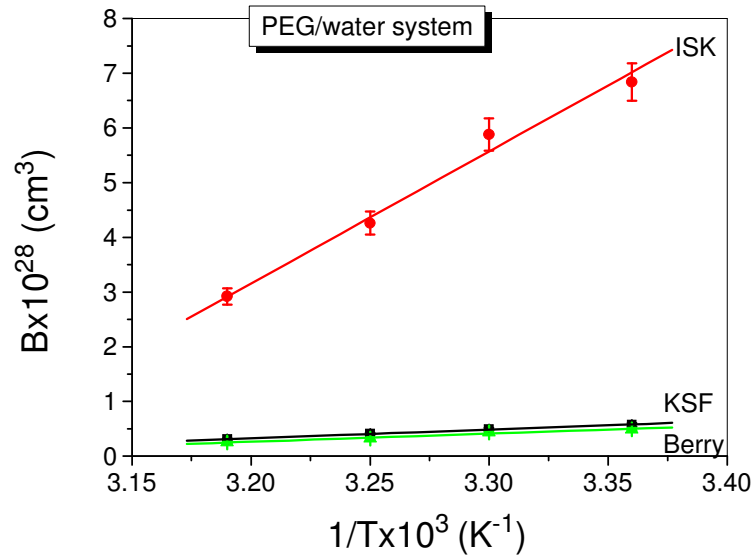


Figure 4.26. Plot of the B , interaction parameter obtained from the KSF, ISK and Berry equations as a function of the reciprocal of the temperature for the PEG/water system.

In order to check the validity of the determined theta temperature or obtain more reliable values of theta temperatures, $(1/2 - \chi)$ and A_2 versus temperature relationship were also investigated individually. Theta temperatures of PEG/solvent systems are determined as the interpolation values at $y=0$ respect to $T - (1/2 - \chi)$ behavior for each extrapolation method (KSF, ISK and Berry) and each solvent (THF, DMSO, water, chloroform and methanol). A typical $T - (1/2 - \chi)$ behavior is given for PEG/water system in Figure 4.27.

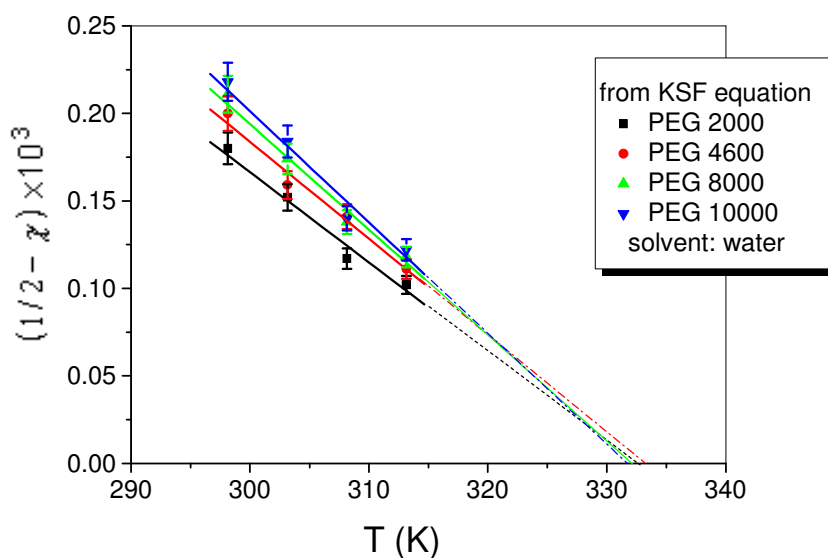


Figure 4.27. Plot of the theta temperature obtained from $T - (1/2 - \chi)$ behavior for PEG/water system.

Typical interpolation graphics with respect to $T - A_2$ behavior by using of A_2 values calculated for K_θ value obtained from each extrapolation method (KSF, ISK and Berry) and for each solvent (THF, DMSO, water, chloroform and methanol) are plotted. As a typical $T - A_2$ behavior is given plot of PEG/water system in Figure 4.29.

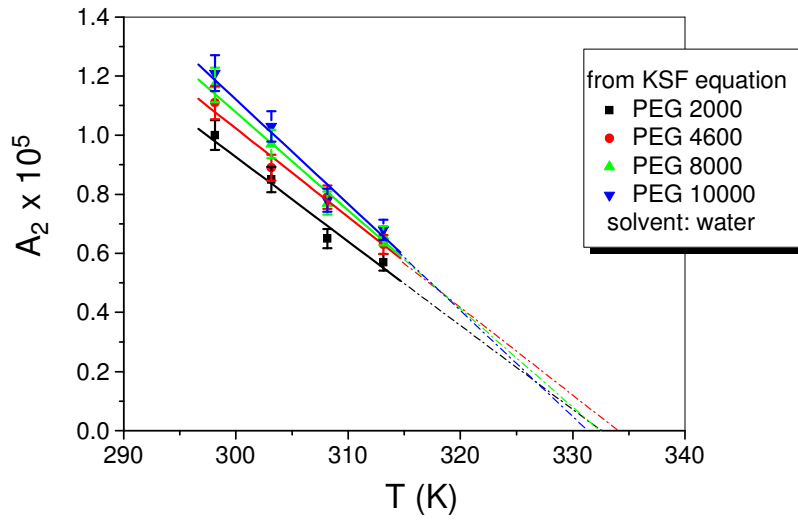


Figure 4.28. Plot of the theta temperature obtained from $T - A_2$ behavior.

The Gibbs free energy of mixing for relation of χ and the second virial coefficient (A_2) is given by Wakker (1991) (Eq.2.55):

$$A_2 = ((1/2) - \chi)(\rho_p^2 V_S)^{-1}$$

where ρ_p is the density of the polymer and V_S is the molar volume of the solvent.

As quite well known, at θ temperature, Flory interaction parameter takes the value of 0.5 whereas the second virial coefficient is zero. Subsequently, the interpolated values at which $\chi = 0.5$ or $1/2 - \chi = 0$ and A_2 is zero may be readily obtained. These values characterize the theta temperature for that system and have been successfully applied to Dx/solvent systems (Güner and Kibarar, 2001; Güner, and Çatıker, 2001). The theta temperatures of studied systems is determined by these two interpolation methods with respect to $T - (1/2 - \chi)$ and $T - A_2$ behaviors have been given in Table 4.30-4.34 for each polymer/solvent pair.

When these tables are examined, it is observed that θ temperatures are quite scattered for $T - (1/2 - \chi)$ and $T - A_2$ behaviors through the use of ISK equation and the θ temperatures thus obtained by these two interpolation methods display rather low values for each five distinct solvent.

Table 4.30. The theta temperatures obtained from KSF, ISK and Berry equations of PEG/water system.

Methods	from KSF equation	from ISK equation	from Berry equation
	T (K)	T (K)	T (K)
1-) from $(1/T)$ - B behavior	336	326	329
average	330 ± 5		
2-) From T - $(1/2 - \chi)$ behavior			
PEG 2000	332	286*	331
PEG 4600	333	303	331
PEG 8000	332	313	331
PEG 10000	332	317	330
average	332 ± 1	311 ± 7	331 ± 1
3-) from T - A_2 behavior			
PEG 2000	332	287*	331
PEG 4600	334	303	332
PEG 8000	333	313	331
PEG 10000	332	317	331
average	333 ± 2	311 ± 7	331 ± 1

*has been ignored with regard to the statistical analysis results.

Table 4.31. The theta temperatures obtained from KSF, ISK and Berry equations of PEG/methanol system.

Methods	from KSF equation	from ISK equation	from Berry equation
	T (K)	T (K)	T (K)
1-) From $(1/T)$ - B behavior	347*	334	334
average	334		
2-) From $T - (1/2 - \chi)$ behavior			
PEG 2000	333	313	328
PEG 4600	336	319	330
PEG 8000	331	320	328
PEG 10000	331	322	328
average	333 ± 3	319 ± 5	329 ± 1
3-) From T - A_2 behavior			
PEG 2000	336	313	329
PEG 4600	337	318	331
PEG 8000	333	320	329
PEG 10000	332	322	328
average	335 ± 2	318 ± 5	329 ± 2

* has been ignored with regard to the statistical analysis results.

Table 4.32. The theta temperatures obtained from KSF, ISK and Berry equations of PEG/DMSO system.

Methods	from KSF equation	from ISK equation	from Berry equation
	T (K)	T (K)	T (K)
1-) From $(1/T)$ - B behavior	352*	347	345
average	346 ± 1		
2-) From T - $(1/2 - \chi)$ behavior			
PEG 2000	342	291*	339
PEG 4600	338	310	336
PEG 8000	337	316	335
PEG 10000	340	322	338
average	339 ± 3	316 ± 6	337 ± 2
3-) From T - A_2 behavior			
PEG 2000	345	291*	341
PEG 4600	340	310	337
PEG 8000	338	316	337
PEG 10000	342	322	340
average	341 ± 4	316 ± 6	339 ± 2

* has been ignored with regard to the statistical analysis results.

Table 4.33. The theta temperatures obtained from KSF, ISK and Berry equations of PEG/chloroform system.

Methods	from KSF equation	from ISK equation	from Berry equation
	T (K)	T (K)	T (K)
1) From $(1/T)$ - B behavior	365*	357	349
average	353 ± 4		
2-) From $T - (1/2 - \chi)$ behavior			
PEG 2000	350	329	338
PEG 4600	347	332	338
PEG 8000	342	331	335
PEG 10000	345	334	337
average	346 ± 4	332 ± 3	337 ± 2
3-) From T - A_2 behavior			
PEG 2000	356	330	341
PEG 4600	351	334	340
PEG 8000	346	334	338
PEG 10000	350	337	341
average	351 ± 5	334 ± 4	340 ± 2

* has been ignored with regard to the statistical analysis results.

Table 4.34. The theta temperatures obtained from KSF, ISK and Berry equations of PEG/THF system.

Methods	from KSF equation	from ISK equation	from Berry equation
	T (K)	T (K)	T (K)
1-) From $(1/T)$ - B behavior	371*	358	356
average	357 ± 1		
2-) From T - $(1/2 - \chi)$ behavior			
PEG 2000	345	312*	340
PEG 4600	347	325	342
PEG 8000	349	334	344
PEG 10000	342	331	339
average	346 ± 4	330 ± 5	341 ± 2
3-) From T - A_2 behavior			
PEG 2000	349	312*	343
PEG 4600	352	326	345
PEG 8000	354	336	347
PEG 10000	346	333	342
average	350 ± 4	332 ± 5	344 ± 3

* has been ignored with regard to the statistical analysis results.

The theta temperatures determined for PEG/solvent systems are collectively presented in Table 4.35 (except for ISK). Besides, for a better overview the θ temperatures are given versus each solvent in terms of statistical bars in Figure 4.29.

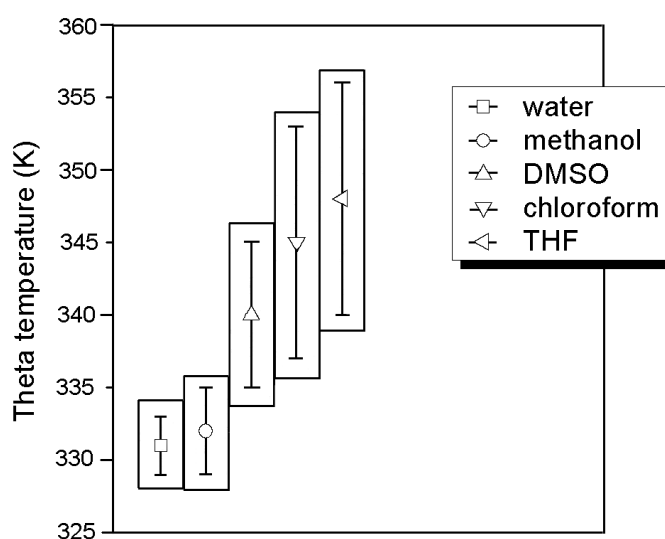


Figure 4.29. θ temperatures are given versus each solvent in terms of statistical bars.

Table 4.35. The theta temperatures obtained from KSF, ISK and Berry equations of PEG/solvent systems.

Solvent	from $(1/T)-B$ behavior	from $T - (1/2 - \chi)$ behavior		from $T-A_2$ behavior		Average
	KSF+ ISK+ Berry	KSF	Berry	KSF	Berry	
Water	330 ± 5	332 ± 1	331 ± 1	333 ± 2	331 ± 1	331 ± 2
Methanol	334	333 ± 3	329 ± 1	335 ± 2	329 ± 2	332 ± 3
DMSO	346 ± 1	339 ± 3	337 ± 2	341 ± 4	339 ± 2	340 ± 5
Chloroform	353 ± 4	346 ± 4	337 ± 2	351 ± 5	340 ± 2	345 ± 8
THF	357 ± 1	346 ± 4	341 ± 2	350 ± 4	344 ± 3	348 ± 8

In this work, three different extrapolation and two distinct interpolation methods have been employed for the determination of θ corresponding to $331 \pm 2K$ for PEG in water. θ temperature of PEG/methanol system has been subsequently found as $332 \pm 3K$, closer to that of PEG/water. θ temperatures of PEG/DMSO, PEG/chloroform and PEG/THF systems all display an increasing trend. Solvent which has lower theta temperature is weakest solvent. According to results in Table 4.35, solvency power of solvents for PEG decreases below order. This order is compatible with algorithmic calculations:

$$\text{THF} > \text{chloroform} > \text{DMSO} > \text{methanol} > \text{water}$$

Among the systems studied, the θ temperatures of PEG/chloroform and PEG/THF solutions have been found to be higher (THF somewhat higher). In a good solvent, the polymer coil is expected to expand. In other words, long-range interactions are greater than short-range interactions. Consequently, polymer-solvent interactions are much more dominant with regard to those of polymer molecule segments, the determination of θ temperature of those solutions seems to be more probable at high temperatures.

Among five different solvents employed in this study, only for PEG (or PEO)/solvent system are theta temperatures present in literature. The determined theta temperatures are scattered between an extremely wide range of temperature such as 280-390 K. While Chew and Couper (1976) are faced with a θ temperature around 280 K for a molecular weight of 1000-6000, Boucher and Hines (1976) and

Ataman (1987b) have obtained a high theta temperature like 369 ± 3 K for PEO with a molecular weight of 20000. On the other hand, Napper (1970) has found a theta temperature corresponding to 390 ± 20 K. In the studies of Saeki group (1976), the θ temperature of PEG/water system has been reported as 371 K. Polik and Burchard (1983) has estimated to be 375 K theta temperature of PEO.

The θ temperatures determined for water/ K_2SO_4 and water/ $MgSO_4$ systems vary around 308-318 K (Barton, 1991). Barton has reported the θ temperature of PEO as 323 K in a series of solvents (methyisobutyl ketone, diethylene glycol diethyl ether).

Theta temperature (ideal temperature) is the temperature at which, for a given polymer-solvent pair, the polymer exists in its unperturbed dimensions. Under these conditions, the long-range forces between polymer molecule segments which cause contraction are just balanced by the polymer-solvent interactions causing the polymer molecular coil to expand. Theta temperature is defined as the temperature at which long-range and short-range interactions balance each other. Cloud point on the other hand, is expressed as the temperature at which short-range interactions are more dominant, in other words, short-range interactions are more effective compared to long-range interactions. In the systems displaying LCST, cloud point (phase separation temperature) is found as the temperature above θ temperature. The “closed loop” phase separation behavior of PEO in water has been confirmed (Saeki et al., 1976) for $MW < 2000$, and for $MW = 10^6$, $LCST = 372$ K (Boucher and Hines, 1978).

Determination of θ temperature through the use of cloud point temperatures have also been achieved via different extrapolation methods by Flory (1953). However, θ temperature values obtained from cloud point studies are rather high when scatterings occurring in extrapolation methods are considered.

4.7.3. Calculation of Mark Houwink exponent “a” for PEG

Mark-Houwink exponents of PEG and PEO in water are being given in Table 4.36. As can be seen from the table “a” exponent is scattered among a quite wide range. Only for PEG, this exponent is observed to be between 0.5-0.82.

Table 4.36. Mark-Houwink exponent for PEG and PEO in water.

t (C°)	MW range	Method	a	Reference
20	60 - 11,000	End group titration ¹	0.76	Brandrup and Immergut, 1989.
25	2,000	Stokes radius- $[\eta]$ – molecular weight relationship	0.67	Wang et al., 2004.
25	630 - 1470	Capillary viscometry and GPC	0.50	Desilets and Pinkerton, 1987.
25	190- 1,000	End group titration ²	0.50	Brandrup and Immergut, 1989.
35	400 - 4,000	End group titration ³	0.82	Brandrup and Immergut, 1989.
25	4,000- 100,000	Vapor pressure osmometer and viscosity	0.90	Amu, 1982.
35	4,000 – 100,000	Vapor pressure osmometer and viscosity	0.85	Amu, 1982.
45	4,000 - 100,000	Vapor pressure osmometer and viscosity	0.78	Bailey and Callard, 1959. Boucher and Hines, 1978.
30	35,000	Limiting viscosity and light scattering	0.78	Quesada, 1997.
30	20,000 - 5,000,000	light scattering, sedimentation and diffusion ⁴	0.78	Brandrup and Immergut, 1989.
30	36,900 - 1,020,000	Light scattering and sedimentation-diffusion	0.78	Bailey et al., 1958.
35	30,000 - 7,000,000	Limiting viscosity number – molecular weight relationship ⁴	0.82	Brandrup and Immergut, 1989.
45	30,000 - 7,000,000	Limiting viscosity number – molecular weight relationship ⁴	0.81	Brandrup and Immergut, 1989.
72	111,000- 633,000	Light scattering, viscosity	0.58	Park and Kim, 1997.

¹ Narrow MWD polymers or well-fractionated polymers, $HI \leq 1.25$.

² Narrow MWD polymers or well-fractionated polymers, $HI \leq 1.25$ and limited to low MW polymers.

³ Poorly fractionated polymers or most probable MWD polymers $1.8 \leq HI < 2.4$ and limited to low MW polymers.

⁴ Poorly fractionated polymers or most probable MWD polymers $1.8 \leq HI < 2.4$.

Practically, Mark-Houwink exponent is a magnitude which characterizes the expansion of the selected polymer in a certain solvent. This exponent exhibits the value of zero in spherical form of the polymer coil whereas its numerical value is 0.5 at θ temperature. In a partly extended polymer chain, $0.5 < a < 1$ and $a = 1.0$ in extended chain. In a semiflexible and/or rodlike structure $1.0 < a < 2.0$ and finally $a = 2.0$ in rodlike structures. Wormlike polymer chains exhibit a values that range from 0.764 to 2.0. High values are encountered with rigid chains of low molar mass. High molar mass, flexible chains have lower a values (Elias, 1997, Sperling, 2001).

Mark-Houwink exponents of PEG and PEO in different solvents are presented in Table 4.37. In literature, no such value exists reported as a Mark-Houwink exponent related with PEG/DMSO system. When the exponents in Table 4.37 are examined, even in the same solvent, different Mark-Houwink exponents are being displayed.

Table 4.37. Mark-Houwink exponent for PEG and PEO in chloroform, methanol and THF.

	t (C°)	MW range	Method	a	Reference
chloroform	25	200-1500	End group titration	0.5	Brandrup and Immergut, 1989.
methanol	20	60-19,000	End group titration	0.72	Brandrup and Immergut, 1989.
methanol	25	-	Light scattering and sedimentation-diffusion	0.57	Brandrup and Immergut, 1989.
THF	25	68000-914000	-	0.42	Sung and Lee, 2001.
THF	30	85,000-860,000	viscosity	0.76	Berek and Tarbajovska, 2002.
THF	72	111,000-633,000	Light scattering, viscosity	0.60	Park and Kim, 1997.

Mark-Houwink exponents with respect to $\overline{M}_n$ and $\overline{M}_w$ values are given in Tables 4.38 and 4.39.

Table 4.38. Mark Houwink exponent “ a ” for PEG /solvent systems according to $\overline{M}_n$.

t (°C)	water	methanol	DMSO	chloroform	THF
25	0.60	0.62	0.61	0.67	0.64
30	0.59	0.62	0.59	0.67	0.63
35	0.58	0.61	0.60	0.66	0.62
40	0.58	0.60	0.59	0.66	0.62

Table 4.39. Mark Houwink exponent “ a ” for PEG /solvent systems according to $\overline{M}_w$.

t (°C)	water	methanol	DMSO	chloroform	THF
25	0.62	0.64	0.62	0.69	0.66
30	0.61	0.64	0.61	0.70	0.65
35	0.60	0.63	0.62	0.68	0.64
40	0.60	0.62	0.61	0.68	0.64

When these tables are examined, Mark-Houwink exponents determined for water have been found to be somewhat closer to or a little higher than 0.60. The values determined for methanol and DMSO have also been obtained again somewhat higher than the “ a ” value encountered in water, when the other two solvents (THF and chloroform) are considered, the highest Mark-Houwink exponent has been found in chloroform. According to polymer geometry definition of Elias (1997) and Sperling (2001), since the a value is about 0.60, its corresponding geometry is called as partly extended.

As may be remembered, during the evaluation of 2-D and 3-D diagrams in algorithmic calculations, THF used to display a better solvent appearance when compared with chloroform and sometimes they both exhibited a similar behavior. If Mark-Houwink exponents are considered, chloroform seems to be the best solvent among the selected five other solvents. Water, on the other hand, strongly supports algorithmic results with its lowest Mark-Houwink exponent.

4.7.4. Calculation of Unperturbed Dimensions of PEG

Calculated $[\eta]_{\theta}$, α_{η} , $\langle r^2 \rangle_o^{1/2}$ and $\langle s^2 \rangle$ values according to KSF, ISK and Berry equations are presented in Tables 4.40 - 4.44 for PEG/solvent systems.

α_{η} and α values calculated according to ISK equation use to fall below 1 from time to time for water and DMSO. However, in all solvent systems, lower values with respect to those obtained from KSF and Berry equations have been encountered. Among the three different extrapolation methods, KSF and Berry equations have yielded much more significant results.

The magnitudes, $[\eta]_{\theta}$, α_{η} , $\langle r^2 \rangle_o^{1/2}$ and $\langle s^2 \rangle$ are the measures of the hydrodynamic volume, intensity of the thermodynamic interactions and the hydrodynamic expansion, contraction of the polymer in solution, respectively.

It is clearly seen in Tables 4.40 - 4.44 that in the hydrodynamic volume, intensity of the thermodynamic interactions and the hydrodynamic expansion of the coil are in a decrement trend by temperature on the interactions between the polymer and solvent molecules in solution. The point which strongly wished to emphasize is that at each selected temperature and molecular weight, being related to the solvent nature, the variations in thermodynamic magnitudes such as hydrodynamic volume and hydrodynamic expansion/contraction of polymer may be followed.

When the hydrodynamic magnitudes of PEG in the selected solvents are regarded, highest values of α , α_{η} , $\langle r \rangle_o^{1/2}$ and $\langle s^2 \rangle_o$ appear in chloroform. However, from time to time these values seem to be somewhat alike both in chloroform and THF. Although sometimes displacements may take place between THF and DMSO, generally, the values found for THF are higher than those found for DMSO. It is not seen a net change being related to the type of solvent when the magnitudes, α , α_{η} , $\langle r \rangle_o^{1/2}$ and $\langle s^2 \rangle_o$ are compared.

Table 4.40. Calculated data for PEG/water solutions from intrinsic viscosity measurements in the temperature range of 25-40 °C according to KSF, ISK and Berry equations.

	$[\eta]_{\theta}$ (dLg ⁻¹)			α_{η}			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle \times 10^6$ (Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
T=25 °C															
PEG 2000	0.07	0.08	0.07	1.05	0.99	1.07	1.07	0.99	1.08	85	91	84	1.38	1.34	1.38
PEG 4600	0.10	0.12	0.10	1.08	1.01	1.09	1.09	1.01	1.11	123	131	122	3.04	2.95	3.06
PEG 8000	0.14	0.17	0.13	1.10	1.03	1.11	1.12	1.04	1.14	168	179	166	5.98	5.80	6.01
PEG 10000	0.17	0.20	0.16	1.12	1.05	1.13	1.15	1.06	1.16	205	218	202	9.19	8.93	9.25
T=30 °C															
PEG 2000	0.07	0.08	0.07	1.05	0.98	1.06	1.06	0.98	1.08	85	90	83	1.34	1.30	1.35
PEG 4600	0.10	0.12	0.09	1.06	1.00	1.08	1.08	1.00	1.10	123	131	121	2.93	2.84	2.95
PEG 8000	0.13	0.16	0.13	1.09	1.02	1.10	1.11	1.03	1.13	167	178	165	5.75	5.58	5.79
PEG 10000	0.16	0.20	0.16	1.11	1.04	1.12	1.13	1.05	1.15	204	217	201	8.86	8.60	8.92
T=35 °C															
PEG 2000	0.07	0.08	0.07	1.04	0.97	1.05	1.05	0.96	1.06	84	91	84	1.30	1.26	1.31
PEG 4600	0.10	0.12	0.10	1.06	0.99	1.07	1.07	0.98	1.08	122	131	121	2.88	2.78	2.88
PEG 8000	0.13	0.17	0.13	1.07	1.00	1.08	1.09	1.00	1.10	167	179	166	5.54	5.35	5.56
PEG 10000	0.16	0.20	0.16	1.09	1.01	1.10	1.11	1.01	1.12	203	218	201	8.44	8.16	8.47
T=40 °C															
PEG 2000	0.06	0.08	0.06	1.04	0.97	1.04	1.04	0.96	1.06	83	88	82	1.25	1.20	1.24
PEG 4600	0.09	0.11	0.09	1.05	0.98	1.06	1.06	0.98	1.08	120	128	118	2.76	2.61	2.71
PEG 8000	0.12	0.15	0.12	1.07	1.00	1.08	1.09	1.00	1.10	163	174	162	5.35	5.07	5.25
PEG 10000	0.15	0.19	0.15	1.08	1.01	1.09	1.10	1.02	1.12	198	212	197	8.19	7.74	8.02

Table 4.41. Calculated data for PEG/methanol solutions from intrinsic viscosity measurements in the temperature range of 25-40 °C according to KSF, ISK and Berry equations.

	$[\eta]_{\theta}$ (dLg ⁻¹)			α_{η}			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle \times 10^6$ (Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
T=25 °C															
PEG 2000	0.05	0.06	0.05	1.07	1.02	1.10	1.09	1.03	1.12	79	82	77	1.22	1.19	1.23
PEG 4600	0.08	0.09	0.07	1.11	1.05	1.13	1.13	1.07	1.17	114	119	111	2.76	2.70	2.80
PEG 8000	0.11	0.12	0.10	1.13	1.08	1.16	1.17	1.10	1.21	155	163	151	5.47	5.35	5.54
PEG 10000	0.13	0.15	0.12	1.16	1.10	1.19	1.20	1.13	1.24	189	198	184	8.53	8.34	8.63
T=30 °C															
PEG 2000	0.05	0.06	0.05	1.07	1.03	1.11	1.09	1.04	1.13	77	80	74	1.16	1.14	1.18
PEG 4600	0.07	0.08	0.07	1.10	1.06	1.14	1.13	1.07	1.17	111	116	107	2.61	2.56	2.65
PEG 8000	0.10	0.11	0.09	1.13	1.08	1.17	1.16	1.11	1.21	151	158	147	5.16	5.06	5.23
PEG 10000	0.12	0.14	0.11	1.16	1.12	1.20	1.21	1.15	1.25	184	192	178	8.21	8.05	8.33
T=35 °C															
PEG 2000	0.05	0.06	0.05	1.07	1.02	1.09	1.08	1.02	1.12	76	80	74	1.14	1.11	1.15
PEG 4600	0.07	0.08	0.07	1.09	1.04	1.12	1.12	1.05	1.15	110	116	108	2.53	2.47	2.56
PEG 8000	0.09	0.11	0.09	1.12	1.07	1.15	1.16	1.09	1.19	151	158	147	5.05	4.93	5.10
PEG 10000	0.12	0.14	0.11	1.15	1.09	1.18	1.19	1.11	1.22	183	193	179	7.86	7.68	7.95
T=40 °C															
PEG 2000	0.05	0.06	0.05	1.05	1.00	1.07	1.07	1.00	1.09	76	81	75	1.10	1.08	1.11
PEG 4600	0.07	0.08	0.07	1.08	1.02	1.10	1.10	1.03	1.12	110	117	108	2.46	2.40	2.48
PEG 8000	0.09	0.12	0.09	1.10	1.04	1.12	1.12	1.05	1.15	151	159	148	4.78	4.65	4.82
PEG 10000	0.12	0.14	0.11	1.13	1.07	1.15	1.16	1.08	1.18	183	194	180	7.50	7.31	7.56

Table 4.42. Calculated data for PEG/DMSO solutions from intrinsic viscosity measurements in the temperature range of 25-40 °C according to KSF, ISK and Berry equations

	$[\eta]_{\theta}$ (dLg ⁻¹)			α_{η}			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle \times 10^6$ (Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
T=25 °C															
PEG 2000	0.07	0.08	0.07	1.05	0.99	1.07	1.07	0.99	1.09	86	91	85	1.40	1.36	1.21
PEG 4600	0.10	0.12	0.10	1.08	1.02	1.10	1.10	1.02	1.12	124	132	123	3.11	3.03	2.54
PEG 8000	0.14	0.17	0.13	1.10	1.04	1.12	1.13	1.05	1.15	170	180	167	6.09	5.93	4.72
PEG 10000	0.17	0.20	0.16	1.12	1.06	1.14	1.15	1.07	1.18	207	219	203	9.45	9.20	6.99
T=30 °C															
PEG 2000	0.07	0.09	0.07	1.05	0.98	1.06	1.06	0.98	1.08	86	91	84	1.38	1.34	1.20
PEG 4600	0.10	0.12	0.10	1.07	1.00	1.08	1.08	1.00	1.10	124	132	122	3.02	2.93	2.51
PEG 8000	0.14	0.17	0.13	1.09	1.02	1.10	1.11	1.03	1.13	169	180	167	5.88	5.71	4.67
PEG 10000	0.17	0.21	0.16	1.11	1.04	1.13	1.14	1.05	1.16	206	219	203	9.14	8.87	6.92
T=35 °C															
PEG 2000	0.06	0.08	0.06	1.05	0.99	1.06	1.06	0.98	1.08	82	88	81	1.28	1.24	1.13
PEG 4600	0.09	0.11	0.09	1.07	1.01	1.08	1.09	1.01	1.10	119	127	118	2.81	2.72	2.37
PEG 8000	0.12	0.15	0.12	1.09	1.02	1.10	1.11	1.03	1.13	163	173	161	5.47	5.30	4.40
PEG 10000	0.15	0.18	0.15	1.12	1.05	1.13	1.14	1.06	1.16	198	211	195	8.54	8.29	6.51
T=40 °C															
PEG 2000	0.06	0.08	0.06	1.04	0.98	1.05	1.05	0.97	1.07	82	88	81	1.24	1.20	1.07
PEG 4600	0.09	0.11	0.09	1.06	0.99	1.07	1.07	0.99	1.09	119	127	117	2.71	2.63	2.24
PEG 8000	0.12	0.15	0.12	1.08	1.01	1.09	1.10	1.01	1.11	162	173	160	5.25	5.09	4.18
PEG 10000	0.15	0.18	0.14	1.10	1.03	1.11	1.12	1.04	1.14	197	210	195	8.15	7.91	6.18

Table 4.43. Calculated data for PEG/chloroform solutions from intrinsic viscosity measurements in the temperature range of 25-40 °C according to KSF, ISK and Berry equations.

	$[\eta]_{\theta}$ (dLg ⁻¹)			α_{η}			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle \times 10^6$ (Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
T=25 °C															
PEG 2000	0.07	0.08	0.06	1.09	1.07	1.15	1.11	1.09	1.19	87	89	83	1.58	1.56	1.62
PEG 4600	0.11	0.11	0.09	1.15	1.13	1.21	1.19	1.16	1.27	126	129	120	3.75	3.71	3.84
PEG 8000	0.15	0.16	0.13	1.18	1.16	1.25	1.23	1.20	1.32	172	176	163	7.53	7.45	7.72
PEG 10000	0.18	0.19	0.15	1.21	1.18	1.27	1.26	1.23	1.35	210	214	199	11.6	11.5	11.9
T=30 °C															
PEG 2000	0.06	0.07	0.05	1.10	1.08	1.17	1.12	1.10	1.21	82	83	77	1.41	1.40	1.45
PEG 4600	0.09	0.09	0.07	1.15	1.13	1.23	1.19	1.17	1.29	119	121	112	3.34	3.32	3.44
PEG 8000	0.12	0.13	0.10	1.19	1.17	1.27	1.24	1.22	1.34	162	165	152	6.74	6.69	6.94
PEG 10000	0.15	0.16	0.12	1.22	1.19	1.29	1.27	1.25	1.37	197	200	185	10.5	10.4	10.8
T=35 °C															
PEG 2000	0.06	0.07	0.05	1.09	1.06	1.14	1.11	1.07	1.17	82	84	78	1.38	1.36	1.41
PEG 4600	0.09	0.10	0.08	1.14	1.11	1.20	1.18	1.14	1.25	119	122	113	3.27	3.22	3.34
PEG 8000	0.12	0.13	0.11	1.18	1.14	1.23	1.22	1.18	1.29	162	166	154	6.50	6.42	6.64
PEG 10000	0.15	0.16	0.13	1.20	1.17	1.25	1.25	1.21	1.32	197	202	188	10.1	9.94	10.3
T=40 °C															
PEG 2000	0.06	0.07	0.05	1.08	1.05	1.13	1.10	1.06	1.17	82	84	78	1.35	1.33	1.38
PEG 4600	0.09	0.10	0.08	1.13	1.10	1.18	1.17	1.12	1.23	118	122	113	3.17	3.12	3.24
PEG 8000	0.12	0.13	0.11	1.16	1.13	1.22	1.21	1.16	1.27	161	166	154	6.30	6.20	6.43
PEG 10000	0.15	0.16	0.13	1.19	1.15	1.24	1.24	1.19	1.31	196	202	188	9.82	9.67	10.0

Table 4.44. Calculated data for PEG/THF solutions from intrinsic viscosity measurements in the temperature range of 25-40 °C according to KSF, ISK and Berry equations.

	$[\eta]_{\theta}$ (dLg ⁻¹)			α_{η}			α			$\langle r^2 \rangle_o^{1/2}$ (Å)			$\langle s^2 \rangle \times 10^6$ (Å)		
	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry	KSF	ISK	Berry
T=25 °C															
PEG 2000	0.06	0.07	0.05	1.07	1.02	1.09	1.08	1.02	1.12	79	83	77	1.23	1.20	1.13
PEG 4600	0.08	0.09	0.08	1.09	1.04	1.12	1.12	1.05	1.15	115	121	112	2.73	2.67	2.87
PEG 8000	0.11	0.13	0.10	1.13	1.07	1.16	1.16	1.09	1.19	157	165	153	5.48	5.35	5.75
PEG 10000	0.13	0.16	0.12	1.15	1.09	1.18	1.19	1.11	1.22	190	200	186	8.49	8.29	8.92
T=30 °C															
PEG 2000	0.06	0.07	0.05	1.06	1.01	1.09	1.08	1.01	1.11	79	84	78	1.21	1.18	1.13
PEG 4600	0.08	0.09	0.08	1.09	1.03	1.11	1.11	1.04	1.14	115	121	112	2.69	2.62	2.80
PEG 8000	0.11	0.13	0.10	1.12	1.06	1.14	1.15	1.07	1.18	156	165	153	5.37	5.23	5.59
PEG 10000	0.13	0.16	0.13	1.14	1.08	1.16	1.17	1.10	1.20	190	201	186	8.29	8.08	8.63
T=35 °C															
PEG 2000	0.06	0.07	0.05	1.06	1.00	1.08	1.07	1.00	1.10	79	83	77	1.20	1.17	1.11
PEG 4600	0.08	0.09	0.08	1.08	1.03	1.10	1.10	1.03	1.13	114	121	112	2.65	2.58	2.72
PEG 8000	0.11	0.13	0.10	1.11	1.05	1.14	1.14	1.07	1.17	156	165	153	5.29	5.15	5.42
PEG 10000	0.13	0.16	0.12	1.13	1.07	1.15	1.16	1.09	1.19	190	200	186	8.12	7.92	8.33
T=40 °C															
PEG 2000	0.05	0.06	0.05	1.06	1.00	1.07	1.07	1.00	1.09	76	80	75	1.10	1.08	1.03
PEG 4600	0.07	0.08	0.07	1.08	1.02	1.10	1.10	1.03	1.12	110	116	108	2.44	2.38	2.48
PEG 8000	0.10	0.12	0.09	1.11	1.05	1.13	1.14	1.06	1.16	150	159	148	4.87	4.75	4.94
PEG 10000	0.12	0.14	0.11	1.12	1.06	1.14	1.16	1.08	1.18	183	193	180	7.44	7.25	7.55

4.7.5. Calculation of Thermodynamic Parameters of PEG Solutions

Calculated Flory interaction parameters are given in Tables 4.45-4.49 for PEG/solvent pairs and it must be equal to 0.5 at the theta temperatures. This stipulation is almost formed as $0.5 \approx 0.499$ for the PEG-solvent systems.

Calculated excess enthalpy and entropy of dilution parameters and Flory interaction parameters for PEG/solvent systems are also presented in Tables 4.45-4.49. Enthalpically, solubility or solvation of polymer in solution is preferred whereas, entropically it is not, due to the surrounding of the polymer chain with regular solvent molecules.

Solvation/association between polymer segments and solvent molecules are disturbed with an increment of temperature for polymer-polar solvent systems. According to determined dynamic and thermodynamic magnitudes it is observed that the strong interactions between polymer and solvent molecules through H-bonding will occur for the PEG/solvent systems. It is obvious that χ_H must be negative. Calculated χ values seem to be a little bit smaller than 0.5, as shown in Tables 4.45 - 4.49 and χ_S is the only indicated force in setting χ numerically to 0.5, which is believed to be the ideal condition for polymer solutions.

Table 4.45. Thermodynamic parameters for the PEG/water system.

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
T=298 K									
PEG 2000	0.5016	-0.0018	0.49982	0.5009	-0.0009	0.50004	0.5021	-0.0023	0.49977
PEG 4600	0.5017	-0.0019	0.49980	0.5015	-0.0015	0.49997	0.5021	-0.0024	0.49976
PEG 8000	0.5018	-0.0020	0.49979	0.5012	-0.0013	0.49994	0.5023	-0.0025	0.49975
PEG 10000	0.5019	-0.0022	0.49978	0.5013	-0.0014	0.49992	0.5023	-0.0026	0.49975
T=303 K									
PEG 2000	0.5016	-0.0017	0.49985	0.5010	-0.0009	0.50005	0.5023	-0.0025	0.49979
PEG 4600	0.5016	-0.0018	0.49984	0.5004	-0.0004	0.50000	0.5022	-0.0024	0.49980
PEG 8000	0.5018	-0.0020	0.49983	0.5011	-0.0012	0.49996	0.5023	-0.0025	0.49979
PEG 10000	0.5020	-0.0021	0.49982	0.5013	-0.0014	0.49994	0.5024	-0.0027	0.49978
T=308 K									
PEG 2000	0.5015	-0.0016	0.49988	0.5014	-0.0013	0.50010	0.5019	-0.0021	0.49986
PEG 4600	0.5017	-0.0019	0.49986	0.5019	-0.0018	0.50003	0.5021	-0.0023	0.49984
PEG 8000	0.5017	-0.0019	0.49986	0.5000	-0.00001	0.50000	0.5021	-0.0023	0.49985
PEG 10000	0.5018	-0.0020	0.49986	0.5006	-0.0006	0.49998	0.5022	-0.0023	0.49985
T=313 K									
PEG 2000	0.5017	-0.0018	0.49990	0.5010	-0.0009	0.50008	0.5023	-0.0024	0.49987
PEG 4600	0.5017	-0.0018	0.49989	0.5010	-0.0010	0.50003	0.5023	-0.0024	0.49987
PEG 8000	0.5019	-0.0020	0.49988	0.5007	-0.0008	0.50000	0.5024	-0.0026	0.49986
PEG 10000	0.5021	-0.0022	0.49988	0.5013	-0.0013	0.49998	0.5025	-0.0027	0.49986

Table 4.46. Thermodynamic parameters for the PEG/methanol system.

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
T=298 K									
PEG 2000	0.5025	-0.0028	0.49970	0.5017	-0.0018	0.49992	0.5043	-0.0048	0.49957
PEG 4600	0.5028	-0.0032	0.49965	0.5025	-0.0026	0.49983	0.5044	-0.0049	0.49953
PEG 8000	0.5033	-0.0036	0.49963	0.5029	-0.0031	0.49979	0.5047	-0.0052	0.49953
PEG 10000	0.5035	-0.0039	0.49962	0.5030	-0.0032	0.49976	0.5048	-0.0053	0.49952
T=303 K									
PEG 2000	0.5031	-0.0033	0.49972	0.5034	-0.0035	0.49989	0.5053	-0.0058	0.49957
PEG 4600	0.5029	-0.0032	0.49969	0.5033	-0.0034	0.49983	0.5050	-0.0055	0.49956
PEG 8000	0.5034	-0.0038	0.49968	0.5036	-0.0038	0.49980	0.5053	-0.0058	0.49957
PEG 10000	0.5041	-0.0044	0.49963	0.5040	-0.0043	0.49975	0.5059	-0.0064	0.49952
T=308 K									
PEG 2000	0.5035	-0.0038	0.49975	0.5036	-0.0036	0.49995	0.5056	-0.0060	0.49964
PEG 4600	0.5035	-0.0038	0.49974	0.5031	-0.0032	0.49989	0.5051	-0.0054	0.49965
PEG 8000	0.5043	-0.0046	0.49971	0.5040	-0.0042	0.49985	0.5059	-0.0062	0.49963
PEG 10000	0.5050	-0.0054	0.49969	0.5040	-0.0042	0.49982	0.5060	-0.0064	0.49962
T=313 K									
PEG 2000	0.5030	-0.0032	0.49981	0.5046	-0.0045	0.50001	0.5055	-0.0058	0.49974
PEG 4600	0.5049	-0.0051	0.49978	0.5096	-0.0097	0.49994	0.5089	-0.0091	0.49973
PEG 8000	0.5063	-0.0065	0.49979	0.5099	-0.0099	0.49992	0.5101	-0.0103	0.49974
PEG 10000	0.5067	-0.0070	0.49976	0.5084	-0.0085	0.49988	0.5102	-0.0105	0.49972

Table 4.47. Thermodynamic parameters for the PEG/DMSO system.

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
T=298 K									
PEG 2000	0.5061	-0.0070	0.49909	0.5035	-0.0034	0.5001	0.5090	-0.0102	0.4988
PEG 4600	0.5077	-0.0087	0.49898	0.5054	-0.0056	0.4998	0.5101	-0.0114	0.4987
PEG 8000	0.5080	-0.0091	0.49895	0.5061	-0.0065	0.4996	0.5101	-0.0114	0.4987
PEG 10000	0.5082	-0.0093	0.49886	0.5064	-0.0069	0.4995	0.5101	-0.0114	0.4987
T=303 K									
PEG 2000	0.5061	-0.0069	0.49921	0.5060	-0.0057	0.5002	0.5091	-0.0101	0.4989
PEG 4600	0.5072	-0.0080	0.49918	0.5009	-0.0009	0.5000	0.5097	-0.0107	0.4990
PEG 8000	0.5077	-0.0085	0.49914	0.5043	-0.0045	0.4998	0.5098	-0.0108	0.4990
PEG 10000	0.5079	-0.0089	0.49904	0.5053	-0.0056	0.4997	0.5099	-0.0110	0.4989
T=308 K									
PEG 2000	0.5068	-0.0076	0.49924	0.5031	-0.0029	0.5002	0.5096	-0.0106	0.4990
PEG 4600	0.5081	-0.0089	0.49922	0.5069	-0.0070	0.5000	0.5104	-0.0113	0.4991
PEG 8000	0.5085	-0.0092	0.49921	0.5070	-0.0072	0.4998	0.5104	-0.0113	0.4991
PEG 10000	0.5088	-0.0097	0.49909	0.5075	-0.0078	0.4997	0.5107	-0.0117	0.4990
T=313 K									
PEG 2000	0.5063	-0.0069	0.49942	0.5042	-0.0039	0.5003	0.5093	-0.0101	0.4992
PEG 4600	0.5131	-0.0137	0.49939	0.4754	0.0247	0.5001	0.5177	-0.0185	0.4993
PEG 8000	0.5138	-0.0144	0.49938	0.5367	-0.0368	0.4999	0.5178	-0.0185	0.4993
PEG 10000	0.5134	-0.0141	0.49929	0.5183	-0.0185	0.4998	0.5170	-0.0178	0.4992

Table 4.48. Thermodynamic parameters for the PEG/chloroform system.

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
T=298 K									
PEG 2000	0.521	-0.025	0.4964	0.527	-0.030	0.4972	0.552	-0.059	0.4931
PEG 4600	0.532	-0.037	0.4948	0.538	-0.042	0.4956	0.563	-0.071	0.4917
PEG 8000	0.537	-0.043	0.4945	0.542	-0.047	0.4953	0.567	-0.075	0.4917
PEG 10000	0.534	-0.040	0.4945	0.539	-0.044	0.4952	0.561	-0.069	0.4919
T=303 K									
PEG 2000	0.522	-0.025	0.4966	0.531	-0.034	0.4973	0.556	-0.063	0.4936
PEG 4600	0.532	-0.037	0.4954	0.541	-0.045	0.4961	0.566	-0.074	0.4924
PEG 8000	0.539	-0.043	0.4951	0.546	-0.050	0.4957	0.571	-0.079	0.4924
PEG 10000	0.536	-0.041	0.4950	0.542	-0.047	0.4956	0.566	-0.073	0.4925
T=308 K									
PEG 2000	0.521	-0.024	0.4971	0.528	-0.030	0.4981	0.551	-0.056	0.4951
PEG 4600	0.533	-0.037	0.4959	0.539	-0.042	0.4969	0.563	-0.069	0.4940
PEG 8000	0.538	-0.042	0.4959	0.543	-0.046	0.4967	0.566	-0.072	0.4942
PEG 10000	0.534	-0.039	0.4958	0.539	-0.043	0.4966	0.560	-0.066	0.4942
T=313 K									
PEG 2000	0.522	-0.025	0.4974	0.530	-0.031	0.4985	0.556	-0.061	0.4956
PEG 4600	0.548	-0.052	0.4964	0.571	-0.073	0.4975	0.606	-0.111	0.4947
PEG 8000	0.560	-0.063	0.4964	0.581	-0.083	0.4973	0.617	-0.122	0.4949
PEG 10000	0.553	-0.057	0.4962	0.570	-0.073	0.4971	0.604	-0.109	0.4948

Table 4.49. Thermodynamic parameters for the PEG/THF system

	KSF			ISK			Berry		
	χ_S	χ_H	χ	χ_S	χ_H	χ	χ_S	χ_H	χ
T=298 K									
PEG 2000	0.5046	-0.0053	0.49927	0.5033	-0.0034	0.49984	0.5076	-0.0086	0.49894
PEG 4600	0.5046	-0.0054	0.49924	0.5032	-0.0035	0.49970	0.5070	-0.0080	0.49898
PEG 8000	0.5051	-0.0060	0.49913	0.5038	-0.0043	0.49954	0.5072	-0.0084	0.49889
PEG 10000	0.5061	-0.0070	0.49910	0.5046	-0.0052	0.49948	0.5082	-0.0093	0.49888
T=303 K									
PEG 2000	0.5046	-0.0053	0.49936	0.5020	-0.0021	0.49994	0.5075	-0.0084	0.49909
PEG 4600	0.5047	-0.0054	0.49932	0.5029	-0.0031	0.49979	0.5070	-0.0079	0.49910
PEG 8000	0.5051	-0.0059	0.49923	0.5035	-0.0039	0.49964	0.5072	-0.0081	0.49904
PEG 10000	0.5062	-0.0070	0.49921	0.5044	-0.0048	0.49959	0.5082	-0.0092	0.49903
T=308 K									
PEG 2000	0.5049	-0.0055	0.49941	0.5022	-0.0023	0.49997	0.5081	-0.0090	0.49916
PEG 4600	0.5049	-0.0056	0.49937	0.5031	-0.0033	0.49982	0.5075	-0.0083	0.49918
PEG 8000	0.5054	-0.0061	0.49928	0.5038	-0.0041	0.49968	0.5077	-0.0086	0.49911
PEG 10000	0.5065	-0.0072	0.49928	0.5048	-0.0051	0.49964	0.5088	-0.0096	0.49912
T=313 K									
PEG 2000	0.5048	-0.0052	0.49951	0.5023	-0.0022	0.50001	0.5078	-0.0085	0.49933
PEG 4600	0.5048	-0.0053	0.49948	0.5032	-0.0033	0.49987	0.5072	-0.0079	0.49934
PEG 8000	0.5053	-0.0059	0.49939	0.5039	-0.0041	0.49974	0.5075	-0.0082	0.49927
PEG 10000	0.5063	-0.0069	0.49941	0.5047	-0.0050	0.49972	0.5085	-0.0092	0.49930

4.8. X-ray Diffraction (XRD) Analysis

Bailey and Koleske (1976), Gray (1991), Tadokoro (1990) and Elias (1997) have emphasized that PEG is found in helix conformation and that it displays a semi-crystalline polymer. Oosterhelt et al. (1999) presented a report to confirm the helical structure of PEG and showed the contributions of water to its stabilization. Begum and Matsuura (1997) showed that the gauche state of the C-C bond, which is typical for the crystalline helical state, is retained when PEG is dissolved in water (Oosterhelt et al., 1999).

In XRD studies, diffractions have been mainly observed at two angles ($2\theta = 19.3^\circ$ and 23.5°). These two angles are in quite good agreement with those found in literature (Corrigan et al., 2002, Petrova et al., 1998).

Qiao et al. (2004) found that PEG shows two main diffraction peaks at about 18.8° and 23.1° whose positions remain unchanged after the cross-linking. The reason for this is that the presence of cross-links does not alter the crystal forms of PEG; it only limits the crystallization of PEG. Secondly, the diffraction peak of cross-linked PEG is lower than that of pure PEG, meaning that the crystallinity of PEG decreases when it is cross-linked.

X-ray diffractogram of PEGs, that of samples PEG 2000, 4600, 8000 and 10000 are shown in Figures 4.30 - 4.33 which shows diffuse areas with sharp band, suggesting uniform crystallization. The XRD spectra of PEGs employed in this study at four different molecular weights and prepared as original, in water and in THF, respectively have been examined.

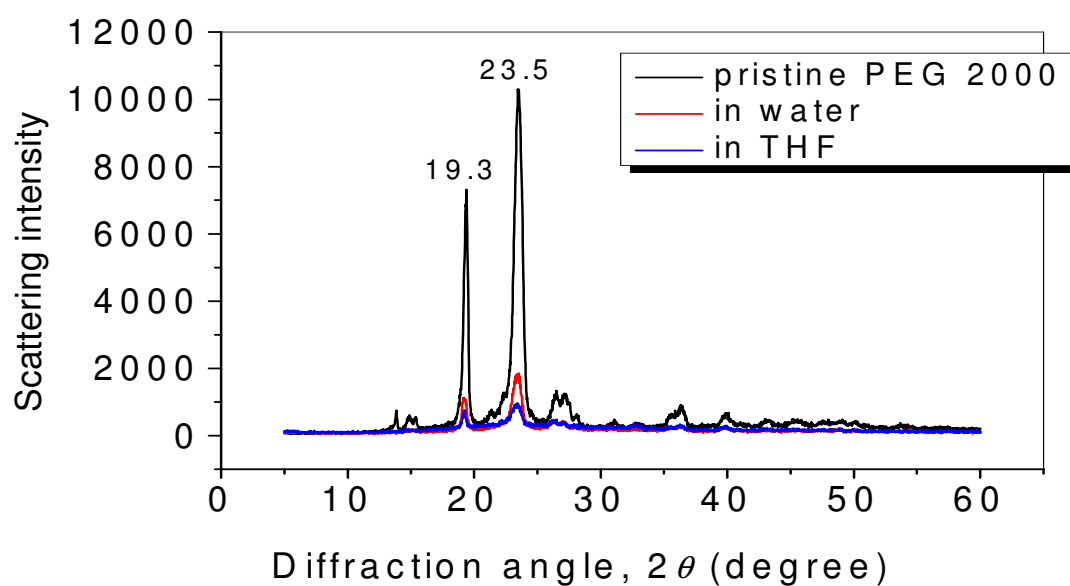


Figure 4.30. XRD patterns of the PEG 2000 powders in the presence and absence solvents.

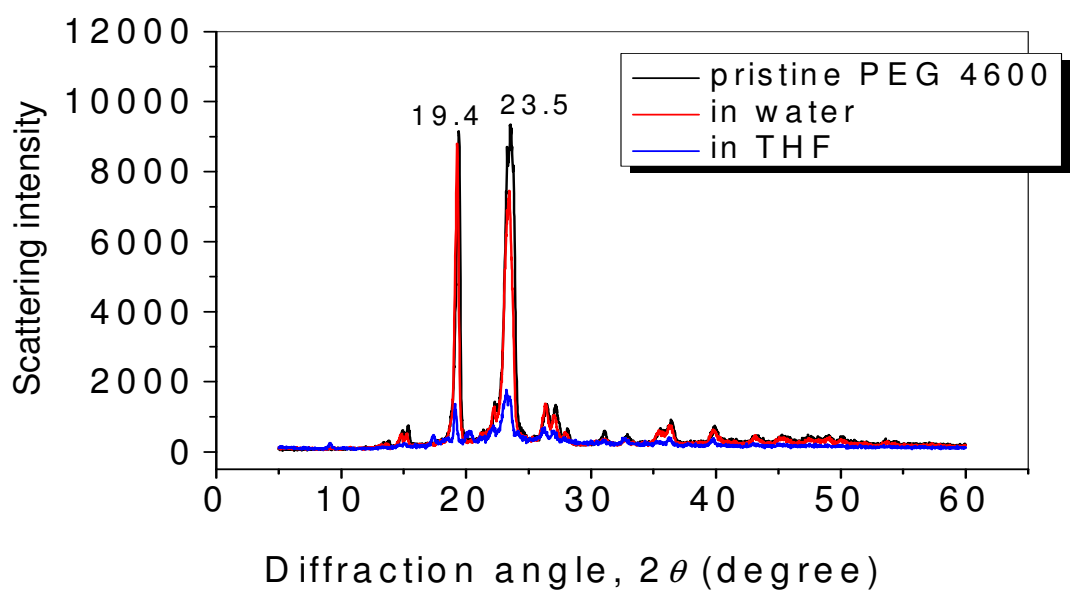


Figure 4.31. XRD patterns of the PEG 4600 powders in the presence and absence solvents.

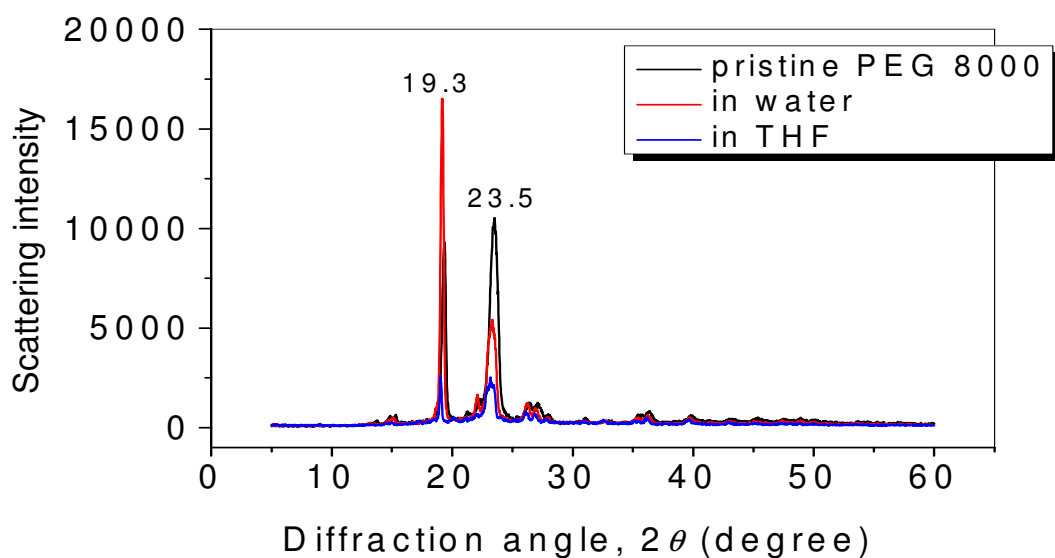


Figure 4.32. XRD patterns of the PEG 8000 powders in the presence and absence solvents.

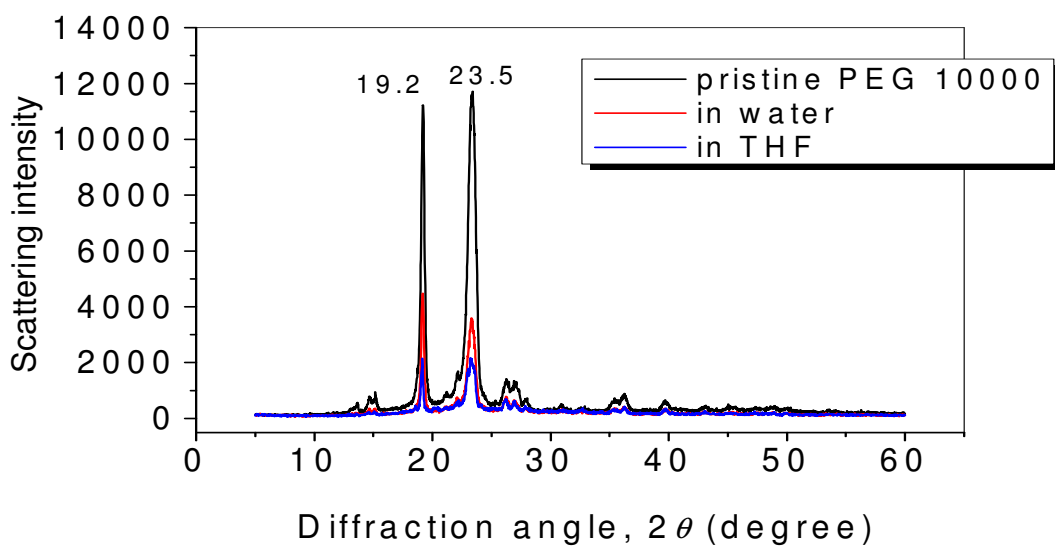


Figure 4.33. XRD patterns of the PEG 10000 powders in the presence and absence solvents.

A useful estimate of the percent crystallinity can be obtained by an approximate method (Alexander, 1969 and Chall et al., 1962) according to which, leaving aside the background scatter from both sides of the crystalline peak, a smooth curve is drawn in the form of an area encompassing all the base points of both sides of the rising crystalline peak to separate the amorphous scatter zone from the crystalline zone. The percent crystallinity is defined as

$$\% \text{ crystallinity} = \frac{\text{area under the crystalline peak } (A_c)}{\text{total area under crystalline and amorphous peaks } (A_c + A_a)} \times 100$$

The most suitable polynomials of 2nd, 3rd or 4th order defined which limit the background of the graph (Polynomial Regression” or “Polynomial Curve Fitting). With each curve draw by these polynomials and the x-axis, an area (A_a) occurs in between, the total of which is calculated by integrating. Each point forming the graph, is joined with consecutive broken lines and with the help of integral work, the total area of the zone remaining between these broken lines and x-axis is thus calculated. A typical polynomial curve fitting is given for PEG/water system in Figure 4.34.

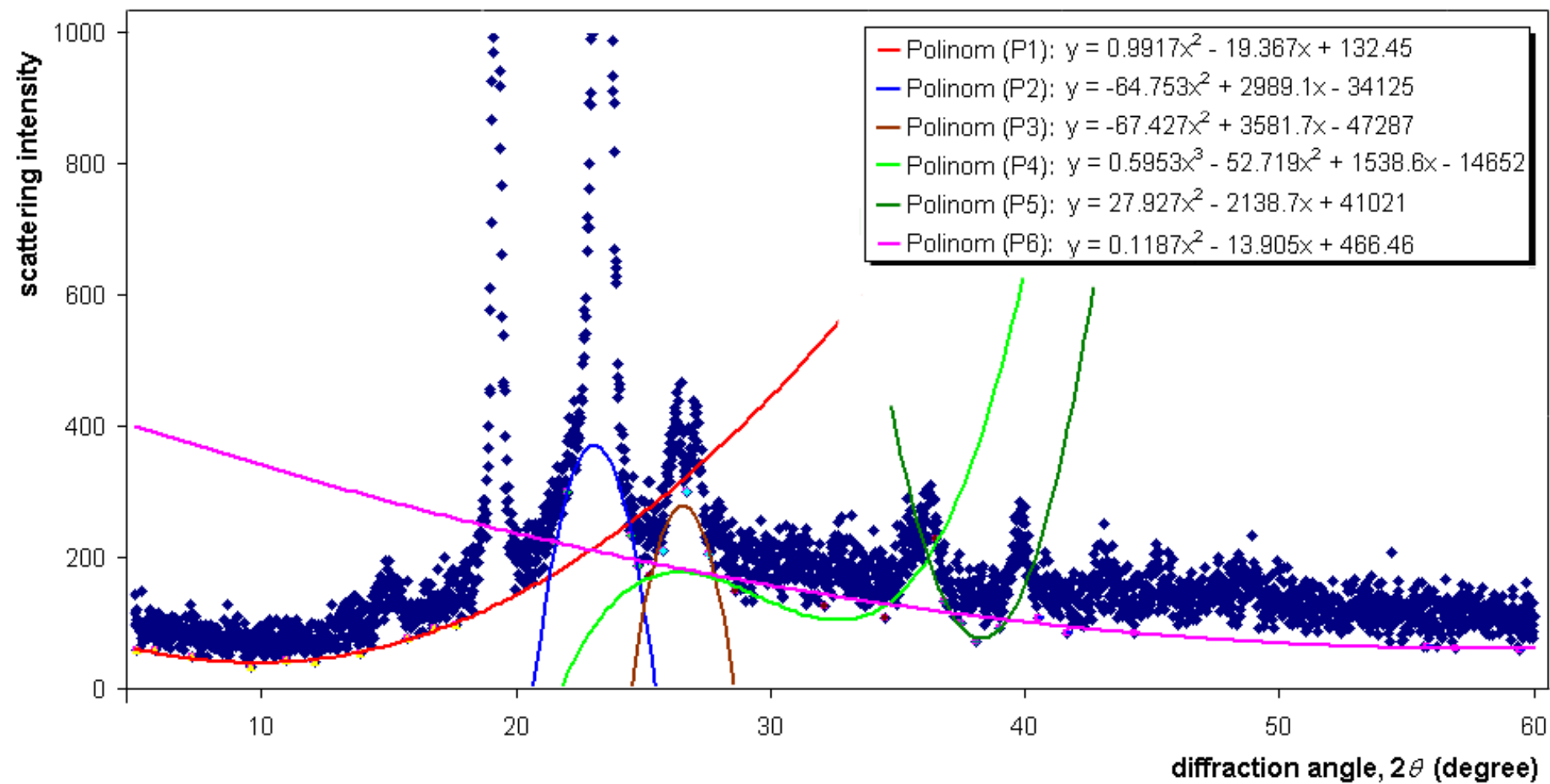


Figure 4.34. Polynomial curve fitting for PEG/water system

A typical calculation of the percent crystallinities of PEG samples are given in Table 4.50.

Table 4.50 . Crystallinity % and variation % of PEG powders in the presence and absence solvents.

	pristine polymer	in water		in THF	
	X_c (%)	X_c (%)	variation (%)	X_c (%)	variation (%)
PEG 2000	62	44	18	33	29
PEG 4600	63	44	19	33	30
PEG 8000	56	46	10	33	23
PEG 10000	56	46	10	32	24

In original polymer samples, % crystallinity for PEG 2000 and PEG 4600 yields 62-63% whereas for PEG 8000 and PEG 10000, this value drops to 56%. For these four molecular weights, when XRD's of samples prepared in water and THF are examined the % crystallinities are observed to drop. % crystallinity varies about 20% for the samples prepared in water with 2000 and 4600 molecular weights compared to the original polymer. This variation is around 10% for PEG 8000 and 10000 prepared in water when compared with that of the original polymer. % crystallinity variations of samples prepared in THF are much more prominent. 30% decrease is observed in crystallinity for PEG 2000 and 4600 samples prepared in THF whereas this change in crystallinity above 20% for PEG 8000 and 10000 samples (Table 4.50).

As a consequence of the dissolution of PEG in water, it is quite obvious that a variation will occur in the polymer conformation and a decrease in % crystallinity. Undoubtedly, THF being more effective than water, will subsequently lead to a greater change in polymer conformation in THF. This behavior, in turn, will end up with the conclusion that % crystallinities of samples prepared in THF are expected to drop more than those in water.

When % crystallinities of PEG samples are calculated, variations are observed between literature values with regard to the selected method. As the crystallinities calculated via X-ray or WAXD are low (60-75%), percent crystallinity values found from DSC measurements are generally higher (> %80).

While Petrova et al. (1998) find the crystallinity as 65% through X-ray studies for PEG samples at a molecular weight of 2000, Qiao et al. (2004) have found this value as 59% for PEG of 1000 molecular weight and 77% for that of 1500 molecular weight as a result of WAXD studies. Percent crystallinity of PEG at 2000 molecular weight has come out to be 86% from DSC measurements by Silva et al. (2003) which is extremely greater than the value obtained by Petrova. Percent crystallinity found as 86-92 % by Pielichowski and Flejtuch (2002) for PEG between a range of 1000-10000 molecular weight reaches extremely high values. Hu et al. (2003) has ended up with such a high value as 95% for % crystallinity from DSC studies with PEG 8000.

4.9. FTIR and Raman Spectroscopy

Infrared spectra have been used as solid evidence for the direct association of the solvents with the etheric oxygen of PEG. In concentrated chloroform or benzene solution, PEG shows strong molecular association through intermolecular H-bonds (Liu and Parsons, 1969). When crystalline PEG is melted or dissolved, some disorder of the polymer chain must be involved. Also, the polymer chain is known to be less ordered for low molecular weight PEG. The interpretations of the chain disorder in PEG by various authors, however, are not consistent. The influence of the solvent medium on the conformational structure of PEG has not been clearly explored previously (Conner and McLauchlan, 1965), although certain peculiar viscosity results in aqueous PEG solutions have been reported (Rösch 1956).

Studies involving the conformational structure variations of PEOs and related work have gained much importance lately and indeed very valuable (Kozielski et al., 2005; Drozdowski et al., 2002; Stevenson et al., 2003).

Topological analysis of the water molecule has also suggested that the attractive electrostatic effect between the positive water O-H zone and the negative PEO lone pairs plays an important role in the H-bonding of the PEO-water system. Thus, the molecular electrostatic potential topology, $V(r)$, which is particularly useful for understanding the hydration process predicts a coil of water molecules around the PEO chain forming H-bonding with two sites of ether oxygen. This coil is formed in such a way that more water molecules accumulate on the cavities surrounding the PEOs oxygen atoms where the minima of the negative zone are located. PEO is characterized by a sequence of monomers, which in water can adopt the local conformation (O-C-C-O dihedral sequences) *tgt*, *tgg*, *tg⁺g⁻*, *ttt*, etc. (with *t*=trans, and *g*=gauche). The same studies (Smith et al., 2000; Dormitondova, 2002) indicate that the *tgt* and *tgg* conformers are favored under low concentration and low temperature conditions. On most systems, the most stable conformation (cis, trans, and/or gauche) is the result of the combination of different factors such as steric repulsions, trans effect, hyperconjugation, H-bonding, and solvent effects (Wade, 1987). In general, H-bonds are the results of a delicate balance between electrostatic interactions, exchange and dispersion forces. In addition, the positive value at the O-H bond in water is 50% bigger than the corresponding value of the C-H in the monomers. These facts suggest that the attractive electrostatic interaction between the positive water O-H bond and the negative PEO lone pairs is the driving force for the H-bonding on PEO-water. In one case, a water molecule forms a H-bond with ether's oxygen on the polymer and another H-bond with an adjacent water molecule. A second kind of interaction, similar to the water molecule is located on each O-C-C-O *tgt* local site forming two H-bonds with the minima lone pairs of the ether oxygen (Aray, 2004).

In this work, original PEG samples (PEG 2000, PEG 4600, PEG 8000 and PEG 10000 g/mol) have been prepared in different solvents (water, methanol, DMSO, chloroform and THF) and followed by the casting of solvents, the prepared solid samples have been employed for FTIR and Raman spectroscopies from which spectral analysis have been made. The aim of spectroscopic studies is to observe the changes in polymer conformation related with solvent character and molecular weight and the interpretation of the characteristic bands appearing at different frequencies. The investigation of spectral evidences with algorithmic calculations

and thermodynamic magnitudes presents another purpose of this study. Spectral differences have been grouped with respect to characteristic fields (O-H stretching, C-H stretching, CH₂ bending, C-O stretching, CH₂ rocking, C-C-O and C-O-C bending, C-O-C angle bending and C-O internal rotation and Far Raman region respectively) and thus evaluated.

The choice of Raman spectroscopy for analysis of chemical composition and structure is based on the high sensitivity of the Raman Effect for certain nonpolar chemical groups. In polymers, these groups are primarily the nearly homonuclear single and multiple C-C bonds that are weak or absent in the FTIR spectra. In this study, the characteristic group frequencies for Raman spectroscopy have been tabulated.

The difference in wavelength between the incident and scattered radiation corresponds to wavelengths in the mid-infrared region. Indeed, the Raman scattering spectrum and infrared absorption spectrum for a given species often resemble one another quite closely. There are, however, enough differences between the kinds of groups that are infrared active and those that are Raman active to make the techniques complementary rather than competitive. For some problems, the infrared method is the superior tool; for others, whereas the Raman procedure offers more useful spectra. For the other, an important advantage of Raman procedure over infrared lies in the fact that water does not cause interference (Koenig, 1992).

4.9.1. O-H stretching

It will be much more helpful to interpret the OH stretching frequency variations both with respect to molecular weight and solvent nature. As a known fact, the stretching vibrations of free OH groups not added to H-bond are observed at higher wavenumbers. As H-bond formation is realized more the followed band shifts to lower wavenumbers and the band broadens. Free OH stretching vibrations may be observed at $\sim 3500\text{ cm}^{-1}$ or higher wavenumbers. The presence of the FTIR transmittance component confirmed that H-bonds exist in the polymer blends. All the hydroxyl bands could be further resolved into "free hydroxyl bands

could be further resolved into “free” hydroxyl peaks ranging from 3450 to 3550 cm^{-1} and the associated “H-bonded hydroxyl” peak ranging from 3300 to 3450 cm^{-1} , which is attributed to a wide distribution of H-bonded hydroxyl-strength frequencies. The H-bonded hydroxyl peak includes intramolecular and intermolecular H-bonding (Wang et al., 2001).

When investigated on the basis of molecular weight as the OH stretching frequency of lowest molecular weight PEG sample (PEG 2000) among PEG samples described as pristine polymer (nosolvent interaction) are being observed at 3426 cm^{-1} , the OH stretching frequency of highest molecular weight PEG sample shifts towards 3504 cm^{-1} . This shift is around $\sim 80 \text{ cm}^{-1}$. In the case of low molecular weight PEG sample, as a consequence of the abundance of OH end groups and H-bond formation of these groups among themselves weakens the OH stretching frequency and the spectrum shifts towards lower wavenumbers (Table 4.51, Figures 4.35, 4.36). As the molecular weight increases peak areas are decreased relatively. This behavior is quite natural because the number of end groups decrease by increasing molecular weight.

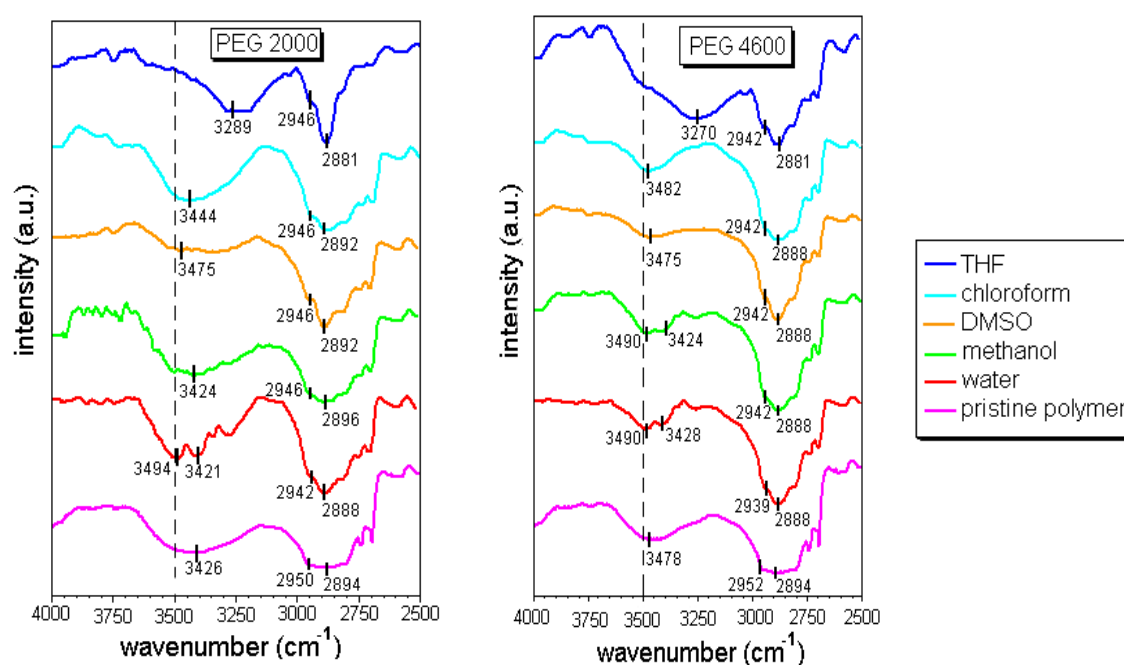


Figure 4.35. Change of the FTIR spectra of OH stretching and CH stretching frequencies in PEG 2000 and PEG 4600 systems cast from different solvents.

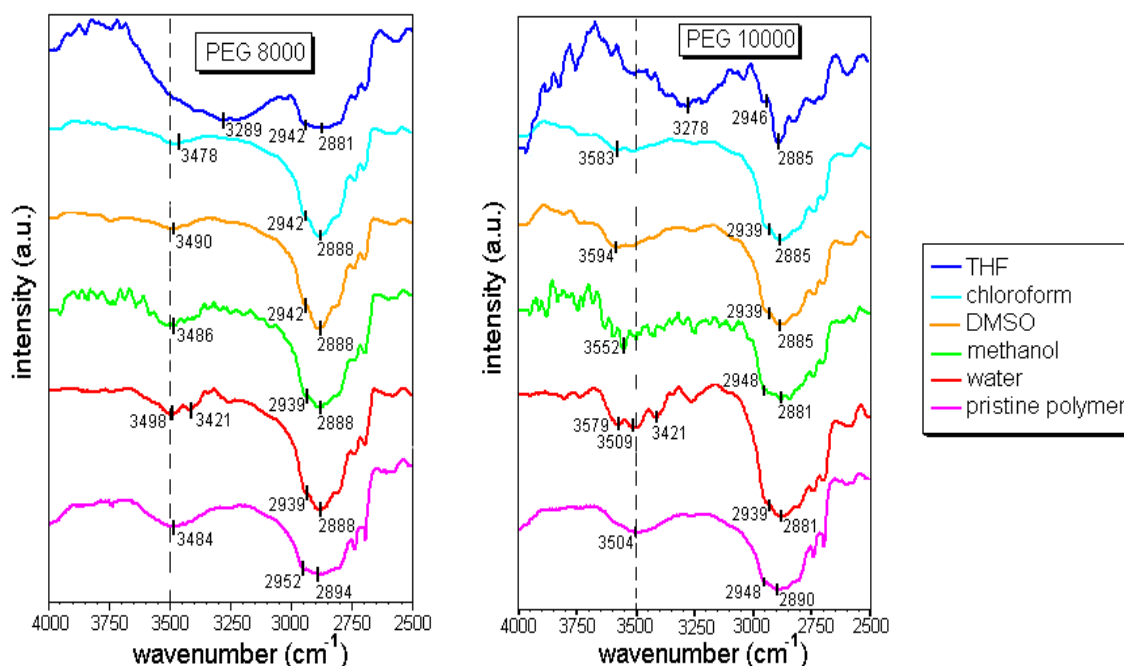


Figure 4.36. Change of the FTIR spectra of OH stretching and CH stretching frequencies in PEG 8000 and PEG 10000 systems cast from different solvents.

The shift of free OH vibrations to higher wavenumbers displayed in original polymer sample with increasing molecular weight is also observed in the samples prepared in solvent medium (Table 4.51, Figures 4.35, 4.36).

Table 4.51. FTIR bands of OH end group stretching for different molecular weight PEG/solvent systems at room temperature.

Polymer	ν_{OH} (cm^{-1})					
	pristine polymer	polymers casting from				
		water	methanol	DMSO	chloroform	THF
PEG 2000	3426(m)	3494 (m) 3421 (m)	3424 (m)	3475 (m)	3444 (m)	3289 (m)
PEG 4600	3478 (m)	3490 (m) 3428 (m)	3490 (m) 3424 (m)	3475 (m)	3482 (m)	3270 (m)
PEG 8000	3484 (m)	3498 (m) 3421 (m)	3486 (w)	3490 (w)	3478 (m)	3289 (m)
PEG 10000	3504 (m)	3579 (m) 3509 (m) 3421 (m)	3552 (m)	3594 (m)	3583 (m)	3278 (w)

m: medium, w: weak.

The free OH vibrations of PEG 2000 sample prepared in water are observed at 3494 cm^{-1} whilst that of PEG 10000 sample has shifted to 3579 cm^{-1} . Similarly, this shift for PEG 10000 samples prepared in methanol is being observed at 3552 cm^{-1} , at 3594 cm^{-1} in DMSO and at 3583 cm^{-1} in chloroform, respectively.

When the spectra are examined carefully, one may also realize the spectral variations of OH groups added to H-bond besides free OH groups. Related to H-bond character (1:1 and 1:2 type H-bond) (Vinogradov and Linnell, 1971) these shifts may be exhibited up to $3200\text{-}3400\text{ cm}^{-1}$ wavenumbers.

The change in polymer conformation, more extensively the mobility of polymer chain also affects the interaction characters of those groups in that polymer chain being related to the type of solvent (Branca et al., 1998; Liu and Parsons, 1969; Kozielski et al., 2005 and Drozdowski et al., 2002).

The increasing strength of solvent for disordering the polymer in the order of THF > chloroform > DMSO > methanol > water may also be observed in the spectra as well. The H-bonded OH stretching vibrations for the PEG 2000 sample prepared in water are observed at 3421 cm^{-1} whereas those of the sample prepared in THF shift towards 3298 cm^{-1} . These shift values for the PEG samples with 4600, 8000 and 10000 molecular weights prepared in THF have been observed at 3270 , 3289 and 3278 cm^{-1} , respectively (Table 4.51, Figures 4.35, 4.36).

4.9.2. C-H stretching

C-H stretching vibrations display a broad and multishouldered spectral behavior in a wide frequency range of $2800\text{-}2950\text{ cm}^{-1}$. As antisymmetrical CH_2 stretching vibration are observed at high frequency values ($\sim 2950\text{ cm}^{-1}$), symmetrical CH_2 stretching may be displayed at lower frequency values ($2850\text{-}2890\text{ cm}^{-1}$) (Bailey and Koleske, 1976; Bermudez et al., 2000; Huang et al., 2002). Matsuura et al. (1973) have emphasized the fact that the shoulder observed at 2952 cm^{-1} may

result as a characteristic band from the antisymmetrical stretching vibrations of CH₂ in crystalline PEG. In FTIR spectra of pristine polymers, this characteristic behavior has been determined as a shoulder between 2942-2952 cm⁻¹. On the other hand, in solvent systems this frequency shifts to lower fields and may occur almost ~10 cm⁻¹ (Table 4.52). This is clear evidence implying that the hydrophobic interactions between the methylene groups of semicrystalline polymer are being destructed in the presence of solvent. Among this narrow region, the shift towards lower frequency values may as well be observed in the spectra of melt polymers (Bailey and Koleske, 1976; Bermudez et al., 1999). However, a systematic change and/or shift have not been determined with respect to the repeated unit number in PEG (Bermudez et al., 2000) who strongly supports this interpretation.

At lower frequencies, CH₂ symmetrical vibrations also exhibit different spectral behavior in varying systems. The characteristic band of pristine polymers observed at 2890-2894 cm⁻¹ shift towards lower frequency values in samples prepared cast from solvent systems. Generally, the frequency values do not vary much for the samples prepared from four solvents apart from THF whilst this shift may occur at much lower frequency values when THF is employed as the solvent (Figures 4.35, 4.36, Table 4.52). This behavior implies that symmetrical stretching will weaken as a consequence of the hydrophobic interactions of methylene groups. Matsuura et al. have estimated that the band observed at 2889 cm⁻¹ may as well characterize the symmetrical stretchings of CH₂ groups in semicrystalline state in the PEG chain. Besides, these characteristic bands may shift towards lower frequency values in melt state as well (Matsuura, et al., 1973; Machida and Miyazawa, 1964 and Bermudez et al. 1999). Whether the stretching deformations occur by thermal effect or the deformation is achieved by solvent effect it points out too common and parallel behavior.

CH₂ symmetrical stretching (~2890 cm⁻¹) and antisymmetrical stretching (~2940 cm⁻¹) vibrations of PEG samples are successfully observed as characteristic bands in Raman studies as well (Bailey and Koleske, 1976). These stretchings are expected to weaken as a result of the interactions of hydrophobic

methylene groups, however, the four different systems and four different molecular weights studied exhibit a spectral variation at 2886 cm^{-1} (strong band) and at $2940\text{-}2945\text{ cm}^{-1}$ (shoulder) frequency range, respectively it was already observed in FTIR studies that the broad band maxima characterizing the CH_2 stretching vibrations between the frequency range of $2890\text{-}2880\text{ cm}^{-1}$ shift towards lower field values (THF sample being the most pronounced $\sim 13\text{ cm}^{-1}$).

Table 4.52. FTIR bands of CH_2 stretching for different molecular weight PEG/solvent systems at room temperature.

Polymer	$\nu_{\text{-CH}_2}$ stretching (cm^{-1})					
	pristine polymer	polymers casting from				
		water	methanol	DMSO	chloroform	THF
PEG 2000	2950 (sh)	2942 (sh)	2946 (sh)	2946 (sh)	2946 (sh)	2946 (sh)
	2894 (s)	2888 (s)	2896 (s)	2892 (s)	2892 (s)	2881 (s)
PEG 4600	2952 (sh)	2939 (sh)	2942 (sh)	2942 (sh)	2942 (sh)	2942 (sh)
	2894 (s)	2888 (s)	2888 (s)	2888 (s)	2888 (s)	2881 (s)
PEG 8000	2952 (sh)	2939 (sh)	2939 (sh)	2942 (sh)	2942 (sh)	2942 (sh)
	2894 (s)	2888 (s)	2888 (s)	2888 (s)	2888 (s)	2881 (s)
PEG 10000	2948 (sh)	2939 (sh)	2948 (sh)	2939 (sh)	2939 (sh)	2946 (sh)
	2890 (s)	2881 (s)	2881 (s)	2885 (s)	2885 (s)	2885 (s)

s: strong, sh: shoulder.

In spectral evaluations, the in-plane and out-of-plane bending vibrations have been taken into consideration during interpretations. These groups have been displayed as shown in Figure 4.37 in order to follow the various bending deformations of this group more comfortably.

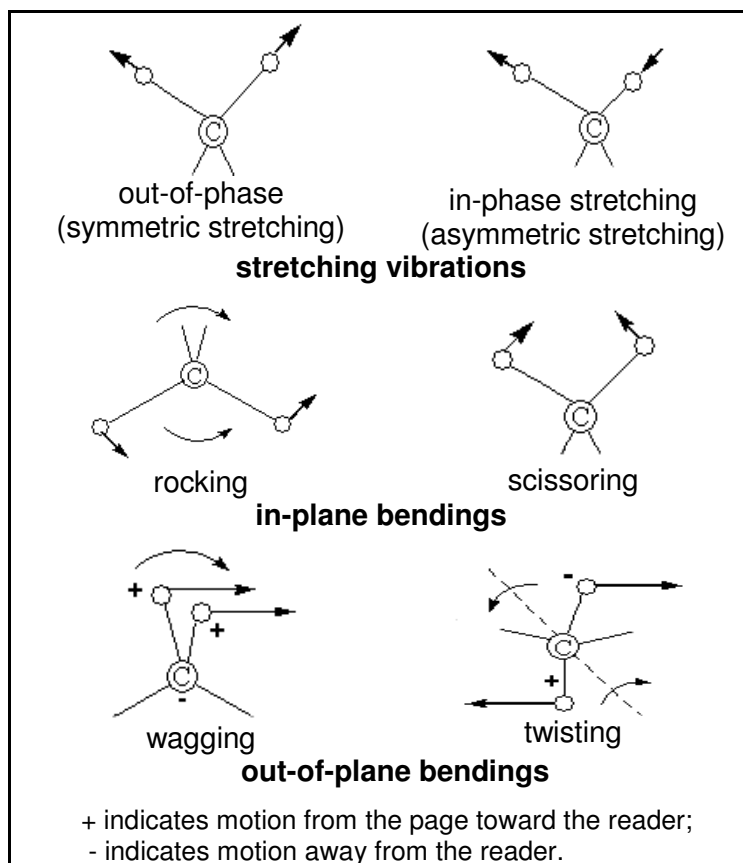


Figure 4.37. Characteristic vibrations of CH₂ group.

4.9.3. CH₂ bending

Scissoring vibrations of methylene groups (in-plane bending) are observed within the range of 1460-1470 cm⁻¹ (Bailey and Koleske 1976; Morssli et al. 1991; Huang et al., 2002). Extremely strong bands displayed in the range 1468-1473 cm⁻¹ for PEG samples are observed to weaken and shift towards lower frequencies (Table 4.53).

Table 4.53. FTIR bands of CH₂ scissoring for different molecular weight PEG/solvent systems at room temperature.

Polymer	ν_{CH_2} scissoring (cm ⁻¹)					
	pristine polymer	polymers casting from				
		water	methanol	DMSO	chloroform	THF
PEG 2000	1473 (s)	1466 (m)	1469 (m)	1467 (m)	1466 (m)	1461 (m)
PEG 4600	1467 (s)	1466 (m)	1465 (m)	1466 (m)	1465 (m)	1465 (m)
PEG 8000	1467 (s)	1466 (m)	1465(m)	1466 (m)	1466 (m)	1462(m)
PEG 10000	1468 (s)	1462 (m)	1465 (m)	1463 (m)	1461 (m)	1463 (m)

s: strong, m: medium.

The highest shift occurs in THF sample. If it is considered that scissoring motion is more flexible, this behavior is quite natural within the measure of disruption of hydrophobic interactions of methylene groups. The previous spectral evaluation of PEG samples (Bailey and Koleske, 1976; Bermudez et al., 2000), the bands observed at 1236-1244 cm^{-1} wavenumbers may be attributed to CH_2 twisting vibrations. However, the spectral difference of the band occurring at 1241 cm^{-1} in FTIR studies has not been observed in the systems studied at hand.

Several implications are proposed for CH_2 in-plane bending vibrations suggesting that they may be observed as a doublet at around 1480 cm^{-1} in Raman studies but almost impossible to detect in FTIR (Koenig and Angood, 1970; Bailey and Koleske, 1976; Kozielski et al., 2004). In this study, within this frequency region, generally doublet peaks are being observed. As no net spectral difference is realized related to solvent character in PEG 2000, 4600 and 8000 samples at 1483-1486 cm^{-1} frequency range, only the peak observed at 1477 cm^{-1} for PEG 10000 sample prepared in THF strongly supports comment in FTIR studies (Figure 4.38).

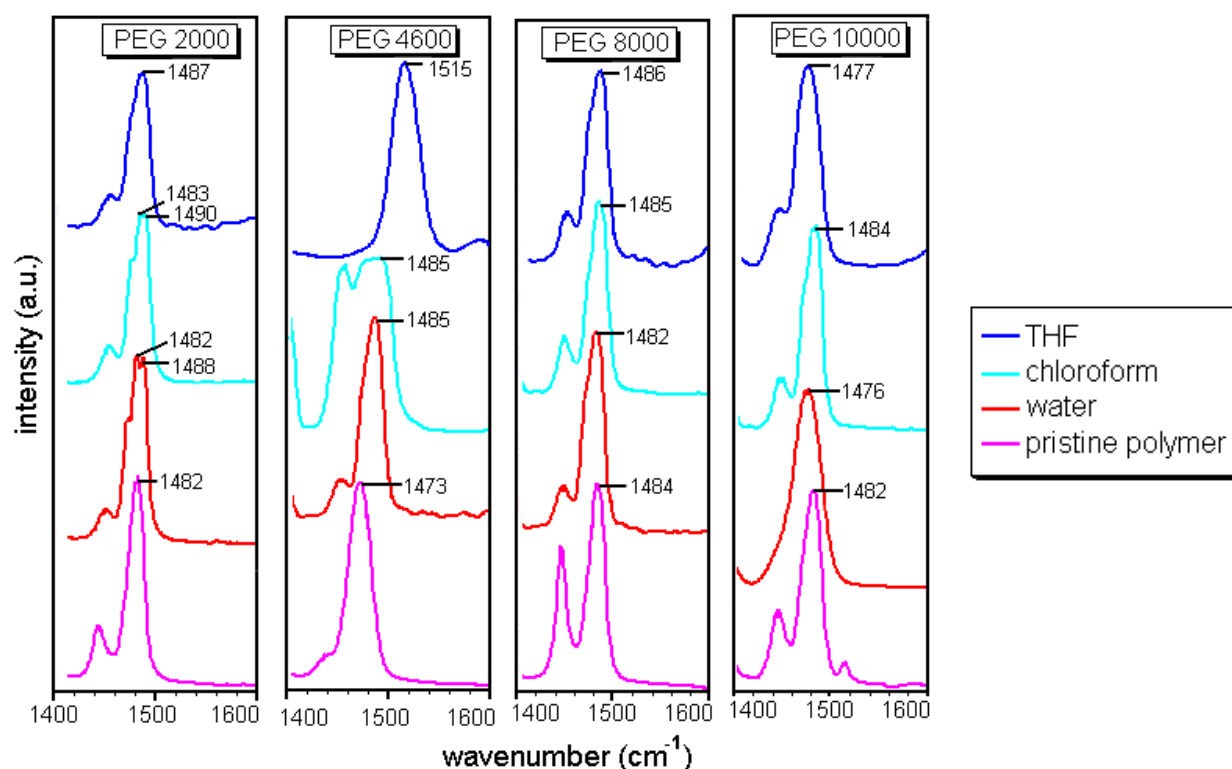


Figure 4.38. Change of the Raman spectra of in-plane bending of CH_2 for PEG samples in the presence and absence of solvents.

CH₂ out-of-plane bending is seen as a doublet at 1230 cm⁻¹ and 1280 cm⁻¹ (Figure 4.39). If Raman evaluations are considered, it is observed that the band appearing at 1280 cm⁻¹ for PEG 2000 and 8000 samples is almost constant in all solvents. However, it may be investigated that the doublet bands observed in PEG 4600 and PEG 10000 samples shift towards lower fields.

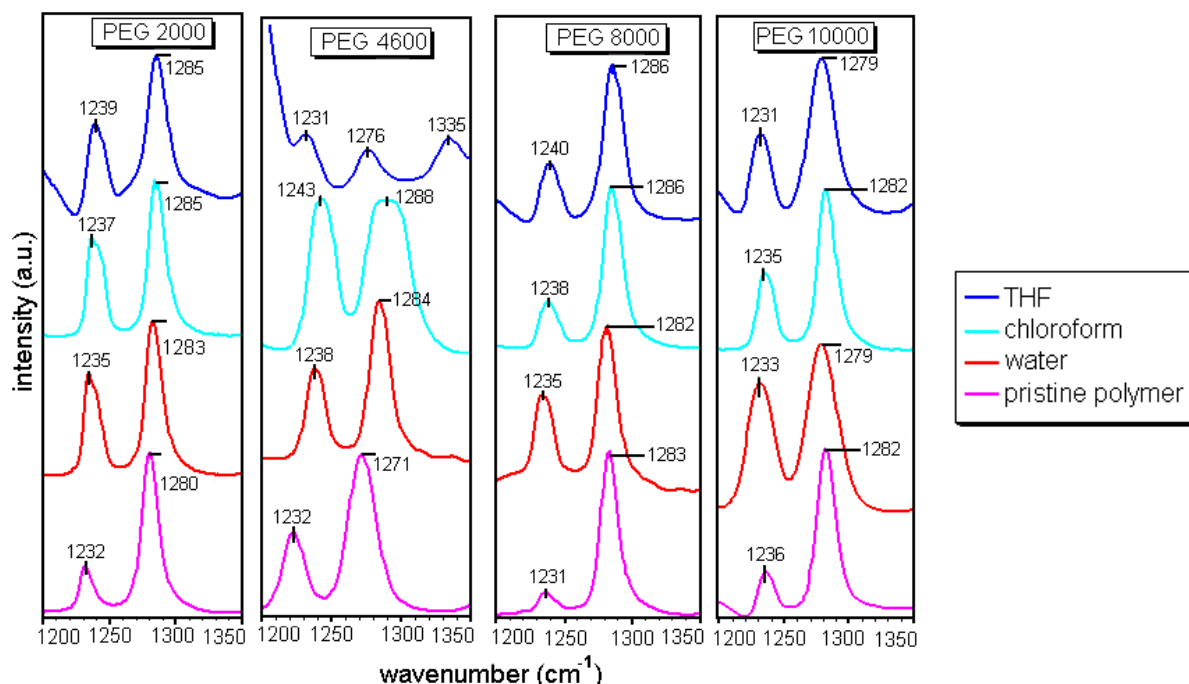


Figure 4.39. Change of the Raman spectra of out-of-plane bending of CH₂ for PEG samples in the presence and absence of solvents.

4.9.4. C-O stretching

C-O stretching vibrations may be evidently observed at ~1100 cm⁻¹ in FTIR. It is a quite widely known fact that as H-acceptor O atom participates actively in the formation of H-bond, C-O bond energy is expected to weaken and shift towards lower frequencies. In spectral evaluations, a broad and highly shouldered behavior is displayed in this region (Figure 4.40).

As a consequence of the complexation of electronegative oxygen atom with cationic structures, CO stretching vibrations shift towards lower wavenumbers (Bermudez et al., 2000; Carlos et al., 1999).

C-O group may either add to H-bond or may not. C-O stretching vibrations with different characters may exhibit a broad and wide band whereas in some cases bands characterizing each formation clearly may also be detected. The bands occurring at 1145-1153 cm^{-1} in pristine PEG are considered as C-O stretchings which do not participate in H-bonding. The shift of these bands in four other solvents apart from THF towards a lower frequency of about 5 cm^{-1} is quite significant (Figure 4.40). However, more important than this, in THF which is considered as the best solvent, this band surprisingly vanishes (PEG 8000 sample shows differentiation). If an interpretation is required, one may imply that polymer coil extends in good solvents thus leading to H-bond formation between etheric oxygen and OH groups, consequently weakening C-O stretching vibration, shifting of spectrum towards a down-field and even with the complete extinction of that band.

The observed bands of PEG samples in this region are extremely broad. Treatment with the solvent, three specific bands become more prominent. The first one among these prominent bands is the band appearing at the wavenumber mentioned above. This region may be described as the region of C-O-C asymmetrical stretching vibrations (Kondo, 1997) and C-O-C asymmetrical stretching vibrations may be observed as two distinct bands (Morssli et al., 1991). The band appearing at a higher frequency value is the one participating in intramolecular H-bond while the latter occurring at a lower wavenumber characterizes the vibrations participating in intermolecular H-bond. The exhibition of this region as a broad band may be explained by the CH_2 rocking modes in this frequency region besides the C-O stretchings (Bermudez et al., 2000). However, it has been widely reported in literature that CH_2 rocking bands may only occur at way low frequency values and most prominently at $\sim 850 \text{ cm}^{-1}$.

According to the spectral interpretation of Morssli and his group (1991), the band appearing in the range of 1145-1153 cm^{-1} wavenumber characterizes the C-O stretching participating with intramolecular H-bond. As stated previously, this region was defined as the free C-O stretching vibrations. The common point of both implications is that, whether those vibration denote the free C-O or the

participating C-O in intramolecular H-bonding, the band in THF sample completely vanishes.

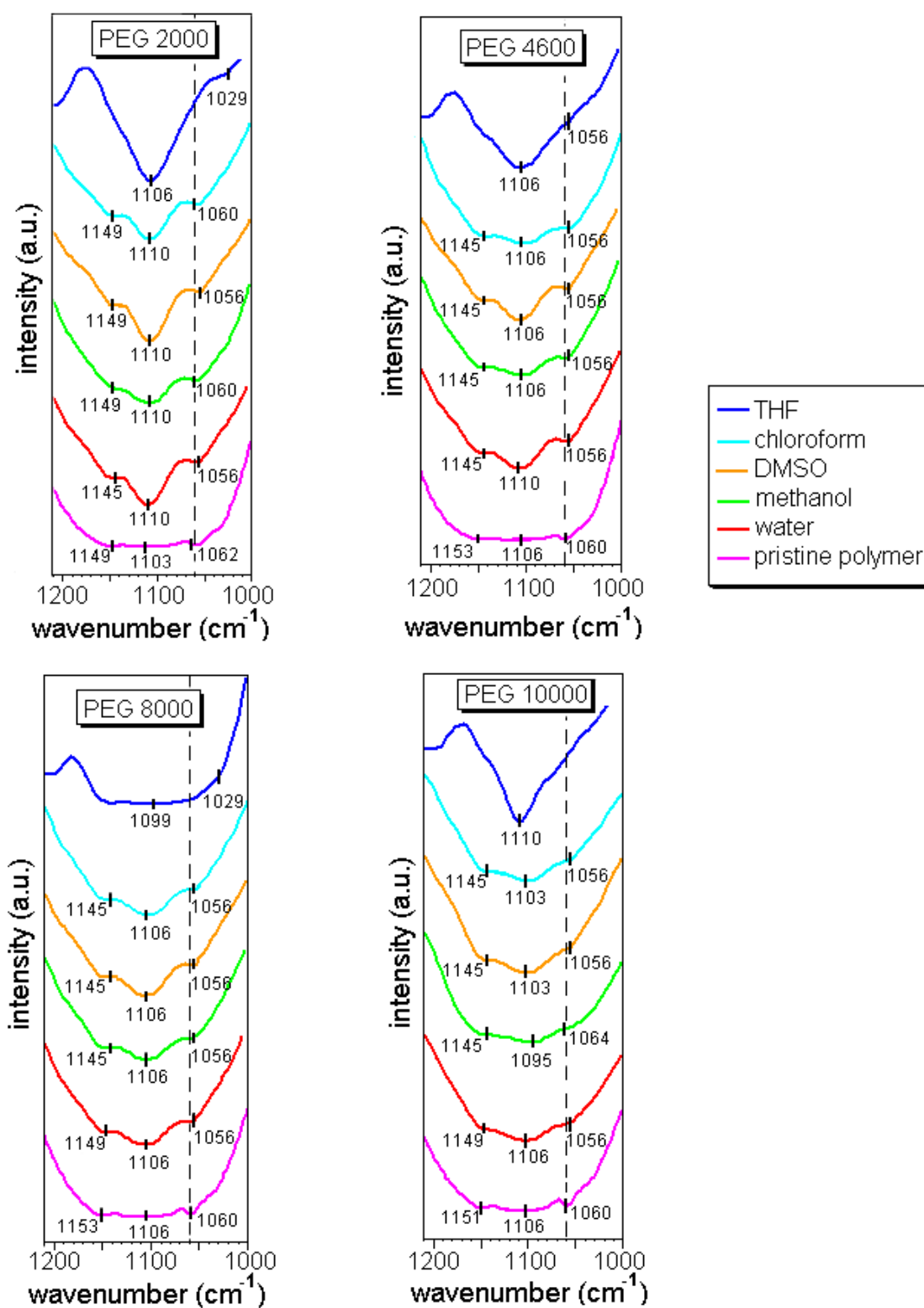


Figure 4.40. Change of the FTIR spectra of C-O stretching frequencies in different molecular weight PEG systems cast from different solvents.

The lower frequency region characterizes the C-O stretchings participating in intermolecular H-bond formation. In all samples, a quite significant band is observed at 1103-1106 cm^{-1} and this band shows somewhat spectral variations although very slight. Extremely different spectral implications have been made for this narrow region. It is reported that this band is said to characterize CH_2 twisting (Kozielski et al., 2004), C-C antisymmetrical stretching (Menna, et al., 2003), C-O-C stretching (Bailey and Koleske, 1976) and only C-O stretching (Bermudez et al., 2000) and have been largely discussed. However, this band may also be considered as the C-O stretching participating in intermolecular H-bond formation together with the hydroxyl group. This opinion is very much alike with the spectral evaluation of Morssli group.

In Raman studies, the frequency range coinciding with 1160-1060 cm^{-1} characterizes that of various vibrations. The table illustrating the spectral characterizations of PEG in Raman studies achieved by different working groups is given below.

Table 4.54. References about Raman stretching vibrations (1057-1073 cm^{-1}) of PEG.

Frequency	Mode	specified by
1064 (m)	C-O stretching C-C stretching CH_2 rocking	Bailey and Koleske, 1976.
1060-1066 (m) 1073 (s)	C-O stretching CH_2 rocking	Koenig and Angood, 1970 (He-Ne and Ar lasers).
1057 (m)	C-OH stretching	Kozielski et al., 2004.
1065 (m)	Solid-melt transition band	Branca et al., 1998.
1065 (m)	C-C stretching	Morssli et al., 1991*.

* α , β and γ -hydroxybutyrate.

s: strong, m: medium.

Table 4.55 . References about Raman stretching vibrations (1118-1140 cm^{-1}) of PEG.

Frequency	Mode	specified by
1126 (m)	CH ₂ rocking C-C stretching	Bailey and Koleske, 1976.
1125-1130 (m)	C-C stretching CH ₂ wagging	Koenig and Angood, 1970 (He-Ne and Ar lasers).
1118-1136 (m)	CH ₂ twisting	Kozielski et al., 2004.
1125-1140 (m)	C-O stretching	Morssli et al., 1991*.

* α , β and γ -hydroxybutyrates.
m: medium.

Table 4.56. References about Raman stretching vibrations (1142-1149 cm^{-1}) of PEG.

Frequency	Mode	specified by
1149 (s)	C-O stretching CH ₂ rocking	Bailey and Koleske, 1976.
1142-1147 (m)	C-O stretching	Koenig and Angood, 1970 (He-Ne and Ar lasers).

s: strong, m: medium.

As can be seen from the table, spectral interpretation is quite difficult at close frequency values where distinct vibrations overlap still, the shoulder displayed at 1072 cm^{-1} for PEG 2000 sample is not observed for that cast from THF. Similarly, the medium strength band appearing at 1075 cm^{-1} in PEG 8000 sample completely vanishes for those prepared in THF. The disappearance of the band observed or shoulders at a higher frequency with respect to 1064-1067 cm^{-1} frequency range in THF samples is quite meaningful.

Although a net spectral distinction is observed in Raman studies at the upper frequency range ($>1100 \text{ cm}^{-1}$) the shift towards a higher frequency (though very little) for the samples prepared from THF (1147 and 1148 cm^{-1}) is a behavior difficult to explain (Figure 4.41).

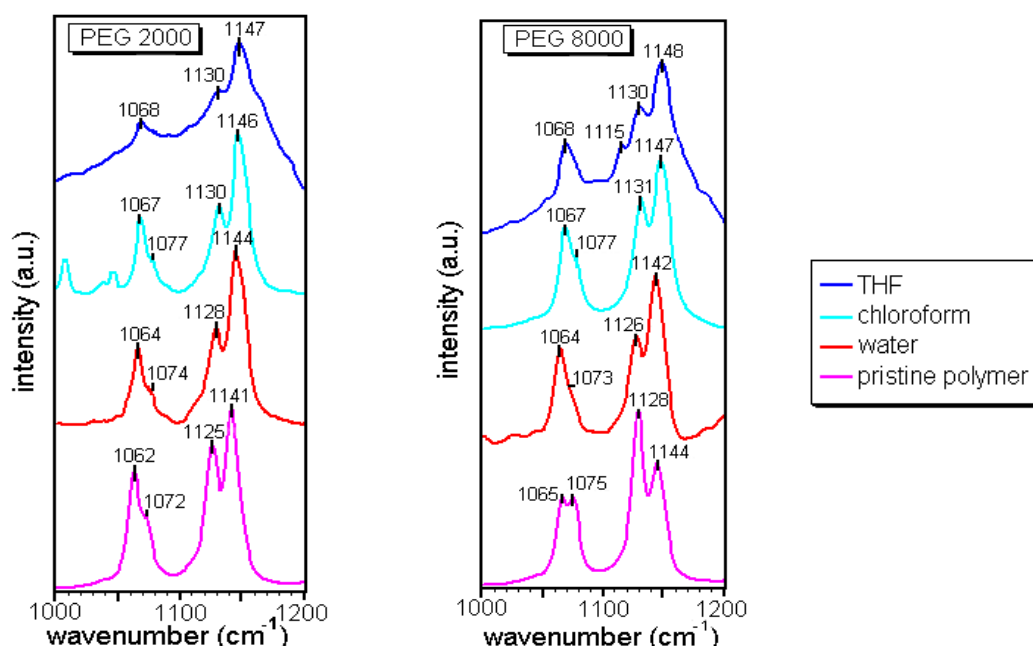


Figure 4.41. Change of the Raman spectra in the region of 1160-1060 cm^{-1} for PEG samples in the presence and absence solvent.

4.9.5. CH_2 rocking

In FTIR studies, spectral distinctions in this region may be observed at two specific wavenumbers (842 and 962 cm^{-1}) (Figure 4.42). These bands appear at exactly the same frequency values for four pristine polymers at different molecular weights. However, for those polymers cast from the solvent, these frequency values seen to shift towards lower regions.

The behavior supporting previous implications exist here as well. As a consequence of the disruption of methylene groups through hydrophobic interactions, it is quite natural that bending vibrations of these groups will certainly be disrupted and the spectrum will shift towards lower frequency values.

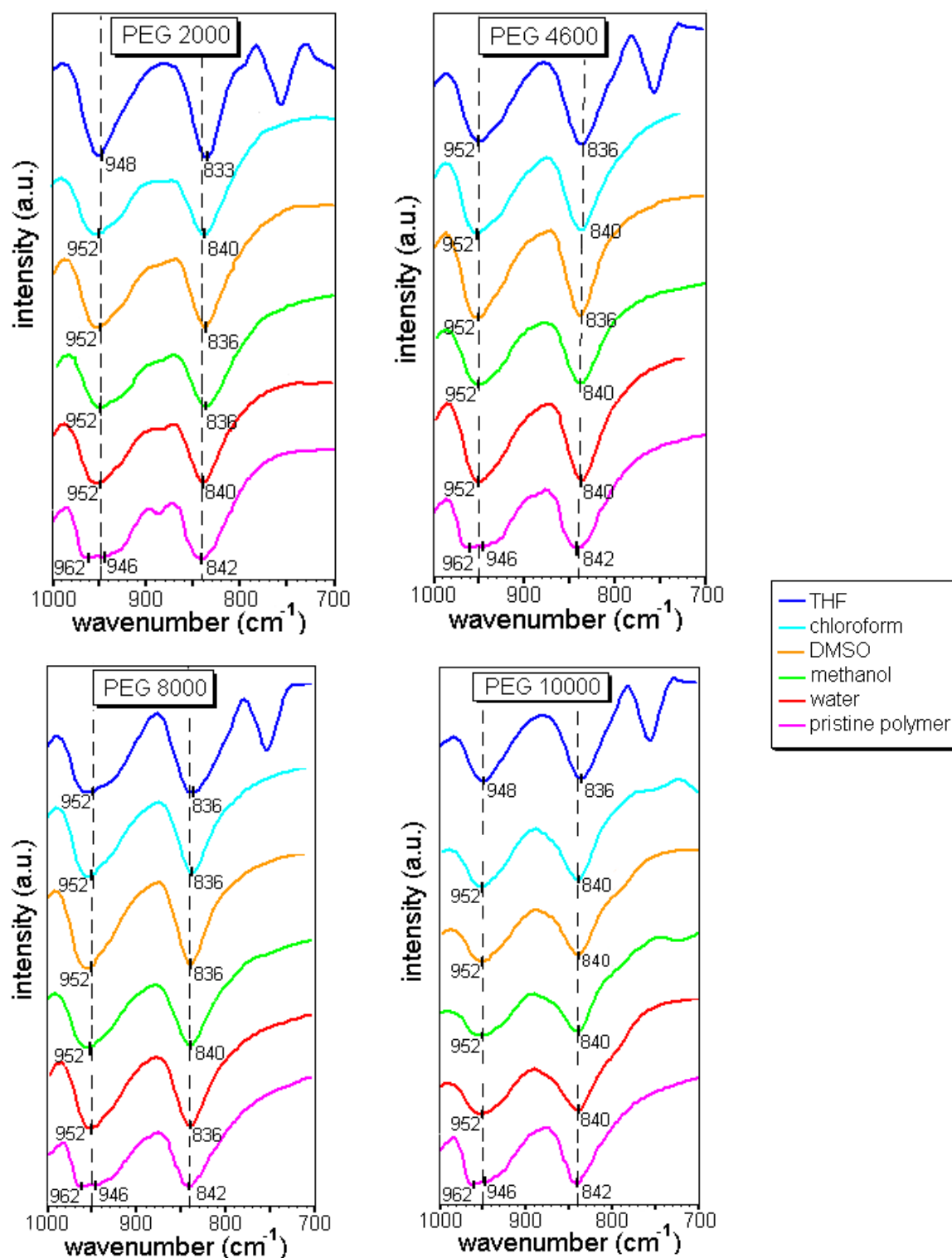


Figure 4.42. Change of the FTIR spectra of ethylene rocking frequencies in different molecular weight PEG systems cast from different solvents.

In Raman studies, the frequency range at 840-860 cm^{-1} is being evaluated to characterize different vibrations. In this narrow region it has been reported that CO stretching, CH_2 rocking vibrations (Matsuura et al., 1973), skeleton vibrations

(Kozielski et al., 2004) and C-CO stretching vibrations (Morssli et al., 1991) may occur but it is not very precise. In other two studies (Frech and Huang, 1995; Bailey and Koleske, 1976) CH₂ rocking modes have been implied to appear in this region.

Frech and Huang (1995) studied CH₂ rocking region ($\sim 750\text{-}900\text{ cm}^{-1}$) and suggested that the frequency up-shift of the band around 860 cm^{-1} with increasing salt concentration is associated with a change in the local conformation of the polymer upon complexation. Ferry et al. (1998) also attributed this peak to changes in the vibrations of the pristine polymer induced by the presence of the cation M⁺. Therefore, the investigation of the Raman peak around 860 cm^{-1} is a useful tool to investigate the extent of secondary interactions.

There is another feature in the Raman spectra of polymeric electrolytes (Silva et al., 2001) around 860 cm^{-1} , which is commonly used to investigate the interactions of the cations and the polymeric chain. This peak was previously attributed to the breathing mode of the ring of oxygens which surrounds the M⁺ cations, but this interpretation has been recently reviewed and some authors have ascribed this band to internal vibrations associated with the local conformation of the polymeric chain affected by the cation complexation.

Carlos et al. (1999) suggest that the absence of the liquid bands mentioned above shows that the semirigidity of the polyether chains probably induces some short-range order in the materials and reduces the fraction of trans structures, characteristic of the molten state, meaning that the conformation of the chains retains the *tgt* sequence characteristic of the crystalline state. Two bands at 1326 and 992 cm^{-1} and the shoulders at 810 and 915 cm^{-1} are not found in the spectra of the doped ureasils. However they may state that the general feature of the spectra of ureasil is substantially identical to that of liquid PEG.

Koenig and Angood (1970) have observed that the strength of the band observed at 811 cm^{-1} decreases as the polymer chain gets longer and they have indicated this band may well characterize the dimer formation whilst the strengths will

substantially diminish in trimer and tetramer structures. In this study, this band has been observed in a few samples. This band at 811 cm^{-1} is probably associated with the hydroxyl end groups in the polymer; although the infrared band has been assigned to the trans form of the methylene groups (Matsuura and Miyazawa, 1969).

For the samples studied at hand, Raman bands may be easily observed in the region very close to the wavenumbers appearing in FTIR but still, it is not very easy to seize spectral discriminations to clarify the up-field or down-field behaviors of these bands.

4.9.6. C-C-O and C-O-C Bending

C-C-O and C-O-C bending vibrations may well be observed in far-Raman region and right at the outside of this region ($<400\text{ cm}^{-1}$) (Koenig and Angood, 1970; Bailey and Koleske, 1976; Bermudez et al., 2000).

As a consequence of the H-bonding of the etheric oxygen of OH end groups of PEG both two bending vibrations are violated and subsequently, the spectrum shifts towards lower frequency values.

In Raman studies, three prominent peaks are easily illustrated in this region at $363\text{-}365\text{ cm}^{-1}$, $536\text{-}538\text{ cm}^{-1}$ and $582\text{-}585\text{ cm}^{-1}$ wavenumbers, respectively (Figure 4.43). The bending vibrations appearing at $363\text{-}365\text{ cm}^{-1}$ for the pristine polymer with 10000 molecular weight and that cast from the solvent media do not display any spectral distinction. Similarly, the vibrations at $536\text{-}582\text{ cm}^{-1}$ remain almost identical. The bending vibrations observed at 365 cm^{-1} for PEG 8000 sample will result with a shift to 368 cm^{-1} in chloroform and to 369 cm^{-1} in THF with a shift value of $\sim 4\text{ cm}^{-1}$. The band appearing at 538 cm^{-1} for the pristine polymer at the same molecular weight will shift towards upper-field at a magnitude of $\sim 4\text{ cm}^{-1}$. Similarly, the band at 585 cm^{-1} shifts towards higher frequency values with a magnitude of $\sim 3\text{ cm}^{-1}$.

Among the studied four samples, this shift value corresponds to 7-8 cm^{-1} for the PEG 2000 sample owning largest number of OH end groups.

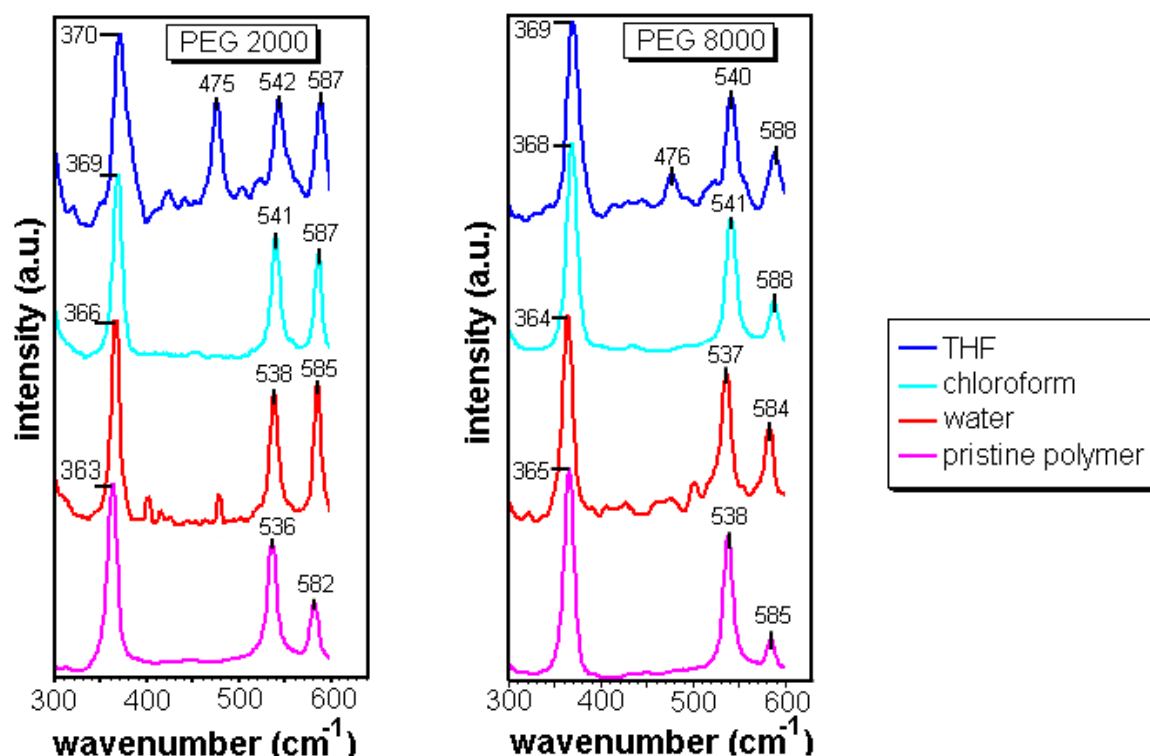


Figure 4.43. Change of the Raman spectra of C-C-O and C-O-C bending frequencies of PEG samples in the presence and absence solvents.

4.9.7. C-O-C angle bending and C-O internal rotation

C-O-C angle bending and C-O internal rotational vibrations may be illustrated a little bit above 200 cm^{-1} in far-Raman region (Koenig and Angood, 1970; Bailey and Koleske, 1976). The bands characterizing these two vibrations within the range of 215-230 cm^{-1} is observed as well (Table 4.57, Figure 4.44). It is seen that these two characteristic wavenumbers appearing at 231 cm^{-1} for the pristine polymer (PEG 2000) shift towards lower fields with an increase in molecular weight, it may well be declared that this behavior is quite natural regarding that the number of OH end groups will decay with increasing molecular weight (except for PEG 8000). Parallel to the interpretations obtained from FTIR studies, one is sure to face with the reality that the interaction will increase with the number of end

groups and that a shift will occur towards higher frequency values at low molecular weights.

Table 4.57. Peak maxima for the pristine PEG and systems cast from chloroform, THF and water (C-O-C angle bending and C-O internal rotation).

Polymer	wavenumbers (cm ⁻¹)			
	pristine polymer	polymers casting from		
		water	chloroform	THF
PEG 2000	-	-	220 (w)	226 (w)
	231 (w)	236 (w)	237 (w)	239 (w)
	278 (m)	282 (m)	284 (m)	285 (m)
PEG 4600	220 (w)	229 (w)	240 (m)	-
	266 (m)	282 (m)	286 (m)	-
PEG 8000	234 (w)	229 (w)	237(w)	242 (w)
	281 (m)	280 (m)	283 (m)	284 (m)
PEG 10000	215 (w)	225 (w) 276 (m)	232 (w)	222 (w)
	231 (sh)		280 (m)	276 (m)
	279 (m)			

m: medium, w: weak, sh: shoulder.

If the spectral evaluations are to be achieved with respect to the solvent type, the spectral behavior of PEG samples cast from solvent media exhibit discriminates significantly from that of the pristine polymer. As the solubility power of the employed solvent rises, a shift towards higher wavenumbers is unavoidable. In chloroform and THF (qualified as good solvents) cast samples, though some little replacements may occur, shifts towards highest wavenumbers have been observed. Besides C-O-C bending and C-O internal rotational vibrations, C-C-O bending vibrations may well be detected in far-Raman region (~ 280 cm⁻¹) (Bailey and Koleske, 1976). The band observed for the pristine polymer (PEG 2000) at 278 cm⁻¹ shifts to wavenumbers 284 and 285 cm⁻¹ in chloroform and THF, respectively (Table 4.57, Figure 4.44).

The band appearing at 266 cm⁻¹ for PEG 4600 sample will shift to 286 cm⁻¹ in chloroform whereas the band observed at 280 cm⁻¹ for PEG 8000 sample will shift to values 283 cm⁻¹ in chloroform and 284 cm⁻¹ in THF.

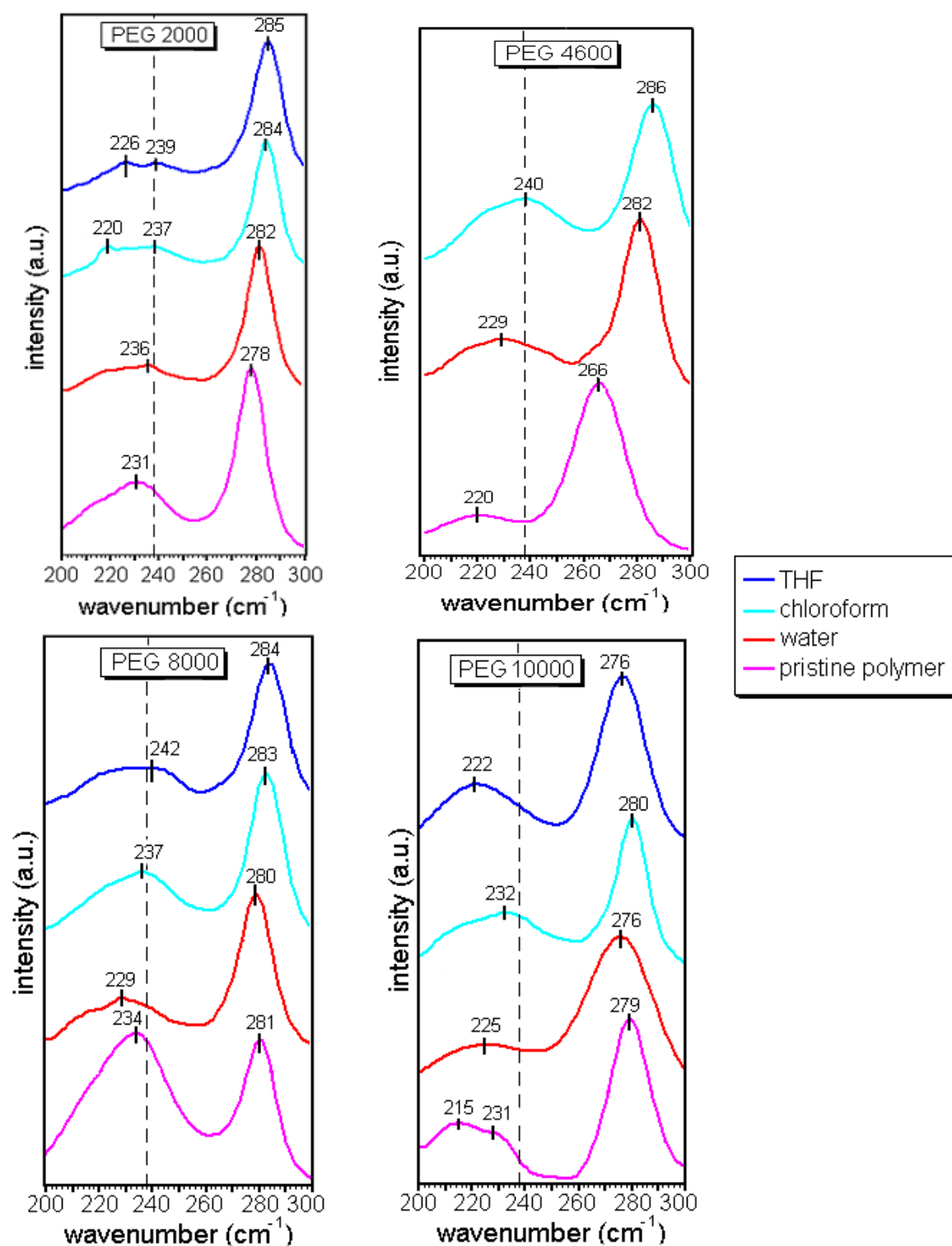


Figure 4.44. Change of the Raman spectra of C-O-C angle bending and C-O internal rotation frequencies of PEG samples in the presence and absence solvents.

4.9.8. Far Raman region ($< 400 \text{ cm}^{-1}$)

In this study, OH...O bending, C-O rotation and C-C-O angle bending vibrations have been investigated in detail within the range of $48\text{--}88 \text{ cm}^{-1}$. This region has been characterized to yield OH...O bending ($\sim 66 \text{ cm}^{-1}$) (Walrafen et al., 1989), C-O rotation and C-C-O angle bending ($\sim 85 \text{ cm}^{-1}$) (Bailey and Koleske, 1976) spectral evaluations highly illustrate the spectral distinctions in the behavior of pristine polymers and those cast from different solvents. Each three characteristic band shifts towards higher frequency values for the samples prepared in solvent medium (Figure 4.45, Table 4.58). The highest frequency shift values are displayed for the samples cast from chloroform and THF.

Table 4.58. Peak maxima for the pristine PEG and systems cast from chloroform, THF and water (Far Raman region).

Polymer	wavenumbers (cm^{-1})			
	pristine polymer	polymers casting from		
		water	chloroform	THF
PEG 2000	-	47.6 (sh)	53.5 (sh)	52.0 (sh)
	57.2 (sh)	60.4 (sh)	65.6 (sh)	67.8 (sh)
	82.1 (w)	83.6 (w)	85.9 (w)	86.1 (w)
PEG 4600	70.9 (w)	84.4 (m)	88.2 (s)	-
PEG 8000	-	-	53.0 (sh)	-
	62.1 (sh)	59.1 (sh)	67.4 (sh)	68.4 (sh)
	84.4 (w)	80.6 (w)	86.0 (w)	85.8 (s)
PEG 10000	77.2 (m)	79.2 (s)	84.2 (w)	79.3 (s)

s: strong, m: medium, w: weak, sh: shoulder.

Within the measure of the H-bond formation it is expected that OH...O in-plane deformation, C-O rotation and C-C-O angle bending vibrations will shift towards higher wavenumbers. This observation is a strong evidence illustrating the achieve role of H-bond for the samples cast from THF and chloroform.

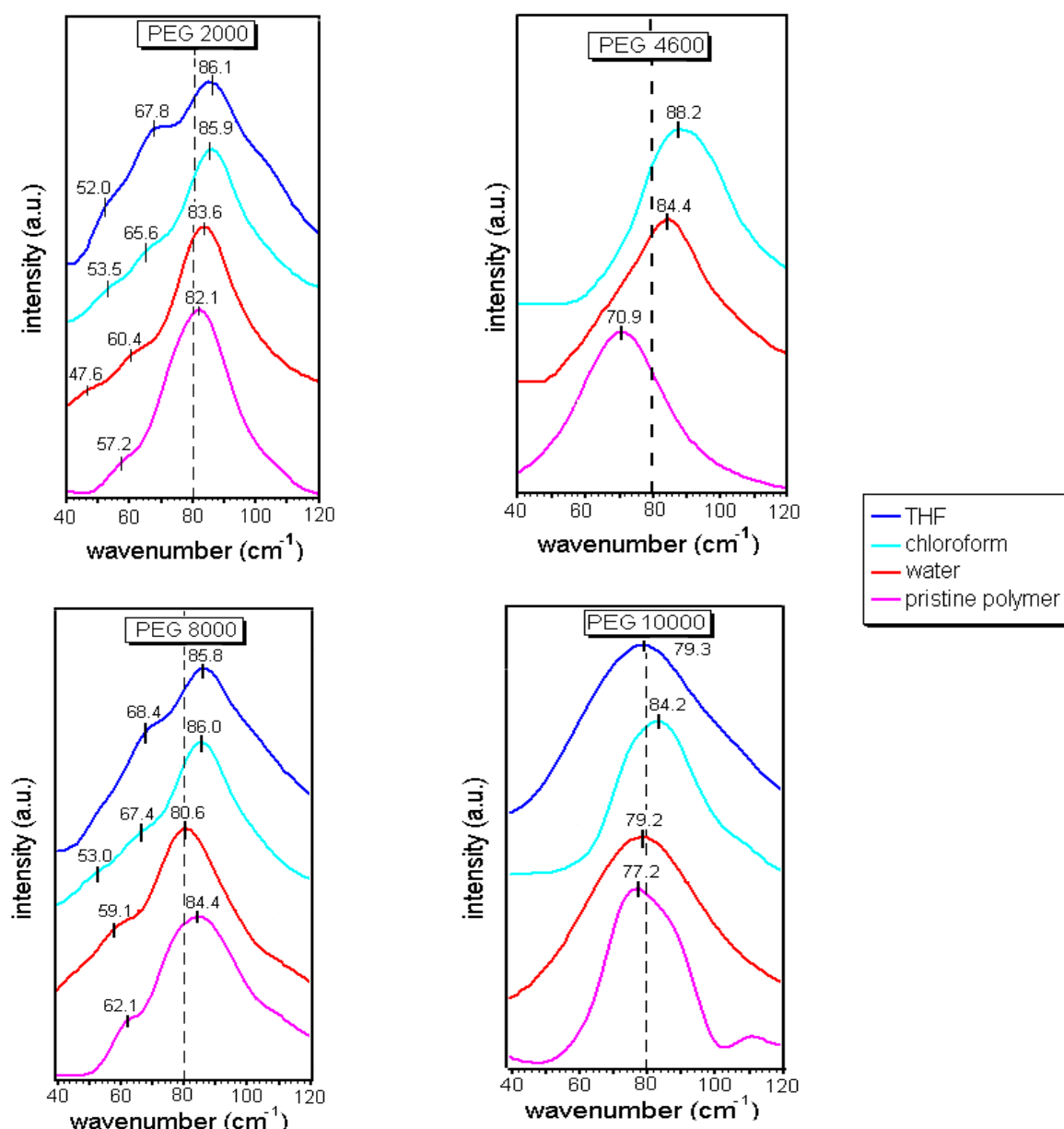


Figure 4.45. Change of the Raman spectra of OH...O bending, C-O rotation, C-C-O angle bending frequencies of PEG samples in the presence and absence solvents.

If a generalization has to be made taking into account the fact that PEG macromolecule employed in Raman studies own two methylene groups, one etheric oxygen and OH end groups, one may propose that bending vibrations (OH...O, C-O, C-C-O and C-O-C) discussed in detail with wavenumbers display spectral discriminations and the spectrum shifts towards higher frequency values within the measure of H-bond achieved by H-acceptor oxygen atom together with OH end groups. This behavior implies that the mentioned vibrations will occur less

favorably as long as the degree of H-bond formations increases. The greatest frequency shifts have been observed for chloroform and THF samples.

Several general trends were noted across all of the FTIR spectra of cyclosporine having four amide groups, all of which are intramolecularly H-bonded and a twisted antiparallel β -sheet involving residues amino acids. First, the studies could be sorted into four general groups according to H-bonding ability. Spectra obtained from solvents incapable of H-bond donating or accepting were similar to that of crystalline material. Polar H-accepting solvents and spray-dried powder exhibited similar structures, representing a second conformational group. Likewise, polar, H-donating solvents comprised a third conformational group. Last, a combination of H-donating and accepting solvents was used to mimic water, and revealed a fourth conformational group. Second, as the solvent polarity increased, the band assignments were observed to shift downwards as the conformation shifts away from the crystalline structure. Decreasing the solvent polarity resulted in increased intramolecular H-bonding, increased β -sheet stability and increased crystallinity (resemblance to the tetragonal crystal conformation). Third, within the class of solvents that were H-bond acceptors, as the solvent dipole increased, the band sharpness and intensity increased, indicating an increase in structural stability (Stevenson et al., 2003).

In spectra obtained from PEG samples in THF and DMSO that were H-bond acceptors, the band sharpness and intensity has been increased (Figures 4.35, 4.39). As the solvent polarity increased, intermolecular H-bonding decrease and band assignments observed to shift downwards (Figures 4.34, 4.37, 4.41, 4.42, 4.43).

CONCLUSION

- 1) In this study, the solubility parameter of PEG has been calculated by the use of several different algorithmic methods. By creating the solubility profiles of the polymer in selected solvents, the dissolving capability of these solvents has been discussed.
- 2) Algorithmic methods, as the computational application of the principle “like dissolves like”, have been employed on the basis of the solution thermodynamics of the polymer, and the type of similarities/agreements displayed on the basis of various thermodynamic magnitudes to interpret the solvent power in PEG/solvent systems.
- 3) Similar agreements have been interpreted by XRD, FTIR and Raman spectroscopic methods from the detections in the solid state.
- 4) δ_t values of the polymer determined in this work from Small, Hoy, VKH, Askadskii and Breitzkreutz algorithmic calculations, respectively, are also in agreement with δ_t values found by some other working groups (Small, Hoy and VKH) as well.
- 5) Small uses the molar attraction constant (F_j) while calculating the total solubility parameter, but he does not take into account the contribution of dipole-dipole interaction which may result from the dipole moment occurring from the heteroatom, most probably present in the structure. Consequently, the solubility parameter is found to be a small value. On the other hand, in Askadskii's approach, dipole-dipole interactions and the cohesive energy density (ΔE) are both considered while calculating the total solubility parameter. When each of these methods are compared dipole-dipole interaction contributes to the total solubility parameter with a value $\sim 3 \text{ (J/cm}^3\text{)}^{1/2}$. In VKH and Hoy approaches, instead of total solubility parameter, the contribution of the components (δ_d , δ_p and δ_h) to the

solubility parameters are considered. According to Small approach the difference is again $\sim 3 (J/cm^3)^{1/2}$. If a comparison has to be made, the total solubility parameter determined by considering the secondary interactions exhibits higher values with respect to those obtained from approaches ignoring these interactions. The interactions which bring polymer segments close to each other are described as secondary interactions. The energy difference corresponding to $3 (J/cm^3)^{1/2}$ may be interpreted as the magnitude characterizing these interactions.

- 6) When the total solubility parameter is taken as the basis; according to Askadskii's approach, THF and chloroform appear to be the best solvents whereas, according to Hansen and Hoy approaches, on the basis of solubility parameter differences THF is the best solvent. Water, on the other hand, possesses the character of the weakest solvent in all of these calculations. As a consequence of the evaluation of 3-D and 2-D solubility profiles, THF and chloroform sometimes exchange positions during determining the dissolving capability of the polymer or from time to time they seem to display similar dissolving behaviors. However, it is most probable to imply that THF is somewhat more effective.
- 7) The theta temperature of PEG/THF system has been found to be somewhat higher than that of PEG/chloroform system but still, Mark-Houwink exponent of PEG/chloroform two-component system appears to be a little bit higher compared to that of PEG/THF system.
- 8) When the hydrodynamic and thermodynamic magnitudes of the polymer in selected solvents are compared, THF and chloroform display similar behaviors. However, we are again faced with the unchanging fact that water still displays its nature as the weakest solvent.
- 9) The crystallinity of a polymer may be determined by various methods. DSC technique is a relative method as in all spectral evaluations. By taking the ratio of enthalpy of fusion of the semicrystalline polymer (which will be

determined) to that of the crystalline polymer, extent of crystallization may be determined. Generally, percent crystallinity obtained from DSC measurements is higher than the percent crystallinity value found by XRD which is an absolute method. In this work, XRD studies of the original polymer and polymer samples cast from water and THF have been made and THF has been observed to be more effective in decreasing the crystallinity of the polymer with respect to water.

- 10) Crystalline structure variations of original polymers in the presence of a solvent may also be detected by spectral studies. Symmetric and asymmetric stretching vibrations together with in-plane and out-of-plane bending vibrations of methylene group shift towards lower frequency values in the samples treated with the solvent which is most significantly observed in THF.
- 11) It is quite logical that C-O stretching vibrations for the samples prepared from solvents apart from THF shift toward lower field values. For the sample cast from THF, this stretching band is by no means observed in the spectrum or may only appear as a nonsignificant shoulder.
- 12) C-C-O and C-O-C bending vibrations are observed to shift towards higher frequency values as a consequence of the interaction of end groups with etheric oxygen resulting from the unfolding of the polymer coil in a good solvent. In practice, this shift indicates that both two bendings (in plane, out of plane) will be much more difficult. Similarly, in C-O-C angle bending and C-O internal rotation vibrations shifts towards upper frequency values are quite significant as well. Due to both FTIR and Raman interpretations, shift towards maximum frequency values are observed in samples prepared from THF and chloroform.
- 13) Shifts towards higher frequency values have been lastly investigated in far-Raman region. The effective role of THF and chloroform has been clearly observed here as well.

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