EFFECTS OF HUMIDITY AND VARIOUS GASES ON THE ELECTRICAL
CONDUCTIVITY OF POLYETHYLENE GLYCOL

by

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ABSTRACT

EFFECTS OF HUMIDITY AND VARIOUS GASES ON THE ELECTRICAL CONDUCTIVITY OF POLYETHYLENE GLYCOL

Characterization of the electrical properties of covalently linked pure, hydrogenated and hydrophobically modified polyethylene glycol (PEG) thin films under changing relative humidity is examined by dc measurements. Perfluoroalkylethylalcohol is used as the hydrophobic additive. At low humidity levels, electronic conduction takes place while the absorbed water contributes to this mechanism and increases the current. At around 70 % relative humidity, as a result of the water clusters formed, the polymer melts from the semicrystalline form and the current shows a steeper increase. The water vapor condenses and conduction takes an ionic nature. For the pure PEG samples, after 75 %, the conductivity shows irregularities with respect to increase in the relative humidity. The irregularities subside in the hydrogenated as well as the hydrophobically modified PEG samples, while in the latter the steep increase in conductivity shifts to higher values of relative humidity with increase of perfluoroalkylethylalcohol concentration in the film. There is a hysterisis between the absorption and desorption of water as the film cannot reach its semicrystalline form in the time interval of desorption. The polymer film could get its pre-absorption form after drying. The response of PEG thin films to exposure to acetone and methanol vapor at changing pressures are observed by dc measurements under vacuum. The conductivity of the polymer increases with the increasing pressure of vapor while this increase reaches a significant value at 1100 Pa. Acetone causes an augmentation in current 10 times greater than methanol due to the difference between their dielectric constants.

ÖZET

NEM VE ÇEŞİTLİ GAZLARIN POLİETİLEN GLİKOL'ÜN ELEKTRİKSEL İLETKENLİĞİNE ETKİLERİ

Kovalent bağlı saf, hidrojene edilmiş ve hidrofobik olarak modifiye edilmiş polietilen glikol ince filmlerinin elektriksel özelliklerinin karakterizasyonu değişen bağıl nem etkisinde doğrusal akım ölçümleri ile yapıldı. Hidrofobik katkı olarak perfloroalkilietilalkol kullanıldı. Düşük nem seviyelerinde elektronik iletkenlik gozlemlenirken, emilen su da iletkenlik mekanizmasına katıldı ve akım değeri yükseldi. Bağıl nemin % 70'e ulaştığı noktada, oluşan su adacıkları sebebiyle polimerin yarıkristal yapısı eridi ve akım daha dik bir artış gösterdi. Su buharı yoğunlaştı ve iletkenlik iyonik bir durum aldı. Saf PEG örneklerin iletkenliği, % 75'den sonra bağıl nemdeki artışla birlikte düzensizlikler gösterdi. Bu düzensizlikler hidrojene edilmiş örneklerde olduğu gibi hidrofobik olarak modifiye edilmiş olan örneklerde de ortadan kalktı, bununla birlikte hidrofobik olarak modifiye edilmiş olan örneklerin iletkenliğindeki gözlenen ani artış, filmlerdeki perfloroalkilietilalkol oranı arttıkça bağıl nemin daha yüksek değerlerine doğru kaydı. Suyun emilim ve geri verilimi arasında, filmin geri verilim zaman aralığında önceki yarıkristal formuna dönememesinden kaynaklanan bir histeri vardı. Polimer film emilim öncesi formunu tavlama sonrasında alabildi. PEG ince filmlerinin aseton ve metanol buharına olan tepkisi vakum altında farklı basınçlarda doğru akım ölçümleri ile gözlemlendi. Polimerin iletkenliği artan basınçla birlikte arttı ve bu artış 1100 Pa'da önemli bir değere ulaştı. Dielektrik sabitleri arasındaki farktan dolayı, aseton akımın metanolden 10 kat fazla artışına sebep oldu.

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LIST OF SYMBOLS/ABBREVIATIONS

a	Penetrant activity
A	Ampere
b	Constant
B	Constant
c	Concentration
C	Carbon
Cl	Chlorine
d	Space
D	Diffusion coefficient
D_0	Diffusion coefficient at zero diffusant concentration
E	Electric field
f	Charge flux
F	Rate of transfer per unit area
H	Hydrogen
I	Current
J	Current density
K	Potassium
m	Constant
N	Nitrogen
n_i	Charge carrier density
O	Oxygen
P	Pressure
p_n	Hopping probability
p/p_0	Relative pressure
q_i	Charge
S	Sulfur
Si	Silicon
t	Time
T	Temperature

T_g	Glass transition temperature
V	Voltage
w	Weight
x	Distance
Zn	Zinc
α	Constant
γ	Fall-off in wave function with distance
ϵ	Dielectric constant
μ_i	mobility
ρ	Average separation of the sites
σ	Conductivity
φ	Volume fraction
χ	Interaction parameter
ΔE	Energy difference
BET	Brunauer, Emmett, Teller
const.	Constant
DC	Direct current
FTIR	Fourier transform infrared spectrum
PAF	Perfluoroalkylethylalcohol
PEG	Polyethylene glycol
QCM	Quartz crystal microbalance
rh	Relative humidity
WAP	Water affinity parameter

1. INTRODUCTION

Polymers are as old as men themselves since in one form or another they are basic constituents of living matter, whether plant or animal. It is only in the present century, however, that as a result of a wide range of scientific studies their existence as a coherent group has come to be recognized and understood. Following this recognition and understanding, the possibility has arisen of actually producing polymers by means of suitable chemical reactions. Originally these synthetic products tended to be regarded as substitutes for existing natural polymers, such as rubber or silk, which were in short supply, but more recent development of the polymer industry has led to the introduction of a vast range of entirely new compounds in the field of plastics, rubbers and fibers, many of which have properties different from those of any existing natural materials. Today's study of polymers, though it includes the original natural polymers, tends to be dominated by these synthetic materials, since it is from the problems associated with the industrial development of such polymers that the main stimulus to scientific research has arisen.

Polymers and polymer composites with hydrophilic properties are being investigated widely as they could be used in medical and industrial applications. Polymer based humidity sensors produced are used in electronics, food industry, and domestic environment; while many researchers work on the use of various polymers in the development of biosensors since they are biocompatible [1, 2, 3, 4].

Polymers attract attention because of their absorption, desorption and swelling behavior under exposure to water vapor and certain chemicals. The diffusion of the penetrants in the polymer networks shows different kinetics depending on environmental conditions such as temperature and humidity as well as the structure of the polymer and the diffusivity of the penetrant. The transport mechanism of the penetrants in the polymer and their effects should be known in detail to get the highest efficiency from the polymers. The examination of sorption and transport properties of small molecules in polymeric materials has long been known to be a promising means to progress to-

ward new concepts. A reasonable degree of success in interpreting the microstructure of polymers has been obtained via these properties; the use of small molecules as microstructural probes is being widely adopted by scientists. The advances achieved appears to be attainable since many of the practical applications of polymers involve sorption and transport of small molecules as fundamental processes. These include a wide variety of applications, ranging from small scale uses such as packaging materials and protective coatings to large scale industrial processes such as membranes for gas separations.

When water molecules penetrate into a polymer sample, the macromolecular chains rearrange themselves towards new conformations. The diffusion rate of the water molecules and the relaxation process determine the nature of the transport process; which in turn affects the polymers' electrical, optical and physical properties. The change in the physical, optical, and electrical properties of polymers with respect to the change in the relative humidity (rh, this is the ratio of the amount of water in the air to the maximum amount which the air can hold at the particular temperature considered) of the environment is being studied in many different aspects. As the rh of the environment changes, water vapor is absorbed by the polymer. Then with the interaction between the polymer and the water vapor, the polymer gets swollen. While all these processes occur, the electrical, physical and optical properties of the polymer change. The swelling induced changes are observed by different methods such as quartz crystal microbalance (QCM) analysis [4, 5, 6], X-ray [5, 6, 7], and neutron reflectivity [5]. These are well-suited techniques to study the swelling of polymer thin films. For example, ellipsometry is used to measure thickness and the refractive index of a thin film [5]. On the other hand, spectroscopic techniques, like infrared spectroscopy, are important to get insight on the structure of the materials in the molecular level, while giving an idea about the intermolecular interactions between the polymers and water vapor [8]. The solvatochromic method [6, 9] is also used to predict the sorption ability of the polymer. The electrical properties are mostly studied by ac impedance spectroscopy [3, 10, 11, 12] by which the capacitance and the conductivity of the polymer films can be obtained.

In this thesis, my aim is to get insight of the conductivity mechanism of polyethylene glycol, i.e., PEG. In order to understand effects of water vapor on the conduction mechanism of PEG, the characterization of the electrical properties of PEG with respect to the rh change is studied and the response of PEG to acetone and methanol vapor and the effects of these gases on the conduction mechanism are observed. The chemical structure of PEG is; $H - (CH_2 - CH_2 - O)_n - H$. Polyethylene glycol is one of the most accepted polymers in the fields described above. Especially, it has been studied intensively for pharmaceutical and biomedical applications, including carriers for controlled drug delivery and materials for prosthetic devices. The mechanism for controlled drug release involves the swelling of a dry polymer network by a biological fluid. The swelling of the polymer network allows the incorporated drug to diffuse out. [13]. Besides being sensitive to the changes in relative humidity and chemicals, PEG helps prevent the adsorption of proteins to the biomaterial surfaces [1, 2, 14]. This improves the medicinal effect and reduces toxicity. However, PEG has a problem of stability as it swells when exposed to water vapor and dissolves easily at high humidity; therefore it is not durable on the substrate. The instability in the long term is a general problem of polymer films produced by the physisorption of polymer molecules to the substrate material. When these films are exposed to water vapor or to a gas, the films get swollen and might be displaced from the surface. However, if the polymer layers are covalently linked to the substrate this problem could be resolved [2]. In this study, gammaisocyanatopropyltriethoxysilane is used to covalently link the polymer layer to the scratched glass surface. The triethoxysilane allows to cross-link the PEG network itself as well as the overlay on the substrate so that it becomes a durable and stable material. As the glass transition temperature of PEG is 207 K, any problems related to the glass transition are not expected to occur as long as the measurements are done at room temperature. Perfluoroalkylethylalcohol (PAF) is used as the hydrophobic additive. As the melting temperatures of hydrophobically modified PEG samples are lower than those of unmodified PEG samples, lower glass transition temperatures are expected for them [15].

The plan of the thesis is as follows; the second chapter of the thesis is devoted to a brief review of the classification of the polymers and a more detailed information of

basic concepts such as the diffusion, the behavior of water and the electrical conduction in polymers to get insight of the mechanisms of absorption, adsorption and desorption of water and gases by the polymer.

In the third chapter of this thesis, the change in the current passing through PEG film is experimentally measured under a constant electric field at rh ranging from 12 % to 90 %. The current changes by 4 orders of magnitude with the increase of rh. It is observed that at low humidity values the electrical conductivity is dominant; as an increase up to 70 % rh is determined, the water molecules condense. At that point, the film changes phase from a semicrystalline form to a gel form, and the ionic conductivity takes place. Beyond 75 % rh, it is experimentally observed that there is an irregular behavior of the current with respect to the changes in rh as a result of the instability of the polymer. To alleviate the instability problem observed in the PEG samples at high rh values, and to increase the range of rh in which measurements can be done with PEG, two different methods are used; the first is to enrich the PEG samples with hydrogen, and the second is to use hydrophobically modified PEG samples. Although the current values decrease somewhat, the conductivity of the samples increases with increase in rh, while the instability problem observed at high values of rh with pure PEG samples disappears. In this way, PEG could be improved to be used in a wider application range.

In the fourth chapter, the current passing through the pure PEG samples is measured in vacuum while the pressure inside the chamber is increased step by step by the vapor of acetone and methanol gases. It is observed that the conductivity increases with the increase in the pressure and when the pressure reaches 1100 Pa the current values show a sudden augmentation. The change in current upon exposure to acetone vapor is 10 times greater than that upon exposure to methanol vapor.

2. REVIEW

The term "polymer" is used for all materials whose molecules are made up of many units; these units may be either a single atom or a small group of atoms in a state of chemical combination. One of the simplest of the polymers, from the standpoint of chemical structure, is polyethylene, in which the repeating unit is the CH_2 group, these units being joined together to form a long chain, as below

$$-CH_2 - CH_2 - CH_2 - .... - CH_2 - CH_2 - CH_2-\ .$$

The original molecule from which the polymer is formed is called *monomer* unit. It is not necessary that all the units in the chain shall be identical. Polymers containing only a small number of units are usually called dimers, trimers, tetramers, etc. according to the number of monomer units involved and the term polymer is reserved for the case in which the number of units is very large like 1000 to 10000.

Natural polymers are divided into three groups; fibers, rubbers and biological polymers. Fibers may be of either plant or animal origin. Rubber is the product of a tree. The animal body makes use of the physical and chemical properties of a variety of biological polymeric materials. Synthetic polymers are fibers, rubbers, crystalline polymers, glasses and inorganic glasses. Rubbers are normally amorphous; their molecules are not arranged in any sort of order. It is this rather loose structure which gives rubbers their softness and flexibility [16]. Large segments are thought to participate in the diffusion process due to internal micromotions of chain rotations and translation. A large amount of free volume in which diffusion may take place is accessible. Crystalline polymers are not wholly crystalline, like an ordinary crystalline solid, but contain a large number of very small crystals existing in close proximity to the remainder of the material, which is disordered or in amorphous state. One of the most generally used and versatile of the crystalline polymers is polyethylene. The crystalline polymers are somewhere in between rubbers, which are soft and highly deformable, and glasses, which are hard and brittle.The crystalline polymers are moderately deformable and tough,

yet they do not easily to retain their shape under moderate stresses. The molecules are not arranged in any geometrical order as in the glass; the structure is amorphous as in rubber. In the amorphous structure of a glass, there are no discontinuities or differences of geometrical arrangement of molecules from one point to another, and hence no internal boundaries from which light can be scattered or reflected; therefore, such materials are transparent. The important difference between a rubber and a glass lies not in geometrical arrangement but in the forces exerted by one molecule on another. In a rubber, these forces are weak, and do not prevent one molecule from moving away from a neighboring molecule; the molecules can move about fairly freely. In a glass, the forces between neighboring molecules are much stronger and the molecules are effectively bound together as a rigid mass. This is intimately related to restricted polymer chain mobility; rotation about the chain axis is limited [17]. Polymers of this type are very dense structures with very little internal void space. Hence, penetrant diffusivities through such a structure are low. Among polymers there are a wide range of materials with mechanical properties similar to those of a glass that do not possess the same degree of optical transparency however. These materials are known as synthetic resins.

2.1. Diffusion in Polymers

The mathematical theory of diffusion in isotropic substances is based on the hypothesis that the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section, given by Fick's law

$$F = -D\partial c/\partial x, \qquad (2.1)$$

where F is the rate of transfer per unit area of section, c the concentration of diffusing substance, x is the space co-ordinate measured normal to the section, and D is called the diffusion coefficient.

When the diffusant component has a molecular size much smaller than the monomer unit of a given polymer and the thermodynamic interaction between the two compo-

nents is very weak, a limited rotational oscillation of only one or two monomer units would be sufficient to give a cross-section for the diffusant molecule to jump thermally from one position to a neighboring one. The diffusion of simple gases, such as hydrogen, argon and nitrogen, in ordinary polymers probably involves such a molecular mechanism. Molecules comparable with, or larger than, the monomer unit of a polymer require for their diffusion a co-operative movement by the micro-Brownian motion of several monomer units to take place. Such substances include most organic vapors, which are either solvents or swelling agents for ordinary polymers. Many features of their diffusion reflect the micro-Brownian motion of long-chain molecules and thus are unique to polymer systems. It has been shown that sorption and permeation, which are typical diffusion controlled processes, of organic vapors in polymer solids exhibit different features in the regions above and below the glass transition temperature, T_g, of a given polymer. In a sense, they are rather simple at temperatures above T_g and exceedingly complex at temperatures below T_g [18].

The distribution of a diffusant, and its change with time, in a given film during sorption or desorption are governed by the one dimensional differential equation for diffusion according to Fick, with the space co-ordinate taken in the direction of the film thickness. The solution to the differential equation depends on the initial and boundary conditions taken for the diffusant concentration, c, as well as on the nature of the mutual diffusion coefficient D which appears in the equation. Solutions appropriate to the initial condition of the sorption experiment were obtained by many authors with the assumptions that D is a function of c and c changes depending on the pressure of the vapor. Sorption curves having characteristics expected from the above mentioned assumptions are called *Fickian* or *normal* type.

Fickian diffusion in polymers is an ideal case of penetrant transport, corresponding to free diffusion of penetrant without interference of polymer chain rearrangement, i.e., structural relaxation. Whether deviations from ideal Fickian behavior occur, depends on the rate of relaxation compared to that of diffusion. If polymer relaxation is much faster than penetrant diffusion, diffusion is followed by instantaneous response of the system, resulting in Fickian behavior. Instantaneous response of the system re-

quires large flexibility of the polymer chains in the system. This is generally accepted to be the case for polymers above their T_g, which are *rubbery* (systems below T_g are *glassy*). The T_g is not a real thermodynamic transition, since its value depends on the speed of heating or cooling the system and it is characteristic of the total system including possible penetrant. Since penetrant absorption may also induce a transition from glassy to rubbery state and vice versa, such transition under isothermal conditions should be considered in terms of glass transition concentration rather than in terms of glass transition temperature [18].

As previously stated molecules having sizes comparable to, or larger than, the monomer unit of a polymer require for their diffusion a co-operative motion of several continuing monomer units of the polymer to take place. This implies that the rate of diffusion of an organic vapor in a polymer solid, and hence the diffusion coefficient of such a system is primarily controlled by the mobility of the polymer segmental unit. Addition of small molecules to the system and raising the temperature weakens the molecular interaction between neighboring polymer molecules. This makes the polymer segment move freely and thus afford it a higher mobility. Therefore, it is to be expected that the diffusion coefficients of polymer-organic vapor systems generally increase with increasing diffusant concentration and temperature.

Crank and Park postulated that the conformation of the polymer molecules in a volume element enclosing a point under consideration and the stress exerted on the element by its surrounding affect the ease of jumping and hence the diffusion coefficient [19]. When a polymer substance absorbs a vapor, the polymer molecules rearrange themselves toward a new equilibrium conformation consistent with the sorbed state. This conformational change may not take place instantaneously. Thus, during a sorption process the instantaneous conformation of a polymer chain in any given volume element generally differs from the one which would be taken if the chain were equilibrated with the particular concentration in the element. This means that the chain conformation in a volume element is not uniquely determined by the diffusant concentration there, but may depend on the time taken by the element to reach the particular concentration.

Internal stresses may be set up when a vapor diffuses into a polymer solid. It is to be expected that the inner, unswollen (or less swelling) part of the solid will exert a compression force on the outer, swelling part, while the swollen part will exert, on the unattacked region, a force which tends to expand the solid. These compression and expansion forces change as sorption proceeds, since the concentration distribution in the solid changes with time and since the polymer chains tend to relieve these stresses by changing their conformations.

At temperatures well above T_g the micro-Brownian motion of the polymer molecules is sufficiently active to enable equilibrium to be reached rapidly. Therefore, at such temperatures, the chains in any volume element of the polymer may take up almost instantaneously an equilibrium conformation consistent with the sorbed state when vapor diffuses into the solid. Depending on that, the time-dependence of D associated with the conformational change of the polymers should disappear. With the micro-Brownian motion of polymer chains being sufficiently active, the time-dependence of D due to internal stresses also should disappear, since the stress set up by swelling immediately decays by a rapid chain relaxation. In this way we can understand that at temperatures well above T_g the diffusion coefficient of a polymer-organic vapor system becomes free from any time-dependent effect and depends only on the diffusant concentration.

The absorption of vapor by the surface layer of a polymer solid necessitates some conformational rearrangement of the polymer molecules in that layer. In circumstances in which the conformation change of the polymer chains inside the solid is rapid enough to make D purely concentration-dependent, it is not unreasonable to postulate that the molecular rearrangement in the surface layer also proceeds at a very high rate. In such a case, the vapor may be taken up quickly into the surface layer until the equilibrium value corresponding to the pressure of the ambient vapor is reached. This implies that the condition of constant surface concentration is established.

The permeation method has been used chiefly for studying diffusion of gaseous substances and water vapor in polymer solids. The theory of permeation assumes that

diffusion is not the only transport process which permits vapor to permeate through a polymer solid. When the solid contains microvoids, convective flow of vapor may take place through a capillary system formed by such voids, and the permeation turns out to be the sum of two contributions, one due to ordinary diffusion through the compact part of the solid and the other due to convection through the capillary part.

For a given polymer-diffusant system D may be written in the form:

$$D = D_0(T)F(c, T), \tag{2.2}$$

where D_0 denotes the value of D at zero diffusant concentration and F is the factor which represents the variation of D with concentration.

There is a sharp distinction between the diffusion coefficients of simple gases and of organic vapors in polymers. The value of D for gases is generally not only much larger for organic vapors but is independent of the gas pressure or concentration. Thus with simple gases the problem is reduced to correlating D_0 with three variables, the nature of the gas, the nature of the polymer and the temperature. On the other hand, the diffusion coefficients of organic vapors are generally concentration-dependent, which requires the diffusant concentration as an additional variable. Thus in terms of the above equation it becomes necessary for organic vapors to correlate both D_0 and F with these four variables.

For most of the polar polymers, D increases with c. Polar polymers are also known as hydrophilic polymers meaning that they can transiently bond with water through hydrogen bonding as this is thermodynamically favorable and makes them soluble in water and polar solvents. Besides that hydrophobic molecules tend to be electrically neutral and nonpolar, and thus prefer other neutral and nonpolar solvents or molecular environments. According to thermodynamics, matter seeks to be at a low-energy state, and bonding reduces chemical energy. Water is electrically polarized, and is able to form hydrogen bonds internally. But, since hydrophobes are not electrically polarized, and because they are unable to form hydrogen bonds, water repels hydrophobes, in

favor of bonding with itself. For several of the less hydrophilic polymers D decreases with increasing concentration. Such a behavior might be explained by postulating clustering of water in the polymer so as to render a proportion of it comparatively immobile. If the proportion of the water immobilized increased with concentration then D will decrease with increasing concentration. Clustering may be initiated at polar centers. Cluster growth in the polymer will differ from that in free space because of the potential field of the surrounding polymer. On the other hand, with polymers of high segmental mobility, association of the water may occur in a completely random fashion throughout the polymer. For the hydrophobic polymers, the solution of water in the polymer appears to be thermodynamically ideal and the mobility factor independent of concentration so that D is constant.

2.2. Water in Polymers

Because of their low cost, stability and permeability to water and easy handling, polymers have been widely investigated as water vapor sensing materials. The change in electrical characteristics with rh is the principle on which many polymer- water vapor sensors are based; variation of capacitance in the case of capacitive devices, variation of the impedance for resistive devices. The former and the latter kind of sensors are, respectively, produced with higher and lower resistance materials. The water sorption changes the dielectric constant of the polymer and this is the basis of capacitive sensors. The conductivities of some polymers increase strongly, due to water sorption, and can be suitable for resistive humidity sensors.

Within the field of polymer physics *equilibrium* usually refers to any equilibrium uptake of vapor or liquid. Brunauer, Emmett and Teller developed a leading classification (the so-called "BET classification") on equilibrium sorption behavior, as reflected by their sorption isotherms [20] Sorption isotherms describe equilibrium sorption in the non-saturated region as a function of the penetrant activity, including adsorption and capillary condensation. The BET classification originally distinguished five types of sorption isotherms (Figure 2.1). These isotherms are plotted as the volume fraction of sorbed penetrant or the mass absorbed versus the relative pressure. Type I is

the well-known Langmuir isotherm, which is applicable to microporous solids. Type II and Type III isotherms describe adsorption of gases on macroporous or non-porous solids, and Type IV and Type V isotherms are applicable to both mesoporous or microporous solids. The presence of hysterisis loops is characteristic for Type IV and Type V, but may also appear in the other isotherms. Brunauer et al. originally stated their theory at least to be valid for gases which do not possess considerable dipole moments [20]. Water molecules possess a large dipole moment. Nevertheless, the BET classification has been adopted in a convincing way for water in polymers. Polymers may show a widely varying appearance of water sorption isotherms. Type II isotherms are commonly encountered with hydrophilic polymers such as wool, silk and cellulose acetate. For less hydrophilic ones Type III isotherms are observed. Linear isotherms are found for hydrophobic polymers. Linear isotherms imply that Henry's law is valid over the entire range of penetrant activities. Since Henry's law expresses the ideality of dissolution, this also implies the insignificance of penetrant-polymer interactions, which is plausible for water sorption in hydrophobic polymers. Non-linear isotherms consequently indicate that the sorption process deviates from ideality, they reflect interactions between water molecules and polymer structure [20].

Brunauer et al. proposed a model to describe the features of five different types of sorption isotherms. According to this model, the penetrant is considered to bind at specific sites in the polymeric structure, e.g. in cracks, pores, or at specific polar groups which are capable of interaction with polar penetrants like water. This is called *localized sorption theory. Dissolution theory* offers another approach to penetrant sorption. The starting point of this theory is that for polymer-penetrant systems that do not display strong interactions, observed deviations from ideal behavior should be attributed to incompatibility of their molecule sizes. This basic concept is given by the following *Flory-Huggins* relation [20]:

$$\ln(a) = 1 - \varphi + \ln(\varphi) + \chi(1 - \varphi)^2 \qquad (2.3)$$

In this model, φ is the volume fraction of dissolved penetrant, and a is the penetrant activity. The compatibility of polymer and penetrant is expressed by a dimensionless
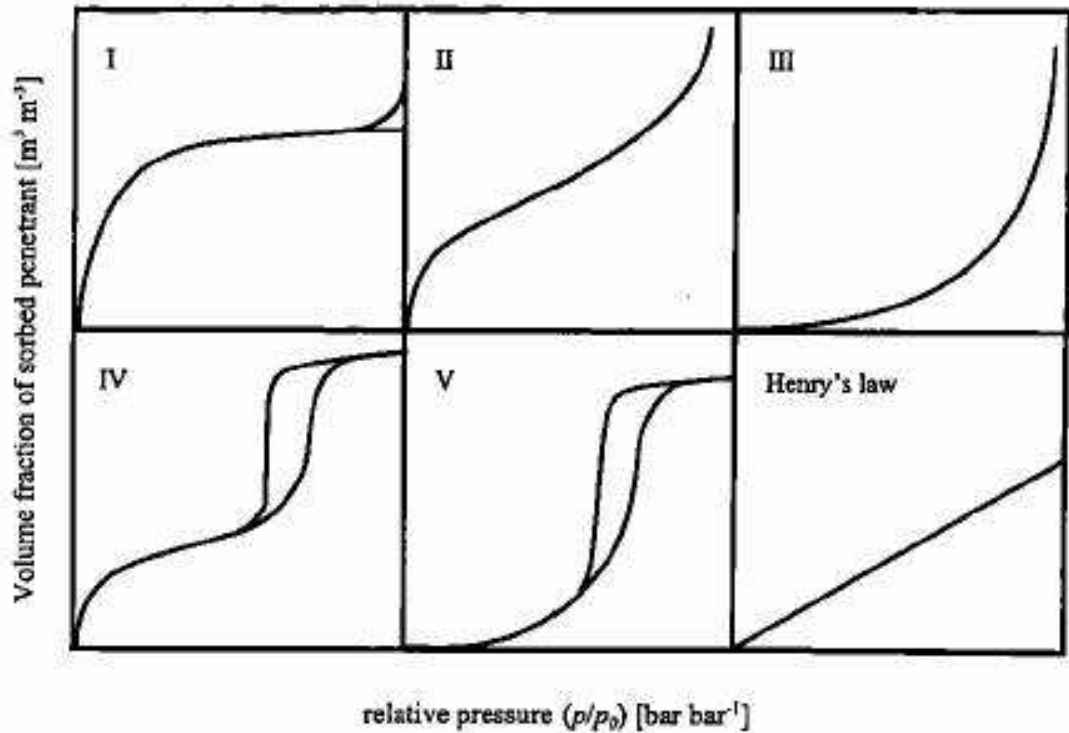
Figure 2.1. Five types of sorption isotherms according to BET classification and the linear isotherm according to Henry's law

interaction parameter χ. According to Flory the theory is limited to relatively apolar systems, interacting only weakly. In contrast to that starting point, the Flory-Huggins relation is also used for fitting water sorption.

The assumption that clustering of penetrant may cause the sorption isotherm to depart from the Flory-Huggins relation for higher penetrant activities, led to another approach by taking penetrant-polymer as well as penetrant-penetrant interactions into account.

The water molecule is relatively small, highly dipolar and in the liquid and solid states is strongly associated through hydrogen bond formation. Partial electrostatic charges due to the difference in electronegativity of oxygen and hydrogen result in strong interactions of water with other charged or polar groups and between water molecules mutually in polymers. Strong localized interactions may develop between the water molecule and suitable polar groups of the polymer; on the other hand, in relatively non-polar materials, clustering or association of the sorbed water is encouraged.

It is generally accepted that for sorbed water molecules at least three different states are possible; the first one is the single water molecule, which neither shows significant interactions with other water molecules nor with their environment, the second one is formation of aggregated water molecules, which interact with other water molecules to form clusters, but usually such clusters are not large enough to resemble bulk water properties, the last one is the existence of localized interactions of water molecules and polymer groups.

Transport of water in hydrophobic systems is normally by single water molecules, especially at low water activities. Interactions of water molecules and hydrophobic polymers are minimal, since the polarizability of water is small, and the dispersion forces only weakly contribute to interaction with non-polar materials.

Clustering of water molecules may cause a marked deviation from Henry's law. Water clusters stem from a high mutual affinity of water molecules combined with a relatively low affinity of water molecules for the polymeric matrix. Consequently, clustering of water is expected primarily in hydrophobic polymers for high water activities. Also for hydrophilic polymers clustering may be expected if the amount of water molecules is higher than the quantity that can be bound to the polymer.

The overall solubility of water in the polymer is determined by the amount and nature of polar groups in the polymer. Hydroxyl, carboxyl and peptide groups were found to bind water molecules strongly. The sorptive capacity depends also on the position of the polymer group at the polymer chain. It is generally excepted that where well-defined crystallites are formed these are inaccessible to water; nevertheless, a significant fraction of the total regain may be associated with the polar groups in the surfaces of the crystallites. As their surface area is a function of their size, it follows that there is no unique relation between the sorptive capacity and degree of crystallinity. If the interchain hydrogen bonds are weak or the degree of order of crystallites relatively low the swelling and eventual disruption of the polymer matrix may occur. These are experimentally observed by many researchers and contradictory results have been obtained. Hodge et al. have observed that water does not inhabit intact crystallites; but

instead contributes to the breakdown of the inter and intra molecular hydrogen bonding and this gives rise to enhanced polymer mobility [21, 22, 23]. However, Assender and Windle indicated that water molecules might well inhabit the crystalline lattice [24]. The more hydrophobic polymers which sorb minute quantities of water obey Henry's law. In general, the more polar groups present in the polymer matrix, the higher will be its sorptive affinity towards water. However, the accessibility of these groups, the degree of crystallinity of the matrix and the relative strengths of water-water and water-polymer bonds are important factors in deciding the total regain.

2.3. Electrical Conduction in Polymers

Polymers are unique because of the range of structural forms that can be synthesized and the way in which changes can be made in the structure in a local or general way. They can exist as amorphous materials, as crystalline materials, or as mixtures of crystalline and amorphous materials. They are molecular materials. Each polymer chain is its own individual identity, and the interaction with other polymer chains is usually weak. Polymer chains can take up different conformations and can be oriented mechanically. Within the individual polymer chains, the chemical units need not have a unique spatial arrangement.

In comparison to well ordered, covalent, or ionically bonded inorganic materials, polymers are weakly bonded, disordered materials. The functional groups from which they are made up need not have unique spatial relationships to each other. These differences have profound effects on most of the properties of polymers. They are heat insulators and are usually soft and easily distorted. Till 1970s all carbon based polymers were regarded as electrically insulating and poor conductors of charge. This view is changing as a new class of polymers known as conductive polymers are being discovered. With this developments, the conductivity of the polymers covers a wide range which changes between 10^5 and 10^{-18} $\Omega^{-1}cm^{-1}$. The conductivity of polyethylene is 10^{-13} $\Omega^{-1}cm^{-1}$ where it is 10^2 $\Omega^{-1}cm^{-1}$ for poly(p-phylene).

As being weakly bonded, disordered materials, polymers may not have a band

structure: there may be arrays of molecular states and molecular ion states, as well as many localized dipole states. Thus, many transport properties exist which are complicated by the existence of molecular ion states and regions of differing polarity or polarizability. The free charges may prefer to exist as molecular ions, they may be trapped in polar regions, or they may be trapped as result of polarization of the surrounding medium.

In this concept, three levels of structure must be considered as stated by Seanor [25]. The basic chemical composition is the first level as the nature of the monomer units will determine the behavior of the polymer. The second level involves the spatial arrangement of the basic polymer units within the individual polymer molecules, the microstructure. This is a function of the polymerization reaction and the precise reaction conditions mostly. The third level is the spatial arrangement of the polymer chains in the solid state, the macrostructure.

The conductivity, σ, is defined as;

$$\sigma = \sum_i q_i n_i \mu_i, \tag{2.4}$$

where q_i is the charge, n_i is the charge carrier density and μ_i is the charge carrier mobility. For the polymers, each parameter n and μ may be ambient sensitive, may be potential sensitive and may be influenced by the precise conditions of fabrication. *Ambient sensitive* means sensitive to all experimental conditions; the sample preparation, the ambient pressure, moisture, temperature. μ is influenced by the interfaces like crystalline-amorphous phase boundaries.

The factor limiting the conductivity is the carrier mobility, not the carrier concentration (Equation 2.4). To contribute to conductivity, the carriers must be mobile. There are at least three elements contributing to the carrier mobility: single chain or intramolecular transport, interchain transport, and the interparticle contact. These three elements comprise a complicated resistive network (Figure 2.2), which determines the effective mobility of the carriers. Process A indicates the intrachain transport of

charge, the interchain hopping of carrier is shown as process B and the carrier transport through the voids on the macroscopic level is shown as process C in Figure 2.2.
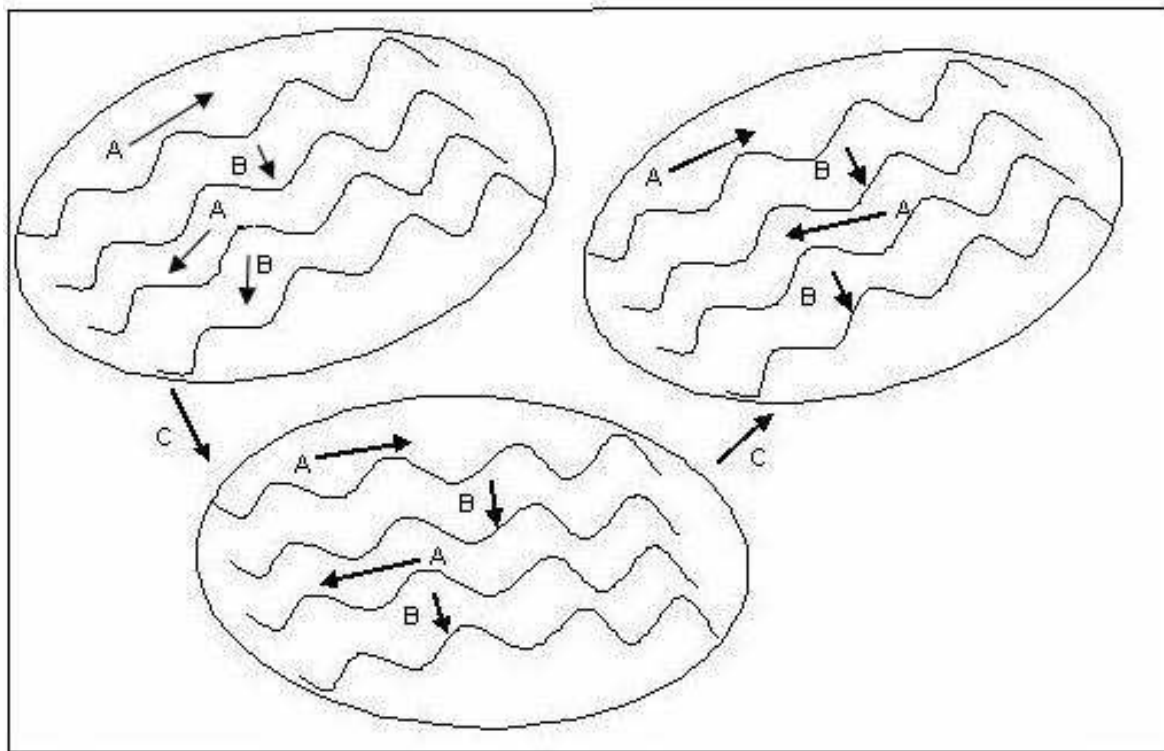

Figure 2.2. Conductivity network of a conductive polymer with A indicating intrachain transport of charge, B indicating interchain transport, C indicating interparticle transport, and arrows showing path of a charge carrier migrating through the material

If polymers are thought in the concept of the band model of solid state physics, the bandwidth of the polymers for a single chain is calculated to be large, but the disorder and the large distances between polymer chains suggest that the limiting step will be the transfer of charge carriers between adjacent polymer segments which may be on the same or on a different polymer chain. Polymers based on carbon, oxygen and nitrogen contain two electrons for each available states, all energy levels are filled like insulators. Intrinsic conduction arises by excitation of an electron from the highest filled molecular orbital to the lowest empty molecular orbital. The intermolecular orbital overlap is small. Consequently, the energy bands are narrow; charge carrier mobility is low. The creation of an electron and a positive hole in the conducting

states can be controlled by an electron donor or an electron acceptor introduced into the host matrix. In the context of band theory, regular arrays of similar atoms exist. In the case of a polymer, the condition of regular spacing of like atoms applies only to the case of the simplest carbon-hydrogen polymers such as polymethylene $(-CH_2-)_n$ and only along the chain axis [26]. Breakdowns exist in the local structure, dipoles exist in the chain and all will impact the system energetics. Thus, it is not to be expected that even the most highly crystalline nondipolar polymers will have high mobilities and that the mobilities will be isotropic. Thus, for such materials the existence of narrow bands similar to those of molecular crystals would be expected. In general, even highly crystalline polymers do not show greater than 90 % bulk crystallinity and even the crystalline regions are likely to be disordered. A semicrystalline polymer contains crystalline lamella where the remainder parts are amorphous. It is convenient to think of semicrystalline polymers as a continuous matrix of an amorphous polymer in which the properties are modified by the crystalline regions that act as sites for reinforcing the amorphous matrix. Carrier trapping can occur at the phase boundaries between the crystalline and amorphous regions. The crystallinity lowers the conductivity; if the conduction is ionic, ion mobility through the crystalline regions will be low; if electronic, the crystalline-amorphous interface may act as a trapping region. Most of the polymers contain polar groups and each dipole can act as an electron or hole trap. The localized states formed by surface states, dipole states, chain ends and branches, broken bonds, impurities, boundaries may act in trapping carriers from the extended states of crystalline region. The localized states deep within the energy gap are an inherent property of the polymer and are related directly to its chemical structure. The lack of long-range order contributes to the range of energy associated with a particular chemical group. Because the energy of closely adjacent sites is unlikely to be the same, both the distance and energy terms in equation describing the hopping probability,

$$p_n \propto \exp(-\Delta E)\exp(-\gamma\rho) \tag{2.5}$$

is small. Here ΔE represents the energy difference between the initial and final states, γ describes the fall-off in wave function with distance, and ρ is the average separation

of the sites.

Besides the charge carriers generated thermally, charge carriers can be generated by the emission from electrodes or under the influence of light.

The number of charge carriers and the local electric field are functions of location in the sample and represented by the terms $n(x)$ and $E(x)$ where x is the distance from a reference electrode. Then the steady-state current density J cannot be a function of position;

$$J = qn(x)\mu E(x) \neq f(x). \tag{2.6}$$

This means that the charge flux is constant across the sample. The relationship between the field gradient and the number of charge carriers is defined by Poisson's equation:

$$dE(x)/dx = qn(x)/\varepsilon, \tag{2.7}$$

where ε is the dielectric constant. The integral of the local field across the sample is the applied potential V:

$$\int_0^x E(x)\,dx = V. \tag{2.8}$$

These three equations, in combination with any set of boundary conditions, define the current-voltage relationships. In the simplest case, $n(x)$ is independent of position. In this case $E(x)$ is not a function of position, and

$$J = qn\mu E. \tag{2.9}$$

An ohmic electrode is an electrode that has no potential barrier to injection and is capable of providing an infinite supply of charge carriers. Thus, the boundary conditions

are

$$n(0) = \infty \ \ and \ \ E(0) = 0. \tag{2.10}$$

Substituting $n(x)$ in Poisson's equation into the equation for current yields

$$J = 9\varepsilon\mu V^2/8d^3. \tag{2.11}$$

This is known as Child's law for a trap free insulator [27]. The deviations from Ohm's law arise because the solid is unable to transport all the injected charge. The accumulated charge (the space charge) builds up adjacent to the ohmic electrode. Consequently, the field distribution changes. The analysis of this space charge limited currents provides a powerful means by which to interpret nonlinear current-voltage characteristics and particularly to qualify the numbers and energies of traps.

If the applied potential is sufficiently low, conduction is ohmic. At some higher potential, the current becomes nonlinear in voltage. If there are traps in the solid, the space charge limited current may be decreased by several orders of magnitude. The equation relating the current to the voltage should be modified by a trap limiting parameter relating the proportion of trapped charge to free charge. As the last traps are filled, the current increases tremendously. It often appears that dielectric breakdown occurs when the traps become filled.

The reason for the interest in space charge limited currents in polymers lies in the wealth of information which can be obtained from the current-voltage curves. The relationship of the number and depth of the traps to the pretreatment of the polymer, its molecular structure, and morphology are of prime importance in understanding the electrical behavior of polymers.

The conduction mechanism can occur by charge transport (either proton or electron). If there is sufficient segmental motion to allow the groups to take up energetically favorable spatial positions, charge transfer can take place [26].

Ionic conduction has been accounted for the low but finite conductivity of many of the more insulating polymers. In some cases, deviations from Ohm's law have also been explained in terms of ionic conductivity [26].

There are polymeric systems in which ionic conductivity can be and has been unambiguously observed. These cases relate primarily to polymers that contain ions, groups capable of ionizing, or to which ionic materials have been added. In all such materials, the presence of water plays an important role as the surface resistivity of the polymer decreases with the increase in the relative humidity (e.g. the surface resistivity of polyamines decrease from 10^{14} Ω to 10^7 Ω with the increase of the relative humidity from 10 % to 80 %) [26]. Water may act as a source of ions, as a high dielectric constant impurity, as plasticizer, or as a local structure modifier. In such cases, the definitive criterion for ionic conduction, that of mass transfer, can unambiguously be demonstrated. Ion content, ion mobility and water content are clearly related. It appears that water aids dissociation, as well as increasing ion mobility. The general relationship between conductivity, σ and moisture content is [28]

$$\ln \sigma = \ln \sigma_{dry} - \alpha w_{ads}, \tag{2.12}$$

where α is constant and w_{ads} is the weight of the water per unit mass of the polymer. This is a widely observed relationship relating the dielectric constant to the water uptake by an equation of the form

$$\alpha w_{ads} = b(1/\varepsilon_{dry} - 1/\varepsilon_{wet}). \tag{2.13}$$

In this equation, b is constant and ε is the dielectric constant.

Eley and Leslie [29] derived another equation,

$$\log \sigma = const. + \log(w_{ads})^{1/2} + B w_{ads}^m. \tag{2.14}$$

This equation is derived from a model in which water contributes to charge density.

Water seems to effect the transport of charge as well as modifying the local structure. The local dielectric constant is expected to increase. The effect of moisture on the mechanical properties of most polymers indicates that plasticization occurs, and it is also possible that the charge carrier hopping distance or path length would increase. Water can also act as an electron donor or source of charge carriers. As the water content increases, there can be a change from electronic to ionic conduction. Ionic conduction in polymers does not appear to follow a simple theoretical analysis. Neither Walden's rule relating charge mobility to viscosity nor the simple concepts of electrolyte conduction, which relate conductance to ion concentration are obeyed. Walden's rule relates the viscous drag on an ion to the accelerating force of the electric field and states that the product of molecular viscosity coefficient and mobility is constant. In case of polymers, macroscopic viscosity measurements will not reflect local density fluctuations which are affected by the ionic motion. Considerations of these ions are reflected in the electrical properties like conductivity and thermodynamic variables like glass transition temperature. At the molecular level, polymers do not provide a continuous matrix either spatially or dielectrically. This is related to the polar or nonpolar regions as well as the the amorphous and crystalline regions.
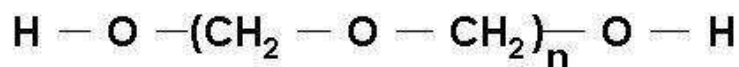
3. EFFECTS OF WATER VAPOR ON PEG THIN FILMS

Polymer, polymer composites and modified polymers with hydrophilic properties have been used in humidity sensor devices. Although polymers containing hydrophilic groups such as $-COOH$, $-SO_3H$ are potentially excellent materials for sensing humidity, these cannot operate at high humidity because of their solubility in water. Such problems have been overcome by blending the hydrophilic polymer with a hydrophobic polymer, or preparing hydrophobic polymers with hydrophilic branches, crosslinking of hydrophilic polymers with a suitable crosslinking agent.
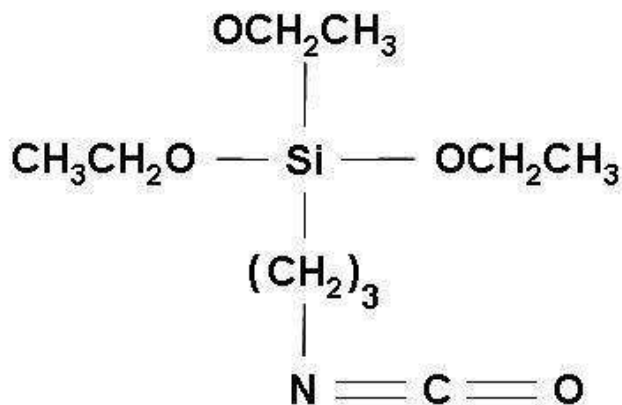
PEG, which is a hydrophilic polymer, is crosslinked with gamma isocyanatropyltriethoxysilane in the experiments and its response to humidity is observed. Afterwards, to solve the problem of stability it is hydrogenated and hydrophobically modified.

3.1. Synthesis of Gamma-isocyanatropyltriethoxysilane Capped Polyethylene Glycol (PEG-Si)
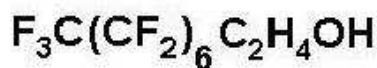
Hydroxyl ended polyethylene glycol (PEG) and isocyanatopropyltriethoxysilane are obtained from Merck and Witco, respectively. Technical toluene is used in the synthesis as a solvent. 3.75 millimoles of hydroxyl ended PEG (4000 g/mole) are dissolved in 180 ml reagent grade toluene. The PEG solution is refluxed in a dean-stark apparatus for 3 hours to remove humidity trapped in PEG. The dried PEG/toluene solution is treated with 7.5 millimoles of gamma-isocyanatropyltriethoxysilane at 323 K overnight. This product is kept in a 125 ml ethanol and 125 ml methanol mixture for 24 hours at 253 K. The precipitate is filtered with a Buchner funnel at 273 K and is dried at room temperature by using a filter paper.

$$H - O - (CH_2 - O - CH_2)_n\, O - H$$

(a)

$$CH_3CH_2O - Si - OCH_2CH_3$$

with OCH_2CH_3 above and $(CH_2)_3$ below connecting to $N = C = O$

(b)

$$F_3C(CF_2)_6 C_2H_4OH$$

(c)

Figure 3.1. (a)PEG, (b)Gamma-isocyanatropyltriethoxysilane, (c)PAF

3.2. Synthesis of Gammaisocyanatropyltriethoxysilane Capped Perfluoroalkylethylalcohol (PAF-Si)

Perfluoroalkylethylalcohol (Fluowet EA612) is provided by Clariant. Reagent grade Tetrahydrofuran is used as a solvent. Tin (II)2-ethyl hexanoate is used as a catalyst. 6 g perfluoroalkylethylalcohol (434 g/mole) and 3.41 g isocyanatropyltri-ethoxysilane (247 g/mole) are dissolved in 42 ml reagent grade tetrahydrofuran. Here, the mole ratio of the reactants is 1 : 1. 4 drops of Tin (II)2-ethyl hexanoate are added to the solution as the catalyst and the solution is mixed well with a magnetic stirrer in an oil bath. The reaction is started by increasing the temperature up to 333 K and it lasts for 5 hours.
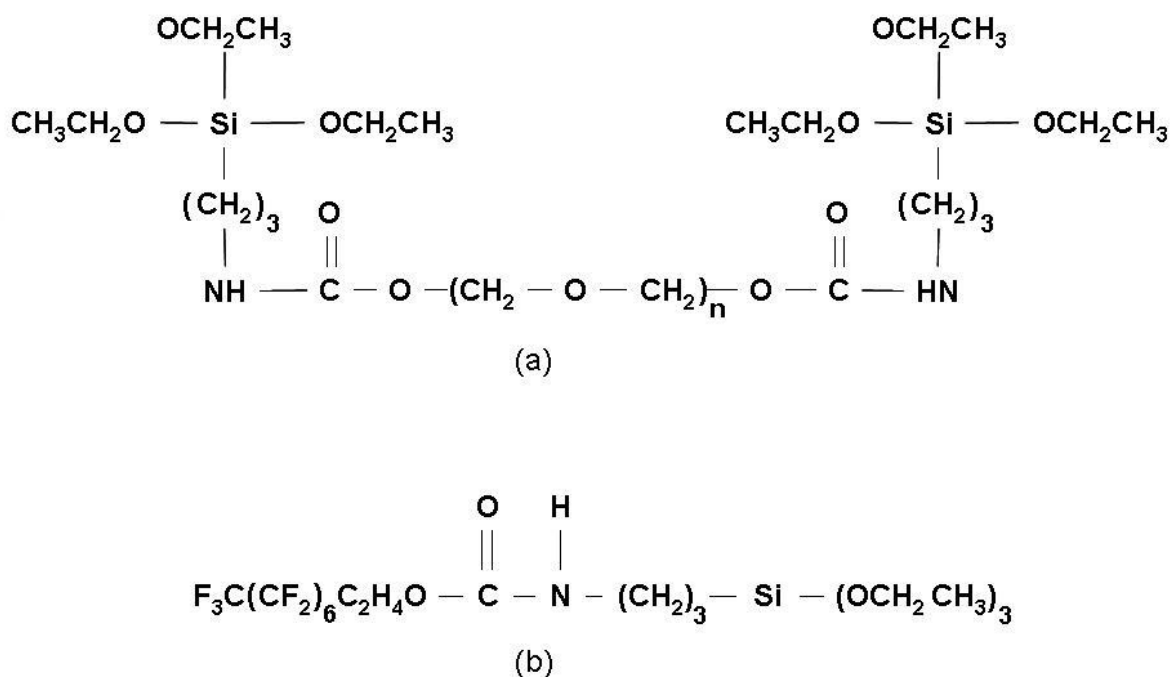
OCH$_2$CH$_3$
|
CH$_3$CH$_2$O — Si —— OCH$_2$CH$_3$
|
(CH$_2$)$_3$ O
| ||
NH — C — O —(CH$_2$ — O — CH$_2$)$_n$ O — C — HN

OCH$_2$CH$_3$
|
CH$_3$CH$_2$O — Si —— OCH$_2$CH$_3$
|
O   (CH$_2$)$_3$
||
C

(a)

O   H
|| |
F$_3$C(CF$_2$)$_6$C$_2$H$_4$O — C — N – (CH$_2$)$_3$— Si — (OCH$_2$ CH$_3$)$_3$

(b)

Figure 3.2. (a)Gamma-isocyanatropyltriethoxysilane capped polyethylene glycol
(b)Gamma-isocyanatropyltriethoxysilane capped perfluoroalkyl alcohol

3.3. Preparation of PEG-Si, Hydrophobically Modified PEG and Hydrogenated PEG Thin Film

2.5 g end group modified PEG is dissolved in 500 ml double distilled water. The solution is mixed until all PEG is dissolved. This solution is used for PEG thin films while a mixed coating solution is prepared by adding proper amounts of PAF solution into PEG solution to obtain PEG films including various percentages of PAF concentration. The PAF solution is also used to prepare the pure hydrophobic films. Two different methods are used to prepare the polymer as a thin film. First, one side of the glass substrate is scratched and the surface becomes rough, then the substrate is immersed into the coating solution for dip-coating of the polymer film. The substrate is kept fixed and the polymer solution is allowed to flow with a constant speed. Afterwards polymer coated glass substrate is dried and kept in an oven at 323 K for 2 hours to cross-link the thin film on the scratched substrate. With this method, samples with

different polymer thicknesses are prepared by scratching the glass substrates in different amounts. As a second method, the sample is prepared by dropping polymer solution directly on a glass substrate and one waits till the sample dries. By that method samples with larger thicknesses are obtained. With the first method, the samples thicknesses varies in the order of 10^1 nm while with the second method, in the order of 10^2 μm.

After the preparation of polymer film, aluminium electrodes are thermally evaporated onto the thin film in a coplanar geometry in an Edwards Coating System at a pressure of 6×10^{-4} Pa. The separation between the electrodes is 0.17 cm. 7 cm long wires are fixed onto the Al electrodes with silver paste for electrical measurements. With this method, samples made of pure PEG, pure PAF and 90 %, 80 %, 70 %, 60 %, 50 %, 40 %, 30 %, 10 % hydrophobically modified PEG by concentration are prepared for measurements.

To hydrogenate pure PEG films, they are first heated in a vacuum chamber for two hours at a pressure of 10^{-4} Pa. Then the chamber is filled with hydrogen gas to a pressure of 10 Pa and the films are kept in it for another 80 minutes.

3.4. Electrical Measurements

The samples prepared are inserted into a closed chamber, Keithley (8002A) High Resistance Test Fixture. This fixture can be used for picoammeter measurements with an offset current less than 10^{-13} A at 40 % rh and it also includes a guarded triaxial jack for meter connections to minimize the effects of undesirable leakage currents. This chamber has a small volume of $15 \times 11 \times 4.5$ cm^3, so that the humidity can be controlled easily by the solutions prepared from the saturated salts, which maintain constant relative humidities in small closed spaces. Different salts give different saturation vapor pressures, hence by choosing a range of different salt solutions it is possible to explore the whole range of humidity. For this purpose, KNO_3 is used to increase the relative humidity up to 90 %, while $ZnCl_2$ is used to decrease the relative humidity to 12 %. This solution, which is inserted into a flat beaker to allow a large surface area to

vaporize the water, is placed into the chamber. The relative humidity in the chamber is monitored by a humidity sensor, placed next to the sample. This sensor, obtained from Honeywell (IH-3610-1), has an accuracy of $\pm$ 2 % from 0 to 100 % relative humidity. A voltage of 5 V is fed to the sensor by a Tes power supply. The output voltage is read through a multimeter (Fluke 8840A). After placing the solution, the chamber is sealed off tightly. The change in humidity is very slow, so that the humidity measured at the sensor is the same as that where the sample is. The rate of rh increase in the chamber changes as the rh value increases. Between 30 % and 40 % rh, it is nearly 0.7 % per minute; between 40 % and 65 % rh, 0.20 % per minute; between 65 % and 75 % rh, 0.05 % per minute; above 75 % rh, 0.01 % per minute. During the drying process, the chamber is opened in parts. Although every effort is made to decrease rh with the same rate of increase, the decrease rate becomes slightly different. The rate of decrease is 0.17 % per minute above 75 % rh, 0.06 % per minute between 65 % and 75 % rh, 0.25 % per minute between 40 % and 65 % rh, 0.10 % per minute between 40 % and 30 % rh, 0.01 % per minute under 30 % rh. A dc electric field of 30 V/cm is applied to the sample by an electrometer-power supply (Keithley 6517A), which instantaneously measures the current passing through the sample. This electrometer is capable to do current measurements from 10×10^{-18} A to 21×10^{-3} A. In the 20×10^{-12} A range, it has a resolution of 10×10^{-17} A. The minimum current values measured are in the order of 10^{-13} A, so that as humidity inside the chamber changes gradually, electrical current flowing through the gap of the polymer film is measured every second, while recording the relative humidity at each point at room temperature. The setup used in the measurements is shown in Figure 3.3.

3.5. PEG Thin Films

8 different pure PEG thin films, prepared by either dip-coating or dropping the polymer on the glass substrate, are used in the measurements. At first the current-time characteristics of all samples are investigated to be sure about the time scale that can be used in current-voltage and current-rh measurements. The period used for data taking in the above measurements has to be longer than the time it takes for the
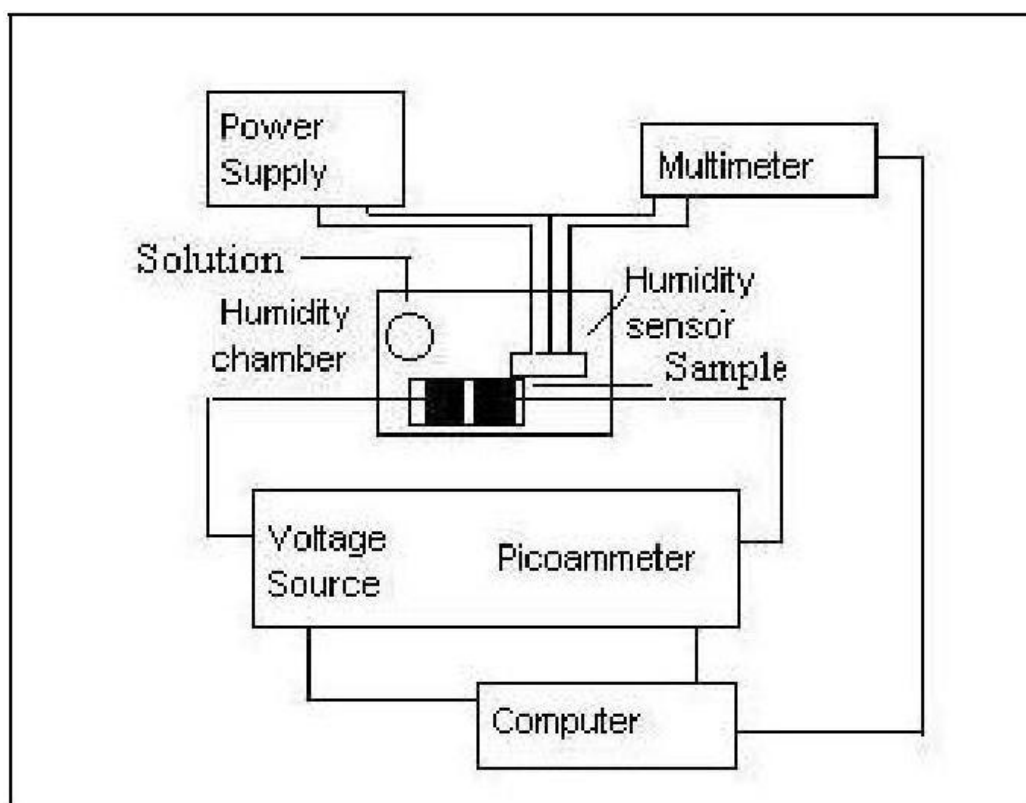
Figure 3.3. Setup used in the measurements

polymer to reach a steady state. The current-time characteristics of a typical sample is shown in Figure 3.4.

After that, the current-voltage (I-V) characteristics of all samples are measured at 30 % rh at 300 K. In Figure 3.5, the I-V characteristic of a PEG thin film (sample 1) which has a thickness of 10 nm is seen. This is typical of the general behavior of all the other samples. They all show ohmic behavior, which is an indication of the electronic nature of the conductivity mechanism.

The process of swelling involves the diffusion of the water molecules into the PEG film. This diffusion is made possible by the freedom of motion of local segments of the PEG chains, which enables the film to accommodate the incoming water molecules. As the amount of water diffusing inside the PEG film increases, the effect of polymer structure comes into play, the swelling leading to an expansion of the network structure. As a result of this expansion the PEG chains are extended in much the same way as if they were subjected to an external force. The expansion is resisted by the tendency
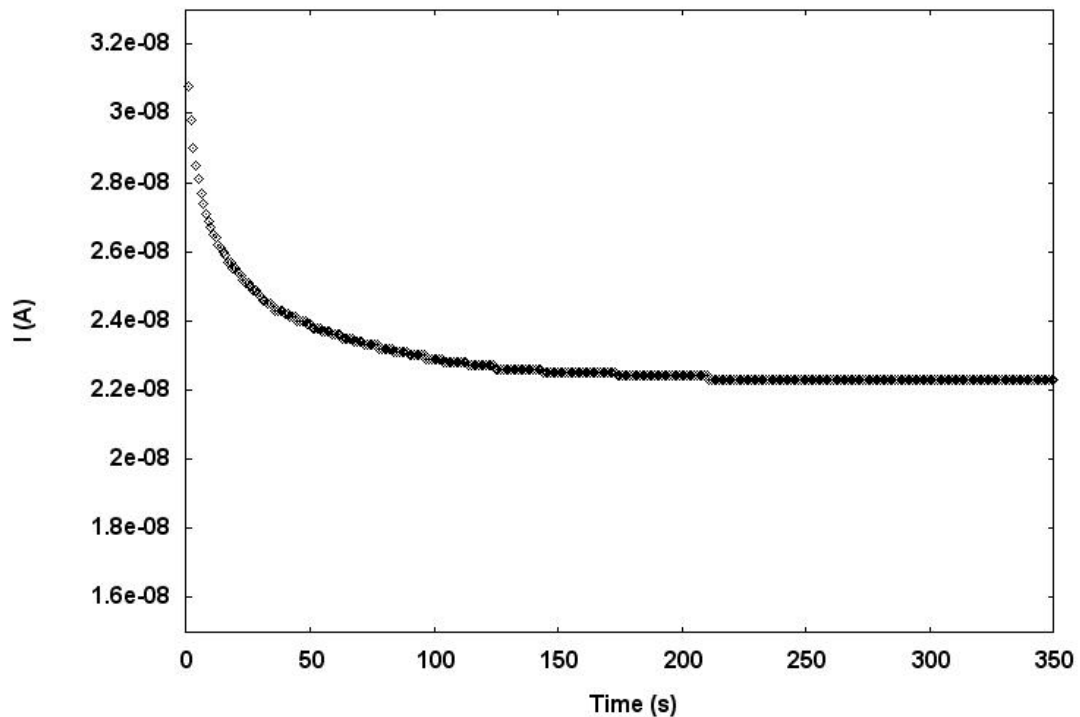
Figure 3.4. The current-time characteristic of pure PEG film

of the chains to a shorter length. The balance of these two effects; the tendency of water molecules to diffuse into the PEG molecules and the tendency of the network to contract to a smaller volume, leads to an equilibrium state corresponding to each rh value. The equilibrium degree of swelling depends on the extent to which the already existing cross-linked network can be expanded.

The conduction inside the polymer can be via intra and interchain transport of charge, and interparticle transport [30]. Water molecules penetrating inside the polymer aid the conductivity either by binding with hydrogen bonds to the polymer polar groups, or forming water clusters as is expected of hydrophilic polymers if the amount of water molecules in the polymer is higher than the quantity that can be bound to it [20]. The crystallinity of PEG was measured to be around 70 % irrespective of its molecular weight by differential scanning calorimetry by Kitano et al [31]. Because gaseous water molecules diffuse and adsorb mostly to amorphous region in the polymeric materials, this data indicated that at least 30 % of the chains were ready to sorb water molecules with a help of van der Waals forces. However infrared spectral analysis of the films suggests that the amount of water sorbed by the van der Waals
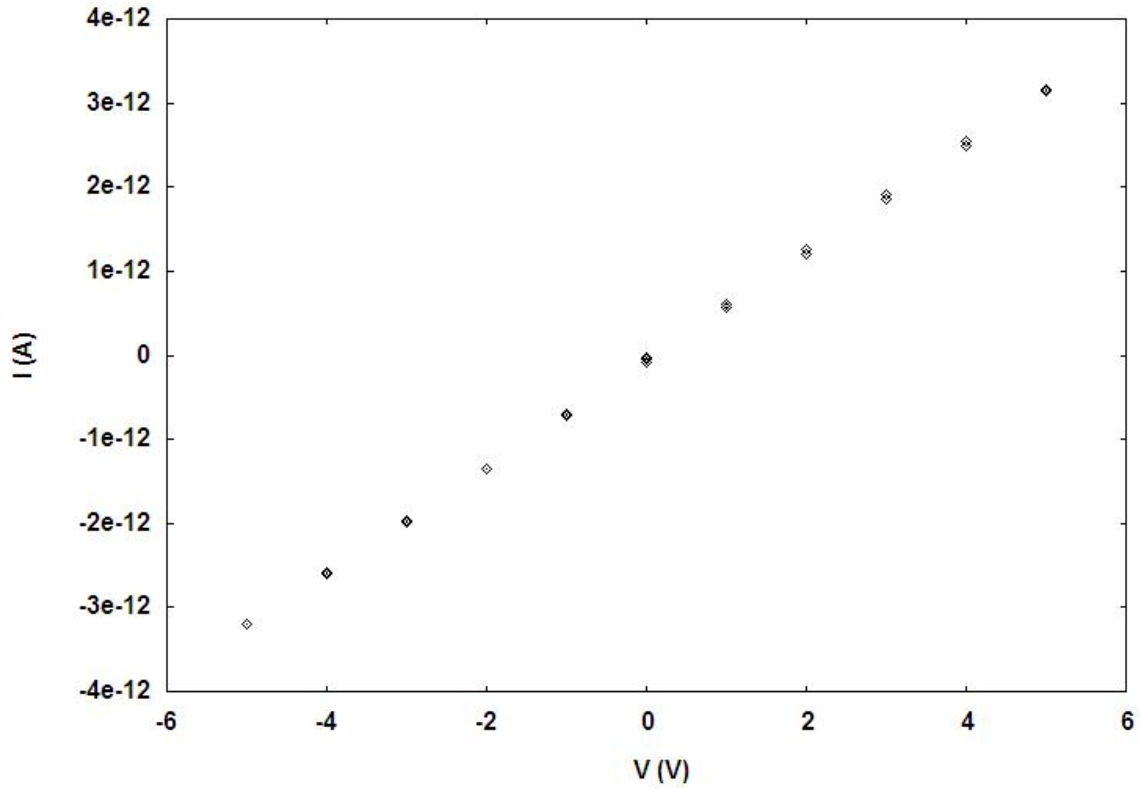
Figure 3.5. The current-voltage characteristic of a sample 1 having a thickness of 10 nm at 30 % rh at 300 K

force would be very small, and water molecules in the PEG films dominantly adsorb to the ether oxygen atom of the PEG chains. This is because the binding energy of the van der Waals interaction is much smaller than that of the hydrogen bonding. The influence of the van der Waals force on the sorption process is negligible [31]. As it is depicted in Figure 3.6, the water sorbed to the PEG films can form a monomeric bonding to the ether oxygen atom of the polymer (binding water). It is also possible that a water molecule can bind to another water molecule which is already bound to PEG with hydrogen bonding (water molecules are dimeric). Besides these, a water molecule can form hydrogen bonds to two PEG chains (bridging water) as well as between two neighboring ether oxygen atoms of the same PEG chain [6]. According to the measurements of Kitano et al., the amount of sorbed water indicates that water molecules bind to the PEG mostly monomolecularly and that the amount of monomeric water in the PEG film is much larger than that of bridging water. The process of sorption of water followed by the penetration into the polymer matrix is explained as follows:

At the polymer surface, monomeric water binds to the oxygen atom of the polymer, the bridging water is formed. The formation of dimer is completed after the water sorption in the polymer matrix is equilibrated. In the polymer matrix, the bridging water is equilibrated first, and subsequently the binding water is equilibrated. Finally, the dimeric water is equilibrated by the attachment of a water molecule to the binding water. But in the long period, it is possible for water to form first small clusters, then larger ones.
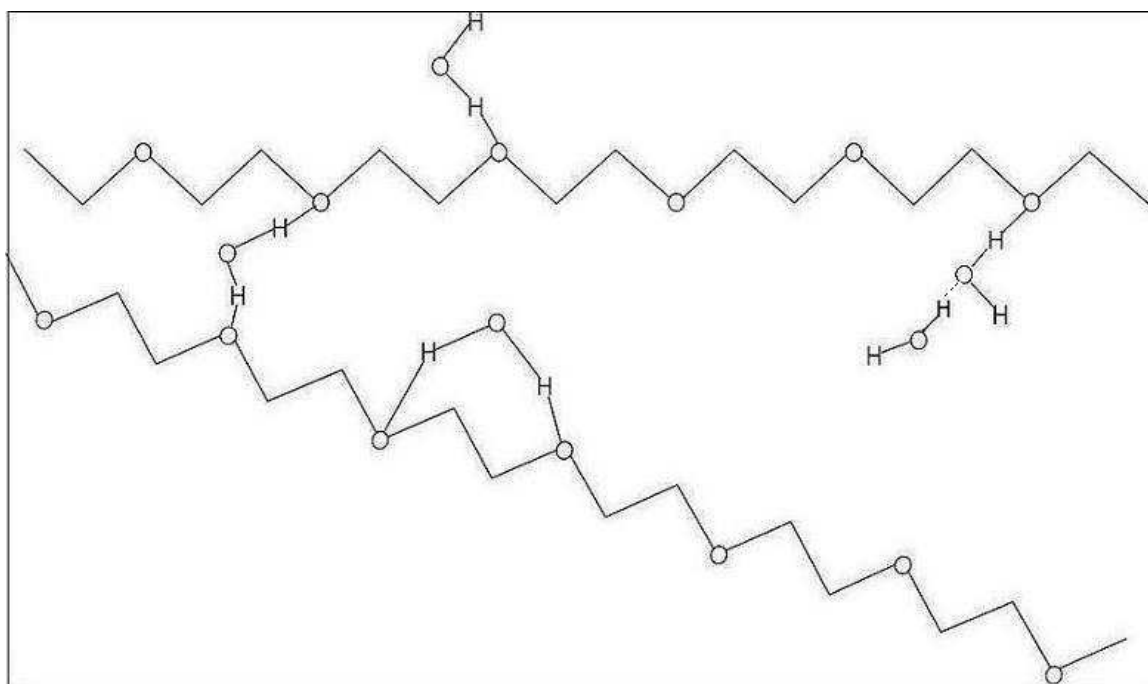

Figure 3.6. This illustration depicts the binding of water molecules to PEG molecules

Afterwards the current measurements under increasing rh are done. During our measurements, the relative humidity changes between 12 % and 90 %. In Figure 3.7, the change in current of sample 1 versus rh from 12 % to 50 % is seen. Even at such low humidity levels the current increases nearly 3 orders of magnitude (the current has a value of 2.6×10^{-13} A at rh=12 % and 8.3×10^{-11} A at rh=50 %). The same characteristic is observed in Figure 3.8 where the dependence of current on rh of sample 2 is shown at low humidity levels. As the rh increases, the thin film starts to absorb water molecules, which are highly dipolar because of the electronegativity of oxygen compared to hydrogen. This difference in the electronegativity causes partial

electrostatic charges, and results in strong interactions between water and other charged or polar groups as well as between the water molecules in the polymer. The degree of the interaction depends on the structure of the polymer. The sorption equilibria can be discussed by treating the sorption process as mixing of the solvent and polymer.

$$\ln a = \ln \varphi + (1 - \varphi) + \chi(1 - \varphi)^2 \tag{3.1}$$

where a is the solvent activity, φ is the volume fraction of solvent, and χ is empirical polymer-solvent interaction parameter. χ depends on concentration and this dependence is ascribed in most cases to an inhomogeneous distribution of solvent molecules and polymer segment. χ shows how strong the interaction between the polymer and the solvent is. It is related to the differences between the water binding energies and increases from negative to positive values in the order of decreasing binding energies. Matsuguchi et al. [6] found that the interaction parameter of PEG has a large positive value with a monotonously decreasing trend with the increase in water content. This indicates that the interaction between the polymer and the absorbed water is not strong, instead, the interactions between the water molecules themselves are rather larger during swelling. The sorbed water starts forming clusters during the initial sorption stage.

At low rh there is a gradual increase in current as shown in Figure 3.9 and Figure 3.10, while a steeper increase starts to be observed at around 70 %. This increase is not very sharp, and this could be the result of using cross-linked PEG film. When the polymer is cross-linked, all the molecules are joined together chemically in the form of a network, this network cannot disperse easily; it swells. The case for a PEG film which is not cross-linked with silane should probably have a very sharp increase at high humidity. It is previously reported that the cross-linking of the polymer with silane effects the crystallinity of the polymer [7]. The distribution of the crystal sizes is broadened and results in a sorption and melting over a broad humidity range. This steeper increase in current which is seen in Figure 3.9 and Figure 3.10 can be a result of a state transition above a certain humidity level. At low humidity levels up to 70 %, the thin film is in a semicrystalline form. As the amount of the absorbed water increases,
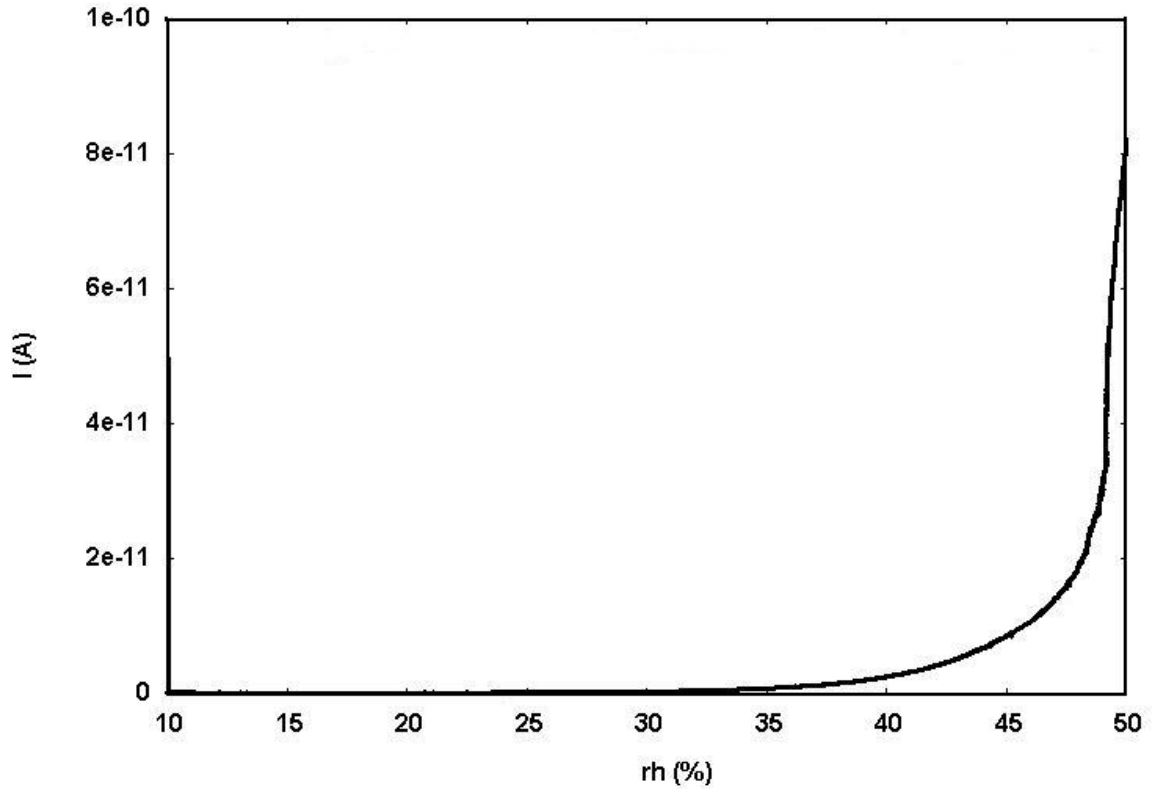
Figure 3.7. Dependence of current of sample 1 on relative humidity at low humidity levels

the crystalline forms in the semicrystalline thin film begin to melt, and at around 75 %, an abrupt absorption takes place where a gel state is formed. In previous studies [6, 8] the FTIR(Fourier transform infrared spectroscopy) measurements were used to indicate the form of the water molecules inside the polymer network. In the FTIR technique, the water affinity parameter (WAP) is estimated using the shift in the streching bands of the sorbed water molecule. Using this parameter, it is possible to clarify the water structures in solid polymer matrices, in another words, the cluster formation propensity of the sorbed water. If the state of the sorbed water is close to that of liquid water (clustered state), the value becomes nearly equal to unity. If the state of the sorbed water molecule is close to that of the vapor (isolated state), a WAP value near zero is obtained. Matsuguchi et al. obtained WAP value changing between 0.55 and 0.60 which increased with an increase in the amount of sorbed water [6]. This may suggest that the water cluster grows as the amount of sorbed water increases and indicates that water molecules take a liquid form as the amount of absorbed water increases. The
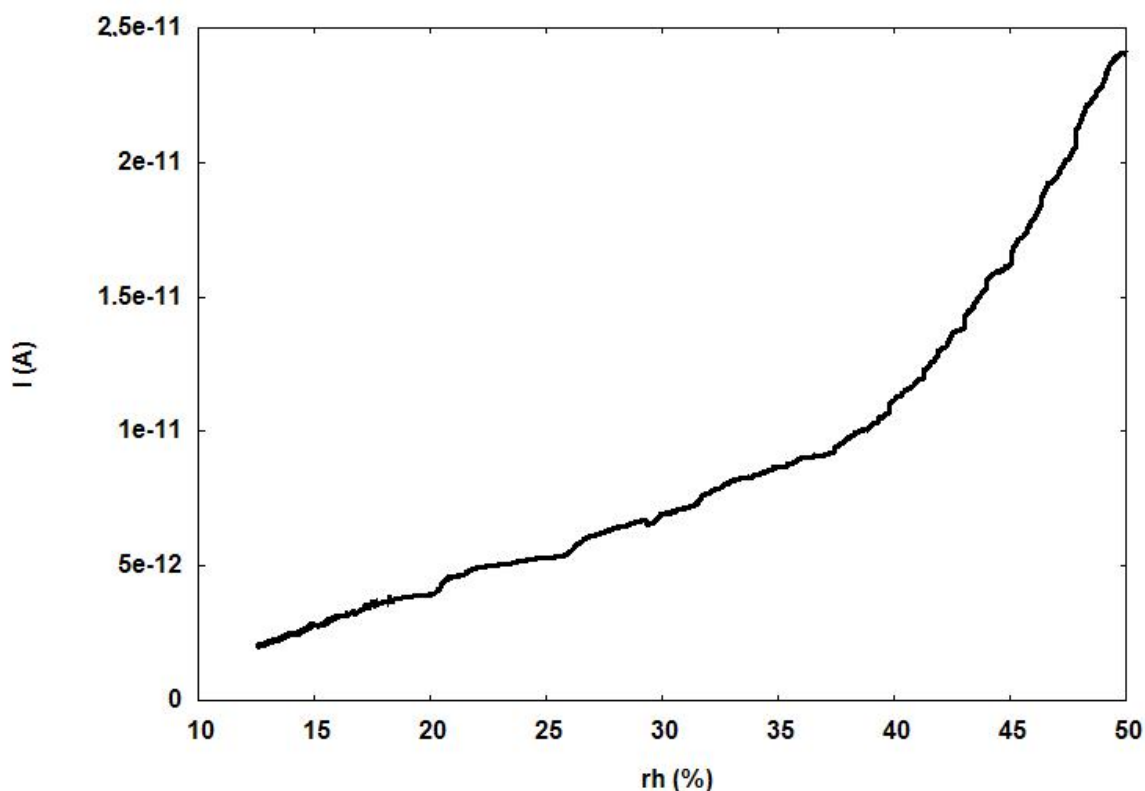
Figure 3.8. Dependence of current of sample 2 on rh at low humidity levels

number of states of water in the polymer has been found to be two or three depending on water concentration and the temperature regime. These are bulk water, weakly bound and strongly bound water, which breaks up the intra and interchain hydrogen bonding of the polymer [32]. At this level, the water condenses in the polymer. As the crystallinity of the polymer is ruined, it swells more. Ionic conductivity starts to dominate at this high humidity level, around 75 %. A very familiar behavior was observed by Chan and Kazarian; up to 70 % rh, the absorbance of water gradually increases, but this trend changes sharply in favor of higher absorbance in the range between 70-80 % [33]. It is stated that below 70 % rh, water molecules enter the PEG matrix, form hydrogen bonds with the ether O atoms in the PEG chain and water does not form clusters when there are still ether O atoms in the PEG available to act as an electron donor for hydrogen bonds with water molecules. It is determined that it is necessary to have at least 0.82 g of water per gram of polymer mass in order to form clusters of water in the PEG. Above 70 % rh, all the ether O atoms in the polymer chain are occupied with water molecules already sorbed in PEG, thus forming clusters.

The plasticizing effect of sorbed water for the polymer is also pointed out in that work. This effect facilitates the growth of water clusters in the polymer due to the increased mobility of polymer chains, and leads to the increase in water sorption at the higher rh values.
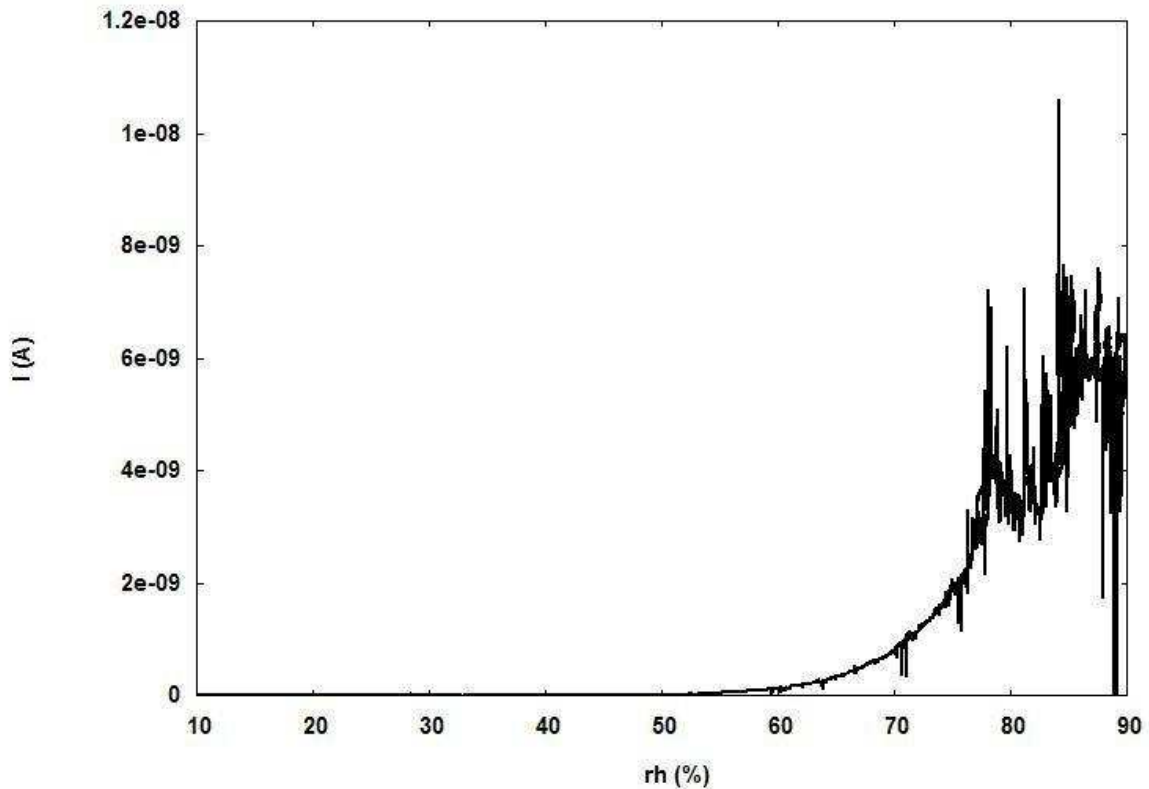

Figure 3.9. The change in the current of sample 1 (10 nm) with respect to increasing rh

Diffusion anomalies occur in polymers at temperatures well above T_g when crystallites are present. Sigmoid sorption curves are obtained at these temperatures and the sigmoid character is more marked the higher the crystalline-amorphous ratio is. It is reported that sigmoid sorption even occurs when all crystallinity has disappeared and the polymer is so weak that it is unable to support its own weight [34, 35]. It appears likely, however, that the effects in crystalline polymers result from slow responses to external changes in the crystalline regions [36]. This could lead, for instance, to a time-dependence in the crystalline-amorphous ratio and so produce time-dependent solubility or diffusion coefficients leading to sigmoid sorption curves.
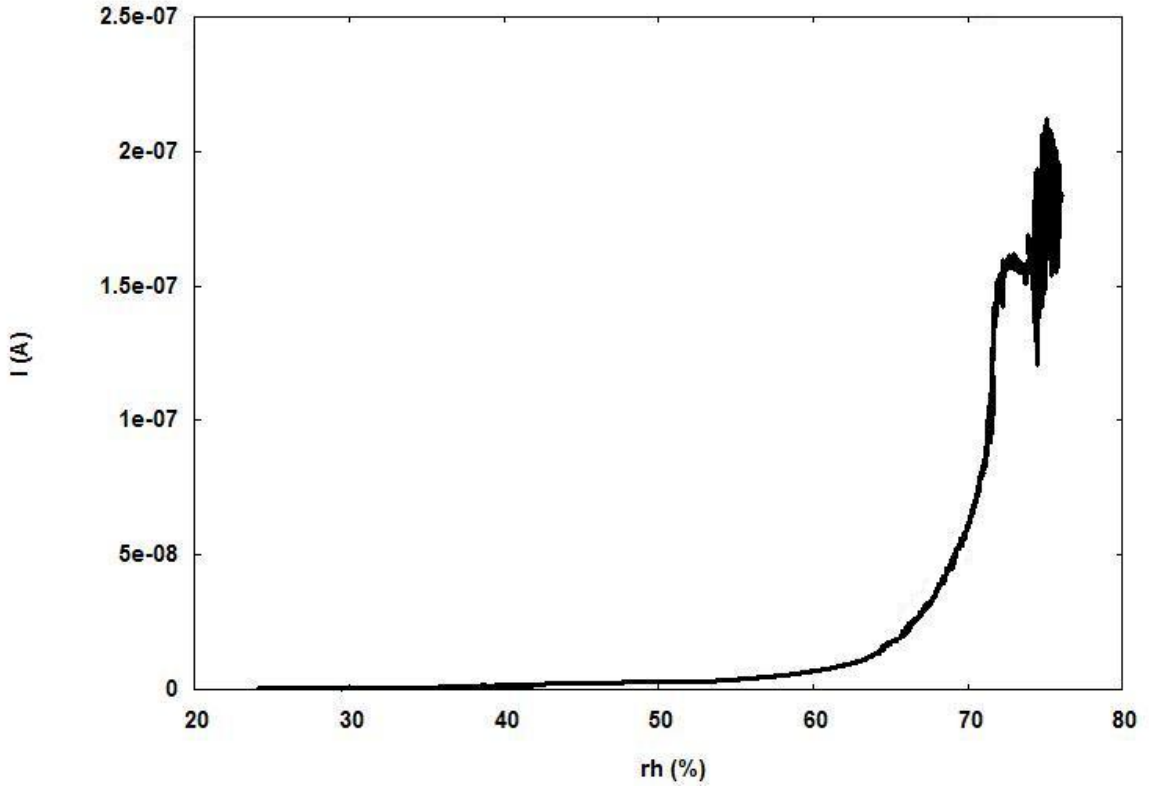
Figure 3.10. The change in the current of sample 3 (200 μm) with respect to
increasing rh

After around 75 % rh, the polymer continues to swell on absorption of more
water molecules, but as its crystalline form is lost, this expansion results in a less
stable structure, where the water molecules are loosely bonded to the PEG chain.
The swelling continues until the elastic force increases the chemical potential of the
sorbed penetrant to such an extent that no further sorption occurs [37]. The elastic
force slowly relaxes. During this relaxation some of the hydrogen bonds are broken,
the clusters are disturbed, and sudden decreases are seen in the current value. The
chemical potential of the sorbed water decreases, and more water is absorbed, causing
a sudden increase in the current value. This process continues as rh increases. As a
result of this process, the I-rh curve does not have a regular sigmoidal shape; instead it
starts to show an unstable and disordered behavior around 75 % rh as seen in Figure
3.9 and Figure 3.10.

The desorption behavior is seen in Figure 3.11. The desorption curve lies above

the one for the increasing humidity. The water absorbed is less easily removed than it would be if the process was perfectly reversible. There is a hysteresis between the absorption and the desorption of water vapor. When the humidity begins to decrease, the same time is needed for the nucleation and growth of crystals of PEG to occur. The rate of humidity decrease is higher than the rate of humidity increase, so that the same crystal form cannot be reached in this limited time. The degree of crystallinity is reduced while the expulsion of water occurs. As a result of the reduced crystallinity the ion mobility increases, so that the conductivity and therefore the current increases in the region where the ionic conductivity occurs. In the regions where the electronic conductivity takes place, the current is also higher as the water inside the polymer film is not totally given off. Some amount of water is kept inside the polymer, even though the humidity decreases. This hysteresis might be seen as a result of the cluster formation of water as reported in previous works [3, 6, 14, 38].

Crank has set up a model capable of producing anomalous sorption and desorption curves of the type seen in 3.11, on the assumption that the surface concentration is constant during sorption and only the diffusion coefficient is a function of time [39]. Changes in the diffusion coefficient are considered to occur in two stages. On increasing the solvent concentration, the increased ease of polymer segmental motion leads to an immediate increase in the diffusion coefficient. A further stage of diffusion coefficient increase is then thought to occur over a period of time as a result of the relaxation processes. As a consequence of these two effects, the value of the diffusion coefficient in any element of a polymer penetrant system at a given time will be *history dependent*, that is the diffusion coefficient will depend on the concentration history of the element.

During the measurements it is observed that, when the measurements are repeated under the same conditions, the current values show little deviations from the previous measurements. This is because of the phase change of the polymer film at high humidity levels. As the semicrystalline form is changed and gets a more amorphous structure, the diffusion constant changes slightly. However, when the second measurement is done after heating the sample in a vacuum chamber at a pressure of 10^{-4} Pa for two hours, the current values do not change from the previously measured

values. When the films are heated, a crystal transformation would be favored thermo-dynamically and would become kinetically possible as the thermal motion increases. In Figure 3.12, two successive measurements are seen. The current takes the same values in both measurements. So it can be said that after increasing the rh when the rh returns back to low values, the polymer could not take its form at the beginning and could not give off all the water molecules that are absorbed. The polymer thin film should be dried to have its pre-absorption structure.
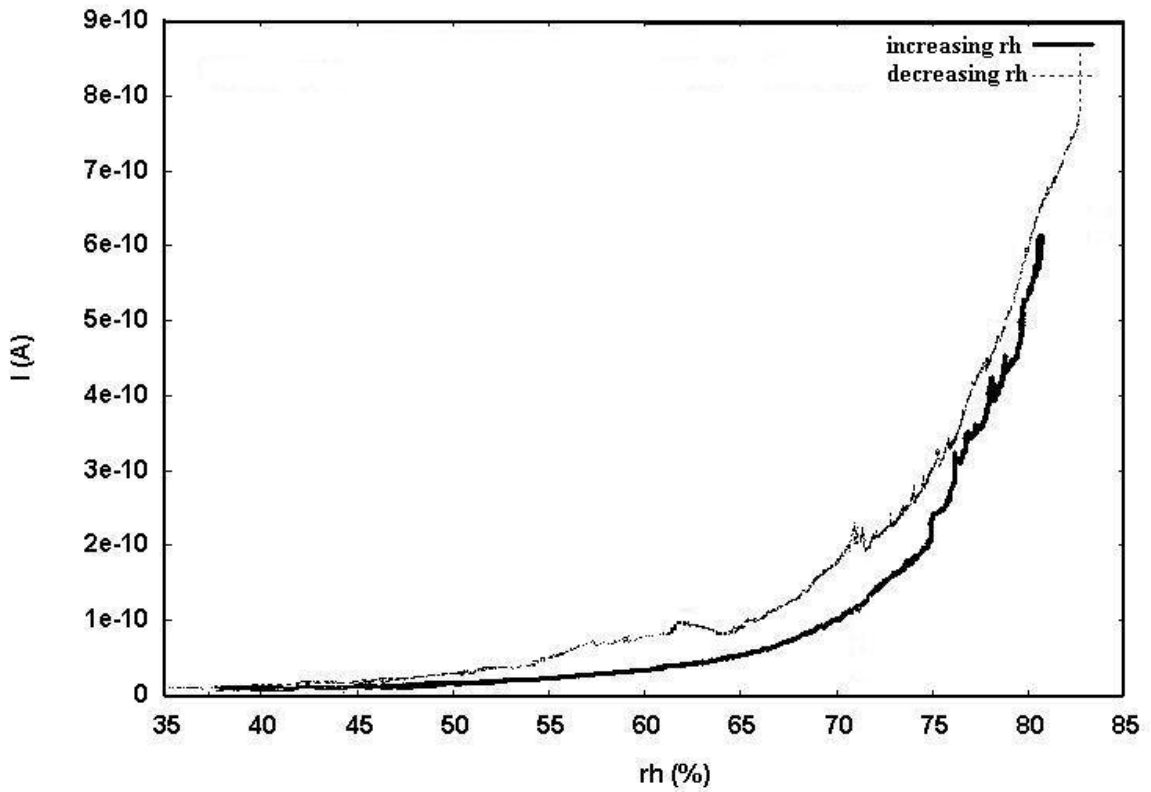

Figure 3.11. The change in the current of sample 2 (50 nm) with respect to increasing and decreasing rh

The thickness of the films does not effect the general behavior of the I-rh curves as can be seen in Figure 3.9, Figure 3.10 and Figure 3.11. This behavior of the PEG film resembles that of type III isotherms, which is observed for less hydrophilic polymers like polyethylene [6]. It is known that the change in the resistance is directly proportional to the mass absorbed for water [40]. The non-linear behavior indicates the interactions between the water molecules and the polymer, although this interaction is not so strong
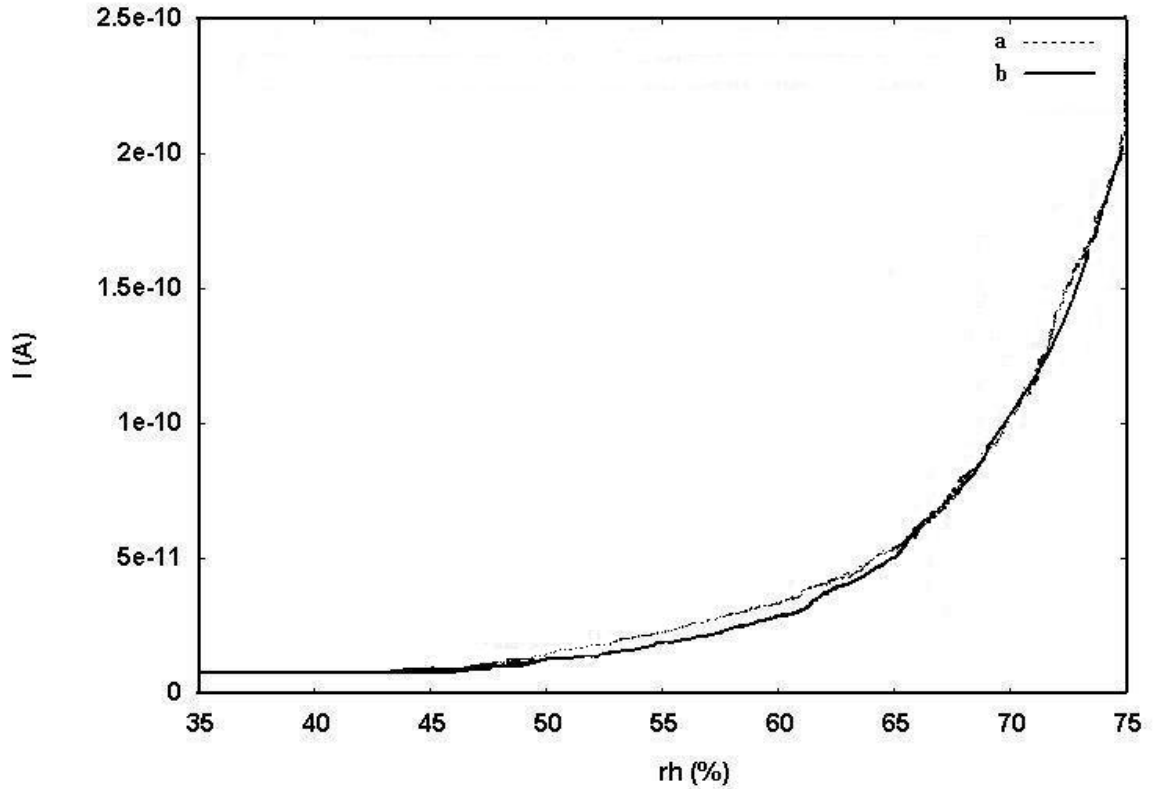
Figure 3.12. Two successive I vs rh measurements of sample 2; a) the first, b) the second measurement done after drying the sample in vacuum

as stated above. The clustering of the water molecules enables the interaction between the water and the polymer as well as the water-water interaction.

3.6. Hydrogenated PEG Thin Films

Beyond 75 % rh, it is experimentally observed that there is an irregular behavior of the current with respect to the changes in rh as a result of the instability of the polymer. To alleviate this problem observed in the PEG samples at high rh values, and increase the range of rh in which measurements can be done with PEG, PEG samples are enriched with hydrogen.

The current-voltage characteristics of the samples are measured. As it is seen in Figure 3.13, the characteristic is nearly the same before and after hydrogenation.
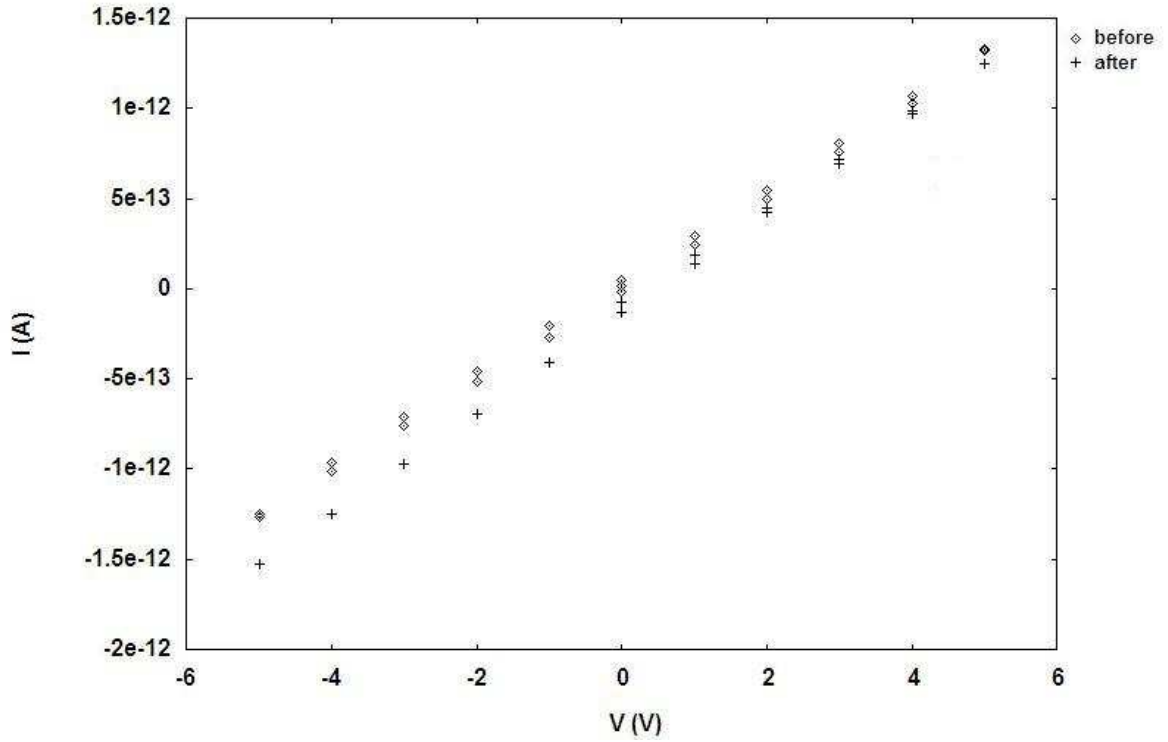
Figure 3.13. The current-voltage characteristics of sample 1 before and after hydrogenation

Measurements on hydrogenated PEG samples show that at the first stages where the rh is low, the I-rh curve is nearly the same as in the previous measurements, while at higher rh values, the problem of instability seen previously is lost, and almost a regular sigmoidal shape is obtained as seen in Figure 3.14. During the preparation of the hydrogenated samples, the pure PEG samples are exposed to hydrogen gas in a vacuum chamber. The hydrogen atoms form bonds with the ether oxygen atoms of the polymer, so the number of ether oxygen atoms available for the binding of water molecules when the sample is exposed to water vapor decreases. The interaction of water molecules with the polymer decreases; consequently the current values also decrease slightly, and the polymer obtains a more stable form than in the pure PEG samples. In this case, the number of water molecules penetrating the polymer network has to be increased to attain the state of phase change. This could happen when rh reaches a higher value. With the penetration of more water molecules, the cluster formation gets accelerated and their contribution to the conductivity increases. After that point, the conductivity gets an ionic nature again, and the I-rh curve shows a

rapid increase. This rapid upward curvature takes place at a higher value of rh with respect to the case seen in pure PEG samples (see Figure 3.14).
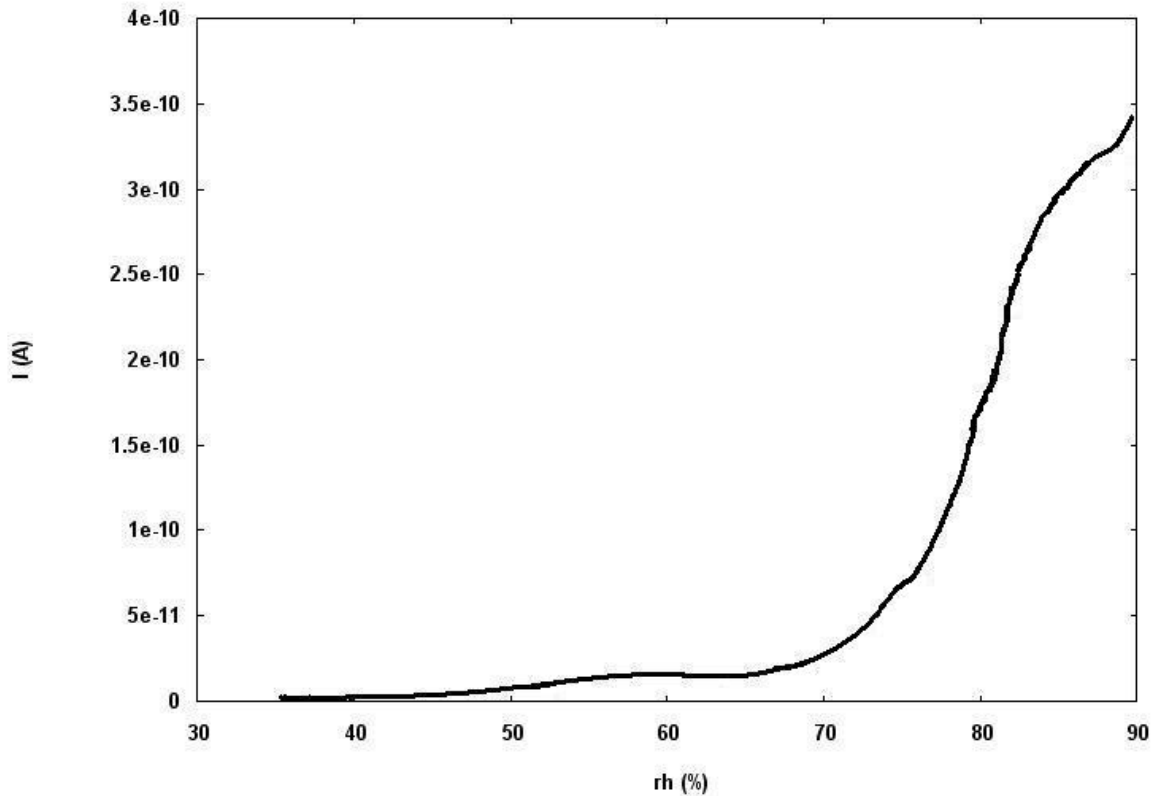

Figure 3.14. The I-rh plot of hydrogenated PEG thin film

3.7. Hydrophobically Modified PEG Thin Films

It is experimentally observed that if the ether oxygen atoms of PEG form bonds with hydrogen by some means before water penetration, it is possible to have a smoother curve, while in sensor applications the dynamic range can be extended to higher values of rh. A small amount of hydrophobic molecules added to PEG may be randomly attached to the PEG chain. The hydrophobic molecules take the place of hydrogen atoms in the hydrogenated PEG films and as a result of this, the hydrophobically modified PEG films show a similar behavior to hydrogenated PEG samples.

At first, the current-time characteristics of the samples are observed. A typical sample is shown in Figure 3.15. Afterwards, the current-voltage (I-V) characteristics of all samples are measured at 30 % rh. In Figure 3.16, the I-V characteristics of

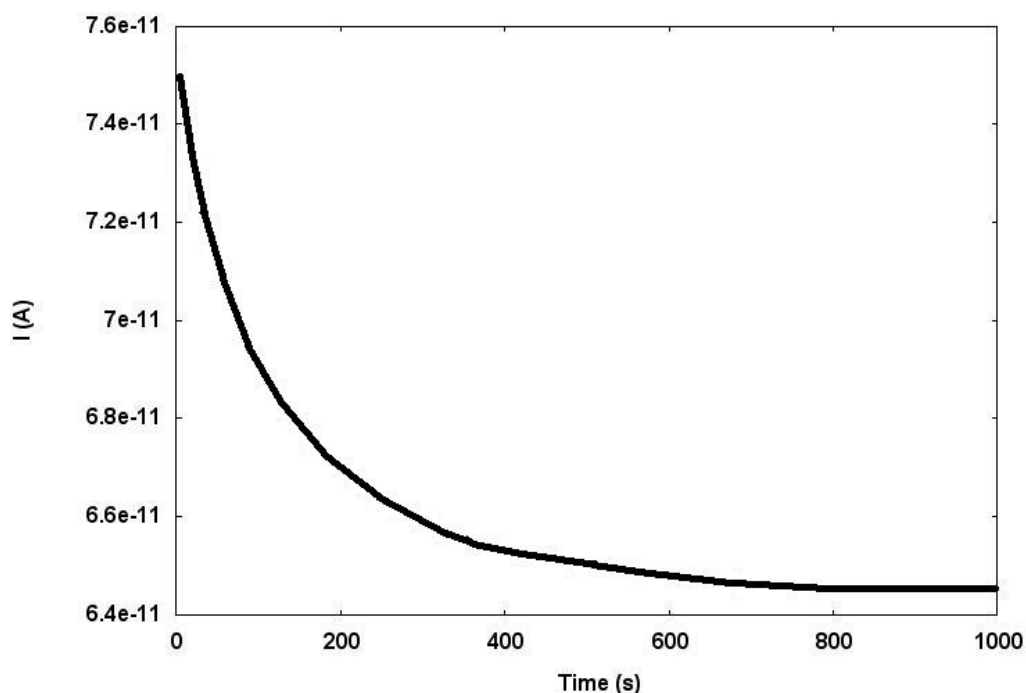hydrophobically modified PEG thin films are seen.

Figure 3.15. The current-time characteristic of a hydrophobically modified PEG film

The I-rh curves of homogeneous PEG and hydrophobically modified PEG thin films are seen in Figure 3.17. The thicknesses of the films presented in this figure are approximately 200 nm. The hydrophobic perfluoroalkylethylalcohol molecules aggregate to minimize their exposure to water [41]. The polarizability of water is small; therefore, the induced momentary dipole is not so strong, hence, the resulting dispersion force is weak. Besides that, the contribution of the dispersion force to the interaction with the hydrophobic molecules is so small that the interaction of water molecules with perfluoroalkylethylalcohol molecules is minimal. At low values of rh, the aggregated state of these molecules is partially disturbed due to the semicrystalline form of PEG polymer. At these values of rh, there is almost no change with respect to pure PEG samples. The current decreases as the content of hydrophilic polymer decreases, this is an expected behavior as the water content that could take role in the conductivity by forming clusters decreases, and instead of water molecules, hydrophobic molecules bind to the oxygen atoms of the polymer. Upon increase of rh, more water molecules are absorbed, the polymer gellifies, and small domains of hydrophobic molecules are formed [42]. As the film was homogeneous in the beginning, some of the
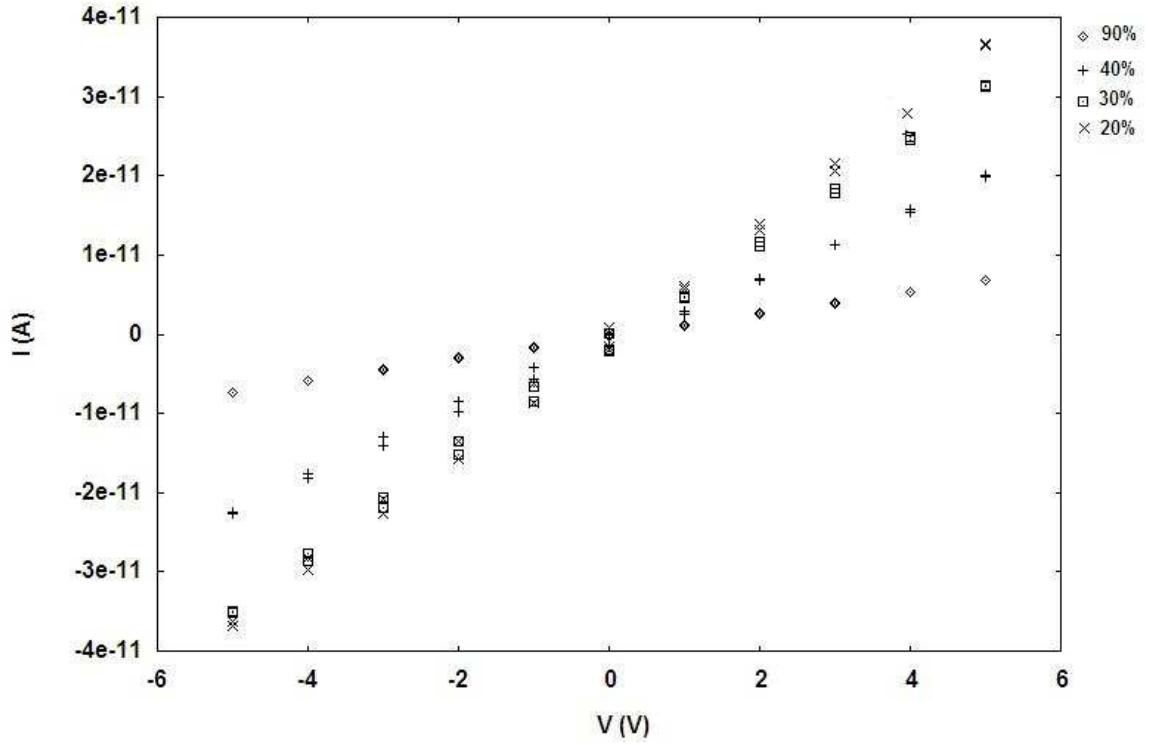
Figure 3.16. The I-V characteristics of 20 %, 30 %, 40 % and 90 % hydrophobically modified PEG thin films

hydrophilic segments get trapped in the hydrophobic domains. This distribution causes a network where the hydrophobic segments are aggregated in small domains with some hydrophilic molecules trapped inside and the rest of the hydrophilic molecules acting as bridges between these hydrophobic domains [43]. The abrupt upward curvature of the current shifts to higher values of rh with increasing perfluoroalkylethylalcohol concentration as a result of the need for more water molecules as the number of hydrophobic molecules in the network increases. The rh value where the phase transition of the polymer occurs increases, and the change of the conduction behavior from electronic to ionic nature is translated to a higher rh value. The instability problem in current at high values of rh seen in pure PEG samples is not observed in these hydrophobically modified PEG samples.

The hysterisis between the absorption and the desorption of water observed in the pure PEG samples is also seen in the hydrophobically modified PEG samples. The current values for the desorption of water are slightly smaller than the values measured for the absorption process. This is shown in Figure 3.18.
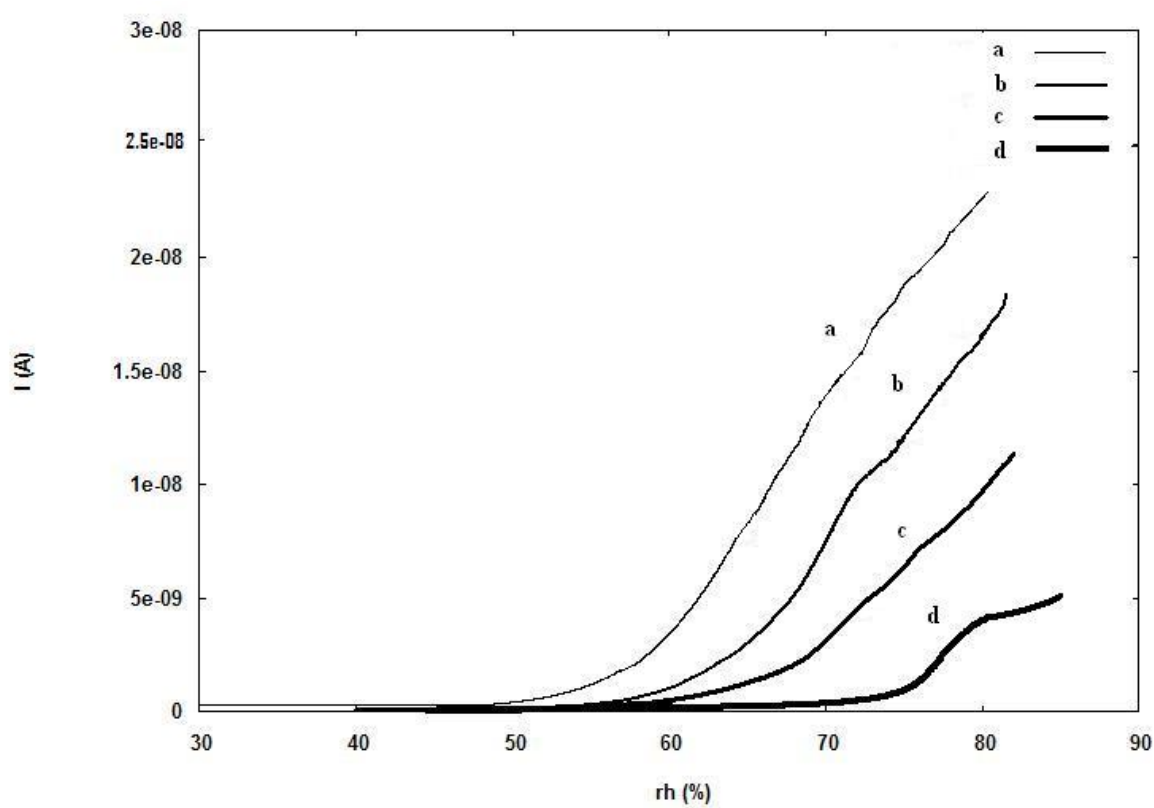
Figure 3.17. The I-rh plot of a) pure PEG, b) 10 % modified PEG, c) 50 % modified
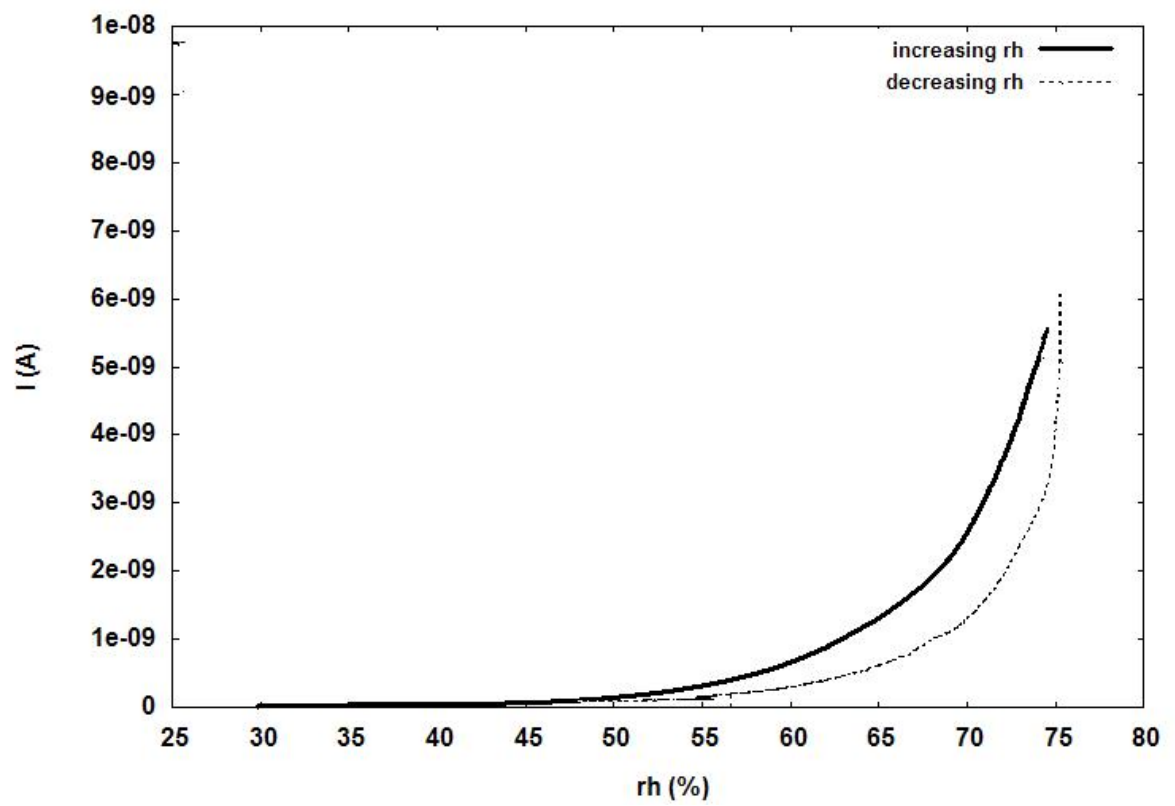PEG, d) 70 % modified PEG thin films

Figure 3.18. The change in the current of 20 % modified PEG thin film with respect to increasing and decreasing rh

4. EFFECTS OF VARIOUS GASES ON PEG THIN FILMS

The growing environmental pollution due to various chemicals used in industry has led to considerable demand for sensing elements. Many chemical sensors and membranes depending on the diffusion and penetration of organic or inorganic solvents in different materials have been reported in the literature [44, 45, 46, 47, 48, 49]. The simplest are those based on the measurements of conductivity or dielectric constant of the sensitive layer when exposed to chemical vapors. The most commonly used materials are oxides of tin, zirconium or titanium with appropriate doping. However, these materials show high sensitivity only at temperatures exceeding 373 K. Research for alternative sensing materials which show high sensitivity under room temperature has to be done. Conducting polymers have shown very promising results, since they exhibit large changes in either the work function or the conductivity over small concentration ranges of certain chemicals [44].

With this in mind, the sensing characteristic of PEG is searched when exposed to acetone and methanol vapor.

4.1. Electrical Measurements

For the measurement of current passing through the polymer sample, placed inside a vacuum chamber, a setup is prepared as shown in Figure 4.1. Dc electric field is applied to the sample by an electrometer-power supply (Keithley 6517A), which instantaneously measures the current passing through the sample. Two pure PEG samples are used in these measurements. First the current-time characteristics of the samples are determined to be sure of the time intervals in the following measurements are appropriate. Then the I-V characteristics of the films are observed. After being sure that they show an ohmic behavior, the pressure inside the chamber is decreased to 10 Pa, and the I-V characteristics are again measured. Afterwards, the gas is let to flow inside the chamber through the gas bleed nozzle while controlling the pressure from the Pirani gauge head. In the experiments, acetone (CH_3COCH_3) and methanol

(CH_3OH) are used to see the response of PEG. The gas is let to flow into the chamber in a controlled way while the pressure inside the chamber is monitored by the Pirani gauge and the pressure is increased step by step. At the same time, the current flowing through the sample under a dc electric field of 30 V/cm is measured with respect to time.
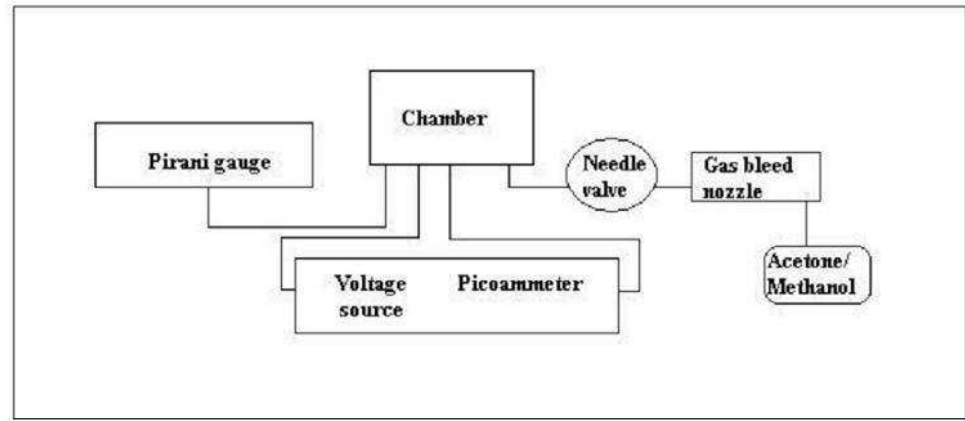

Figure 4.1. Setup used in the measurements

4.2. The Response of PEG to Various Gases

Before starting to take data with acetone, the pressure inside the chamber is decreased to 10 Pa, then through the gas bleed nozzle acetone is let to flow into the chamber. The pressure inside the chamber begins to increase from 10 Pa. When the pressure reaches 500 Pa, the current-time characteristic of Sample 4 is measured and this measurement is repeated at six different pressure values as seen in Figure 4.2. For the first 500 s, the pressure is 500 Pa; between 500 s and 2890 s, 700 Pa; between 2890 s and 4270 s, 800 Pa; between 4270 s and 5480 s, 900 Pa; between 5480 s and 6480 s, 1000 Pa; after 6480 s, it is 1100 Pa. When gas dissolves into the sample, it weakens the attraction between polymer molecules and changes their entanglement, making the molecular movements more active [50]. Thus, the mobility of the polymer chains and the conductivity of PEG thin film increase as the acetone vapor in the chamber increases. The current value increases by nearly 2 orders of

magnitude with the increase of pressure from 500 Pa to 1100 Pa. In Figure 4.3 and Figure 4.4, the response of sample 5 to acetone vapor is seen showing the same kind of characteristic. The current increases by more than 2 orders of magnitude between 800 Pa and 1500 Pa. It was stated by Nylander et al. [51] that the electron donating or accepting species will decrease or increase, respectively, the conductivity of some polymers. Many studies exist suggesting that the chemical sensing effect is due to electron density moving between the polymer film and the penetrating vapor, and the relative magnitude of the electronegativity of the vapor and the work function of the polymer determines the direction of transfer [40, 52].

For a sorption process a polymer film does not immediately attain the equilibrium structure consistent with the new solvent pressure in the gas phase. The sorption curves exhibit an overshoot in the current before leveling off to the equilibrium value. It seems that solvent can be absorbed into the sample before the polymer chains have a chance to completely relax, and the structural rearrangements which the sample experiences as the chains eventually reorient themselves lead to rejection of some of the solvent from the sample. This partial exclusion of the penetrant will be more pronounced in instances when the diffusion rate is faster than the rate of chain relaxation since most of the solvent absorption is into an unrelaxed polymer network [53]. All chains will eventually relax after a sufficiently long period of time. Each time the pressure inside the chamber is increased by one step, it takes nearly a period of 7 minutes for the current to reach an equilibrium value. Once the equilibrium is attained, the current value does not change any more. It is clearly seen that as the pressure due to the acetone vapor increases, the current flowing through the sample takes higher values. In Figure 4.5, this behavior of sample 4 is seen as the current changes with respect to the pressure in an exponential way.

To be able to use the same samples for the exposure to methanol vapor, the samples are heated in the vacuum chamber at a pressure of 10^{-4} Pa for two hours. The I-V characteristics of the samples are controlled in order to be sure that the samples returned to their initial structure. It is observed that as in the first experimental part, drying the samples helps them to attain their previous semicrystalline forms as the
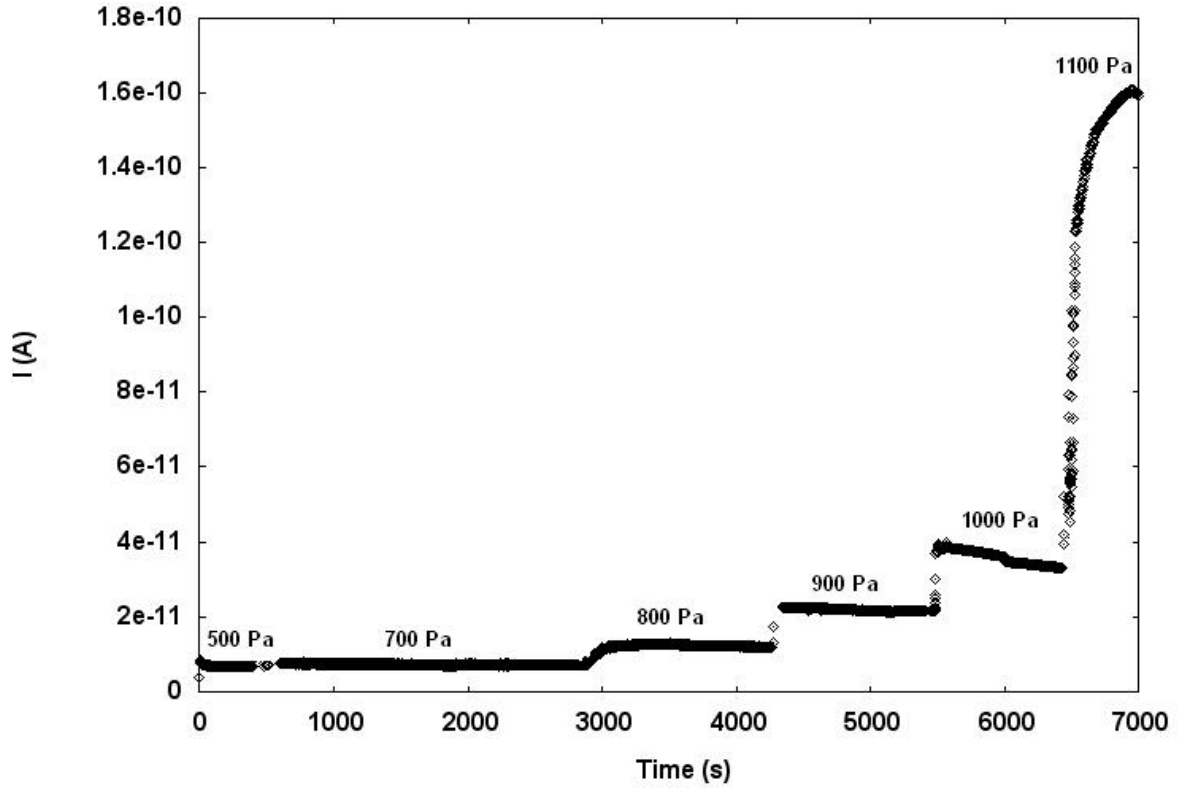
Figure 4.2. The response of sample 4 to acetone vapor under changing pressures

absorbed gas molecules is given off the polymer film totally, thus the I-V characteristics of the samples before and after drying process do not show any difference. The chamber pressure is again decreased to 10 Pa and the methanol vapor is started to be introduced into the chamber while the pressure of the vapor is increased under control step by step. In Figure 4.6 and Figure 4.7, the change of current flowing through the sample with respect to time upon exposure to methanol vapor is seen. As seen in these figures, the pressure inside the chamber is 800 Pa up to 1800 s; 900 Pa, between 1800 s and 3220 s; 1000 Pa, between 3220 s and 4260 s; 1100 Pa between 4260 s and 7800 s; 1200 Pa, between 7800 s and 9950 s; 1300 Pa afterwards. The current values, thus the conductivity of the polymer increases with the increase of the pressure inside the chamber. The current flowing through sample 4 at 1000 Pa acetone vapor is 3×10^{-11} A while for the same sample at the same pressure of methanol vapor, the current value is 3×10^{-12} A. This is a typical example of the difference between responses of sample to two gases, there is a factor of 10 between the current values upon exposure to acetone and methanol vapor for the same pressure values. The current through sample 4 increases by 3 orders of magnitude when the pressure increases from 800 Pa to 1300
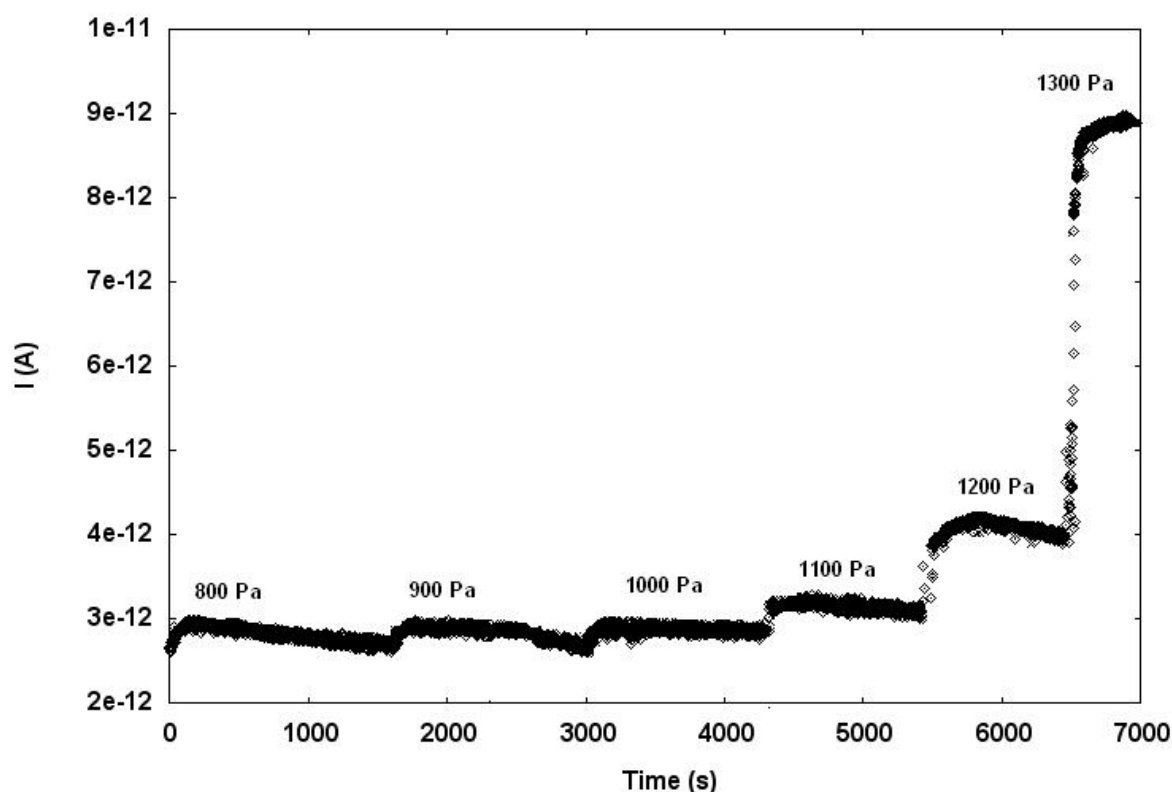
Figure 4.3. The response of sample 5 to acetone vapor under changing pressures

Pa. The methanol vapor shows the same effect on the sample as the acetone vapor and as illustrated in Figure 4.8, again an exponential relation is observed between the current and the pressure. As seen in the acetone exposure, the current needs some time to reach its equilibrium value. It is seen in Figure 4.9 that there is a sharp increase in conductivity immediately after exposure and gets a stable value extending over a period of 7 minutes.

From these figures, it can be concluded that the responses of the polymer film to both acetone and methanol vapor are showing the same characteristics except that the increase in the current values upon the absorption of acetone vapor is nearly ten times greater than the increase upon the absorption of methanol vapor. The responses of the samples to both gases show that the current increases slightly at the smaller values of the pressure, but when the pressure reaches 1100 Pa, the current increases abruptly and for the higher values of pressure marked increases are observed. During the measurements, the temperature is always above the glass transition temperature, therefore the polymer is assumed to be rubbery and it is known that the solvent
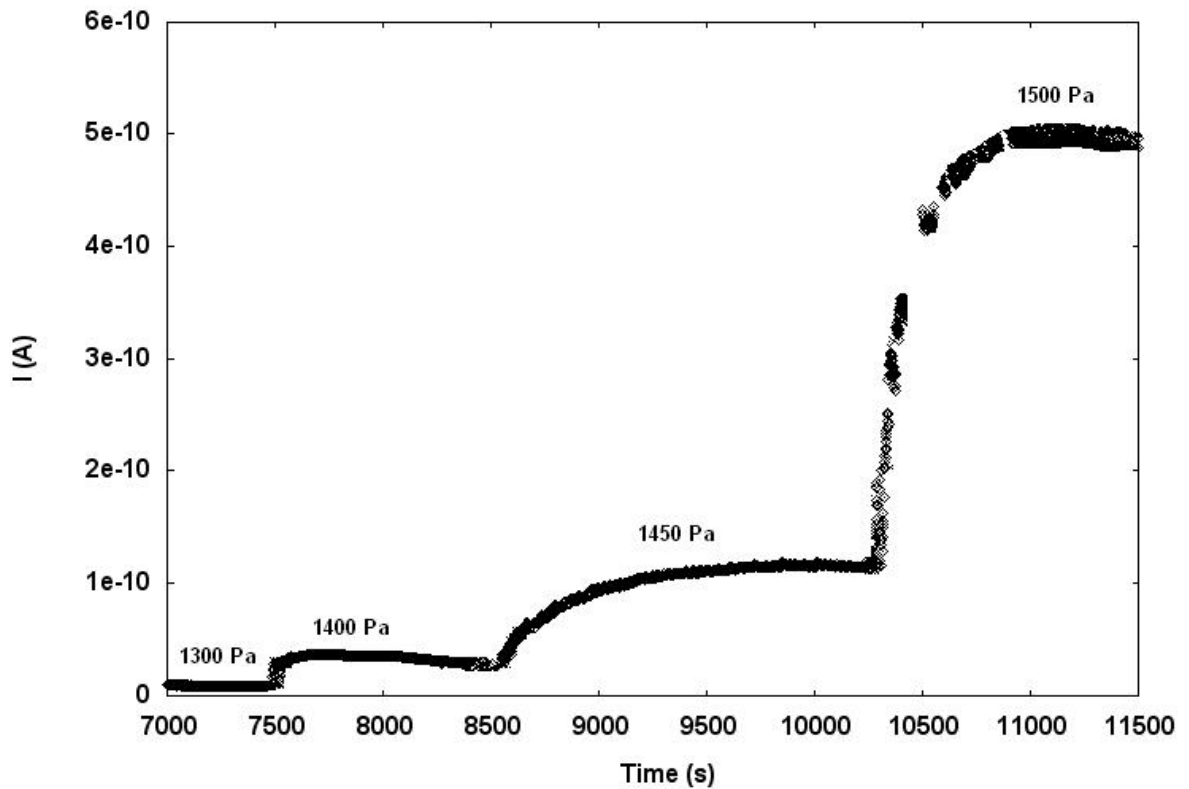
Figure 4.4. The response of sample 5 to acetone vapor under changing pressures

penetration decreases the crystallinity because of the swelling and commensurate with the formation of gel. Hence, as in the first experimental part, the vapor of acetone and methanol might destroy the semicrystalline form of PEG and result in a gel form when the pressure, in another words, the concentration of the acetone and methanol molecules inside the polymer network reaches a certain value. In this case, this happens when the pressure inside the chamber becomes 1100 Pa. In view of acetone's and methanol's high polarity and ability to form hydrogen bonds, this would not be so surprising [32].

Charlesworth et al. [40] proposed a model which seeks to explain the influence of dielectric constant of the vapor on the conductivity of the polymer. In the polymer, there will be defects due to the reactions between the polymer and impurities that lead to a breaking up of the π-bond network within the polymer chains and regions where one polymer chain ends and another begins. To ensure continuous conduction through the bulk of the polymer, an electron encountering one of these defects must hop around it, either to another part of the same chain or to a new chain. Secondly, regardless
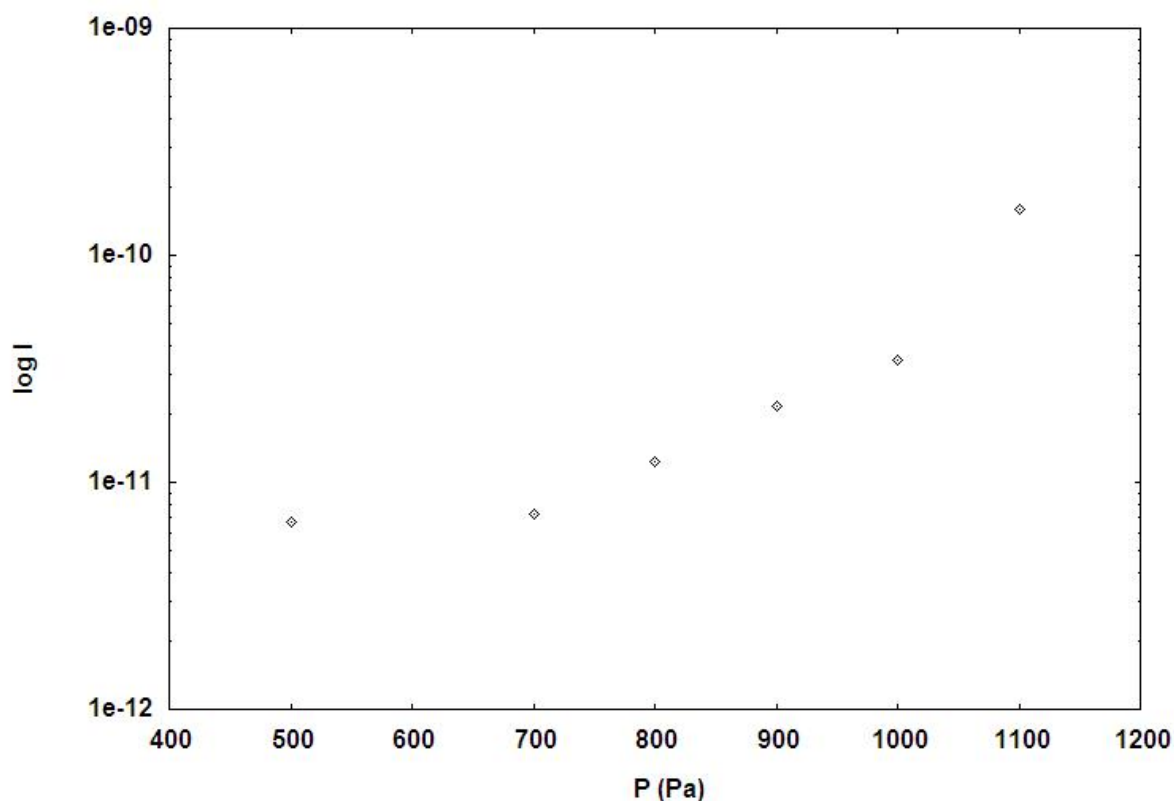
Figure 4.5. Dependence of current on the pressure of acetone vapor for sample 4

of any such physical defects in the system, if the variable-range-hopping mechanism for conduction may be considered as an appropriate description of the behavior of the polymer, then the conformational variations of the polymer segments introduce effective flaws into the conduction pathway. In either case because electron hopping is equivalent to an electron transfer reaction, the rate of hopping, which is inversely proportional to the resistance, can be analyzed using the modern electrochemical theory for electron transfer rate constants. This theory predicts that there is a strong correlation between the rate constant, which is inversely proportional to the specific resistance change (measured by the fractional change in resistance divided by the fractional change in mass), and the dielectric constant. There is a log-linear relationship between the rate constant and reciprocal of dielectric constant. It is known that the dielectric constant of acetone and methanol is 20.7 and 32.6 respectively. Depending on that, the rate constant for acetone is expected to be higher than the rate constant of methanol. As the rate constant is linearly proportional to conductivity, the conductivity for the case of acetone has to be greater than for methanol. This is what is observed in the above measurements. The current values are 10 times greater for the same polymer film when
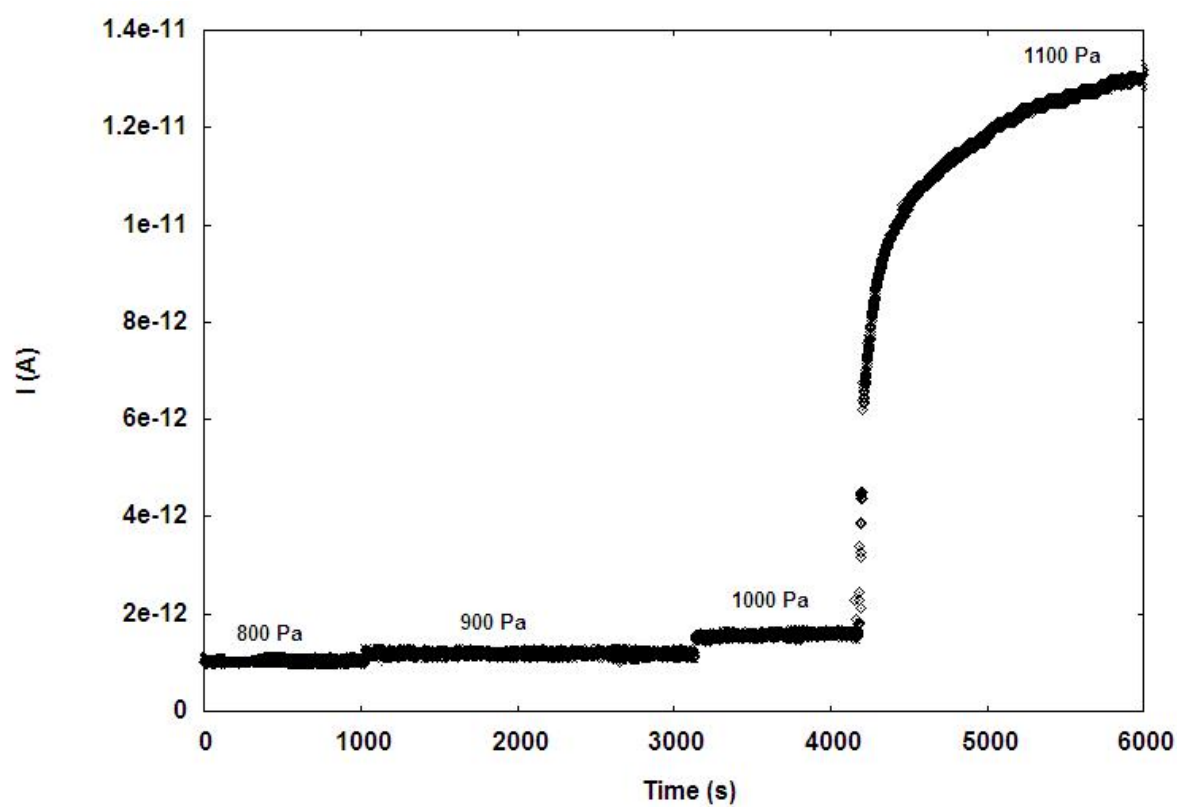
Figure 4.6. The response of sample 4 to methanol vapor under changing pressures
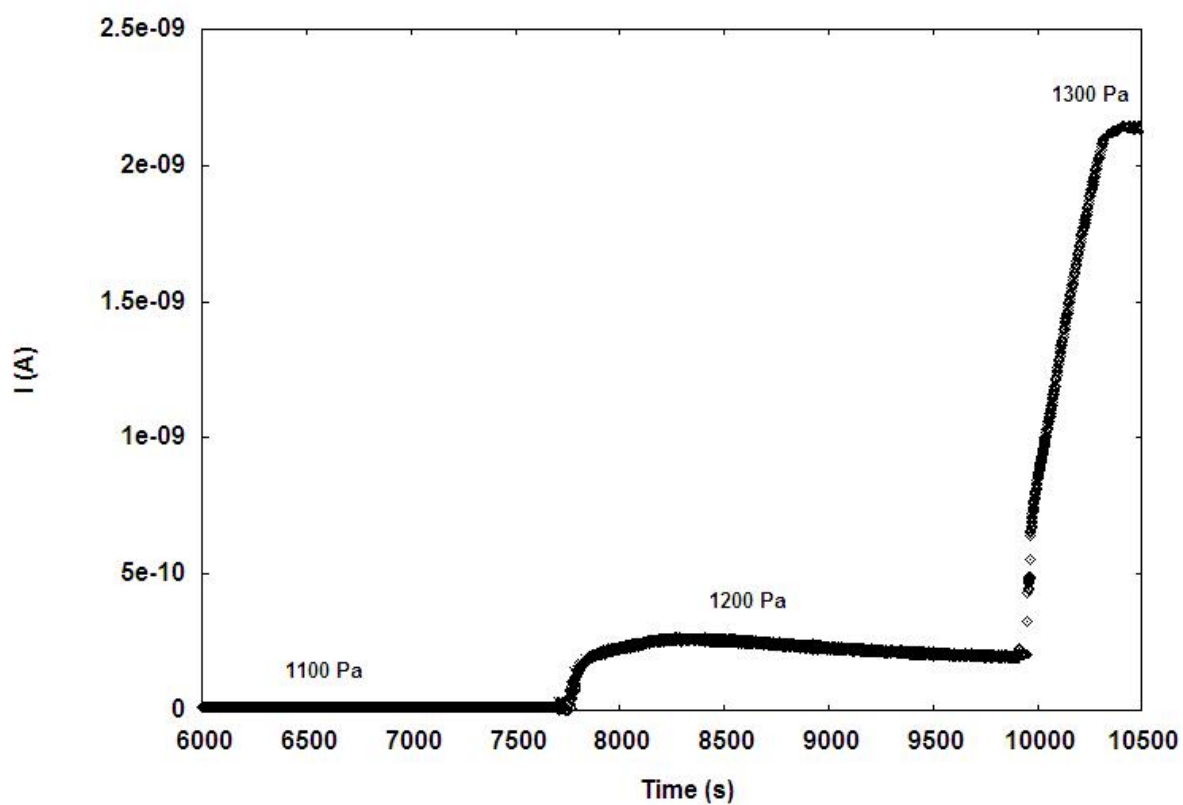
it is exposed to acetone vapor.

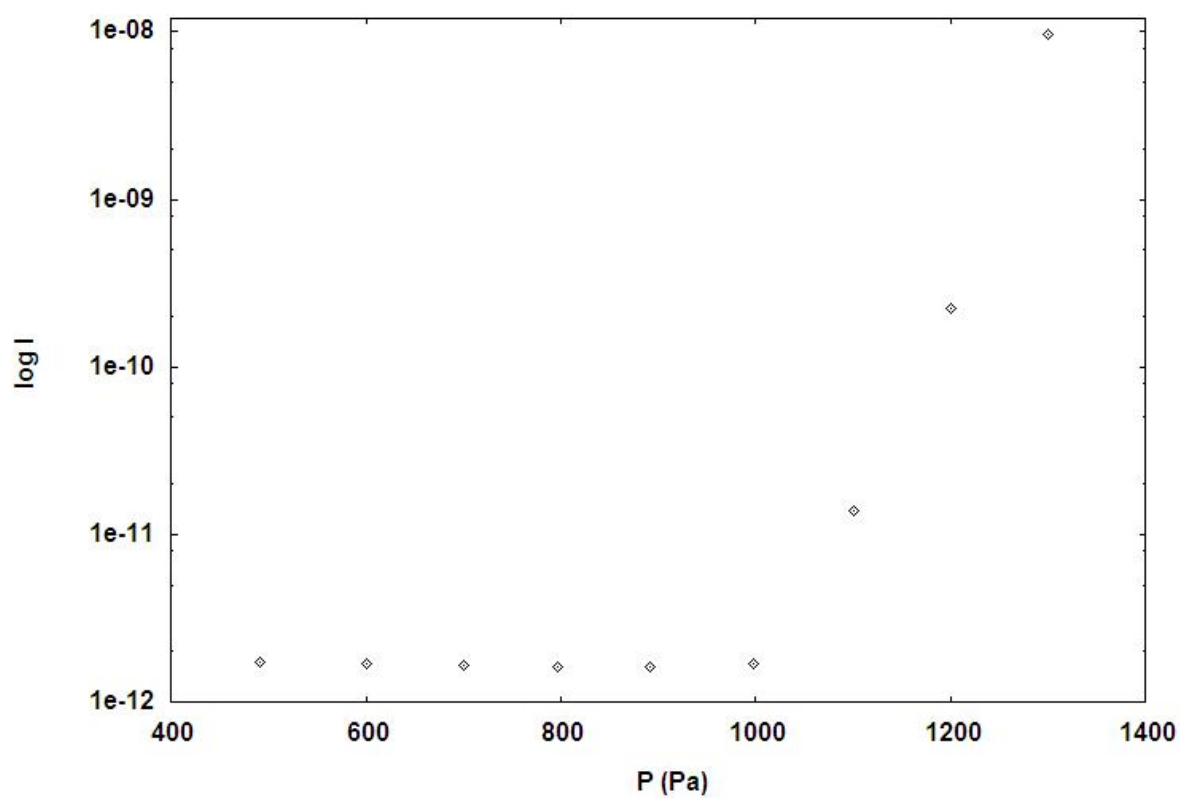Figure 4.7. The response of sample 4 to methanol vapor under changing pressures

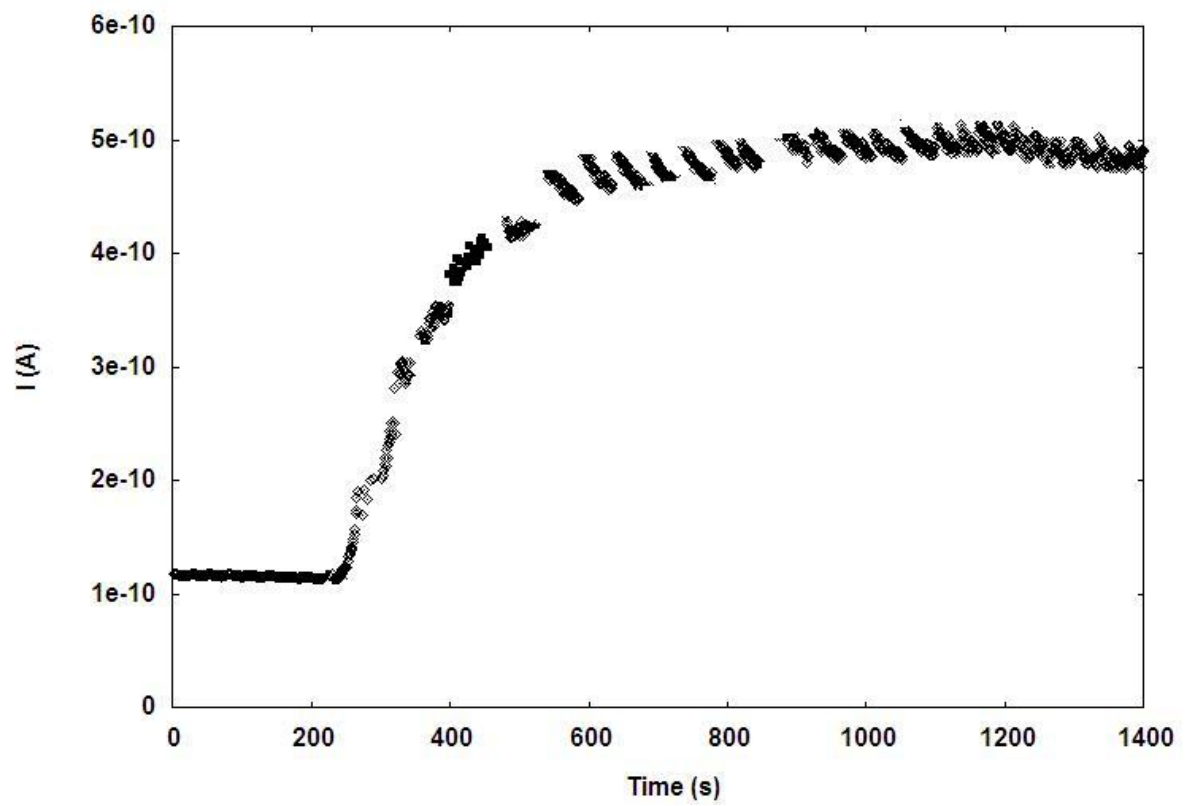Figure 4.8. Dependence of current on the pressure of methanol vapor

Figure 4.9. Variation in current with time for sample 5

5. CONCLUSIONS

In the first part dc electrical measurements of pure, hydrogenated and hydrophobically modified PEG thin films are performed under changing rh between 12 % and 90 % in this work. It is observed that PEG is sensitive to the changes in rh. The current passing through it under a constant electric field increases in a way resembling that of type 3 isotherms. At the first stage the water vapor contributes to the increase of electronic conduction while water clusters begin to form and the film swells. Then at around 70 % rh, the polymer melts from the semicrystalline form, and from that point on, the current shows a steeper increase. The water condenses in the polymer and conduction takes an ionic nature. Like pure PEG samples hydrogenated and hydrophobically modified PEG samples also show sensitivity to rh. At low rh values, the current increases gradually with respect to the change in rh for both samples. As rh increases, the current starts to increase abruptly. There is an irregular behavior of the current with respect to the changes in rh after around 75 % for the pure PEG samples. This is because of the instability of the polymer at rh levels above 75 %. Although the current values decrease somewhat, the hydrogenated PEG samples show a more stable behavior than the pure PEG samples as the hydrogen molecules form bonds with the oxygen atoms of the PEG chain. For the hydrophobically modified PEG samples, the current values decrease as the PEG concentration decreases, but the samples begin to show a smoother and more stable characteristic as the hydrophobic additive inside them increases. Like the hydrogen molecules in hydrogenated PEG samples, the hydrophobic perfluoroalkylethylalcohol molecules occupy the sites on ether oxygen atoms of the PEG chain, and the current shows a sudden upward curvature at a higher rh value. Thus, the abrupt increase of the current shifts to higher rh values as the concentration of perfluoroalkylethylalcohol molecules inside the polymer increases.

Upon decreasing rh, it is determined that the current takes higher values than it has during the swelling; as the sample cannot reach its semicrystalline form in this time interval and has a more amorphous structure. Therefore, the successive measurements show little deviations, but this problem could be resolved by drying the film after each

measurement. By this way the polymer film could get its pre-absorption form and give off all the water molecules absorbed. It is also observed that the thickness of the polymer film does not change the general trend of the conductivity.

In spite of the little decrease in the sensitivity of the current with respect to rh, the hydrogenated and the hydrophobically modified PEG samples could be used at higher rh values than the pure PEG samples. By making an optimization based on these two properties, PEG, a low-cost, easily produced, nontoxic and biodegradable polymer could be a more appropriate material for various applications in humidity sensors and pharmaceutical formulations.

In the second part, the response of pure PEG film to the vapor of acetone and methanol is studied. These measurements were done under vacuum. It is observed that the conductivity of PEG thin films increases with the increase in the pressure of vapor. At 1100 Pa, there is a marked difference in the conductivity whereas up to that value of pressure there is only a slight change. Although the response of PEG films to both of the gases shows the same characteristics, the results indicate that the differences in polymer-solvent interactions result in a much larger adsorption of acetone than methanol. The current increases 10 times more for the measurements done with acetone than for the measurements done with methanol. The resistance change has a positive correlation with the dielectric constant of the gases. This can be explained by treating the variable range hopping process responsible for the conductivity as an electron-transfer mechanism, for which the electrochemical theory predicts a relationship between the rate constant and the dielectric constant of the medium.

PEG might probably show sensitivity to various other gases which have different chemical structures and could be developed to be used as a gas sensor.

From all these experimentally observed properties, it can be concluded that PEG has a potential for use in humidity and gas sensing devices. It is a polymer of choice for the engineering of some tissues, the formation of membranes between them, and polymeric controlled drug delivery systems besides its usage in many industrial fields.

Determination of the sorption and diffusion properties of water and many different organic solvents, and the swelling dynamics in PEG systems are important as it is a smart material. These properties still need to be studied on and developed to have a tailored and optimal structure for every different solvent to meet the needs in the above fields.

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