SYNTHESIS OF ACROLEIN BASED COPOLYMERS AND THEIR MODIFICATIONS

by

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ABSTRACT

SYNTHESIS OF ACROLEIN BASED COPOLYMERS AND THEIR MODIFICATIONS

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Copolymerization of acrolein with N-vinylpyrrolidone (NVP) and its modification were aimed in this study. Polyacrolein is a polymer that its reactive aldehyde groups can easily be converted into oxime, amine, enamine, imine and bisulfite derivatives and has a potential on biological applications. There is very little information on poly (acrolein-*co*-vinylpyrolidone) in the literature.

At the first stage, the free radical copolymerization of acrolein with N-vinylpyrrolidone (NVP) was carried out by using potassium persulfate ($K_2S_2O_8$), as an initiator in water at 65°C. The conversion of monomer mixtures in different mole ratios (58/42, 62/38 and 74/26) to polymers was studied in various time periods.

The conversions of monomer mixtures to polymer were obtained in 192 h as 23%, 19% and 31% respectively.

At the second stage, the monomer reactivity ratios were determined by using Fineman Ross (FR), Kelen Tüdos (KT), Extended Kelen Tüdos (E-KT), Mayo Lewis (M-L), and PREVM methods. The copolymer compositions were determined using elemental analysis and FT-IR analysis data method. By using elemental analysis data $r_{1=}$ 0.44 and r_2= -0.082 (FR), $r_{1=}$ 0.47 and r_2= -0.065 (KT), $r_{1=}$ 0.46 and r_2= -0.064 (E-KT), $r_{1=}$ 0.49 and r_2= -0.065 (M-L), $r_{1=}$ 0.49 and r_2= -0.049 (PREVM) were obtained. By using FT-IR analysis data $r_{1=}$ 0.36 and r_2= -0.077 (FR), $r_{1=}$ 0.41 and r_2= -0.031 (KT), $r_{1=}$ 0.41 and r_2= -0.033 (E-KT), $r_{1=}$ 0.36 and r_2= -0.0010 (M-L), $r_{1=}$ 0.46 and r_2= 0.004 (PREVM) were obtained.

At the third stage, the aldehyde groups of acrolein in acrolein/NVP copolymers having different compositions (A74/NVP26 A62/NVP38 and A58/NVP42) were modified with hydroxylamine and phenylhydrazine reactions. The degree of modifications of modified copolymers synthesized at different times (24, 72, 120 and 168 h) was calculated by using elemental analysis results. The maximum degree of modification of oxime derivative copolymers was obtained in 168 h as 35%, 50% and 73% in increasing content of acrolein in copolymers. The maximum degree of modification of phenylhydrazone derivative copolymers was obtained in 168 h as 27%, 30% and 39% in increasing content of acrolein in copolymers.

All copolymers and their derivatives were characterized by FT-IR and NMR (^{1}H-NMR, ^{13}C-NMR) spectroscopy. Thermal properties and thermal stabilities of copolymers and their derivative were investigated by using DSC and TGA techniques.

Solubility of copolymers and their derivatives were tested in various polar and non-polar solvents. Copolymers and their derivatives were found to be insoluble in common organic solvents. Results indicated that the poly(acrolein-co-vinylpyrrolidone) copolymers could only dissolve efficiently in trichloroacetic acid at 180^{o}C, and partly soluble in aprotic polar solvents, such as in DMF, DMSO and pyridine around 180^{o}C. Furthermore their modification did not considerably affect the solubility behavior of copolymers.

Keywords: Copolymerization, acrolein, N- vinylpyrrolidone (NVP), reactivity ratio, oxime, phenylhydrazone.

ÖZET

AKROLEİN BAZLI KOPOLİMERLERİN SENTEZİ VE MODİFİKASYONLARI

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Bu çalışmada akrolein ile N-vinilpirolidonun (NVP) kopolimeriazyonu ve elde edilen polimerlerin modifikasyonu hedeflendi. Poliakrolein reaktif aldehit grubundan dolayı kolayca oksim, amin, enamin, imin ve bisülfit türevlerine dönüştürülebilen ve biyoteknolojik uygulama potansiyeli olan bir polimerdir. Literatürde poli (akrolein-*ko*-vinilpirolidon) ile ilgili çok az bilgi vardır.

İlk aşamada, N-Vinilpirolidon (NVP) ile akroleinin serbest radikal kopolimerizasyonu sulu ortamda potasyum persülfat ($K_2S_2O_8$) başlatıcısı ile 65^oC de gerçekleştirildi. Farklı mol oranlarındaki (58/42, 62/38 ve74/26) monomer karışımlarının polimerlere dönüşümleri 65^{o}C’de farklı zaman periyotlarında çalışıldı. Monomer karışımının polimere dönüşümü 192 saat de sırasıyla 23%, 19%

ve 31% olarak belirlendi.

İkinci aşamada, monomer reaktiflik oranları, elementel analiz ve FT-IR analiz verileri kullanılarak Fineman Ross (FR), Kelen Tüdos (KT), Extended Kelen Tüdos (E-KT), Mayo Lewis (M-L), ve PREVM metotları ile belirlendi. Kopolimer bileşimi elementel analiz verileri kullanılarak $r_{1=}$ 0.44 ve r_2= -0.082 (FR), $r_{1=}$ 0.47 ve r_2= -0.065 (KT), $r_{1=}$ 0.46 ve r_2= -0.064 (E-KT), $r_{1=}$ 0.49 ve r_2= -0.065 (M-L), $r_{1=}$ 0.49 ve r_2= -0.049 (PREVM) belirlendi. FT-IR analiz verileri kullanılarak $r_{1=}$ 0.36 ve r_2= -0.077 (FR), $r_{1=}$ 0.41 ve r_2= -0.031 (KT), $r_{1=}$ 0.41 ve r_2= -0.033 (E-KT), $r_{1=}$ 0.36 ve r_2= -0.0010 (M-L), $r_{1=}$ 0.46 ve r_2= 0.004 (PREVM) belirlendi.

Üçüncü aşamada, farklı kompozisyonlarda (A74/NVP26 A62/NVP38 ve A58/NVP42) akrolein/NVP kopolimerlerindeki akroleinin aldehit grubu hidroksilamin ve fenilhidrazin ile modifiye edildi. Farklı zamanlarda (24, 72, 120 ve 168 s) sentezlenen modifiye kopolimerlerin modifikasyon derecesi elemental analiz sonuçları kullanılarak hesaplandı. Kopolimerlerin oksim türevleri için maksimum modifikasyon derecesi 168 saat de sırasıyla 35%, 50% 73% olarak belirlendi ve kopolimerlerin fenilhidrazon türevleri için 168 saat de sırasıyla 27% 30% ve 39% olarak belirlendi.

Bütün kopolimerler ve türevleri FT-IR ve NMR (^{1}H-NMR, ^{13}C-NMR) spektroskopisi ile karakterize edildi. Kopolimerlerin ve türevlerinin termal özelikleri ve termal kararlılığı DSC ve TGA teknikleri kullanılarak incelendi.

Kopolimerler ve türevlerinin çözünürlükleri çeşitli polar ve apolar çözücülerde test edildi. Kopolimerlerin ve türevlerinin genelde organik çözücülerde çözünmediği bulundu. Sonuçlar, poli (akrolein-ko-vinilpirolidon) un tamamıyla yalnızca 180^{o}C trikloroasetik asit de çözündüğü, DMF, DMSO ve piridin gibi aprotik polar çözücülerde kısmen çözünür olduğunu, bununla beraber kopolimerlerin modifikasyonlarının çözünürlük davranışına etki etmediğini gösterdi.

Anahtar Kelimeler: Kopolimerizasyon, akrolein, N-vinilpirolidon (NVP), reaktiflik oranı, oksim, fenilhidrazon.

To My Parents

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ABBREVITIONS

A	Acrolein
NVP	N-Vinylpyrrolidone
FTIR	Fourier Transform Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance
r_1	Reactivity ratio of acrolein monomer in copolymer
r_2	Reactivity ratio of NVP monomer in copolymer
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis
H	Phenyl Hydrazone
O	Oxime
FR	Fineman Ross
KT	Kelen Tüdos
E-KT	Extended Kelen Tüdos
M-L	Mayo-Lewis
DMSO	Dimethylsulfoxide
DMF	Dimethylformamide
FA	Formic acid
TCA	Trichloroacetic acid

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1. INTRODUCTION

Functional polymers have benefited great importance in many fields of research as well as industrial applications. Acrolein, methacrolein and crotonaldehyde are the vinylic monomers containing aldehyde groups. Those which acroleins (propenal, acrylaldehyde) are the simplest vinylic aldehyde can be polymerized to prepare some functional polymers or copolymers. Both homo and some copolymerization of acrolein have been investigated since the ease of modifying the aldehyde pendant groups offers considerable scope to make polymers with new properties. Unfortunately, its homopolymer and copolymers except copolymers with styrene and divinylbenzene are either slightly soluble or insoluble in common solvents at normal conditions.

Polyacrolein presents an additional disadvantage when one would like to modify the aldehyde groups. It is difficult to modify successfully in high yield, because it cyclizes intra- and intermolecularly to acetal and hemiacatels leaving only a few suitable isolated aldehyde groups. The desired distribution of free aldehyde groups along the polymer chain may be achieved by the copolymerization of acrolein with vinyl comonomers [1]. By this way, the copolymerization enhances the relative concentration of free aldehyde groups in the copolymer chain to levels desirable for modification reactions [2]. Acrolein have been copolymerized radically with acrylamide, ethyl acrylate, acrylic acid, acrylonitrile, 2-vinyl pyridine, vinyl acetate vinyl chloride, methyl methacrylate, butyl acrylate methacrylonitrile, styrene and many other vinylic monomers as seen in the literature [3].

The reactive aldehyde pendant groups of polyacrolein and copolyacrolein can be converted into the amine derivatives of it, such as oxime, amine, enamine, imine, hydrazone, semicarbazide and some other adducts. These can be employed in many areas of applications, such as the selective chelating of heavy metal ions, enzyme immobilization, and binding of pharmaceuticals, antibodies and proteins.

N-Vinylpyrrolidone copolymers and homopolymer have been studied extensively and they have found many fields of applications in recent years due to their unusual properties, especially in the pharmaceutical, cosmetics and food industry as well as for numerous technical applications [4]. Many of them are soluble in common solvents and processable easily.

A study of NVP-Acrolein copolymers and their modified derivatives are of great interest since there is very little information on these polymers in the literature.

The object of this work was to synthesize the copolymers of acrolein with N-vinyl pyrrolidone and investigate some properties of them and to modify these copolymers with phenylhydrazine and hydroxylamine, and examine the properties of modified copolymers.

2. THEORY

2.1. Some definitions

Polymer

The word polymer is derived from classical Greek poly meaning “many” and meres “parts. Thus a polymer is a large molecule (macromolecule) built up by the repetition of small chemical units**.**

Monomer

A monomer which is defined as any molecule that can be converted to a polymer by combining with other molecules of the same or different type.

Oligomer

An oligomer is a low-molecular-weight polymer. It contains at least 10 to100 repeating units.

Repeating unit

The repeating unit of a linear polymer is a portion of the macromolecule such that the complete polymer (except for the ends) might be produced by linking a sufficiently large number of these units through bonds between specified atoms [5].

Homopolymer

Polymers composed of only one typical repeating unit in the polymer molecules [6].

Copolymer

A copolymer consists of two or more constitutional repeating units [7]. Several classes of copolymer are possible block copolymers, alternating copolymers, graft copolymers, random copolymers.

2.2. Free radical polymerization and copolymerization

2.2.1. Free radical polymerization

Free radical polymerization has three principal steps:

- Initiation of the active monomer
- Propagation or growth of the active (free radical) chain by sequential addition of monomers.
- Termination of the active chain to give a final product

Initiation

Initiation in a free-radical polymerization consists of two steps

Step 1. Dissociation of the initiator to form two radical species,

Step 2. Association followed by addition of a single monomer molecule to the initiating radical.

The dissociation of the initiator (I-I) to form two free radical initiator species ($I^{\cdot}$) can be represented as

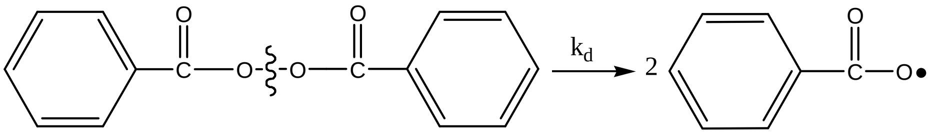
$$I-I \xrightarrow{k_d} 2\ I\bullet \qquad \textbf{(2.1)}$$

Here the initiator I decomposes to yield two radicals, where k_d is the dissociation rate-constant. The dissociation rate-constant follows an Arrhenius dependence on temperature given as

$$k_d = A\exp(-E_a/RT) \qquad \textbf{(2.2)}$$

Where E_a is the activation energy for dissociation. In addition to a strong dependence on temperature, dissociation rate-constants for different initiators vary with the nature of the solvent used in solution polymerization.

Initiators for free-radical polymerizations include any organic compound with a labile bond, such as an azo (-N=N-) disulfide (-S-S-), or peroxide (-O-O-) compound. The labile bond of the initiator can be broken by heat or irradiation, such as ultraviolet or gamma irradiation. An important example of a free radical initiator is benzoyl peroxide whose dissociation is

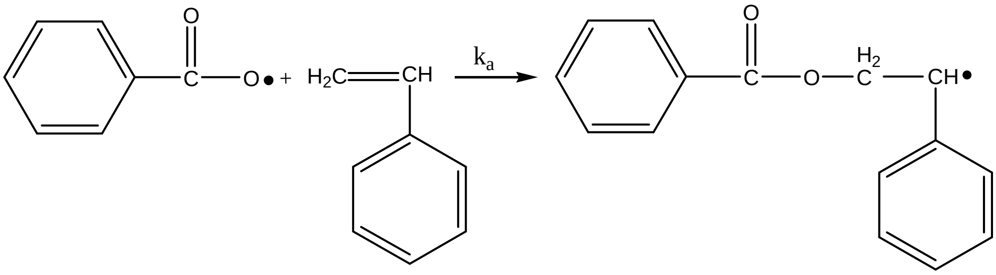


(2.3)

In the second step of initiation (association), a monomer molecule (M) is attached to the initiator radical [8]. This addition step may represented as

$$I\bullet + M \xrightarrow{k_a} IM\bullet \qquad \textbf{(2.4)}$$

where k_a is the rate constant for monomer addition. In the specific case of the polymerization of styrene initiated by benzoyl peroxide, the addition occurs as



(2.5)

Propagation

By definition, a propagation step in a chain reaction is that the number of repeating unit in polymer chain increases and the product in high molecular weight forms.

The sites of the reactive center changes but the number of radicalic active sites remain constant. There are two major propagation reactions under the conditions of most free-radical polymerizations. These are addition and atom transfer reactions.

i) Addition Reactions

Successive monomer additions after the initiation step of reaction can be represented as,

$$M_1^{\bullet} + M \longrightarrow M_2^{\bullet} \tag{2.6a}$$

$$M_2^{\bullet} + M \longrightarrow M_3^{\bullet} \tag{2.6b}$$

$$M_i^{\bullet} + M \longrightarrow M_{i+1}^{\bullet} \tag{2.6c}$$

where M_i represents the radical R-$(M)_{i-1}M^{\bullet}$. Each reaction in the sequence involves the addition of a monomer to a monomer-ended radical, and each is assigned the same rate constant k_p on the reasonable assumption that the rate of the addition reaction does not depend on the size of the participating macroradical. Values of the propagation rate constant k_p for most monomers are of the order of 10^2- 10^3 L/s.mol under practical polymerization conditions.The rate of propagation R_p is given by

$$R_p=k_p[M\cdot][M] \tag{2.7}$$

where $[M^{\bullet}]$ stands for the sum of the concentrations of all monomer-ended radicals in the system. This expression for R_p can be written as shown since the radical concentrations can be lumped together if k_p does not depend on the size of M_i.

ii) atom transfer reactions

Radicals can undergo other reactions as well as monomer addition. Atom abstraction reactions usually involve transfer of hydrogen or halogen atom. An example from micromolecular chemistry involves the chlorination of hydrocarbons at about 200°C or during irradiation with light of wavelength less than 4875×10^{-10} m.

$$Cl_2 \longrightarrow 2Cl^\bullet \qquad \textbf{(2.8)}$$

$$Cl^\bullet + CH_4 \longrightarrow HCl + {}^\bullet CH_3 \qquad \textbf{(2.9)}$$

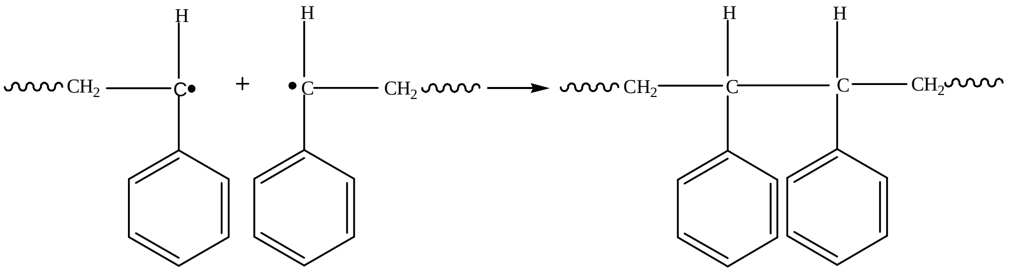
$$CH_3^\bullet + Cl_2 \longrightarrow Cl^\bullet + CH_3Cl \qquad \textbf{(2.10)}$$

iii) Other propagation reactions

Radicals can undergo other reactions such as rearrangements and fragmentations.

Termination

Propagation will continue until some termination process occurs. The sequence of monomer additions is terminated by the mutual annihilation of two radicals. Such termination reactions can occur if the radicals combine to form a bond as in



(2.11)

This process is called termination by combination and would be written in general terms as in with k_{tc} as the corresponding rate constant.

$$M_n\bullet + M_m\bullet \xrightarrow{k_{tc}} M_{n+m} \qquad \textbf{(2.12)}$$

Alternatively the two radicals can form two new molecules by a disproportination reaction in which a hydrogen atom is transferred [9]. Generally for this case,

$$M_n\bullet + M_m\bullet \xrightarrow{k_{td}} M_m + M_n \qquad \textbf{(2.13)}$$

where k_{td} is the rate disproportination rate constant.

Termination may also occur by a mixture of disproportination and combination.

The rates of these reactions are additive for a given polymerization, because both terminations are bimolecular and have second-order rate constants. Thus we can write

$$M_n\bullet + M_m\bullet \xrightarrow{k_t} \text{dead polymer} \qquad \textbf{(2.14)}$$

With the overall rate constant k_t given by

$$k_t = k_{td} + k_{tc} \qquad \textbf{(2.15)}$$

The termination rates R_t corresponding to the different modes of termination are

$$R_{tc} = 2\,k_{tc}\,[M\bullet]^2 \qquad \textbf{(2.16)}$$

from Eq. (2.12)

$$R_{td} = 2\,k_{td}\,[M\bullet]^2 \qquad \textbf{(2.17)}$$

from Eq. (2.13)

$$R_t = 2\,k_t\,[M\bullet]^2 \qquad \textbf{(2.18)}$$

from Eq. (2.15)

2.2.2. Methods of free radical polymerization

There are various ways to carry out free radical polymerization**.**

2.2.2.1. Bulk polymerization

Bulk polymerization is a homogenous system. The simplest technique and the one that gives the highest-purity polymer is bulk polymerization. Only monomer, a monomer-soluble initiator, and a chain-transfer agent to control molecular weight are used. In the case of homogenous bulk polymerization, the product polymer and monomer are miscible. Since polymerization reactions are generally exothermic, the temperature of polymerization depends on the polymerization system. Mixing and heat transfer become difficult as the viscosity of the reaction mass increases [7, 8].

2.2.2.2. Solution polymerization

Solution polymerization is a homogenous system. Solution polymerization may involve a simple process in which a monomer, initiator, catalyst, a solvent are stirred together to form a solution that reacts without the need for heating or cooling, or any special handling. Solvent choice is important because it may be influenced by other factors such as flash point, cost and toxicity. Often, the polymerization can be conducted under conditions of solvent reflux to maximize heat removal. Reactors are usually stainless steel or glass lined. The obvious disadvantages of solution polymerization are the small yield per reactor volume and requirement for a separate solvent-recovery step.

2.2.2.3. Suspension polymerization

Suspension polymerization involves the dispersion of the monomer, mainly as a liquid in small droplets, into an agitated stabilizing medium usually consisting of water containing small amounts of suspension or dispersion agents. The catalyst or initiator is dissolved in the monomer if the monomer is a liquid or included in the reaction medium if a gaseous monomer is used. Near the end of the polymerization, the particles harden and then can be recovered by filtration, which is followed by a final washing step. Although solvent cost and recovery operations are minimal in comparison with solution polymerization, polymer purity is low due to the presence suspending and other stabilizing additives that are difficult to completely remove. In addition, reactor capital costs are typically higher than for solution polymerization.

2.2.2.4. Emulsion polymerization

Emulsion polymerization is widely used commercially for the production of a large variety of polymers. In general, an emulsion polymerization system would consist of the following ingredients: monomer, dispersing medium, emulsifying agent, water-soluble initiator, and a transfer agent. Water serves as the dispersing medium in which the various components are suspended by the emulsifying agent. The water also acts as a heat transfer medium. The final product in an inverse emulsion polymerization is colloidal dispersion of a water swollen polymer in the organic phase [8].

2.2.3. Simple copolymer equation

In the copolymerization by chain-growth reaction, we shall concentrate only on the propagation step in which a monomer adds to an active site at the end of a macromolecular species and the active site is transferred to the new terminal unit created by this addition.

$$M^{*} + M \rightarrow MM^{*} \tag{2.19}$$

Here M denotes a monomer and the asterisk means an active site which could be a radical, ion (with an appropriate counterion), or a carbon-metal bond. For simplicity, the simple copolymer equation will be developed for the case of free radical reactions. The four possible propagation reactions with monomers M_1 and M_2 are

$$M_1^{\bullet} + M_1 \xrightarrow{k_{11}} M_1^{\bullet} \qquad \text{rate= } k_{11}[M_1^{\bullet}][M_1] \tag{2.20}$$

$$M_1^{\bullet} + M_2 \xrightarrow{k_{12}} M_2^{\bullet} \qquad \text{rate= } k_{12}[M_1^{\bullet}][M_2] \tag{2.21}$$

$$M_2^{\bullet} + M_2 \xrightarrow{k_{22}} M_2^{\bullet} \qquad \text{rate= } k_{22}[M_2^{\bullet}][M_2] \tag{2.22}$$

$$M_2^{\bullet} + M_1 \xrightarrow{k_{21}} M_1^{\bullet} \qquad \text{rate= } k_{21}[M_2^{\bullet}][M_1] \tag{2.23}$$

In these expressions M_i stands for a radical of any size ending in a unit derived form monomer M_i and $[M_i]$ denotes the total concentration of all such radicals, regardless of molecular chain length or structure. Similarly k_{ij} is the propagation rate constant for addition of monomer M_j to radical M_i. (Then k_{ii} is the propagation rate constant k_p for homopolymerization of M_i under the given reaction conditions.)

If we now assume that the only significant changes in monomer concentrations result from propagation reactions (i.e., changes in $[M_i^{\bullet}]$ from initiation and transfer reactions are negligible), the rates of monomer disappearance according to the reaction schemes of (2.20)-(2.23) are

$$-d[M_1]/dt = k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1] \tag{2.24}$$

$$-d[M_2]/dt = k_{22}[M_2^\bullet][M_2] + k_{12}[M_1^\bullet][M_2] \tag{2.25}$$

Similarly the time dependence of the concentration of radical $M_1^\bullet$ is

$$-d[M_1^\bullet]/dt = -k_{12}[M_1^\bullet][M_2] + k_{21}[M_2^\bullet][M_1] \tag{2.26}$$

Under steady-state conditions $[M_1^\bullet]$ is sufficiently small that $d[M_1^\bullet]/dt$ is negligible compared to the rates of change of concentration of the reactants. Hence, setting $d[M_1^\bullet]/dt = 0$

$$k_{21}[M_2^\bullet][M_1] = k_{12}[M_1^\bullet][M_2] \tag{2.27}$$

and

$$[M_1^\bullet]/[M_2^\bullet] = k_{21}[M_1]/k_{12}[M_2] \tag{2.28}$$

The relative rates of incorporation of the two monomers into the copolymer at any instant follow by dividing Eq. (2.24) by (2.25):

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1]}{k_{22}[M_2^\bullet][M_2] + k_{12}[M_1^\bullet][M_2]} \tag{2.29}$$

Now divide the right-hand side of Eq. (2.29) by $[M_2^\bullet]$, insert expression (2.28) for $[M_1^\bullet]/[M_2^\bullet]$, and divide through by k_{21} to obtain

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1][(k_{11}/k_{12})[M_1] + [M_2]]}{[M_2][(k_{22}/k_{21})[M_2] + [M_1]]} \tag{2.30}$$

Define the reactivity ratios r_i as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, so that the preceding equation becomes

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2][(r_2[M_2]+[M_1])} \qquad \textbf{(2.31)}$$

as equivalent expression can of course be derived in terms of mole fractions rather than concentrations. If f_1 and f_2 are the respective mole fractions of monomers M_1 and M_2 in the reaction feed and F_1 and F_2 are the corresponding mole fractions in the copolymer formed from this mixture, then

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad \textbf{(2.32)}$$

and from the definition of mole fraction

$$F_2 = 1 - F_1 \qquad \textbf{(2.33)}$$

Equations (2.31) and (2.32) are alternative versions of the simple copolymer equation Measurements of corresponding feed and copolymer compositions should yield values of r_1 and r_2 which can be used to predict the relative concentrations of monomer in copolymers formed from any other mixtures of the particular monomers [5].

2. 3. Copolymer structure inferences from reactivity ratios

2.3.1. Random copolymer

A random copolymer is one in which the monomer residues are located randomly in the polymer molecule. If we represent the repeating units by A and B, then the random copolymer might have the structure shown below

-A-A-B-A-B-A-B-B-A-B-A-A-A-B-A-B-

A better term in general is statistical copolymer. These are primarily copolymers that are produced by simultaneous polymerization of a mixture of two or more comonomers.

According to reaction (2.20) M_1M_1 bonds are formed only by reaction. The probability that a radical ending in an M_1 unit adds an M_1 unit is equal to the rate of this reaction divided by the sum of the rates of all reactions available to this radical. This is the probability P_{11} that an M_1 unit follows an M_1 unit in the copolymer, and since the only other reaction assumed important for this radical is (2-21),

$$P_{11} = \frac{k_{11}[M_1^\bullet][M_1]}{k_{11}[M_1^\bullet][M_1] + k_{12}[M_1^\bullet][M_2]} = \frac{r_1[M_1]}{r_1[M_1] + [M_2]} \qquad \textbf{(2.34)}$$

Similarly, the probability P_{21} that an M_1 unit follows an M_2 unit in the polymer is

$$P_{21} = \frac{k_{21}[M_2^\bullet][M_1]}{k_{21}[M_2^\bullet][M_1] + k_{22}[M_2^\bullet][M_2]} = \frac{[M_1]}{r_2[M_2] + [M_1]} \qquad \textbf{(2.35)}$$

If, however, $r_1r_2=1$, then P_{11} and P_{21} defined above are equal. That is to say, the likelihood that an M_1 unit equals the likelihood that is follows an M_2 unit in the product. The absolute value of this probability depends on the relative concentrations of monomers in the feed. But the equivalence of probabilities is independent of the feed and copolymer composition. Random monomer distributions are obtained more generally if k_{11}/k_{12} is approximately equal to k_{21}/k_{22}. That is to say, $r_1 \cong 1/r_2$.

If $r_1r_2=1$, copolymer equation (2.31) reduces to

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]}{[M_2]} = \frac{[M_1]}{r_2[M_2]} \qquad \textbf{(2.36)}$$

2.3.2. Alternating copolymer

In an alternating copolymer each monomer of one type is joined to monomers of a second type.

-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-

If each radical prefers to add the monomer of the opposite type both reactivity ratios will tend to zero, and the copolymer equation becomes

$$d[M_1]/d[M_2]=1 \qquad \textbf{(2.37)}$$

or

$$F_1 = F_2 = 0.5 \qquad \textbf{(2.38)}$$

The tendency to alternation increases as the r_1r_2 product nears zero, as long as both r_1 and r_2 are less than unity. Such copolymerizations occur in free radical systems when two monomers have opposite polarities.

2.3.3. Block copolymer

Block copolymer have backbones consisting of fairly long sequences of different repeating units [5]. Possible structures of copolymers containing A and B repeating units are shown as;

-A-A-A-A-B-B-B-B-B-B-B-B-A-A-A-A-

If both reactivity ratios are greater than one, there will be tendency for formation of sequences of uniform composition in the copolymers. Such reactivity ratio combinations are not known in free-radical copolymerizations when both monomers are simultaneously in the reaction vessel, but they can be made in other systems.

Table 2.1. Copolymer structure and r_1r_2 product [5]

r_1	r_2	r_1r_2	Copolymer structure
$r_1 = 1/r_2$	$r_2 = 1/r_1$	1	Random (ideal)
<< 1	<<1	$\rightarrow 0$	Alternating
>>1	<1	<1	Tends to be homopolymer of M_1

The comonomer sequence is one of the main factors that influence copolymer behavior and properties. Copolymer composition depends on the monomer feed composition, and the relative monomer reactivity [10]. Therefore, it is very important to study the comonomer reactivity in copolymerization system.

Table 2.2. Reactivity ratios of acrolein (monomer 1) with some monomers for radical copolymerization

Monomer 2	r_1	r_2	Ref.
Acrylamide	1.95	0.80	[11]
	1.59	0.18	[12]
Acrylate,butyl	1.86	0.64	[13]
	2.29	1.12	[14]
Acrylate,ethyl	1.2	0.6	[13]
	1.98	1.09	[14]
Acrylate, methyl	-0.07	7.86	[11]
	1.41	0.83	[13]
	2.54	1.08	[14]
Acrylic acid	2.48	0.08	[15]
	0.5	1.15	[15]
Acrylonitrile	1.16	0.88	[11]
	1.07	0.71	[11]
	1.52	0.48	[12]
	1.28	0.60	[16]
Methacrylate,methyl	0.76	1.14	[13]
	0.59	1.33	[14]
Methacrylonitrile	0.68	1.17	[12]
	0.72	1.20	[17]
Pyridine,2-vinyl-	2.64	-0.12	[12]
Styrene	0.22	0.26	[13]
	0.02	0.22	[14]
	0.32	0.21	[18]
Styrenesulfonate,p,sodium	0.39	0.33	[15]
	0.26	0.047	[15]
	0.113	0.01	[15]
Vinyl acetate	3.04	-0.02	[11]
Vinyl chloride	5.22	0.03	[19]

Table 2.3. Reactivity ratios of NVP (monomer 1) with some monomers for radical copolymerization

Monomer2	r_1	r_2	Ref.
Caprolactam, N-vinyl-	2.80	1.70	[20]
Crotonate, hydrocortisone 21-	0.75	0.05	[21]
2-Oxazoline, 2-isopropenyl-	0.01	3.50	[22]
Acrylamido-2-methylpropane sulfonate sodium salt	0.13	0.66	[23]
Acrylate, cyclohexyl	0.122	1.297	[24]
Carbamate, N-vinyl-t-butyl-	0.40	2.40	[25]
Ethene, 2-phenyl-1, 1-dicyano- ıtaconates, bis(tri-n-butyltin)	0.21	0.065	[26]
Methacrylate, 2-acetylsalicylicoyloxy-3-hydroxypropyl	0.34	0.85	[45]
Methacrylate,furfuryl	0.0036	5.16	[27]
Methacrylate, glycidyl	0.003	4.29	[28]
Methacrylate, methyl	0.006	4.78	[29]
	0.014	5.93	[30]
	0.027	2.07	[30]
	0.066	4.04	[30]
Methacrylate, phenyl	-0.026	4.17	[31]
Pyridine, 2-methy-5-vinyl-	0.039	13	[32]
Pyridine, 2-vinyl-	0.014	12.4	[32]
Pyridine, 4-vinyl-	0.01	9.8	[32]
Quinine	2.20	0.37	[33]
Styrene sulfonate, sodium salt	0.084	7.19	[23]
Vinyl trimehylammonioethyl ether iodide	11.6	0	[34]

2.4. Determination of reactivity ratios

2.4.1. Linear least-square methods

The monomer reactivity ratios (r_1 and r_2) are deduced by using Fineman-Ross [35], Kelen-Tüdos [36], Extended Kelen-Tüdos [37], and Mayo-Lewis [38] methods. The simple copolymer equation can be solved in a linear graphical manner by substituting, $x = \frac{[M_1]}{[M_2]}$, $z = d\frac{[M_1]}{[M_2]}$ so that Equation (2.31)

$$z = x\frac{(r_1[M_1]+[M_2])}{(r_2[M_2]+[M_1])} \qquad \textbf{(2.39)}$$

$$\frac{z}{x} = \frac{(r_1[M_1])}{(r_2[M_2]+[M_1])} + \frac{[M_2]}{(r_2[M_2]+[M_1])} \qquad \textbf{(2.40)}$$

$$\frac{z}{x} = \frac{1}{\frac{(r_2[M_2]+[M_1])}{(r_1[M_1])}} + \frac{1}{\frac{(r_2[M_2]+[M_1])}{[M_2]}} \qquad \textbf{(2.41)}$$

$$\frac{z}{x} = \frac{1}{\frac{(r_2[M_2])}{(r_1[M_1])} + \frac{[M_1]}{(r_1[M_1])}} + \frac{1}{\frac{(r_2[M_2])}{[M_2]} + \frac{[M_1]}{[M_2]}} \qquad \textbf{(2.42)}$$

$$\frac{z}{x} = \frac{1}{\frac{(r_2)}{(r_1)x} + \frac{1}{(r_1)}} + \frac{1}{\frac{(r_2)}{1} + x} \qquad \textbf{(2.43)}$$

$$f = z = x\frac{(1+r_1x)}{(r_2+x)} = F\frac{(1+r_1F)}{(r_2+F)} \qquad \textbf{(2.44)}$$

Equation (2.36) can be linearized in the alternative forms

$$f\ r_2 + f\ F = F + r_1\ F^2 \qquad \textbf{(2.45)}$$

2.4.1.1. Fineman-Ross method

Fineman and Ross (FR) utilized a graphical method for evaluating the reactivity ratios r_1 and r_2 of a given pair of monomers. A plot of G versus H is a straight line whose slope gives r_1 and the intercept gives $-r_2$. Here

$$F(f-1)/f = r_1(F^2/f) - r_2 \tag{2.46}$$

$$G = r_1 H - r_2 \tag{2.47}$$

where $G = F(f-1)/f$ and $H = (F^2/f)$.

$$f = m_1/m_2 \tag{2.48}$$

$$F = \frac{[M_1]}{[M_2]} \tag{2.49}$$

m_1= Mole fraction of monomer (1) in copolymer

m_2= Mole fraction of monomer (2) in copolymer

$[M_1]$= Mole fraction of monomer (1) in feed

$[M_2]$= Mole fraction of monomer (2) in feed

2.4.1.2. Kelen–Tüdos method

Using the equations of Fineman and Ross, the experimental points are often not equally distributed on the resulting line, but rather are concentrated at the initial part, which can result in rather large uncertainties in the estimate for the reactivity ratios.

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{2.50}$$

where η and ξ are mathematical functions of the comonomer molar fractions in the feed [36] and in the copolymer, respectively:

$$\eta = \left[F(f-1)/f\right]/(F^2/f+\alpha) \tag{2.51}$$

$$\alpha(arbitrary\ \ parameter) = \sqrt{\left(F^2\!\!\diagup\! f\right)_{\min}\left(F^2\!\!\diagup\! f\right)_{\max}} \tag{2.52}$$

$$\xi = \left(F^2/f\right)/\left(F^2/f+\alpha\right) \tag{2.53}$$

α is the geometrical mean value of the smallest (H_{max}) and the largest (H_{min}) H-values. r_1 and r_2 were obtained from the plots of η as function of ξ, r_1 being the intercept at $\xi = 1$ and $-r_2/\alpha$ the intercept at $\xi = 0$.

2.4.1.3. Extended Kelen –Tüdos

Extended Kelen Tüdos method is linear least-square method [37], can only be applied to experimental data at sufficiently low conversion, because the calculation is based on differential copolymerization equation. The only exception is the extended KT method, which involves a rather more complex calculation. Where the conversion is directly in determination of G, H and subsequently, η and ξ by definition of the parameter Z.

$$Z = \frac{\log(1-\varsigma_1)}{\log(1-\varsigma_2)} \tag{2.54}$$

where ς_1 and ς_2 are partial molar conversion given by

$$\varsigma_1 = w\frac{(\mu+F)}{(\mu+f)} \tag{2.55}$$

$$\varsigma_2 = \xi_1\frac{F}{f} \tag{2.56}$$

where μ shows the molecular weight of NVP to Acrolein, w is the total conversion (by weight).

$$G = \frac{(F-1)}{Z} \quad H = \frac{F}{Z^2} \tag{2.57}$$

The rest of the calculation is similar to the Kelen-Tüdos method.

2.4.1.4. Mayo-Lewis method

Mayo-Lewis (M-L) method [38] uses the calculated values of G and H in F-R method. The difference is that, for each G and H value, the corresponding line should be plotted using equation (2.50) by substituting an arbitrary value for r_1 in the range of 0.10-1.00 (for low conversion). Then the position of the crossing point of all lines will show a real amount of reactivity ratio.

$$r_1 = Hr_2 - G \tag{2.58}$$

2.4.2. Non-linear least-square method

The most generally useful methods and the data only statistically correct procedures for calculating reactivity ratios from binary copolymerization data involve nonlinear least squares analysis of the data or application of the error in variables (EVM) method. Effective use of either procedure requires more iterations than can be performed by manual calculations. An efficient computer program for nonlinear least squares estimates of reactivity ratios has been published by Tidwell and Mortimer [39].

Reactivity ratios have been determined for many important combinations of monomers and have been tabulated in polymer handbook. Some representative values are given in Table 2.2-2.3. Reactivity ratios for less common monomer-pairs can be calculated by means of the Q-e scheme proposed by Alfrey and Price [40]. The Q-e scheme is an attempt to express free radical copolymerization data on a quantative basis by separating reactivity ratio data for monomer pairs into parameters characteristic of each monomer pairs into parameters characteristic of each monomer.Under this scheme, radical-monomer reaction rate constant k_{12} is written as

$$k_{12} = P_i Q_j \exp(-e_1 e_2) \qquad \textbf{(2.59)}$$

where P_i is a proportionally constant, Q_j is a measure of the monomer reactivity

e is the polarity of the radical $M_1^\bullet$ and $M_2^\bullet$. Both P and Q are determined by the resonance characteristics of radical and monomer [41]. It is assumed that both the monomer and its radical have the same e value consequently,

$$k_{11} = P_1 Q_1 \exp(-e_1^2) \qquad \textbf{(2.60)}$$

Therefore

$$r_1 = \frac{k_{11}}{k_{12}} = \left(\frac{Q_1}{Q_2}\right)\exp[-e_1(e_1 - e_2)] \qquad \textbf{(2.61)}$$

similarly

$$r_1 = \frac{k_{22}}{k_{21}} = \left(\frac{Q_2}{Q_1}\right)\exp[-e_2(e_2 - e_1)] \qquad \textbf{(2.62)}$$

where e_1 and e_2 describe the polarization of the radical and the reacting monomer, respectively.

It is assumed that the polarization of the growing radical end group and its monomer are indistinguishable, then all other monomers can be related to styrene as a Standard, for which Q=1 and e= -0.8 are selected. In general, the value of a reactivity ratio is independent of the nature of the initiator and solvent in a free radical copolymerization: however there is weak temperature dependence.

In Table 2.4 gives values of Q - e for some monomers.

Table 2.4. Q - e Values of some monomers for free radical copolymerization

Monomer	Q	e
Acrolein	0.80	1.31
N-vinylpyrrolidone	0.088	-1.62
Acrylamide	0.23	0.54
Vinyl acetate	0.026	-0.88

2.5. Polymerization of acrolein

Acrolein (2-propenal) is a vinyl monomer with molecular weight 56.06, mp= -87^{o}C, bp = 53^{o}C, Specific gravity: 0.839. Acrolein is usually stabilized with quinone derivatives preventing spontaneous polymerization during storage. The handling of acrolein in fume hoods or in fully closed glass systems is advised [42]. Polyacrolein, formed by spontaneous polymerization of acrolein, was first described in 1843. Such polymers were termed disacryl and were infusible, highly insoluble materials.

Acrolein can introduce aldehyde functionality directly into a vinyl copolymer. Acrolein has 1,3 conjugated unsaturation and can polymerize through the carbonyl as well as the vinyl groups. Ionic polymerizations proceed through the carbonyls, but free radical polymerization has been reported to proceed almost exclusively through the vinyl unsaturation to produce polyacrolein. Polyacrolein is insoluble because neighboring aldehydes in polyacrolein spontaneously condense into six-membered tehrahydropyran rings [43]. According to the Schulz, acrolein polymers prepared by free-radical methods are essentially head-to-tail vinyl polymers modified by cyclization of the pendant aldehyde functions in varying degrees. Thus among the structural subunits thought to be present are, in addition to the simple aldehyde group (I), individually hydrated aldehyde groups (II), dihydroxytetrahydropyran rings (III), and fused tetrahydopyran rings (IV). Similar hemiacatel ether bridges (V) also connect chains. It should be noted that all these substructures represent various degrees of hydration of the basic acrolein unit [44].

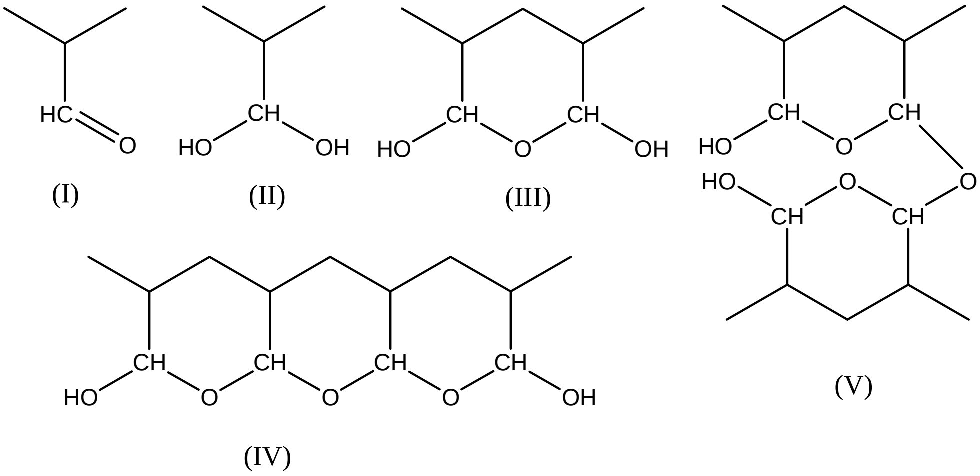


Figure 2.1. The possible structures of polyacrolein.

Acrolein is very reactive against oxidizing agents, reducing agents, oxygen, a variety of chemicals, and sensitive against light [45]. Acrolein is soluble in water, alcohol, ether, and acetone. The aldehyde groups in polyacrolein chains are easily hydrated forming the structures shown in Figure 2.2.

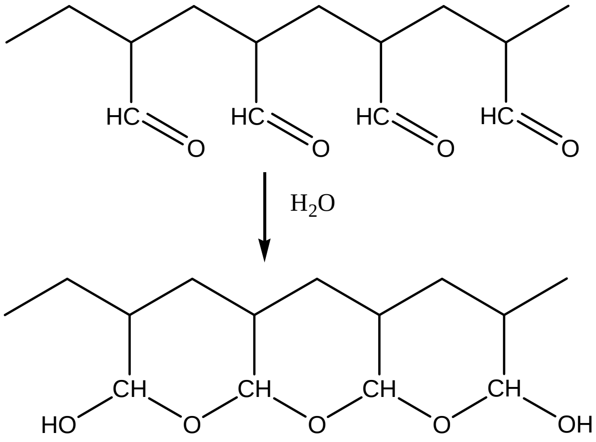


Figure 2.2. Hydrated form of polyacrolein.

The polymer disacryl obtained spontaneously from acrolein, and the polymer resulting from radical initiation or redox systems are colorless powders. They discolor, upon being heated in the presence of air at about 170 ^{o}C, to yellow or brown and sinter without melting at about 220 ^{o}C. Since profound changes take place, polyacrolein cannot be reversibly processed as a normal thermoplastic material**.** There is no glass transition temperature, T_g, value of polyacrolein in the literature**.** Polyacroleins are usually insoluble in water and organic solvents.

2.6. Copolymerization of acrolein in literature

2.6.1. Radical copolymerization of acrolein

Acrolein can be copolymerized radically with vinylic monomers such as acrylamide, ethyl acrylate, acrylic acid, acrylonitrile, 2-vinyl pyridine, vinyl acetate, vinyl chloride, methyl methacrylate, butyl acrylate, methacrylonitrile, styrene (Table 2.5). Usually random copolymers are formed.

Table 2.5. Parameters of the radical copolymerization

Monomer (M_2)	r_1	r_2	Temp. (°C)	Inıtiator	Solvent	Ref.
Acrylic acid	0.50	1.15	54	AIBN	Water[a]	15
	2.40	0.05	75	AIBN	Water[b]	15
	6.70	0.00	80	AIBN	Water[c]	15
Acryl amide	2.0	0.76	20	$K_2S_2O_8$+$AgNO_3$	Water	11
	1.69	0.21	50	AIBN	DMF	12
Acryl nitrile	1.09	0.77	20	$K_2S_2O_8$+$AgNO_3$ H_2O_2+$NaNO_2$	Water	11
	1.60	0.52	50	AIBN	DMF	12
Butyl acrylate	1.60	0.60	50	$K_2S_2O_8$	Water	13
	1.60	0.60	60	AIBN	Dioxane	14
	1.20	0.60	60	AIBN		
Ethyl acrylate	1.60	0.60	50	$K_2S_2O_8$	Water	13
				AIBN	Dioxane	14
Maleic Hydrazide	16	0.00	60	AIBN	DMSO	18
Maleimide	3.20	0.12	60	AIBN	DMSO	18
Methacryl nitrile	0.72	1.20	50	AIBN	Dioxane	12
Methyl acrylate	≈ 0	7.70	20	$K_2S_2O_8$+$AgNO_3$	Water	11, 12
	1.60	0.60	50	$K_2S_2O_8$	Water	13
	1.20	0.60	60	AIBN	Dioxane	14
Methyl methacrylate	0.50	1.00	50	$K_2S_2O_8$	Water	13
	0.80	1.20	60	AIBN	Dioxane	14
Styrene	0.034	0.32	50	$K_2S_2O_8$	Water	13
	0.25	0.25	60	AIBN	Dioxane	14
	0.22	0.33	50	AIBN	Dioxane	18
Vinyl acetate	3.33	0.10	20	$K_2S_2O_8$+$AgNO_3$	Water	11
2-Vinyl pyridine	≈ 4	≈ 0	50	AIBN	DMF	12

[a] pH 3
[b] pH 5
[c] pH 7

2.6.2. Graft copolymerization of acrolein

Grafting was performed by various procedures. Three of these are,

- A foil of poly (methyl methacrylate) was swollen in aqueous acrolein solution and then exposed to γ-radiation of a ^{60}Co source. Graft polymers with aldehyde groups were formed, which show the specific aldehyde reactions [46].

- Cellulose dispersed in an acrolein aqueous solution was treated with γ-radiation of a ^{60}Co source at 40 to 43°C. In addition to the formation of a network of cellulose, homopolymerization of acrolein was observed [47].
- Acrolein was grafted onto poly (ethylene) which was exposed to electron beams. The remaining aldehyde groups could be transformed into hydrazone, oxime, and oxyacid units [48].

2.6.3. Oxidative copolymerization of acrolein

Acrolein and acrylic acid were copolymerized in aqueous H_2O_2 solution at 60 to 90°C to form poly(aldehyde carbon acids). The Canizzaro reaction took place if an aqueous solution or suspension of this polymer material was treated with aqueous NaOH. The aldehyde functions disproportionated into carboxylate and alcohol groups to form poly (hydroxyl carboxylates) [49, 50].

2.6.4. Anionic copolymerization of acrolein

Acrolein was anionically copolymerized with acryl amide and methyl vinyl ketone at 0°C in THF with imidazole as an initiator [51]. Copolymerizations of acrolein with various aldehydes (e.g., acetaldehyde and benzaldehyde) were carried out in THF at -30°C with NaCN as initiator [52.]

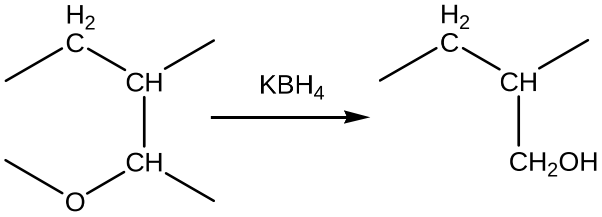
2.6.5. Cationic copolymerization of acrolein

Cationic copolymerization of acrolein with styrene took place in methylene chloride, toluene, and 1-nitropropane with bortrifluoride-etherrate as a catalyst at different temperatures (-78°C to 0°C) [53].

2.7. Some reactions of polyacrolein

Reduction

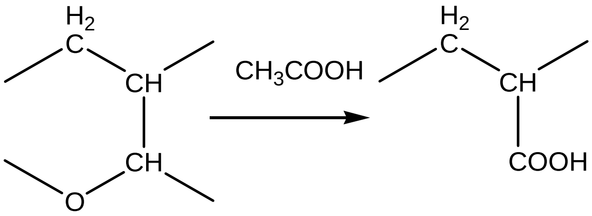
Treatment of polyacrolein suspended in water with potassium borohydride causes reduction of over % 90 of all monomeric units and results in the formation of high-molecular-weight polyallyl alcohol [54];



The primary hydroxyl groups may be esterified, etherified.

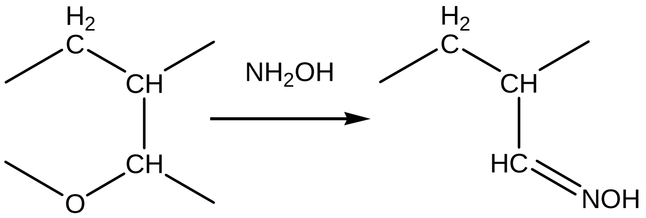
Oxidation

Polyacroleins dissolve at higher temperatures in dilute acid, resulting in the formation of polymeric acid that has largely composition and properties of polyacrylic acid [55];



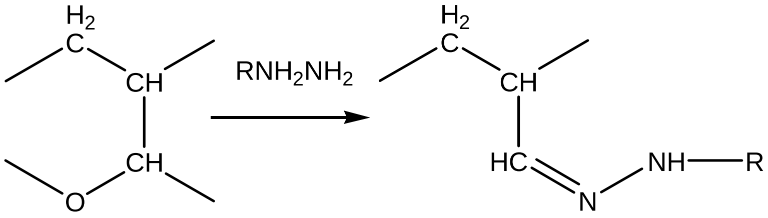
Oximation

The reaction with hydroxylamine hydrochloride gives practically quantitative formation of the oxime [56];



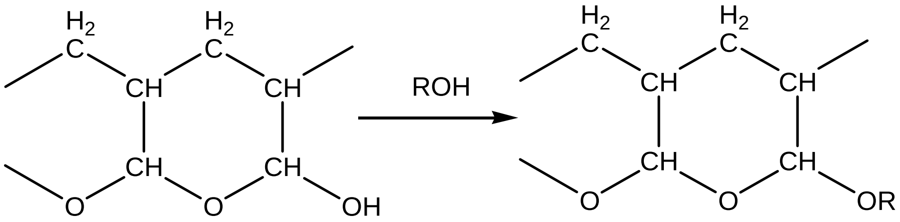
Formation of hydrazones

Phenylhydrazine or its derivatives convert 70 to 90 mole % of the aldehyde groups, depending on the conditions used to the corresponding phenyl hydrazone [57];



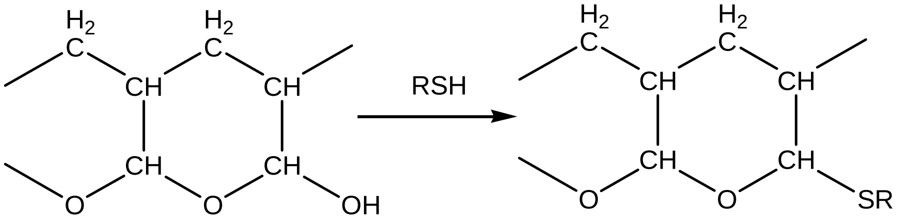
Acetalization

Polyacrolein dissolve in primary alcohols at somewhat elevated temperatures and in the presence an acidic catalyst, acetal forming [58];



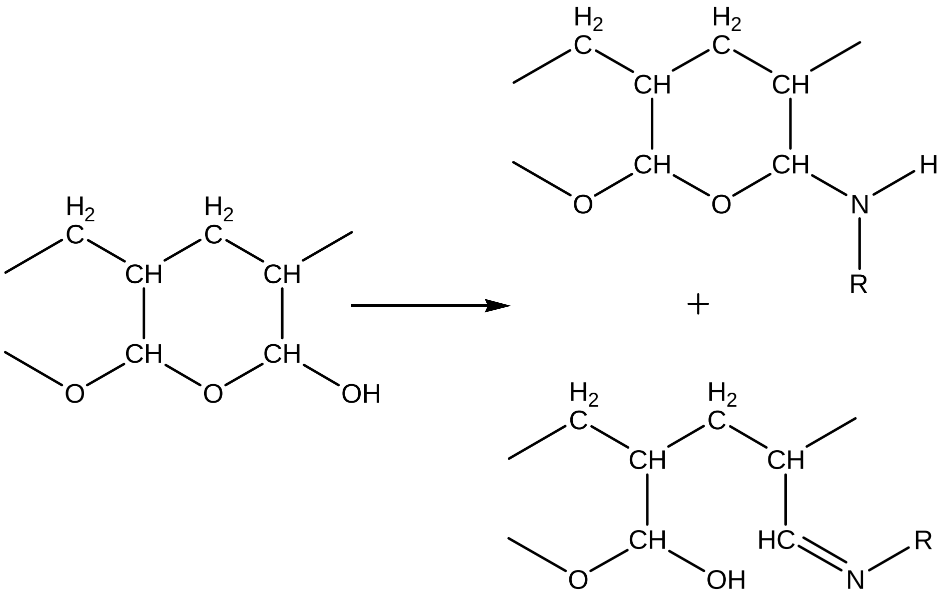
Mercaptalization

The reaction of polyacrolein with mercaptans proceeds under conditions similar to those useful with alcohols and yields, likewise, soluble derivatives [59].



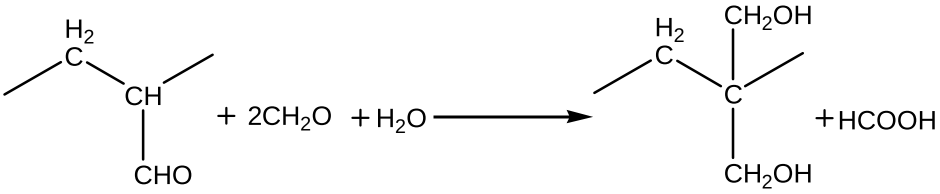
Reaction with ammonia and amines

Polyacrolein reacts exothermically with gaseous or dissolved ammonia. The reaction, products are yellow to brown but completely insoluble [57]. The nitrogen content is about 15 to 17%.



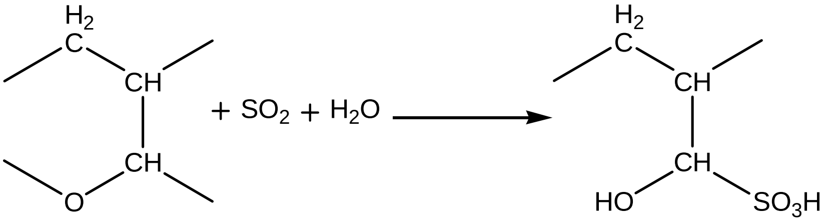
Aldol condensation

The reactions of the free radical-produced polymers described above involved only the carbonyl groups. The alfa hydrogen atom, which is present in each monomeric unit, is also capable of undergoing reaction [60].



Bisulfite adducts

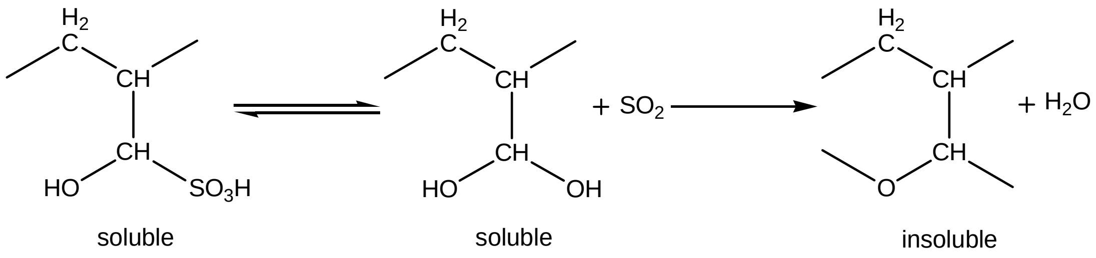
The polyacrolein bisulfite adducts are particularly noteworthy because of their versatile reactivity. If polyacrolein is suspended in a 10% aqueous sulfur dioxide solution, it is insoluble in nearly all organic solvents a clear colorless solution results in several hours at room temperature [61].



insoluble in water

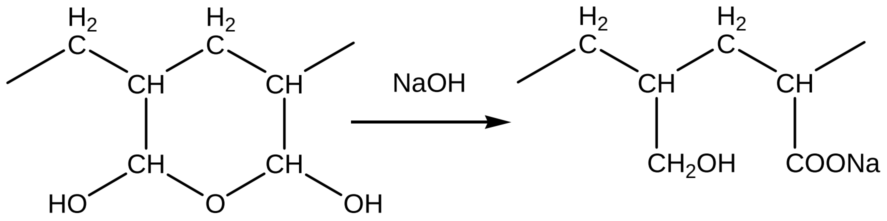
soluble in water

The polyacrolein-sulfurous acid adduct is in equilibrium with its components; apparently a hydrated form of the polymer is generated thereby since, in contrast to the starting polyacrolein, it is soluble in water.



Disproportionation

Disproportionation proceeds under very mild conditions and yields a water-soluble salt of a polyhydroxy polycarboxylic acid. Upon acidification the acid precipitates and is rapidly cross-linked by intermolecular esterification [62].



2. 8. Some application of acrolein copolymers

Polyacrolein containing microspheres can be used for diagnostic test for the detection in various body fluids (e.g., in blood serum or urine) [42].

Manchıum Chang et al. have reported that a series of hydrophilic microspheres by the copolymerization of acrolein - Hydroxyethyl Methacrylate (HEMA) of different ratios in the presence of emulsifier. Ionizing several radiations (Co 60) was selected as the polymerization initiation mechanism to avoid undesirable contamination. The biomedical properties of PA and PHEMA copolymer microspheres were evaluated by immobilizing horseradish peroxidase (HRP), a model enzyme commonly used in the enzyme-linked immunosorbent assay (ELISA), on their surface [63].

Copolymerization of acrolein with acrylic acid in aqueous solution has been reported by J.M. Gadgil et al. The reactivity ratios for acrolein (0.5) with acrylic acid (1.5) have been examined in water at 30^{o}C without pH control [1].

A.Yu. Menshikova et al. have reported that Emulsifier-free emulsion copolymerization of acrolein with styrene and methyl methacrylate to prepare microspheres with surface aldehyde groups. This results of study allow control over the size of monodisperse microspheres (370-1000 nm), hydrophobicity of their surface, and content of the aldehyde groups providing the covalent binding of biologically active compounds [64].

Polyacrolein-co-polystyrene microspheres synthesized via the emulsifier free copolymerization of styrene and acrolein were used for a model slide agglutination test in which particles having attached human serum albumin were used for the detection of anti-HSA (Human serum albumin) in serum from goats immunized with HSA [65].

The copolymerization of vinyl ether and acrolein has been carried out under the influence of boron trifluoride/ether. The copolymer obtained had limited solubility in organic solvents, in contrast to the readily soluble polymers of vinyl ether and the insoluble polyacrolein [66].

2.9. Polymerization of polyvinylpyrolidone

Vinylpyrrolidone polymers have been extensively used, especially in the pharmaceuticals (coating and disintegrated for tablets stabilizer), cosmetics (Film formers for hair sprays) and food (stabilization of beverages) as well as numerous technical applications. In these various fields PVP has rather different functions.

Polyvinylpyrolidone (PVP) having molecular weights (MW) from 2500 to about 1 million is mainly obtained by radical polymerization in solution. The molecular weight distribution of soluble PVP is broad due to transfer reactions. An unusual property of PVP is its solubility in water as well as in various organic solvents. The glass transition temperature of high molecular weight polymers (MW=1 million) is about 175^{o}C and falls to values under 100^{o}C with decreasing molecular weight (MW=2500). Vinylpyrrolidone can be polymerized either in bulk, in solution or in suspension. The structure of PVP is given in Figure 2.3. Copolymers can be formed with numerous monomers by radical polymerization, vinylcyclohexane-co-vinyl pyrrolidone, phenacyl methacrylate-co-vinyl pyrrolidone [67]. However there are only few copolymers which are produced technically in large amounts.

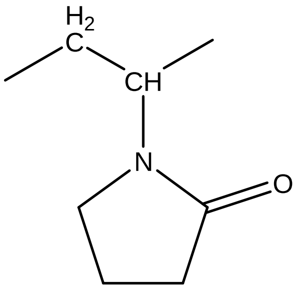


Figure 2.3. The structure of polyvinylpyrolidone.

2.10. Copolymers of acrolein-vinylpyrrolidone

There are some studies on the copolymers of acrolein and N-vinylpyrrolidone which have not been explored recently. Some of these studies found in literature are as follows;

Acrolein has been copolymerized with N-vinylpyrrolidone in an inverted emulsion to give spherical hydrophilic copolymer beads and used to immobilize trypsin presumably via imine bond formation [68].

Another study is that an acrolein-N-vinyl-2-pyrrolidone copolymer and an acrolein-N-vinyl-2-pyrrolidone-vinyl acetate copolymer have been prepared in dilute aqueous solution and used as is or as cationic derivatives prepared by treatment with a small amount of betaine hydrazide chloride, to improve the wet strength (e.g., up to >30%) of paper [69,70].

3. EXPERIMENTAL

3. 1. Materials

Acrolein (>%95) was obtained from FLUKA.

N-vinyl pyrolidone (%98) was obtained from Across Organics. Acrolein and NVP were passed through neutral alumina to remove the inhibitor before use.

Potassium persulfate ($K_2S_2O_8$) was used as initiator. Their molecular structures are given in Figure 3.1-3.2.

Ethanol, 1.4-dioxane, pyridine, ethyl acetate, methanol, formic acid, etc. were used as received. *Triple distilled water* was used as solvent in polymerization.

Phenylhydrazine and hydroxylamine hydrochloride salt were obtained from ALDRICH and MERCK respectively.

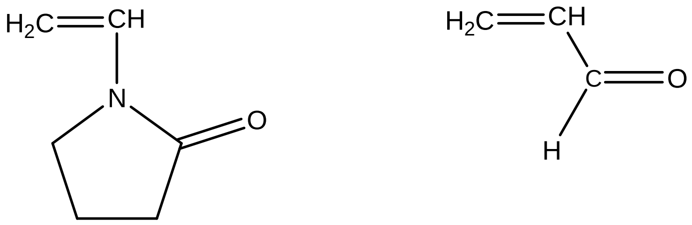


Figure 3.1. The molecular structures of N-vinylpyrrolidone and acrolein.

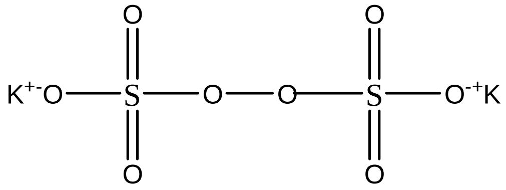


Figure 3.2. The molecular structure of initiator potassium persulfate.

3.2. Synthesis

3.2.1 Synthesis of acrolein / N-vinyl pyrrolidone (NVP) copolymers

Copolymers of acrolein with N-vinyl pyrrolidone (NVP) were prepared by following procedure.

A 100 ml round-bottomed flask was equipped with a reflux condenser, thermometer and nitrogen inlet. The monomer mixtures prepared at different mole ratios were dissolved in water and initiator ($K_2S_2O_8$) was added to flask. The reaction mixture was heated to 65 °C with constant stirring at a definite time interval.

The polymer was precipitated in ethanol-ethyl acetate (1:4) mixture and decanted. Purification of the copolymers was achieved by dissolution in water and reprecipitation with ethanol-ethyl acetate (1:4) mixture for several times. Copolymer samples were dried under high vacuum at 40 °C for 10 days.

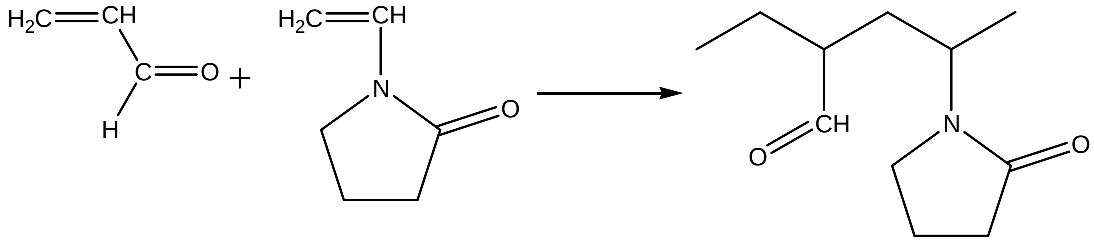


Figure 3.3. The structure of poly (acrolein-*co*-vinyl pyrrolidone).

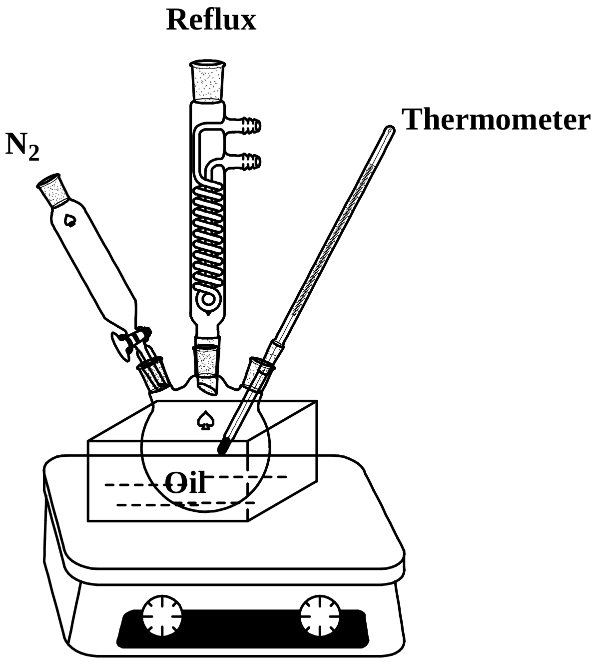


Figure 3.4. The experimental setup for the copolymerization of acrolein with NVP.

3.2.2. Synthesis of phenylhydrazone derivative of copolymers

Phenylhydrazine derivative of copolymers were prepared by following procedure of Zhang et al. [71].

To a 100-ml round-bottomed flask was equipped with a mechanical (or magnetic) stirrer, reflux condenser and thermometer, 0.25 g of poly(acrolein-co-vinyl pyrrolidone) was swollen in 30 ml of absolute ethanol and 0.5 ml acetic acid for 3 h. Phenylhydrazine (1 ml) dissolved in absolute ethanol (30 ml) was added. The mixture was allowed to react at 55-60°C for 16 h. The light yellow colored product was filtered off and washed sequentially with warm water (35°C) and hot ethanol (55°C). Modified copolymers were dried at 40°C for 10 days under high vacuum.

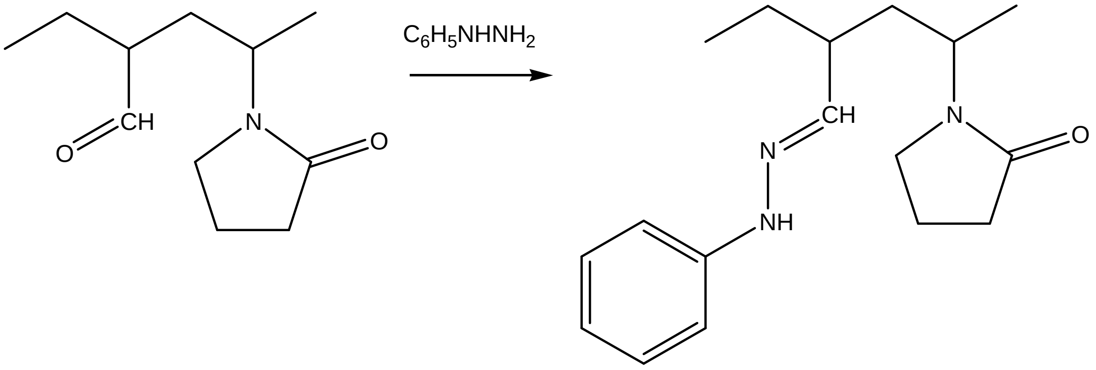


Figure 3.5. Proposed structure of the phenylhydrazine modified copolymers.

3.2.3. Synthesis of oxime derivative of copolymers

Oxime derivative of copolymers were prepared by following procedure of Scampini et al. [72].

The 0.50 g of poly(acrolein-co-vinyl pyrrolidone) was kept swelling in 10 ml of methanol overnight. The aqueous solution of free hydroxylamine was prepared from its hydrochloride salt ($NH_2OH.HCI$) in the following way. Hydroxylamine hydrochloride (0.25 g) was dissolved in water (10 ml) and the HCI was neutralized by the addition of NaOH aqueous solution (1 M) until pH 12. The reaction mixture was refluxed at pH 12 for 27h. The modified copolymer was neutralized, filtered off, thoroughly washed with hot water and methanol to remove excess of reagents and dried at 40^oC for 10 days under high vacuum. Same procedure was applied in the modification of polyacrolein.

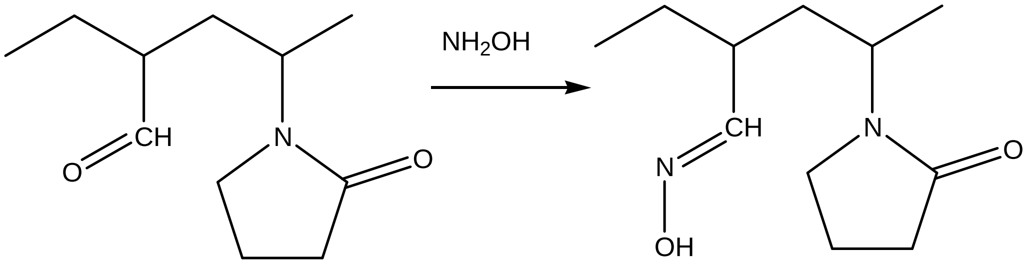


Figure 3.6. Proposed structure of the oxime modified copolymers.

3.3. Characterization of the copolymers and modified copolymers

3.3.1. FT-IR analysis

Fourier transform infrared (FTIR) spectra (KBr Pellets) of the copolymers and modified copolymers were recorded with FTIR Shimadzu Spectrometer in the range of 400-4000 cm^{-1} wavelength, where 30 scans were taken at 4 cm^{-1} resolution.

3.3.2. NMR analysis

^1H-NMR and^{13}C-NMR spectra were recorded on Bruker400MHz spectrometer. Deuterated dimethylsulfoxide (DMSO) was used as NMR solvent.

3.3.3. Thermal analysis

The thermal stability of copolymers and modified copolymers were studied by thermogravimetric analysis (TGA) over a temperature range from 25 at 900°C under nitrogen atmosphere at heating rate 20°C/min using Perkin Emler Pyris 1 model.

Differential scanning calorimetry (DSC) analysis of copolymers and modified copolymers were performed in the range of on a DSC (TA instruments Q10 series) under nitrogen atmosphere at a heating rate 10^oC/min.TGA.

3.3.4 Elemental analysis

The elemental analyses were done on the homopolymers and copolymers in different mol ratio in feed composition by using Eurovector EA 3000 elemental analyzer. It was noted by the elemental analyses results that degree of modifications of copolymers.

3.3.5. Solubility studies

Solubility of copolymers and modified copolymers were tested in various polar and non-polar solvents. About 20 mg of the polymer was added to about 10 ml of solvent in a flask and mixture was kept in cold for 2h and hot for another 2h. The findings were noted soluble or not.

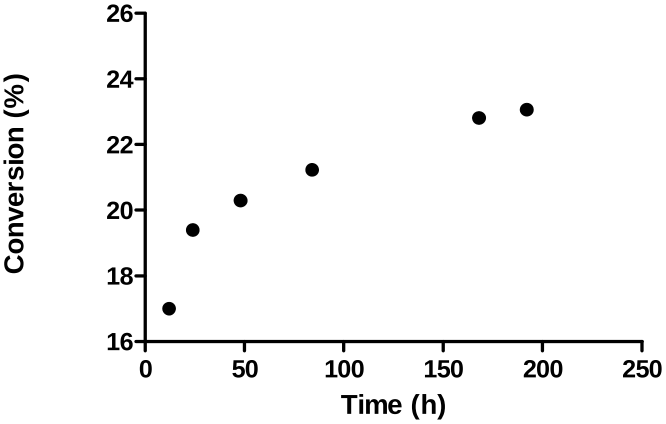
4. RESULTS AND DISCUSSION

4.1. Investigation of copolymerization kinetics

The copolymerization kinetics of poly(acrolein-*co*-vinylpyrrolidone) was investigated. Percentage conversion of monomer mixtures to polymer was studied gravimetrically. The experiments were performed in different mol ratio of monomers in feed as shown in Table 4.1 for different reaction times.

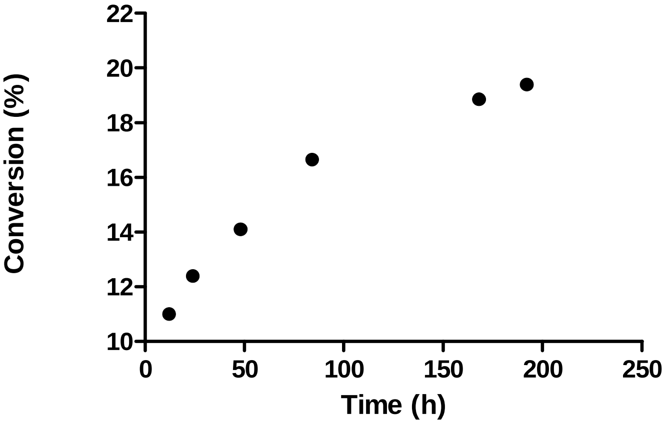
Table 4.1. Feed molar fraction and copolymer composition data of acrolein-NVP copolymers

Feed Molar Fraction		Copolymer composition	
F_1	F_2	f_1	f_2
20	80	58	42
40	60	60	40
50	50	62	38
60	40	64	36
80	20	74	26



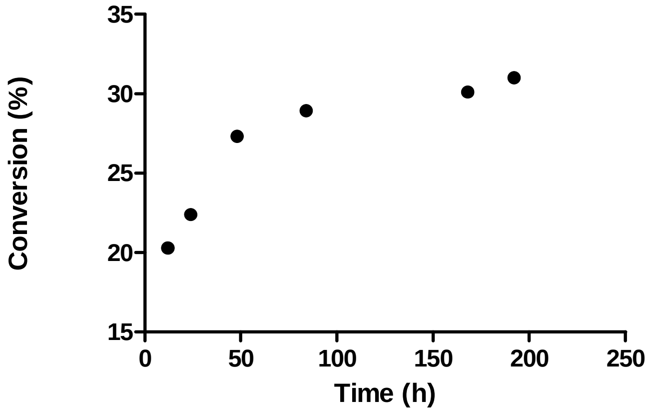
Reaction Time (h)	Conversion (%)
12	17
24	19.40
48	20.30
84	21.23
168	22.81
192	23.06

Figure 4.1. Variation of monomer conversion in the copolymerization of acrolein with NVP (58:42) with reaction time ($[M]_{total}$ =3.53 mol.L^{-1}; $[K_2S_2O_8]$ = 10.22 x 10^{-3} mol.L^{-1}) .



Reaction Time (h)	Conversion (%)
12	11.00
24	12.40
48	14.10
84	17.16
168	18.85
192	19.40

Figure 4.2. Variation of monomer conversion in the copolymerization of acrolein with NVP (62:38) with reaction time ($[M]_{total}$ =3.53 mol.L^{-1}; $[K_2S_2O_8]$ = 10.22 x 10^{-3} mol.L^{-1}).



Reaction Time (h)	Conversion (%)
12	20.30
24	22.40
48	27.33
84	28.93
168	30.10
192	31.00

Figure 4.3. Variation of monomer conversion in the copolymerization of acrolein with NVP (74:26) with reaction time ($[M]_{total}$ =3.53 mol.L^{-1}; [$K_2S_2O_8$] = 10.22 x 10^{-3} mol.L^{-1}).

As can be seen in Figures 4.1 to 4.3, the conversion to polymer increased in time and the shape of conversion curves was quite similar for all polymerizations.

It was observed that the final conversion for copolymer A74/NVP26 is close to 31% after 192 h. whereas, the polymerization was much slower and the final conversion about 20% for copolymer A62/NVP38 under the same conditions. Possibly, it is related with the relative reactivity of monomers.

4.2. Determination of the monomer reactivity ratios

For determining the reactivity ratios, five sets of copolymers of different compositions with <10% conversion were prepared using varying proportions of monomers in the feed. The copolymerization reaction is shown in Figure 4.4.

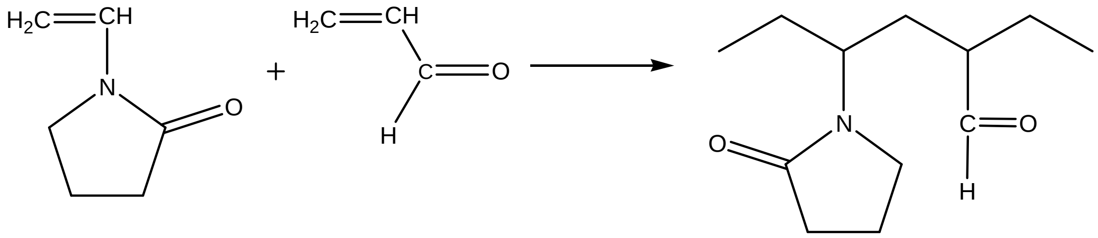


Figure 4.4. The constituent monomeric units of the copolymer.

The determination of the compositions of the copolymers was achieved by using the data from both elementary analysis and FT-IR analysis. Mainly, their percent nitrogen contents obtained by elemental analysis were exploited in calculations to determine the composition of the copolymers. Further, comparable peak intensities on FT-IR spectra were used for the same purpose. Monomer reactivity ratio values were calculated by using the monomer feed ratios and the copolymer composition. The, Fineman–Ross (FR), Kelen-Tüdos (KT), Extended Kelen-Tüdos (E-KT), Mayo–Lewis and non-linear error-in- variables methods were used to determine monomer reactivity ratios for acrolein-NVP pair.

Calculations on the basis of elemental analysis data

Fineman-Rose (FR) method

Molar percentages (mol %) of comonomer units (m_1 and m_2) in poly(acrolein-*co* vinylpyrrolidone) using elemental analysis data were calculated according to the following equations;

$$\%M_2 = \frac{BxM_2}{AN} \qquad \textbf{(4.1)}$$

$$\%M_1 = 100 - \%M_2 \qquad \textbf{(4.2)}$$

$$m_1 = \frac{\%M_1}{M_1}, \quad m_2 = \frac{\%M_2}{M_2} \qquad \textbf{(4.3)}$$

$$\%m_1 = \frac{m_1}{m_1 + m_2}, \ \%m_2 = \frac{m_2}{m_1 + m_2} \qquad \textbf{(4.4)}$$

where M_2 and M_1 are the molecular weight of NVP and acrolein unit; AN is the atomic weight of nitrogen; B is the content of nitrogen in the copolymers (%);

Fineman and Ross method was used to determine the reactivity ratios of r_1 (Acrolein) and r_2 (NVP).

$$f = m_1 / m_2 \qquad \textbf{(4.5)}$$

$$F = \frac{[M_1]}{[M_2]} \qquad \textbf{(4.6)}$$

m_1= Mole fraction of Acrolein in copolymer

m_2= Mole fraction of NVP in copolymer

[M_1]= Mole fraction of Acrolein in feed

[M_2]= Mole fraction of NVP in feed

$$F(f-1)/f = r_1(F^2/f) - r_2 \tag{4.7}$$

r_1 (Acrolein) and r_2 (NVP) are the reactivity ratios, the plot of $F(f-1)/f$ vs. (F^2/f) will give a straight line with r_1 as the slope and $-r_2$ as the intercept (Figure 4.5).

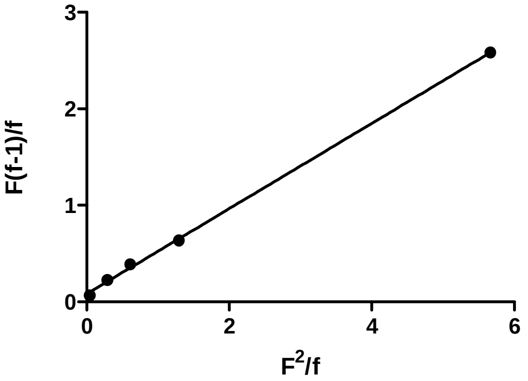


Figure 4.5. Fineman-Ross plot for the copolymerization of acrolein with NVP.

Kelen –Tüdos (KT) method

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{4.8}$$

where η and ξ are mathematical functions of the comonomer molar fractions in the feed and in the copolymer, respectively:

$$\eta = [F(f-1)/f]/(F^2/f + \alpha) \tag{4.9}$$

$$\alpha(arbitrary\ \ parameter) = \sqrt{\left(\frac{F^2}{f}\right)_{\min}\left(\frac{F^2}{f}\right)_{\max}} \tag{4.10}$$

$$\xi = (F^2/f)/(F^2/f + \alpha) \tag{4.11}$$

The experimental data were treated by the above method to find r_1 and r_2.The plot of η versus ξ will give a straight line with $r_1 + r_2/\alpha$ as the slope and $-r_2/\alpha$ as the intercept (Figure 4.6).

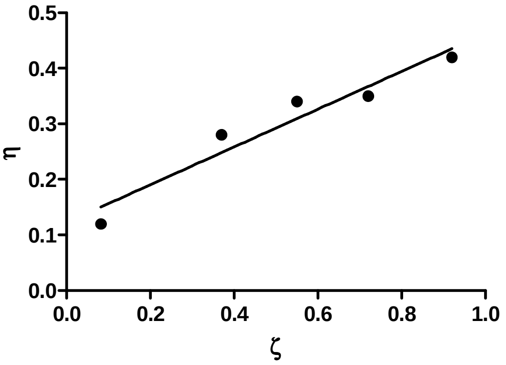


Figure 4.6. Kelen-Tüdos plot for the copolymerization of acrolein with NVP.

The Fineman-Ross (F-R) and Kelen-Tüdos (K-T) methods were used to determine the monomer reactivity ratios. F-R and K-T parameters and the reactivity ratios of this system calculated are summarized in Table 4.2.

Table 4.2. The Kelen-Tüdos and Fineman-Ross parameters for the copolymerization of acrolein with NVP

Monomer feed[a]		Elemental Analysis	Copolymer composition		Parameters of FR-eq.		Parameters of KT-eq		
$\frac{[M_1]}{mol-\%}$	$\frac{[M_2]}{mol-\%}$	%N	$\frac{m_1}{mol-\%}$	$\frac{m_2}{mol-\%}$	F^2/f	$F(f-1)/f$	$F^2/f+\alpha$	ξ	η
20	80	7.458	57.70	42.30	0.046	0.067	0.56	0.082	0.12
40	60	7.135	60.25	39.75	0.29	0.23	0.80	0.37	0.28
50	50	6.890	62.08	37.92	0.61	0.39	1.12	0.55	0.34
60	40	6.716	63.46	36.54	1.29	0.64	1.81	0.72	0.35
80	20	5.196	73.85	26.15	5.66	2.58	6.18	0.92	0.42

[a] $[M]_{total}$ =3.53 mol.L^{-1}; $[K_2S_2O_8]$ = 10.22 x 10^{-3} mol.L^{-1}

Extended Kelen –Tüdos (E-KT) method

The reactivity ratios were also calculated by the extended Kelen–Tüdos method (E-KT) where the effect of conversion is considered directly in determination of G, H and subsequently, η and ξ by definition of the parameter Z (4.8).

$$Z = \frac{\log(1-\varsigma_1)}{\log(1-\varsigma_2)} \tag{4.12}$$

$$G = \frac{(F-1)}{Z} \tag{4.13}$$

$$H = \frac{F}{Z^2} \tag{4.14}$$

Where ς_1 and ς_2 are partial molar conversion given by

$$\varsigma_1 = \frac{w(\mu + F)}{(\mu + f)} \tag{4.15}$$

$$\varsigma_2 = \varsigma_1 \frac{F}{f} \tag{4.16}$$

where μ shows the molecular weight ratio of NVP to Acrolein, w is the total conversion (by weight). The Extended K-T Parameters are provided in Table 4.3.

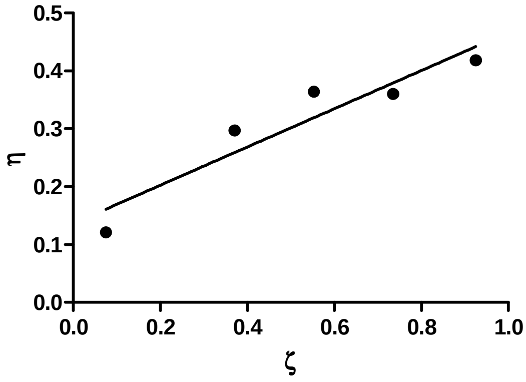


Figure 4.7. Extended KT plot for the copolymerization of acrolein with NVP.

Table 4.3. Extended KT Parameters for the copolymerization of acrolein with NVP

Copolymer composition	ς_1	ς_2	G	F	ξ	η
A58/NVP42	0.208	0.0380	0.061	0.038	0.075	0.121
A60/NVP40	0.101	0.0444	0.221	0.276	0.371	0.297
A62/NVP38	0.113	0.0688	0.381	0.580	0.553	0.364
A64/NVP36	0.0540	0.0466	0.636	1.297	0.735	0.360
A74/NVP26	0.0307	0.0434	2.605	5.763	0.925	0.418

Mayo – Lewis (M-L) method

Mayo – Lewis (M-L) method is another linear method used in calculation. Instantaneous copolymer composition is used in equations. Reactivity ratios are given by the least summation of the root distance of the point from the lines.

The M-L plot r_1 versus r_2 is given in Figure 4.8.

$$r_1 = Hr_2 - G \tag{4.17}$$

$$H = \frac{F^2}{f} \quad G = \frac{F(f-1)}{f} \tag{4.18}$$

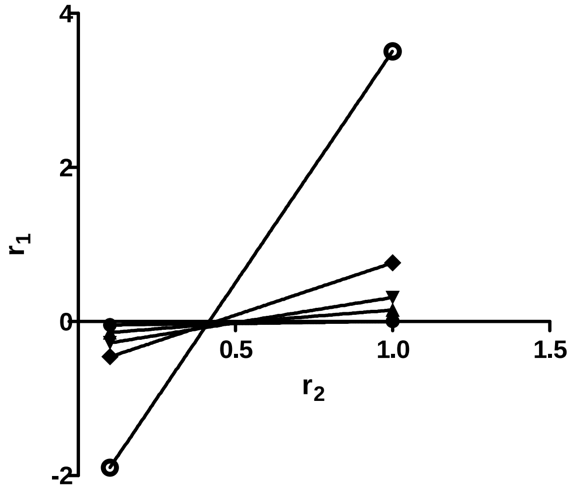


Figure 4.8. r_1 versus r_2 in the Mayo Lewis method.

Non-linear error variables model (EVM)

To determine monomer reactivity ratios, a non-linear error-in-variables model (EVM) method was used utilizing the computer program (PREVM) [73].

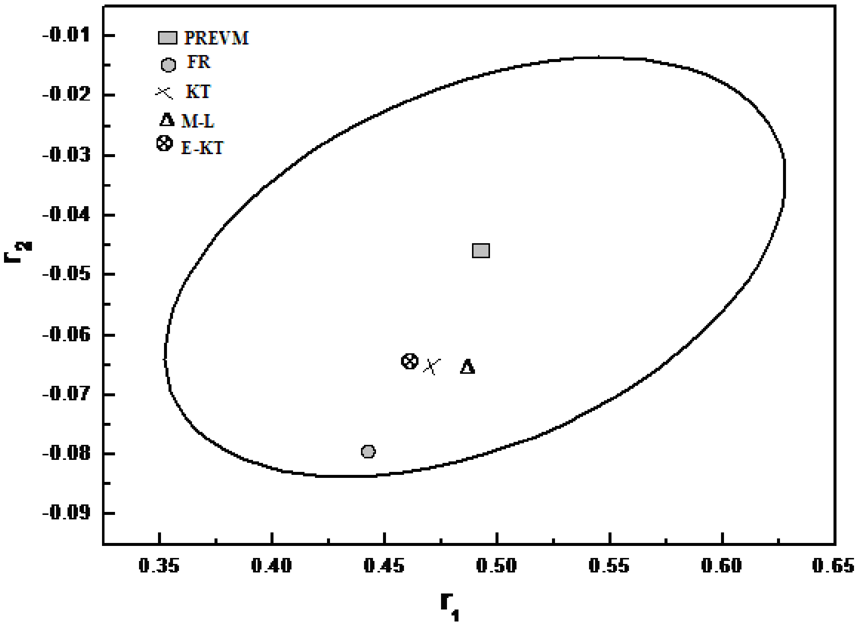


Figure 4.9. Monomer reactivity ratios and 95% joint confidence limits for the reactivity ratios of acrolein and NVP obtained by □PREVM, ○FR, ×KT, ΔM-L, ⊗E-KT.

Table 4.4. A summary of the calculated reactivity ratios by different methods

Methods of Determination and Calculation	r_1	r_2	$r_1.r_2$
Fineman-Ross	0.44	-0.082	-0.0360
Kelen-Tüdos	0.47	-0.065	-0.0306
Ext. Kelen-Tüdos	0.46	-0.064	-0.0294
Mayo Lewis	0.49	-0.065	-0.0318
PREVM	0.49	-0.049	-0.0240

The monomer reactivity ratio of acrolein and NVP obtained by various methods are given in Table 4.4. The reactivity ratios for acrolein (r_1) obtained by Fineman-Ross, Kelen-Tüdos, Extended Kelen-Tüdos, Mayo Lewis and PREVM methods were in excellent agreement with each other but reactivity ratio of NVP showed little deviation for Fineman-Ross and PREVM method.

As shown in the Table 4.4 the higher value of acrolein confirms the higher reactivity of acrolein than NVP.

Calculations on the basis of FT-IR analysis data

Further, molar fractions of comonomer units (m_1 and m_2) in acrolein (M1)-NVP (M2) copolymers were calculated according to the following equations, using FTIR analysis data [74].

$$\Delta A^i = A^i / A^{733} \text{ (Standard band)} \tag{4.19}$$

$$m_1 = \frac{\Delta A^{620} / M_1}{\Delta A^{1286} / M_2 + \Delta A^{620} / M_1} \times 100 \tag{4.20}$$

$$m_2 = \frac{\Delta A^{1286} / M_2}{\Delta A^{1286} / M_2 + \Delta A^{620} / M_1} \times 100 \tag{4.21}$$

A^{620} : C-H out-of- plane bending band in acrolein unit

A^{1286}: C-N stretching band in NVP unit

A^{733} : the least changing absorption band in copolymer

Table 4.5 The Kelen-Tüdos and Fineman-Ross parameters for the copolymerization of acrolein with NVP, calculated by using FTIR analysis data

Monomer feed		Copolymer composition		Parameters of FR-eq.			Parameters of KT-eq	
$\frac{[M_1]}{mol-\%}$	$\frac{[M_2]}{mol-\%}$	$\frac{m_1}{mol-\%}$	$\frac{m_2}{mol-\%}$	F^2/f	$F(f-1)/f$	$F^2/f+\alpha$	ξ	η
20	80	51.40	48.60	0.059	0.014	0.68	0.087	0.02
40	60	59.01	40.99	0.31	0.20	0.95	0.33	0.22
50	50	61.13	38.87	0.64	0.37	1.27	0.50	0.29
60	40	62.20	37.80	1.37	0.59	2.01	0.68	0.30
80	20	71.25	28.75	6.46	2.39	7.09	0.91	0.34

Table 4.6. Extended KT Parameters for the copolymerization of acrolein with NVP, calculated by using FTIR analysis data

Copolymer composition	ς_1	ς_2	G	F	ξ	η
A58/NVP42	0.177	0.0418	0.0132	0.051	0.0801	0.021
A60/NVP40	0.0975	0.0453	0.197	0.288	0.333	0.228
A62/NVP38	0.110	0.0701	0.356	0.611	0.514	0.295
A64/NVP36	0.0525	0.0477	0.590	1.360	0.702	0.304
A74/NVP26	0.0290	0.0468	2.406	6.560	0.919	0.337

Table 4.7. A summary of the calculated reactivity ratios by different methods, calculated by using FTIR analysis data

Methods of Determination and Calculation	r_1	r_2	$r_1.r_2$
Fineman-Ross	0.36	-0.077	-0.0277
Kelen-Tüdos	0.41	-0.031	-0.0127
Ext. Kelen-Tüdos	0.41	-0.033	-0.0135
Mayo Lewis	0.36	-0.010	-0.0036
PREVM	0.46	0.004	0.0018

Reactivity ratios calculated using elemental analysis data (Table 4.4.) were closely in agreement with those obtained from FTIR analysis (Table 4.7).

The calculated reactivity ratio r_2 is in negative value for all the methods. This is absurd since the minimum value theoretically possible for the reactivity ratio is zero [5]. There are some reactivity ratios reported with negative sign in literature [11, 12, and 75]. It was found that the copolymer was relatively enriched with acrolein. NVP caused a decrease in the apparent copolymerization rate, and this was consistent with the observed trends in the reactivity ratios.

4.3. The degree of modification of modified copolymers

4.3.1. Determination of the degree of modification of phenylhydrazone derivative of copolymers

The degree of modifications of phenylhydrazone derivative of copolymers was calculated by using Elemental Analysis data. The results were given in Table 4.8-4.10. It was noted that the rate of modification reaction was quite fast up to 20-24 h. But, it slowed down in time and significant changes were not observed in percent modification later than 200 h.

Table 4.8. Results for phenylhydrazone derivative of copolymer A58/NVP42

	% Nitrogen	Reaction Time (h)	(%) Modification
A58 /NVP42 Hydrazone	6.61	0	-
	12.01	24	23
	12.34	72	24
	12.75	120	26
	13.03	168	27

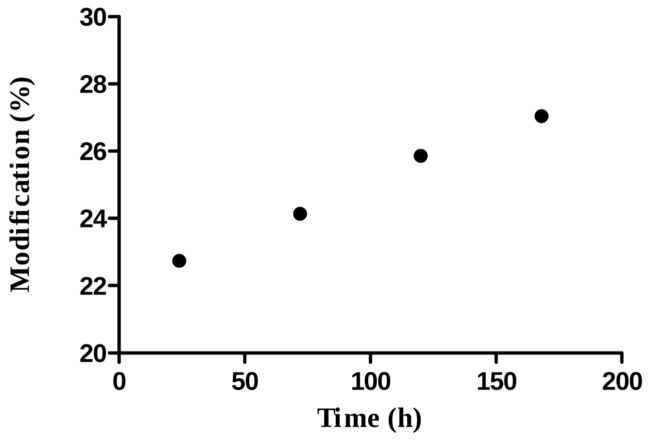


Figure 4.10. Time-dependent change of degree of modification for phenylhydrazone derivative of copolymer A58/NVP42.

Table 4.9. Results for phenylhydrazone derivative of copolymer A62/NVP38

	% Nitrogen	Reaction Time (h)	(%) Modification
A62/NVP38 Hydrazone	5.98	0	-
	12.29	24	24
	12.98	72	27
	13.37	120	28
	13.79	168	30

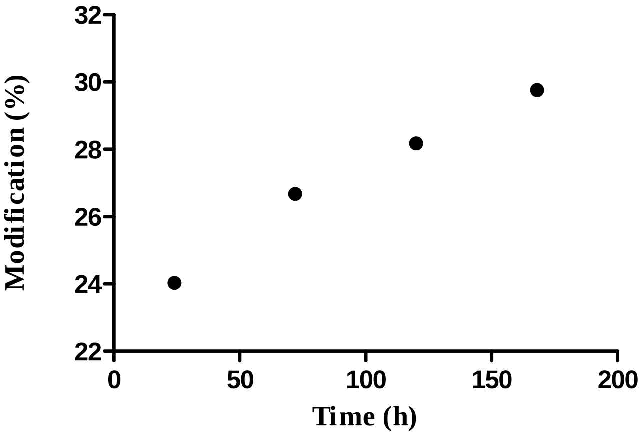


Figure 4.11. Time-dependent change of degree of modification for phenylhydrazone derivative of copolymer A62/NVP38.

Table 4.10. Results for phenylhydrazone derivative of copolymer A74/NVP26

	% Nitrogen	Reaction Time (h)	(%) Modification
	2.40	0	-
	15.31	24	32
A74/NVP26	16.25	72	34
Hydrazone	17.40	120	37
	18.11	168	39

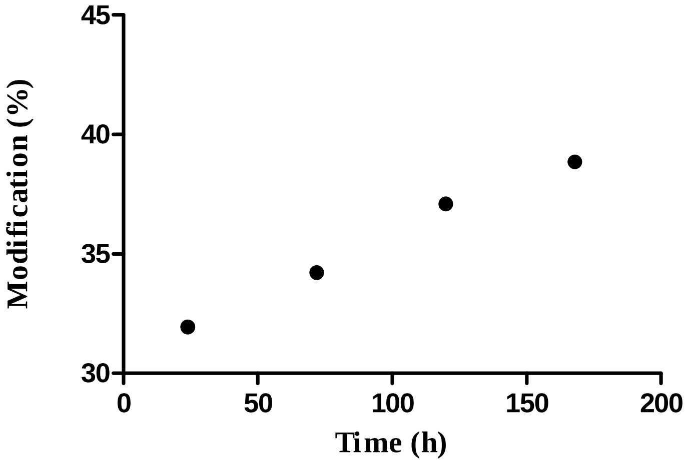


Figure 4.12. Time-dependent change of degree of modification for phenylhydrazone derivative of copolymer A74/NVP26.

These results confirm that degree of modification of an acrolein-NVP copolymer is directly dependent to the amount of aldehyde units in it.

4.3.2. Determination of the degree of modification of oxime derivative of copolymers

The degree of modification of oxime derivative of copolymers was calculated by using elemental analysis data. The results were given in Table 4.11 to 4.13. It was also noted that the rate of modification reaction is fast up to 20-24 h. But, it slowed down in time and significant changes were not observed in percent modification later than 200 h as in the case of previous modification of copolymers.

Table 4.11. Results for oxime derivative of A58/NVP42 copolymer

	% Nitrogen	Reaction Time (h)	(%) Modification
A58/NVP42 Oxime	6.61	0	-
	9.03	24	20
	9.71	72	26
	10.25	120	31
	10.74	168	35

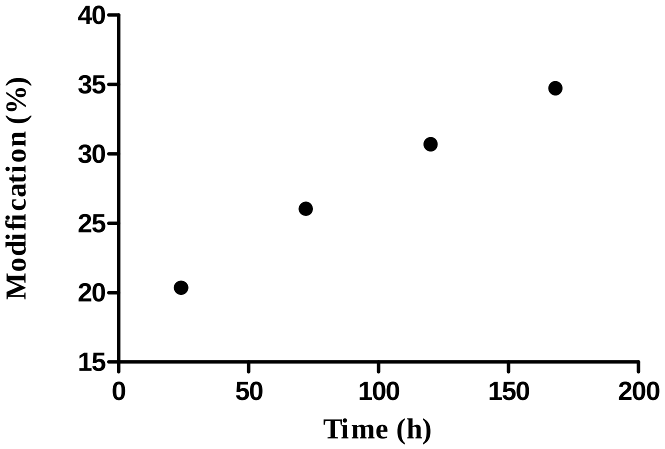


Figure 4.13. Time-dependent change of degree of modification for oxime derivative of copolymer A58/NVP42.

Table 4.12. Results for oxime derivative of copolymer A62/NVP38

	% Nitrogen	Reaction Time (h)	(%) Modification
A62 /NVP 38 Oxime	5.98	0	-
	11.44	24	42
	11.94	72	45
	12.26	120	48
	12.60	168	50

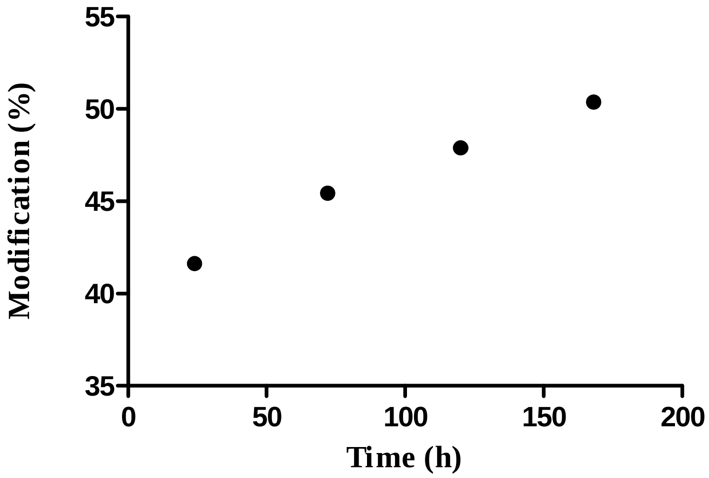


Figure 4.14. Time-dependent change of degree of modification for oxime derivative of copolymer A62/NVP38.

Table 4.13. Results for oxime derivative of copolymer A74/NVP26

	% Nitrogen	Reaction Time (h)	(%) Modification
A74/NVP26 Oxime	2.40	0	-
	17.12	24	66
	16.78	72	69
	16.42	120	71
	15.78	168	73

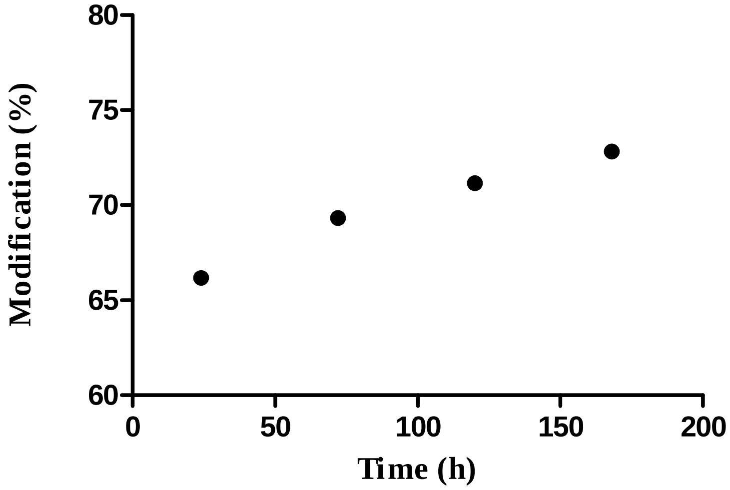


Figure 4.15. Time-dependent change of degree of modification for oxime derivative of copolymer A74/NVP26.

These results also confirm that degree of modification of an acrolein-NVP copolymer is directly dependent to the amount of free aldehyde units in it, as in the previous study for modification of copolymers.

It was observed that the modification with hydroxylamine was more successful than the modification with phenylhydrazine for the same time intervals of modification reaction since hydroxylamine molecules with their smaller size with respect to phenylhydrazine molecules could interact effectively with aldehyde groups in copolymer chains.

4.4. FT-IR Characterization

4.4.1. Characterization of homopolymers

The FT-IR spectrum of polyacrolein is shown in Figure 4.16. The presence of aldehyde groups could be confirmed by the appearance of band at 1725 cm^{-1} range, attributed to C=O stretching, and by absorptions corresponding to the asymmetrical deformation of C-H between 1330-1390 cm^{-1} [76]. This is similar for the band asymmetric stretching of the C-H of aldehyde groups at 2719 cm^{-1}, aliphatic C-H stretching at 2935 cm^{-1}.A broad band from 950 to 1150 cm^{-1}characterizing the –C-O-C- bonds of cyclized aldehyde [77].

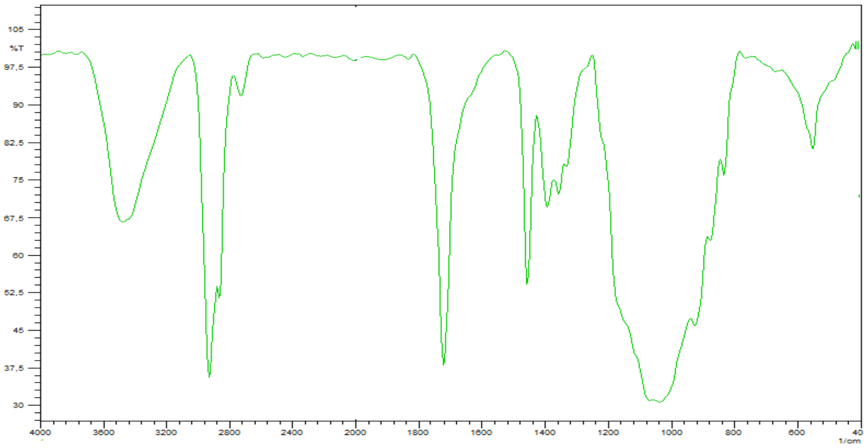


Figure 4.16. FT-IR Spectrum of polyacrolein.

Table 4.14. FT-IR data of polyacrolein

Type of vibration	Wavenumber/cm^{-1}	
	A (this work)	B (literature) [78]
Aldehydic C-H bending	1330-1390	~1375
C=O stretching of aldehyde	1725	1650-1780
O-H stretching	3450	3200-3500
Aldehydic C-H stretching	2719	2719
Aliphatic C-H stretching	2935	~2900

The Infrared spectrum of polyvinylpyrolidone (PVP) is given in Figure 4.17, strong C=O absorption peak from the amide group of PVP at 1680 cm^{-1}, C-N group appeared at 1286 cm^{-1}, C-H stretching and bending vibration frequencies were observed 2800-3000 and 1430-1495 cm^{-1}, respectively [79].

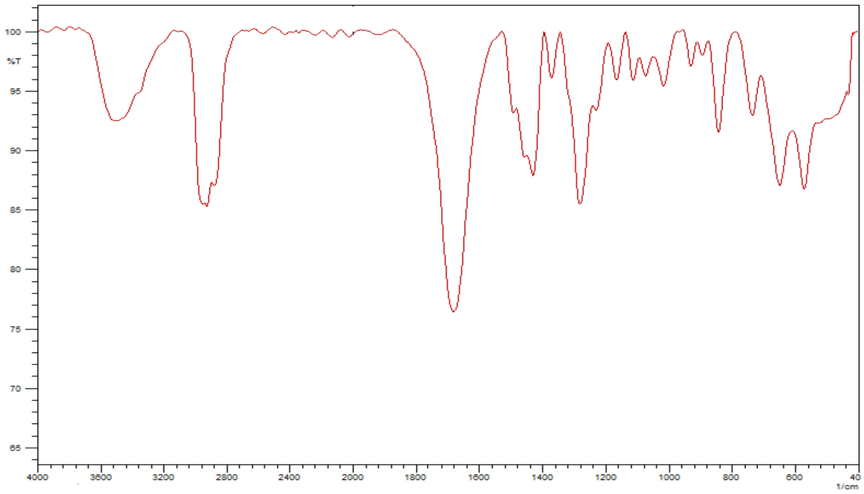


Figure 4.17. FT-IR spectrum of PVP.

Table 4.15. FT-IR data of PVP

Type of vibration	Wavenumber/cm^{-1}	
	A (this work)	B (literature)[78]
C=O stretching of amide	1680	~1680
C-H stretching	2800-3000	2800-3000
C-H bending	1430-1495	1450
C-N stretching	1286	~1300

4.4.2. Characterization of copolymers

The Fourier Transform Infrared spectra of copolymers of Acrolein with NVP having different mole ratios are shown in Figure 4.18. Carbonyl groups of aldehyde and amide group were overlapped consecutively, so carbonyl group of pyrrolidone rings was indicated by the broad absorption peak at 1680 cm^{-1}. But overlapped carbonyl peaks of amide and aldehyde groups split in A74NVP26 copolymer, depending on the acrolein content in copolymer. Also the peak at 3300 cm^{-1} was due to C-H stretching of acrolein and NVP units. Moreover, the intensity of a broad band between 1000-1200 cm^{-1} characterizing the –C-O-C- bonds of cyclized aldehyde increases when aldehyde content of copolymer is increased.

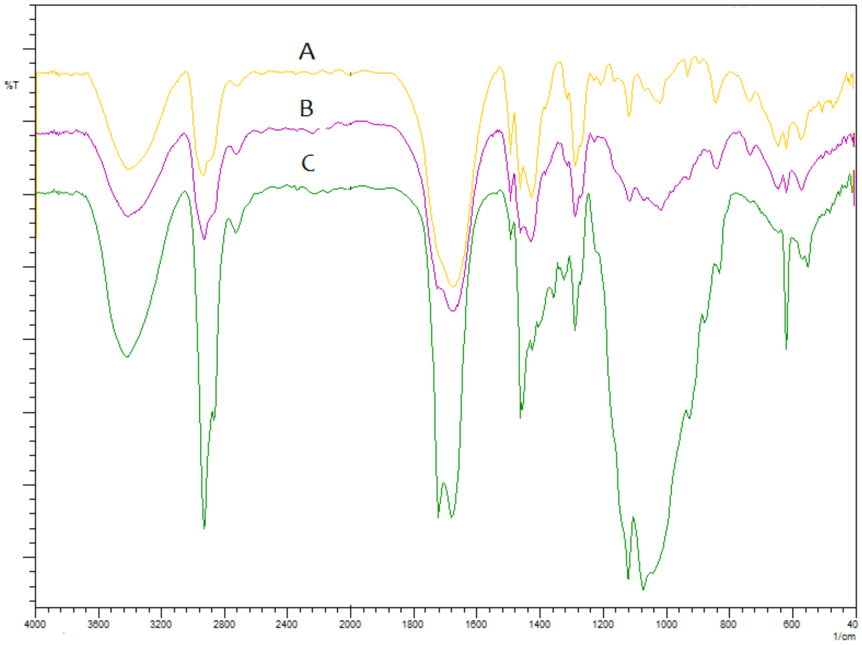


Figure 4.18. FTIR spectra of copolymers A) A58/ NVP 42 B) A62/NVP38 C) A74/NVP26.

Table 4.16. FT-IR data of poly (acrolein-*co*-vinyl pyrrolidone)

Type of vibration	Wavenumber/cm^{-1}
	A (this work)
C-H stretching	2950
Aldehydic C-H stretching	2719
C=O stretching of amide	1680
C=O stretching of aldehyde	1720
C-H bending	1495-1430
C-N stretching	1286

To determine the monomer reactivity ratios, five sets of copolymers were synthesized with <10% conversion (Figure 4.19).

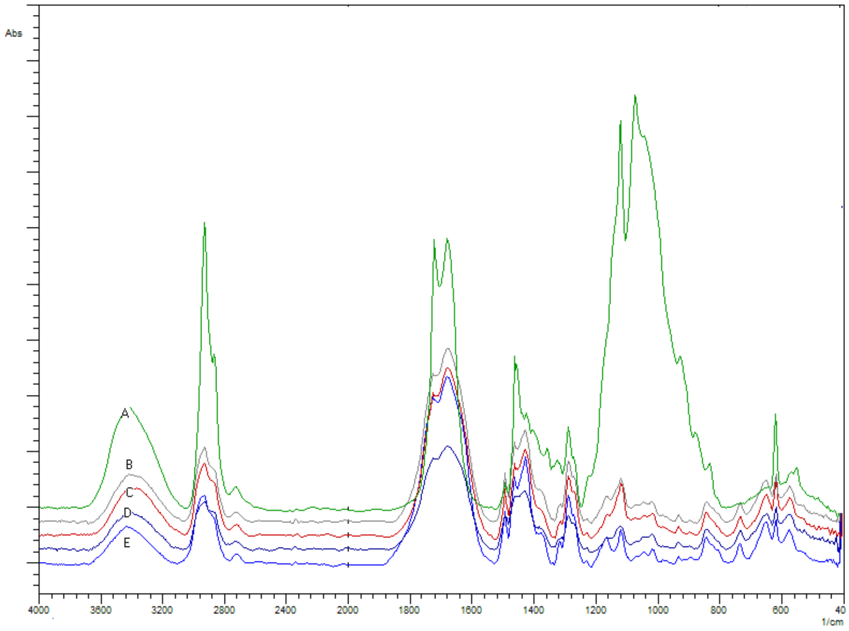


Figure 4.19. FTIR spectra of copolymers (less than <10% conversion).

A) A74/NVP26 B) A64/ NVP 36 C) A62/NVP38 D) A60/NVP40

E) A58/ NVP 42.

4.4.3. Characterization of phenylhydrazone derivative of copolymers

FTIR spectra of phenylhydrazone derivative of copolymers A58/NVP42, A62/NVP38 and A74/NVP26, are shown in Figure 4.20. The absorption band around 1720 cm^{-1} which was the characteristic band belonging to aldehyde groups of acrolein unit disappeared in comparing with the FTIR spectra of unmodified copolymers, in Figure 4.18. This result implied that most of free aldehyde groups in copolymers were converted to phenylhydrazone moieties. Further, the absorption peak at 1650cm^{-1} was due to C=N stretching band of the hydrazone group , peak at 2900 cm^{-1} aliphatic (-CH_2-), and 1600 cm^{-1} (C=C) for aromatic ring of phenyl groups. Absorption peak at 3400 cm^{-1} was because of absorbed water or hydrated aldehyde group (-OH), peak at 3300 cm^{-1} belonged to stretching vibration of hydrazone group (-NH-), and peak at 3050 cm^{-1} was due to aromatic (-CH-) vibration. A wide absorption band at 1650 cm^{-1} was due to overlapping of C=N stretching band of the hydrazone group and C=O stretching of amide group of PVP units.

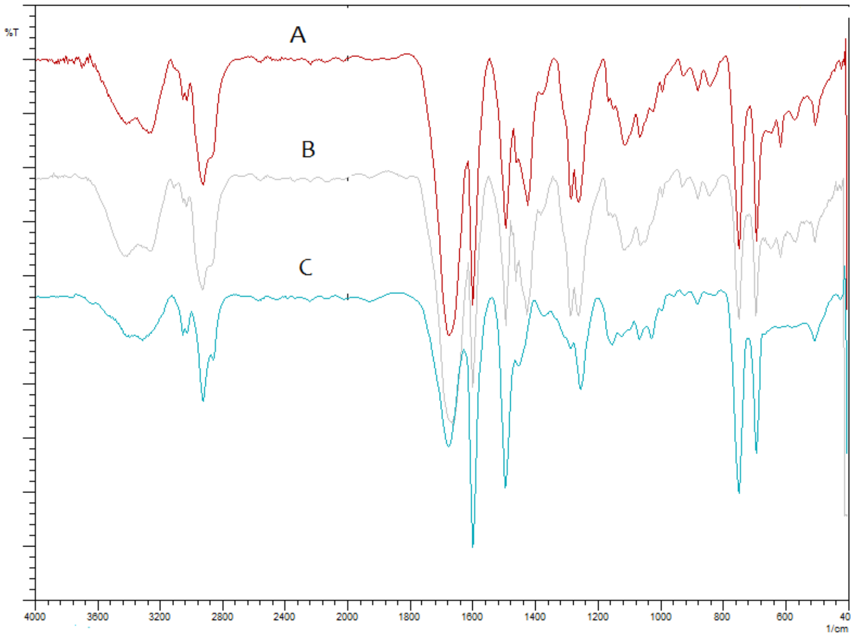


Figure 4.20. FTIR spectra of A) phenylhydrazone derivative of copolymer A58/NVP42 B) phenylhydrazone derivative of copolymer A62/NVP38 C) phenylhydrazone derivative of copolymer A74/NVP26.

4.4.4. Characterization of oxime derivative of copolymers

FTIR spectra of oxime modified of copolymers A58/NVP42, A62/NVP38 and A74/NVP26, are shown in Figure 4.21. Both the absorption band around 1720 cm^{-1} belonging to aldehyde groups of acrolein units and the asymmetric stretching band of the C-H of aldehyde groups at 2719 cm^{-1} also disappeared in comparing with the FTIR spectra of unmodified copolymers, in Figure 4.18. This result implied that most of free aldehyde groups in copolymers were converted to oxime moieties. There were absorption bands in the 3450 cm^{-1} (-OH), 2940 cm^{-1} (-CH$_2$-), 900 cm^{-1} (-N-O-) regions. A wide absorption band at 1650 cm^{-1} was also due to overlapping of C=N stretching band of the oxime group and C=O stretching of amide group of PVP units.

Further, it was observed that the peak intensities belonging to (-N-O-) and –C=N of oxime group increased when acrolein content in copolymers increased.

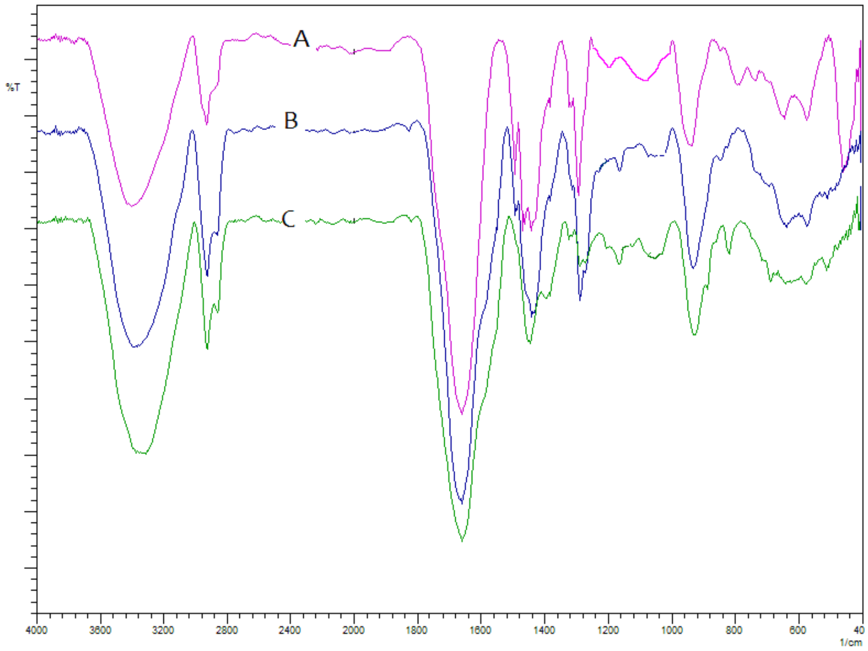


Figure 4.21. FTIR spectra of A) oxime derivative of copolymer A58/NVP42

B) oxime derivative of copolymer A62/NVP38

C) oxime derivative of copolymer A74/NVP26.

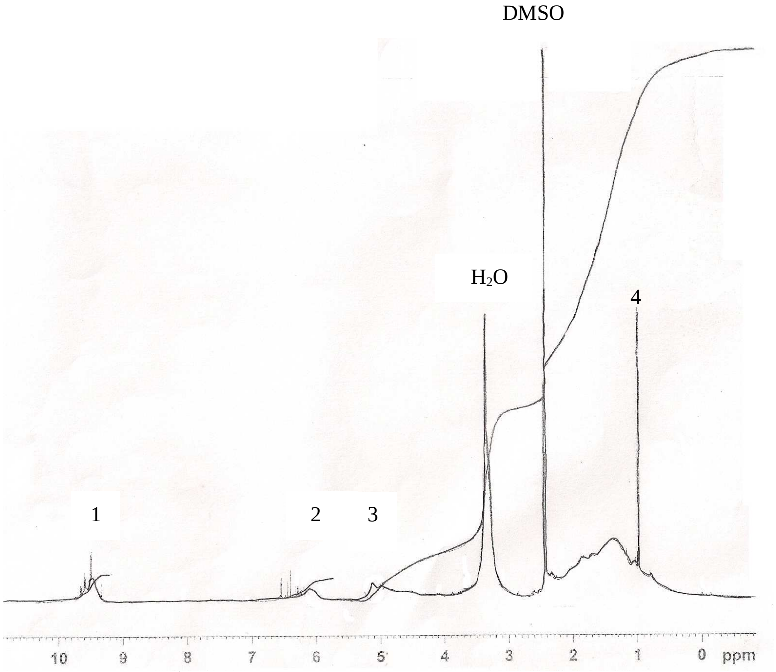
4.5. NMR Characterization

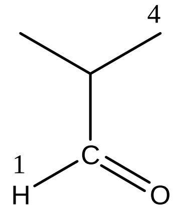
^{1}H and ^{13}C NMR spectra were used to elucidate the structure of homopolymers, copolymers and modified copolymers.

4.5.1. ^{1}H-NMR Characterization

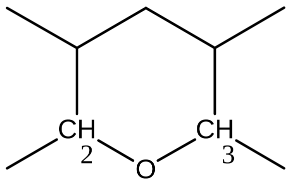
4.5.1.1. Characterization of homopolymers

^{1}H NMR spectrum of polyacrolein is shown in Figure 4.22. The peak at δ = 9.3 ppm was assigned to the aldehyde group proton, but the peaks at 6.3 ppm and 5.0 ppm belonged to ether group protons in the polymer [80]. The presence of these peaks implied that soluble polymer contained structural units (I) and few of structure (II). The peaks at 1.30 and 2.05 ppm were assigned as the backbone protons of repeating units.





(I)



(II)

Figure 4.22. ^{1}H NMR spectrum of polyacrolein.

Figure 4.23 shows ^{1}H NMR spectrum of polyvinylpyrolidone. The peak at 1.80 ppm was assigned the -CH_2- backbone protons of the vinylpyrrolidone units. Protons of C_2 in pyrrolidone group appeared at 3.5 ppm .The peak at 2.10 ppm were attributed to methylene protons in C_4 group [81,82].

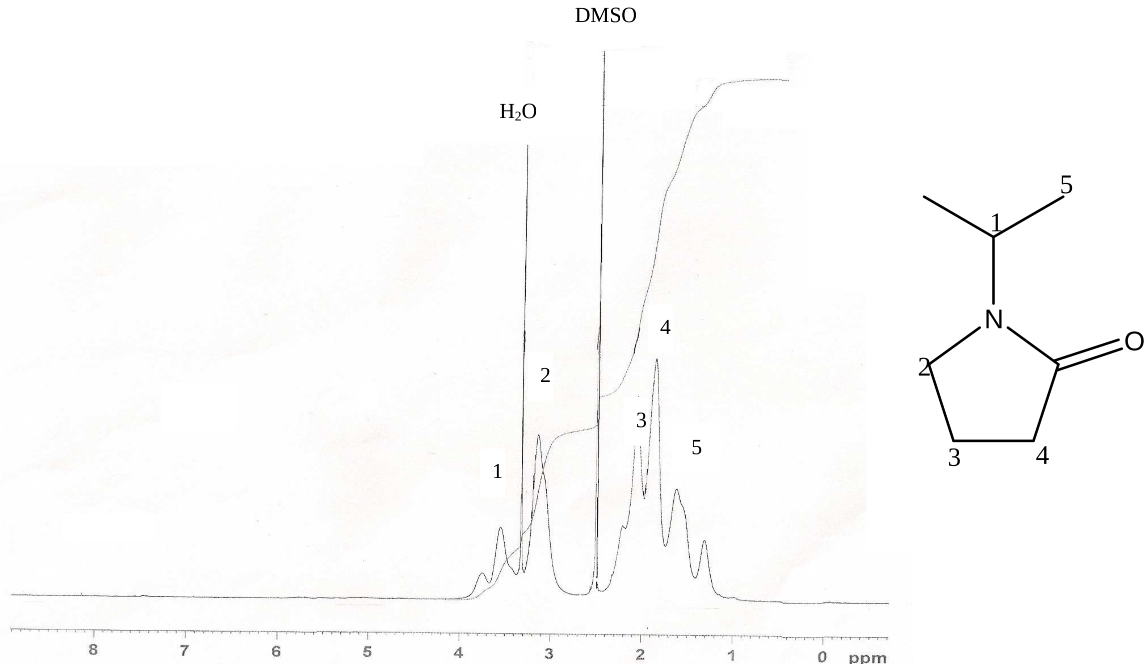


Figure 4.23. ^{1}H NMR spectrum of PVP.

4.5.1.2. Characterization of copolymers

^{1}H-NMR spectrum of the poly (acrolein-vinylpyrrolidone) (62:38) is shown in Figure 4.24. The peak at 9.6 ppm was assigned to the CHO group proton of the acrolein. The signals at 1.5 and 1.8 ppm were assigned to the -CH$_2$- backbone protons of the VP and acrolein. Resonance signal of –CH-N- protons (1) shifted to higher field, and so it was observed at 3.80-4.0 ppm due to the electronegative effect of nitrogen . Characteristic proton resonance peaks for all copolymers synthesized were observed at the same shift values, Figure 4.25.

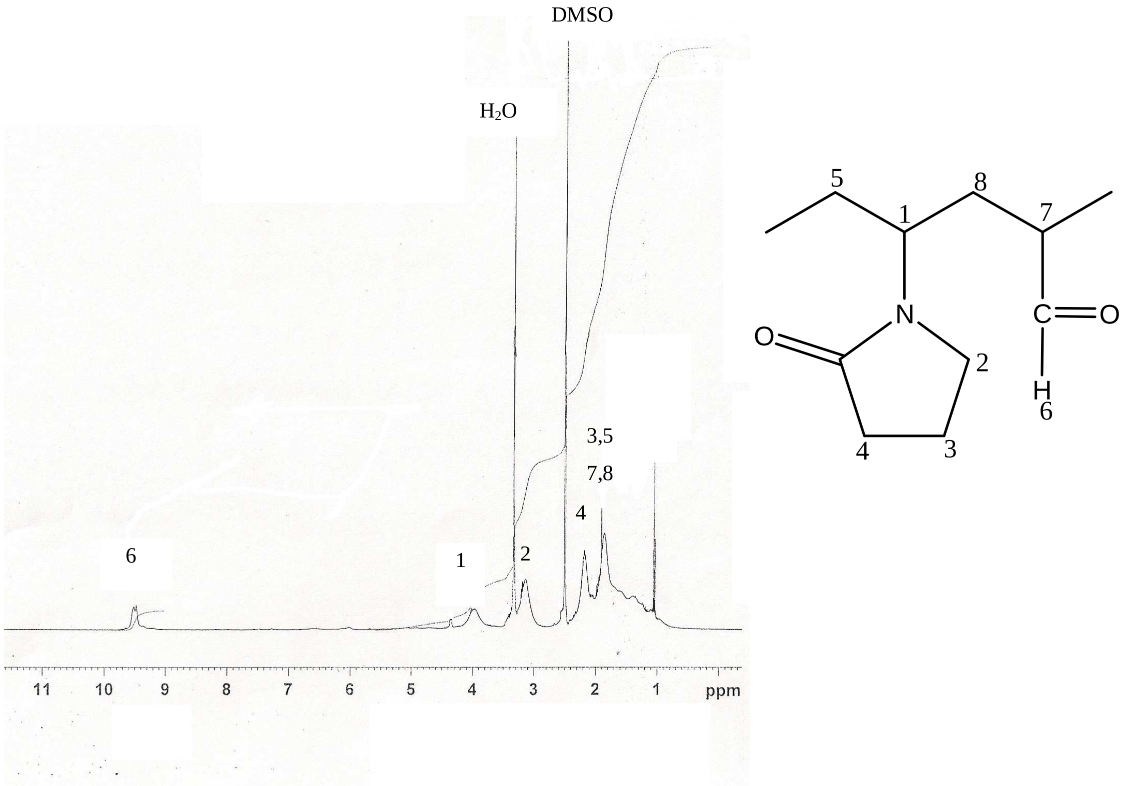
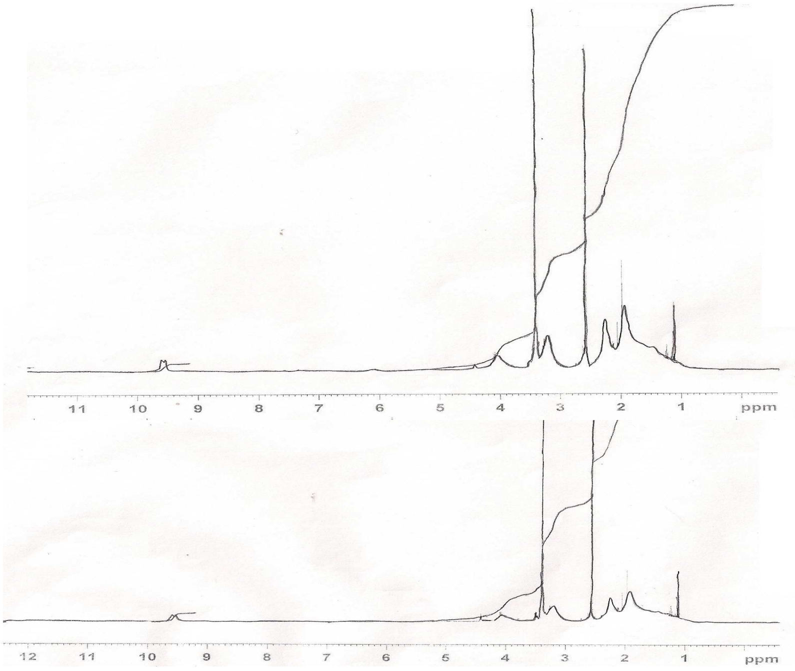
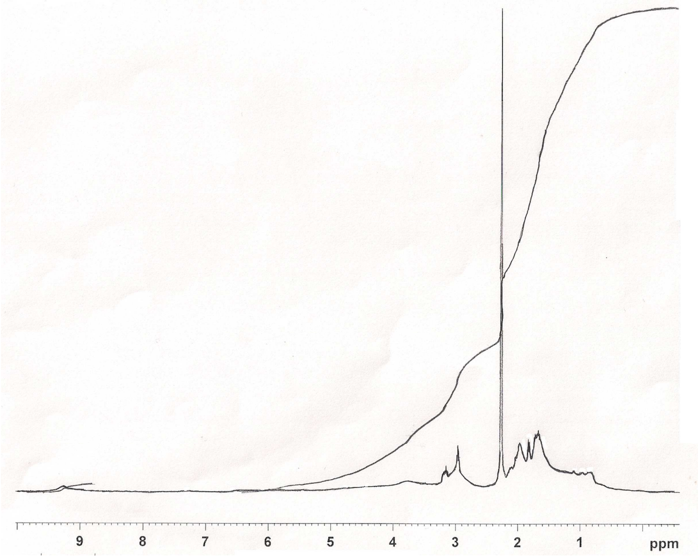


Figure 4.24. ^{1}H NMR spectrum of soluble fraction of A62/NVP38.

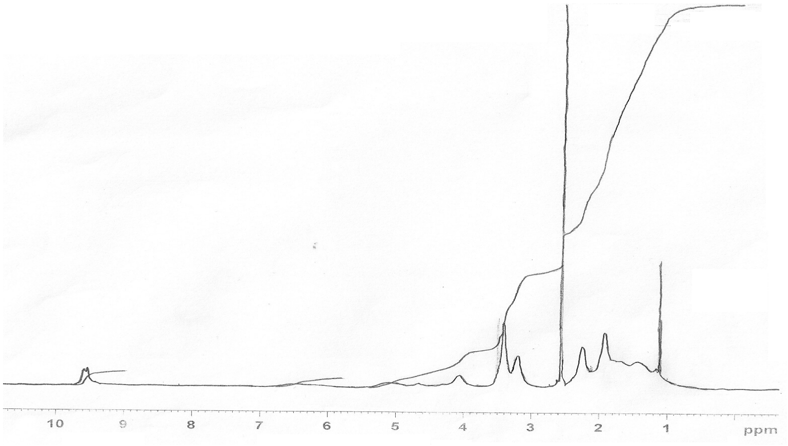


A58/NVP42
(A)

A60/NVP40
(B)



A64/NVP36
(C)



A74/NVP26
(D)

Figure 4.25. ^{1}H NMR spectra of soluble fraction of A) A58/NVP42 B) A60/NVP40 C) A64/NVP36 D) A74/NVP26 copolymers.

4.5.1.3. Characterization of phenylhydrazone derivative of copolymers

As a representative, Figure 4.26 shows the ^{1}H NMR spectrum of phenylhydrazone derivative of copolymer A74/NVP26. It was not observed any peaks around 9.5 ppm for aldehydic proton. This means that aldehyde group was almost converted completely to phenylhydrazone units. A broad peak at 7.2 ppm belonged to aromatic protons together with the protons bonded to nitrogen (10) and iminic carbon (6).

The peak at 1.3 ppm was assigned to the -CH_2- (8, 9) backbone protons of the VP and acrolein. The signal at 4.0 could be assigned to the protons (1,2) of NVP unit protons.

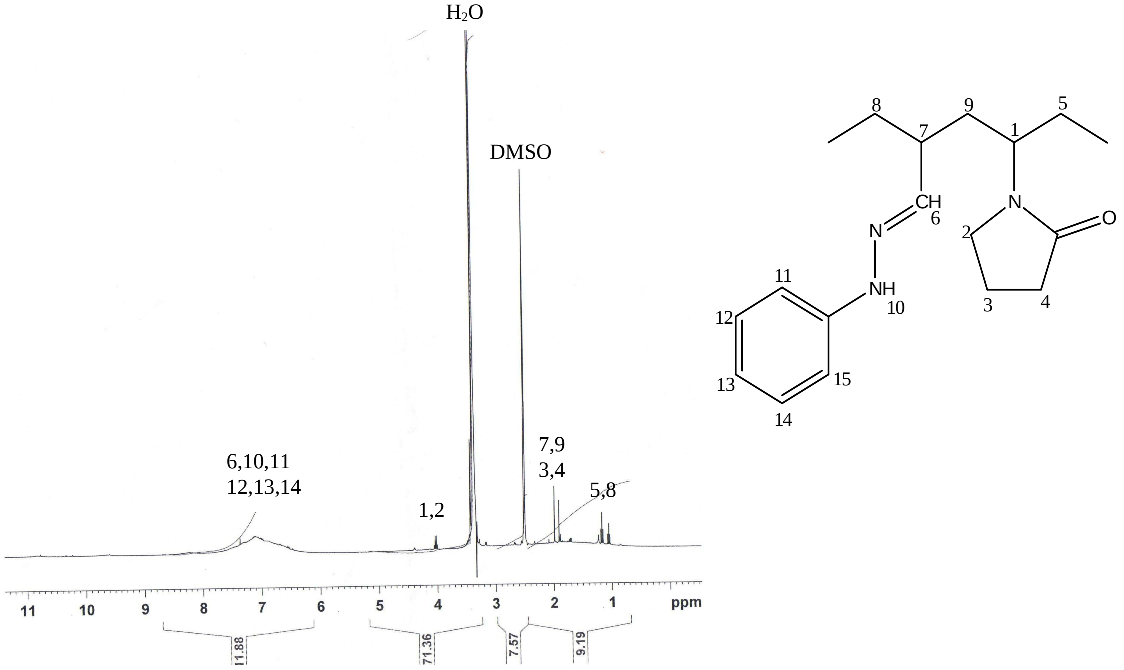


Figure 4.26. ^{1}H NMR spectrum of soluble fraction of phenylhydrazone derivative of copolymer A74/NVP26.

4.5.1.4. Characterization of oxime derivative of copolymers

As can be seen from Figure 4.27 the ^{1}H NMR spectrum of oxime derivative of A74/NVP26 copolymer. There was no peak at 9.5 ppm which belonged to aldehyde proton of acrolein unit. The peak at 10.2 ppm was assigned to the (-NOH-), 3.90 ppm (1), 3.2 ppm (2) (-N-CH-) (1), CH_2 of backbone protons of VP and Acrolein unit at 1.50 ppm.

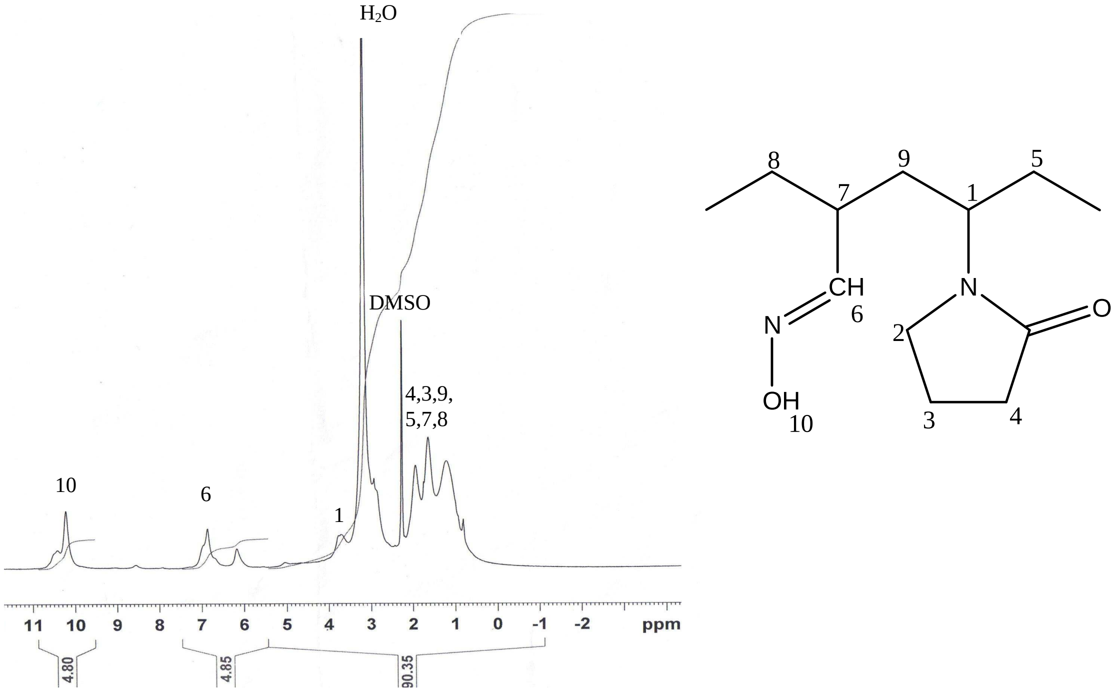


Figure 4.27. ^{1}H NMR spectrum of soluble fraction of oxime derivative of copolymer A74/NVP26.

4.5.2. ^{13}C-NMR Characterization

4.5.2.1. Characterization of homopolymer

The ^{13}C spectrum of polyacrolein is shown in Figure 4.28. The aldehyde carbon of the acrolein unit appeared at 210 ppm. But there was a peak at 79 ppm assignable to the unsaturated ether group protons in the polymer as seen below. This meant that polymer contained structural units (I) and few of structure (II) [83]. The backbone carbon gave a signal at 20 ppm and at 33 ppm respectively.

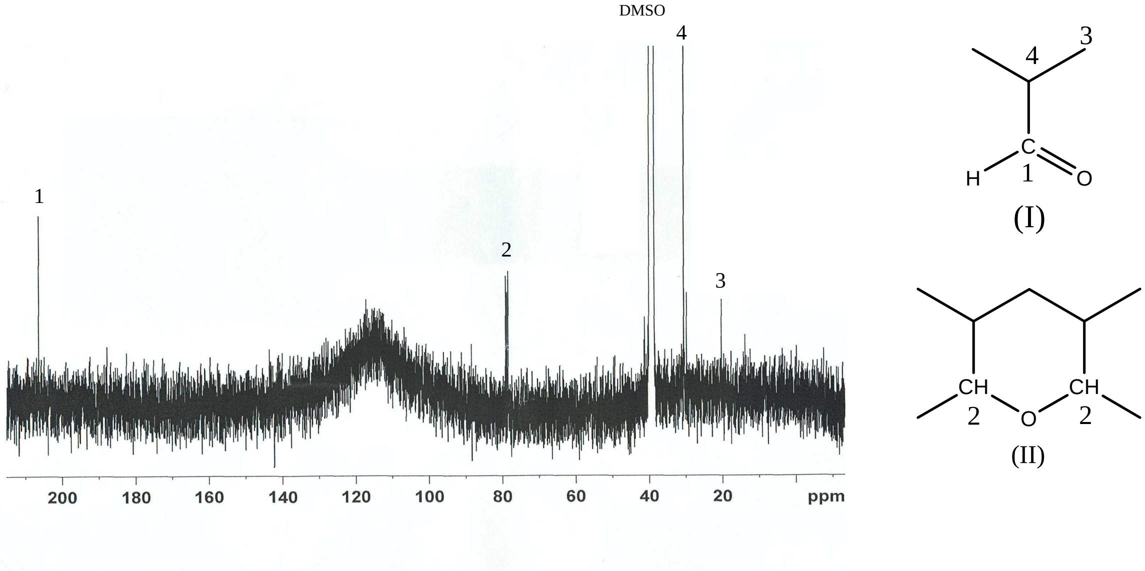


Figure 4.28. ^{13}C NMR spectrum of polyacrolein.

The ^{13}C spectrum of Polyvinlypyrrolidone is shown in Figure 4.29. The carbonyl group of the VP unit appeared at 175 ppm [84]. The backbone carbon gave a signal at 45 ppm and at 17 ppm respectively.

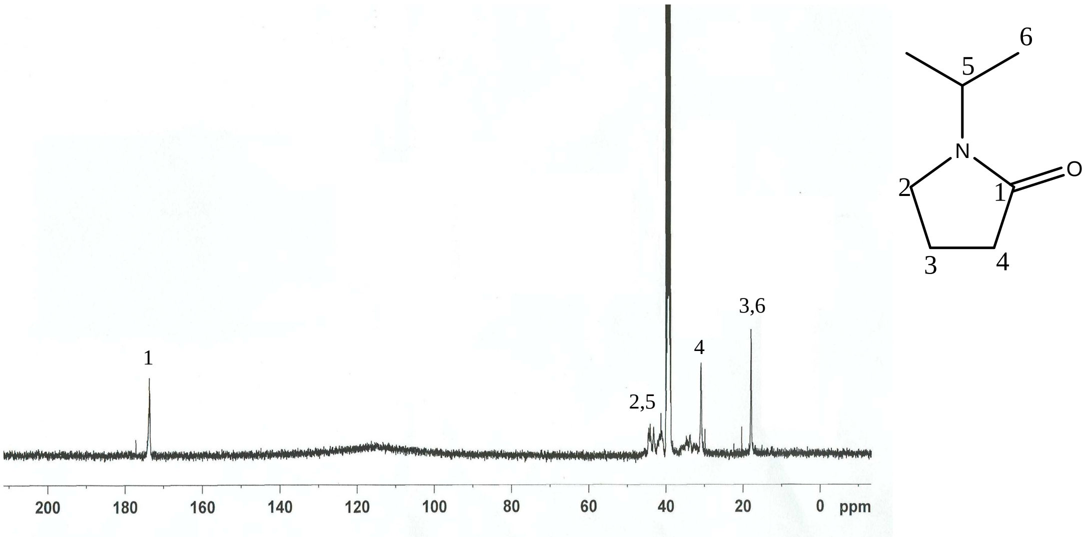


Figure 4.29. ^{13}C NMR spectrum of PVP

4.5.2.2. Characterization of copolymers

The ^{13}C spectra of copolymers are given in Figures 4.30-4.31. The ^{13}C spectra of the copolymers had the characteristics peaks of the monomer units but the chemical shifts assignments for the copolymer were based on the chemical shifts observed for the respective homopolymers. The amide carbon of the NVP unit gave at 175 ppm. The aldehyde carbon of the acrolein unit appeared at 210 ppm. The peak at 45 ppm shifted 55 ppm for the (-CH-) and (-N-CH-) correspond to the NVP unit.

Characteristic carbon-13 resonance peaks for all copolymers synthesized were observed at the same shift values, Figure 4.31**.**

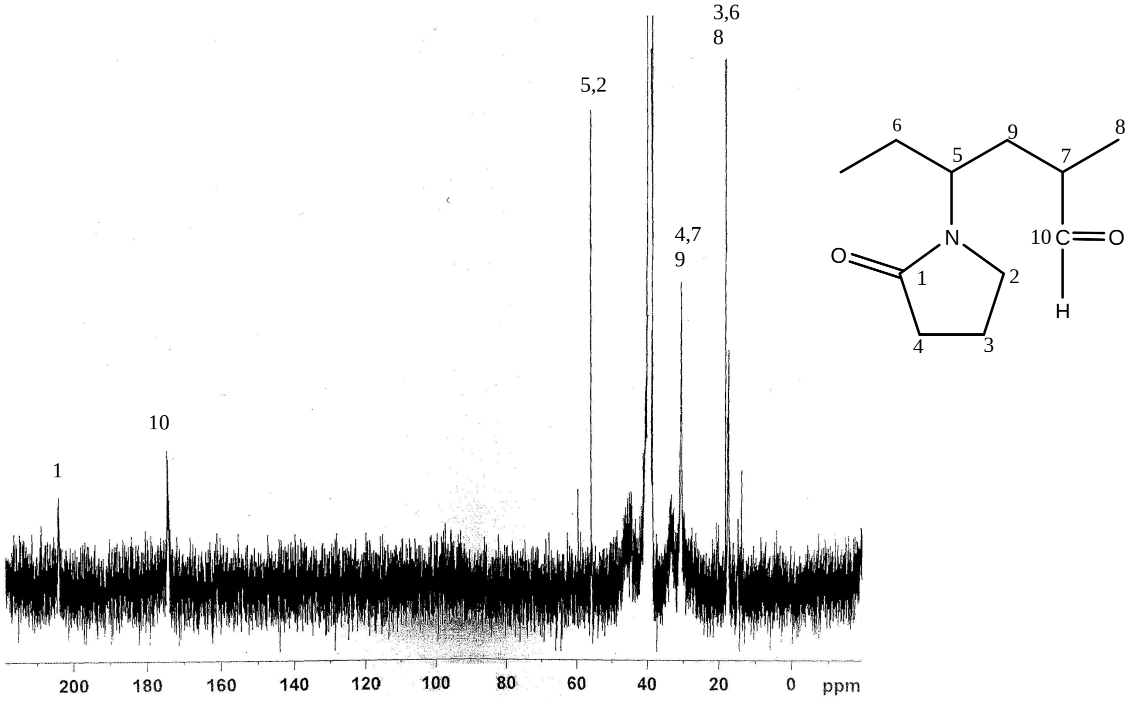


Figure 4.30. ^{13}C NMR spectrum of A74/NVP26 copolymer.

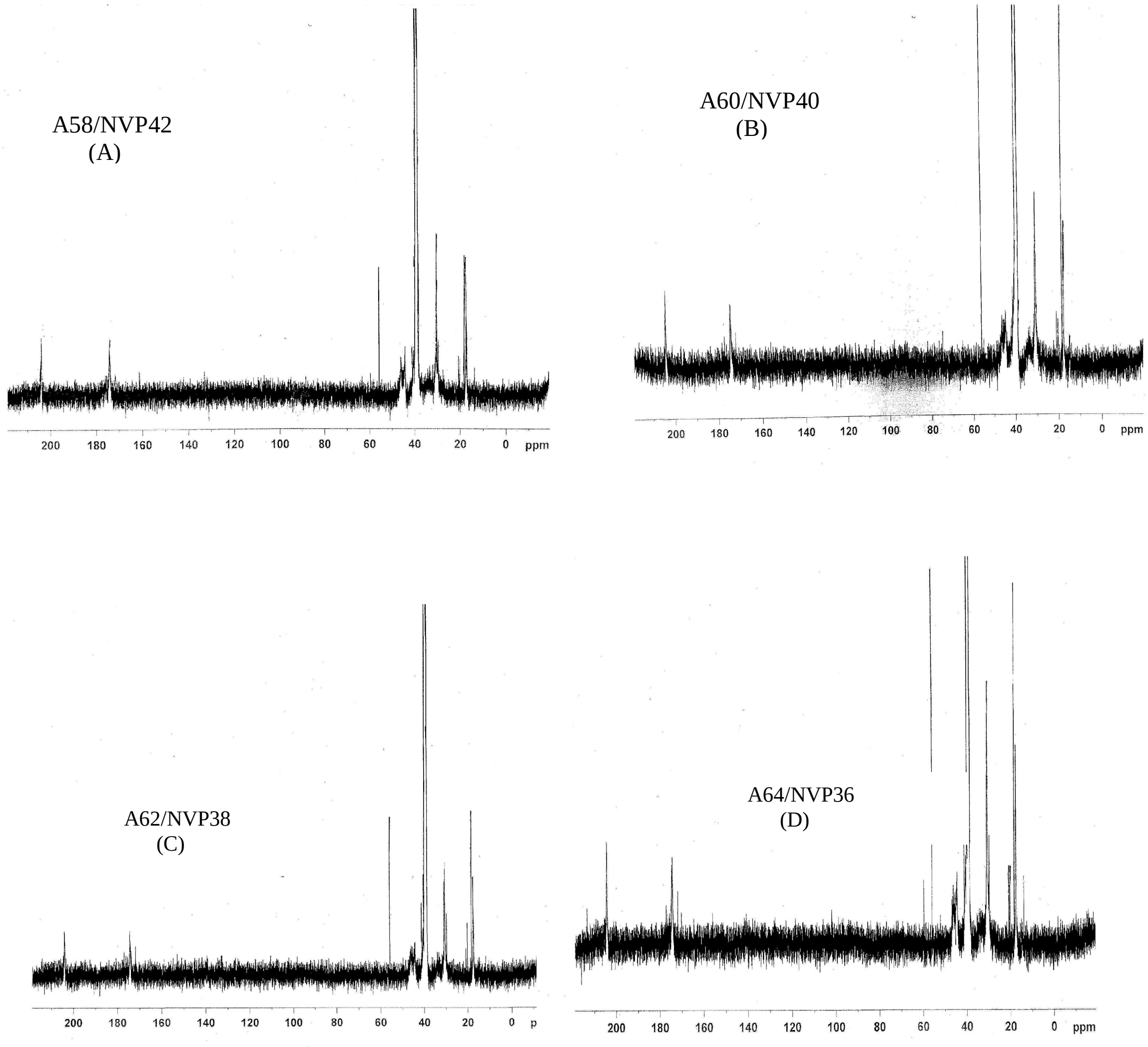


Figure 4.31. ^{13}C NMR spectrum of A) A58/NVP42 B) A60/NVP40 C) A62/NVP38 D) A64/NVP36 copolymers.

It was concluded that low solubility of copolymers in DMSO prevented to define a close relationship between peaks in both ^{13}C and ^{1}H NMR spectra, in order to calculate the copolymer composition and subsequently, the reactivity ratio of copolymers.

4.6. Thermal characterization

4.6.1. Thermogravimetric analysis

The thermal stabilities and the thermal degradation of samples were investigated by thermogravimetric analysis (TGA) in nitrogen atmosphere at a heating rate of 20 C/min.

4.6.1.1. Thermogravimetric analysis of homopolymers

The curve in Figure 4.32 shows three stages of decomposition, first stage begins at about 168^{o}C and ends at about 280^{o}C with weight loss about %15. The next stage ends at about 422^{o}C, with total weight loss about 55%, followed by third stage which is finished at about 631^{o}C. According to the literature [76] no chemical changes take place in polyacrolein up to 75-80^{o}C and the loss in weight that occurs in that temperature region is due to evaporation of traces of monomeric acrolein trapped by the polymer. This means that up to 80^{o}C a physical process occurs. Then, dehydration of hydrated aldehyde groups occurs in the region from 80^{o}C to 130^{o}C, A strong weight loss is observed at 130-180^{o}C by the degradation of pyrone ring structures in the polyacrolein. At temperatures of approximately 250^{o}C side carbonyl groups undergo thermal oxidation and decarboxylation with a considerable weight loss occurs, subsequently the main chain degrades at 350^{o}C [85].

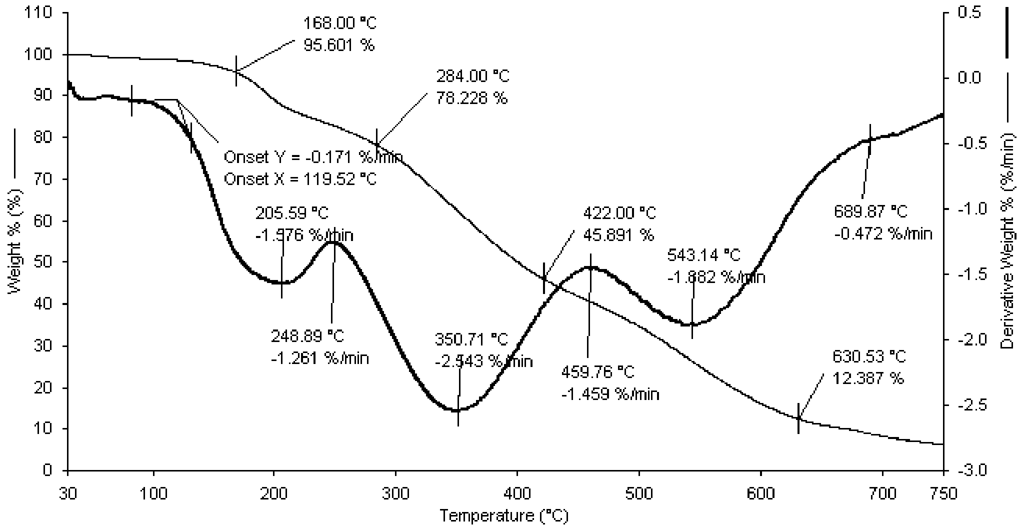


Figure 4.32. TGA curve of polyacrolein.

The TGA curve of polyvinylpyrolidone (PVP) is shown in Figure 4.33. The thermal degradation behavior of PVP is well known in the literature [79, 86]. It has high thermal stability and degrades in one stage, starting about 380^{o}C and ending at about 520 ^{o}C with T_{max} 480^{o}C and weight loss % 80.

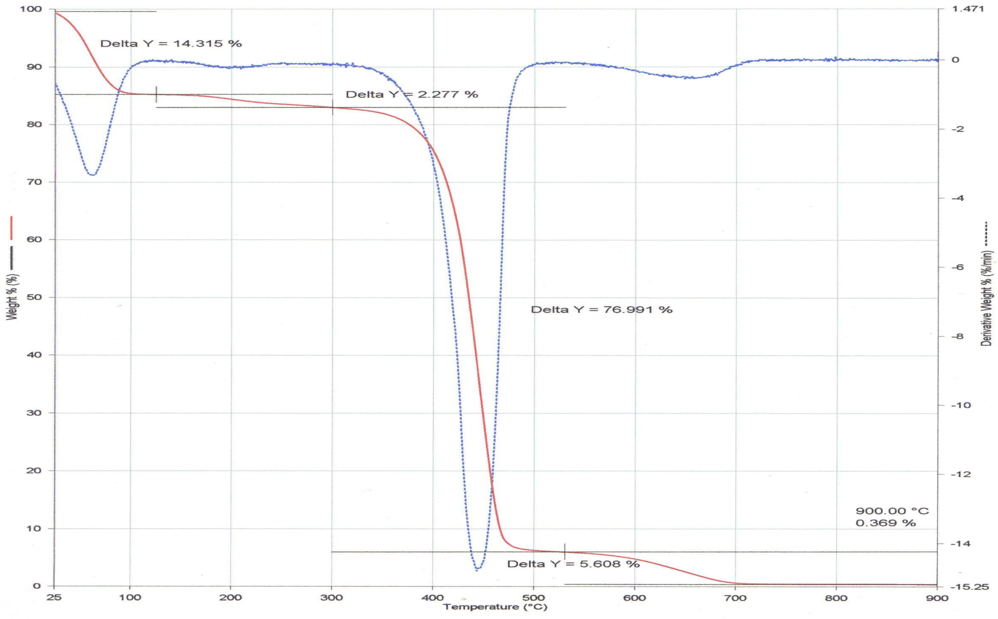


Figure 4.33. TGA curve of PVP.

4.6.1.2. Thermogravimetric analysis of copolymers

The TGA thermograms of (under 10% conversion) poly (acrolein-co-NVP) (58/42, 60/40, 62/38, 74/26 are shown in Figure 4.34 to 4.38. Copolymers of poly (acrolein-co-vinyl pyrrolidone) showed a similar thermal behavior like that of their homopolymers. Two degradation stages for the copolymers were observed. First stage began at about 258°C and ended at about 412°C with weight loss about 22%. The next stage started at 451°C and ended at 533°C giving a maximum peak at 505°C and 15% residue at 700°C.

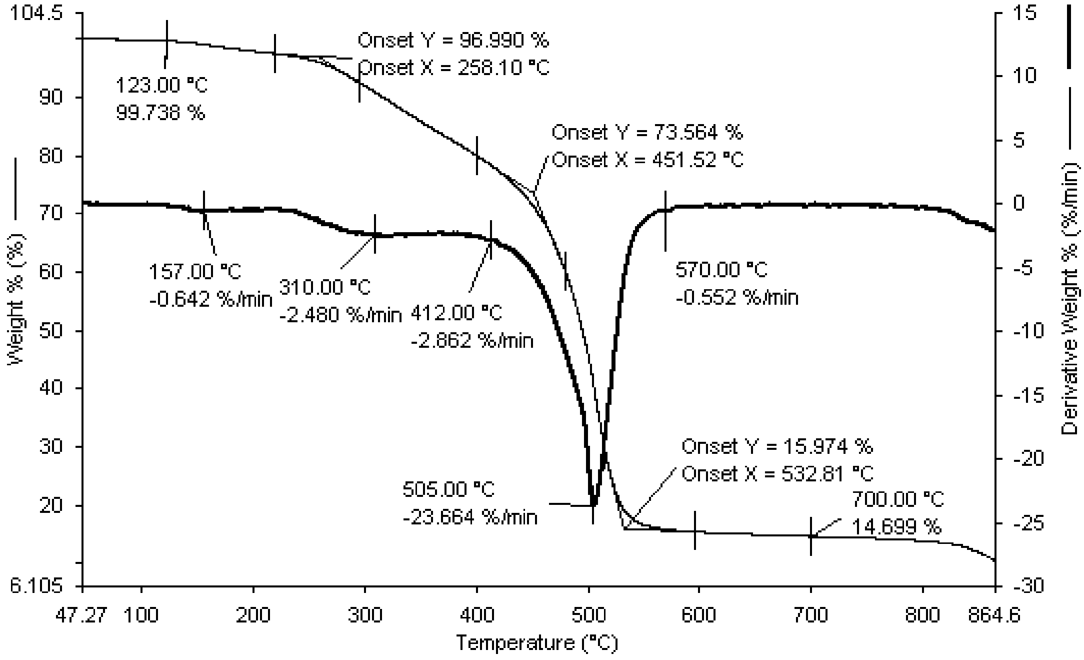


Figure 4.34. TGA curve of copolymer A58/NVP42.

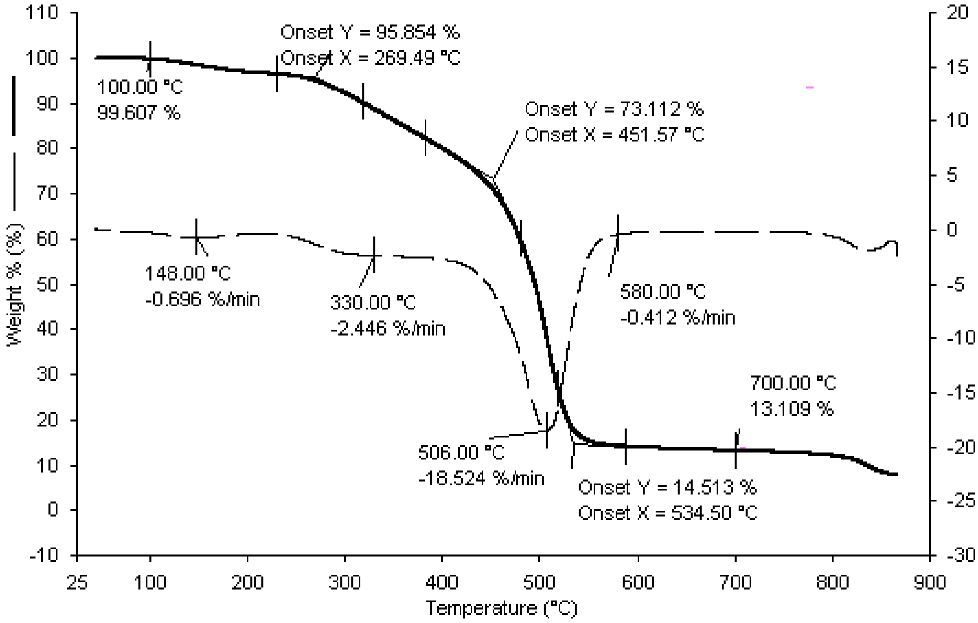


Figure 4.35. TGA curve of copolymer A60/NVP40.

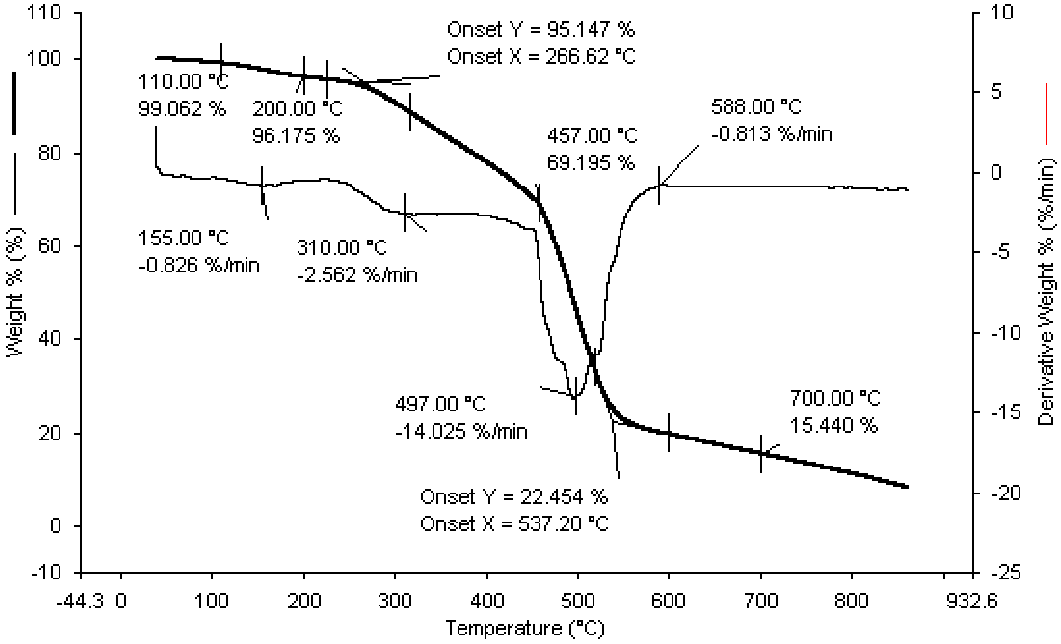


Figure 4.36. TGA curve of copolymer A62/NVP38.

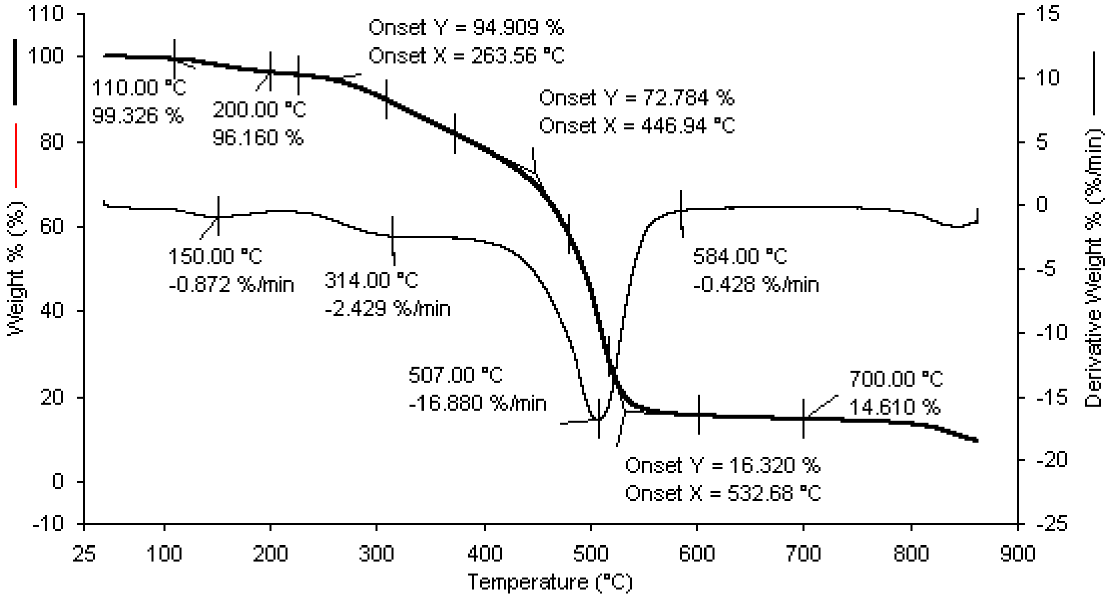


Figure 4.37. TGA curve of copolymer A64VP36.

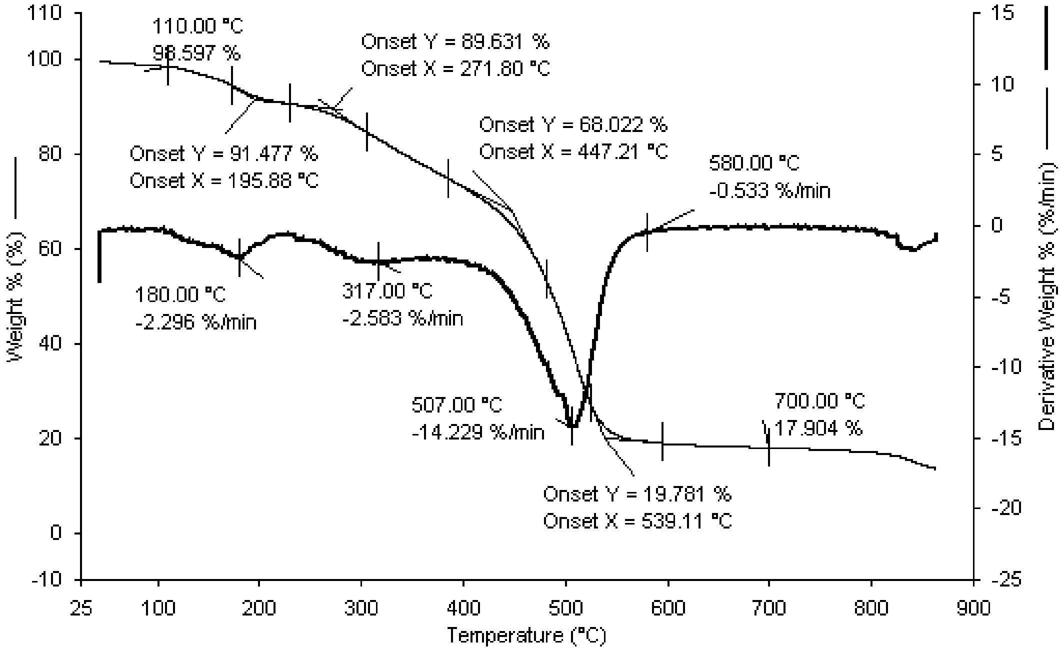


Figure 4.38. TGA curve of copolymer A74/NVP26.

Table 4.17. Thermal degradation behavior of homopolymers and copolymers

Polymer	First stage		Second stage		Third stage	
sample	T_{max} (°C)	wt loss(%)	T_{max} (°C)	wt loss (%)	T_{max} (°C)	wt loss (%)
Polyacrolein	205	15	350	55	543	90
A58/NVP42	310	22	505	84		
A60/NVP40	310	22	506	85		
A62/NVP38	310	22	497	78		
A64/NVP36	314	22	507	84		
A74/NVP26	317	20	507	80		
PVP	450	95				

No significant difference was noted in the decomposition temperature range of the prepared copolymers, as reported in Table 4.17. In addition, the result indicated that thermal stability of poly (acrolein-co-vinyl pyrrolidone) was higher than homopolymers.

4.6.1.3. Thermogravimetric analysis of phenylhydrazone derivative of copolymers

The TGA thermogram of phenylhydrazone derivative of copolymer A58/NVP42 is shown in Figure 4.39. The thermal degradation proceeds with two steps with maximum degradation temperatures at 288°C, 432°C. First step degradation started at about 230°C and ended around 342°C with weight loss about 33%. The next stage started at about 372°C and ended around at 468°C with weight loss about 76%.

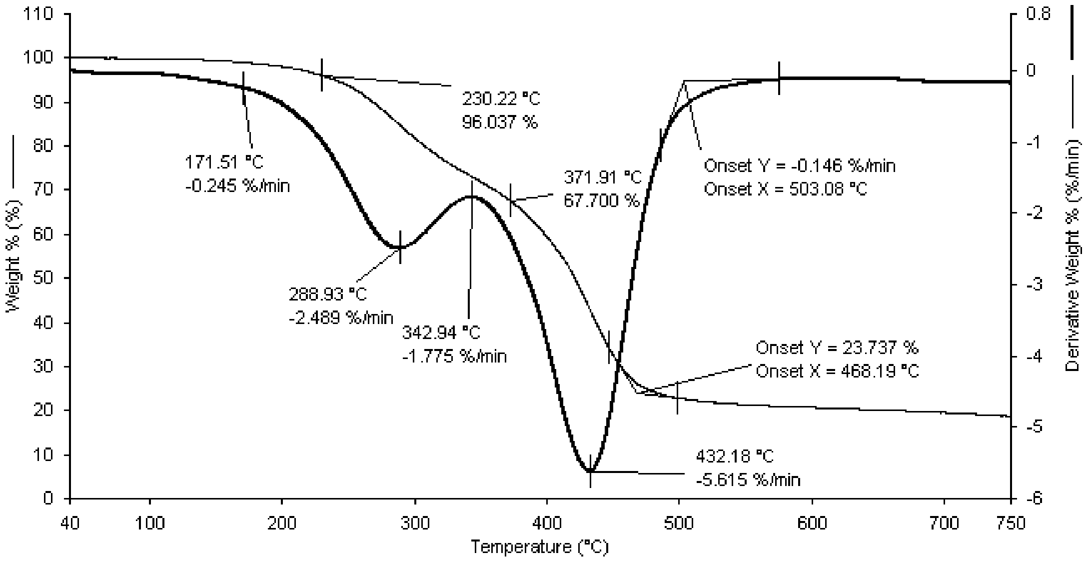


Figure 4.39. TGA curve of phenylhydrazone derivative of copolymer A58/NVP42.

The TGA thermogram of phenylhydrazone derivative of copolymer A62/NVP38 is shown in Figure 4.40. The thermal degradation proceeds with two steps with maximum degradation temperatures 299°C, 428°C. First step degradation started at about 180°C and ended around 354°C with weight loss about 33%. The next stage started at about 392°C and ended around 478°C with weight loss about 76%.

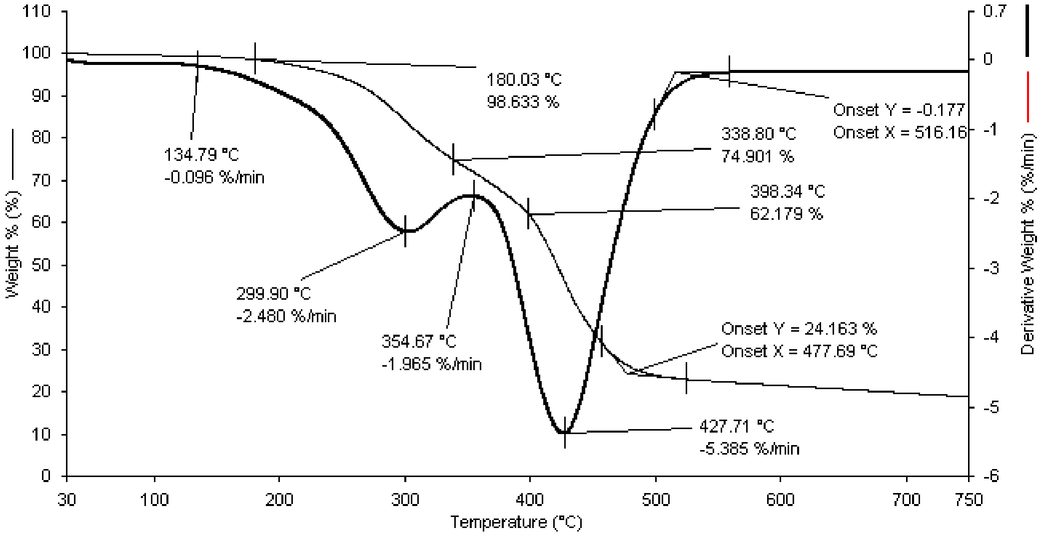


Figure 4.40. TGA curve of phenylhydrazone derivative of copolymer A62/NVP38.

The TGA thermogram of phenylhydrazone derivative of copolymer A74/NVP26 is shown in Figure 4.41. The thermal degradation proceeds with two steps with maximum degradation temperatures 270°C, 560°C. First step degradation started at about 238°C and ended around 361°C with weight loss about 30%. The next stage started at about 455°C and ended around 700°C with weight loss about 65%.

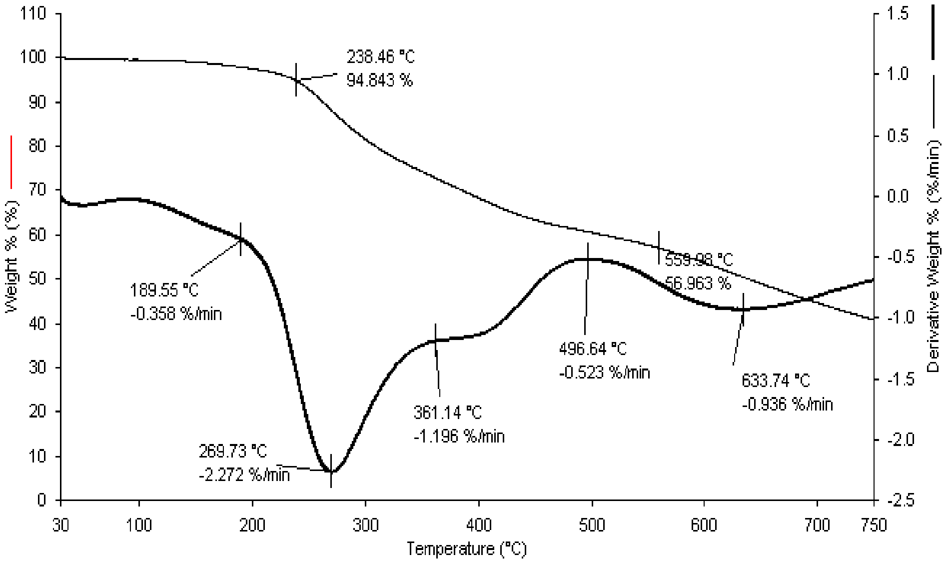


Figure 4.41. TGA curve of phenylhydrazone derivative of copolymer A74/NVP26.

4.6.1.4. Thermogravimetric analysis of oxime derivative of copolymers

The TGA thermogram of oxime derivative of copolymer A58/NVP42 is shown in Figure 4.42. The thermal degradation proceeds with two steps with maximum degradation temperatures 202°C, 433°C. First step degradation started at about 140°C and ended around 355°C with weight loss about 18%. The next stage started at about 404°C and ended around 491°C with weight loss about 33%.

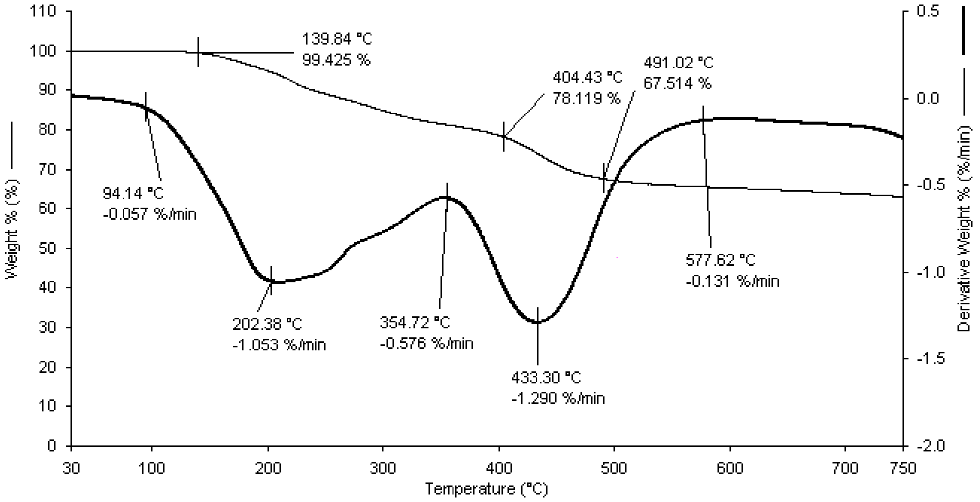


Figure 4.42. TGA curve of oxime derivative of copolymer A58/NVP42.

The TGA thermogram of oxime derivative of copolymer A62/NVP38 is shown in Figure 4.43. The thermal degradation proceeds with two steps with maximum degradation temperatures 212°C and 445°C. First step degradation started at about 130 °C and ended around 340°C with weight loss about 24%. The next stage started at about 402°C and ended around 519°C with weight loss about 51%.

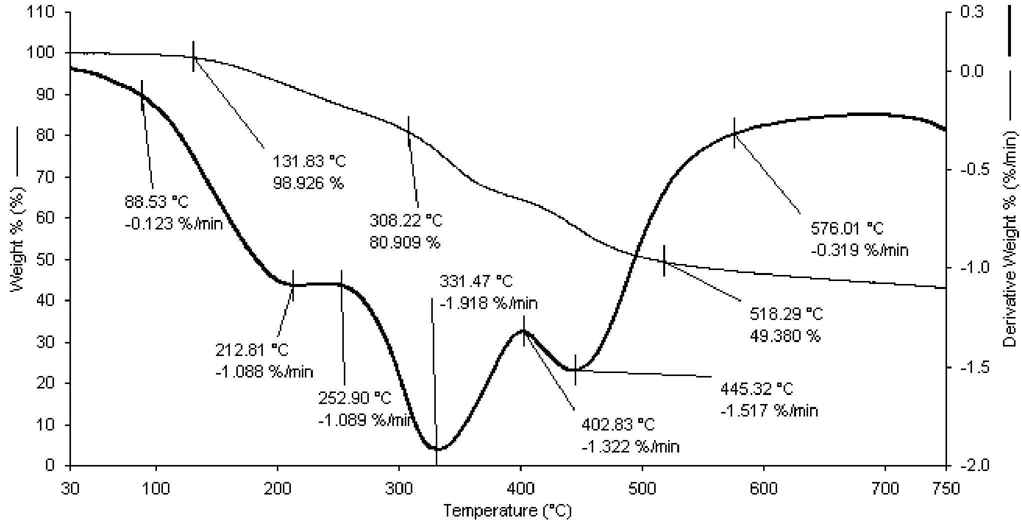


Figure 4.43. TGA curve of oxime derivative of copolymer A62/NVP38.

The TGA thermogram of oxime derivative of copolymer A74/NVP26 is shown in Figure 4.44. The thermal degradation proceeds with two steps with maximum degradation temperatures 247°C, 433°C. First step degradation started at 195°C and ended around 319°C with weight loss about %18. The next stage degradation started approximately at 390°C and ended around 480 °C with weight loss about %65.

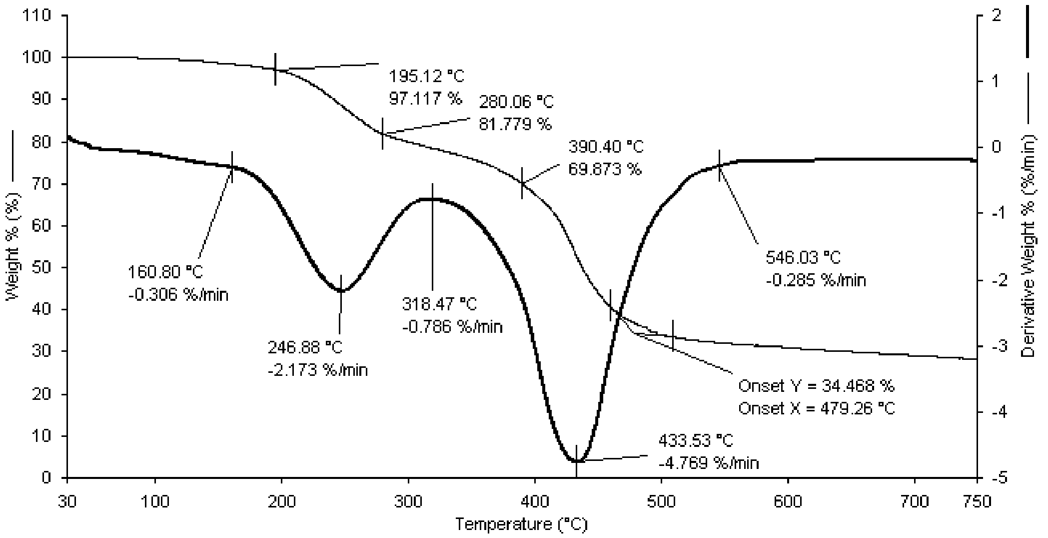


Figure 4.44. TGA curve of oxime derivative of copolymer A74/NVP26.

Thermal behavior of pristine and modified copolymers were given in Table 4.18

Table 4.18. Thermal degradation behavior of pristine and modified copolymers

*Pristine and modified copolymer	First stage		Second stage		Residue
	T_{max} (^{o}C)	wt loss (%)	T_{max} (^{o}C)	Total wt loss (%)	at 750^{o} C
A58/NVP42	280	22	456	85	12
A58/NVP42 oxime	202	18	433	33	62
A58/NVP42Hydrazone	288	33	432	76	18
A62/NVP38	294	55	456	92	8
A62/NVP38Oxime	212	24	445	51	46
A62/NVP38Hydrazone	299	33	422	75	18
A74/NVP26	290	30	436	74	20
A74/NVP26Oxime	246	18	433	66	28
A74/NVP26Hydrazone	270	30	560	65	24

* polymers at high conversion

It was noted that oxime derivative of copolymer gave higher residue than that of pristine copolymers and hydrazone derivative of it. Moreover, percent residue is inversely proportion to percent acrolein in oxime modified copolymers.

4.6.2. Differential scanning calorimetry analysis

4.6.2.1. Differential scanning calorimetry analysis of homopolymers

Differential Scanning Calorimetry (DSC) was performed at a heating rate of 10 ^{o}C/min under nitrogen atmosphere.

As can be seen in Figure 4.45, glass transition temperature (T_g) of polyacrolein was not determined. However Tg for polyacrolein is not reported in literature.

This result may be explained by formation of crosslinking polyacrolein which results in the restrictions of segmental motions of the polymer chain.

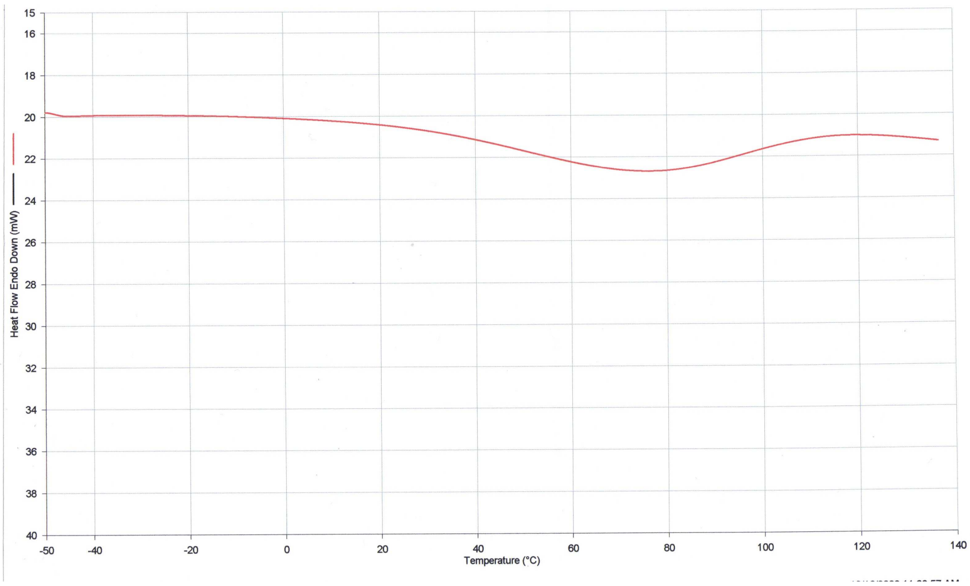


Figure 4.45. DSC curve of polyacrolein.

As shown in Figure 4.46, the Tg value of polyvinylpyrolidone is about 169 °C. This value agrees with the data reported in the literature [67].

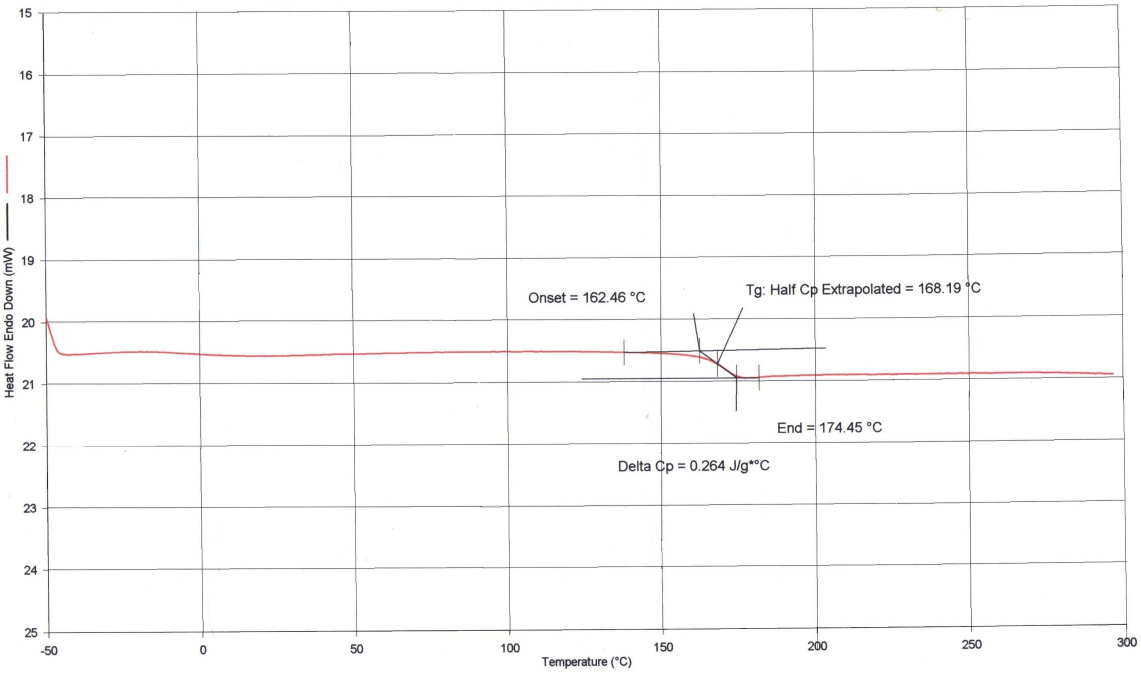


Figure 4.46. DSC curve of PVP

4.6.2.2. Differential scanning calorimetry analysis of pristine and modified copolymers

Differential Scanning Calorimetry (DSC) of copolymers and their derivatives were performed at a heating rate of 10 °C/min under nitrogen atmosphere. It was observed that both unmodified and modified copolymers showed no transition temperature. This situation indicated that the copolymers and modified copolymers exhibit crosslinked behaviors, as expected, because of the formation of inter and intra molecular –C-O-C- bond linkages in polymers and modified polymers.

4.7. Solubility of copolymers and their derivatives

The solubility behavior of copolymers and modified copolymers were tested in various polar and non-polar solvents and shown in Table 4.19.

Table 4.19. Solubility of copolymers and their derivatives

Polymer*	FA	DMF	DMSO	Pyridine	AA	NaOH (1M)	1.4 Dioxane	TCA	M
Polyacrolein	+	+	+	+	-	S	-	+	-
A74	+	+	+-	+	-	S	-	+	-
A74H	+	+	+-	+	+-	-	+	+	-
A74 O	+	-	+-	-	-	+-	-	+	-
A62	+-	+-	+-	+	S	S	-	+	-
A62H	+	+	+-	+	+	-	+-	+	-
A62 O	+	-	+-	-	S	+-	-	+	-
A58	+-	+-	+-	+-	S	S	-	+	-
A58H	+	+	+-	+-	+	-	-	+	-
A58 O	+	-	+-	-	S	+-	-	+	-
PVP	+	+	+	+	+	+-	-	+	+

FA: formic acid, DMF: Dimethylformamide, DMSO: Dimethyl sulfoxide, TCA:Trichloroacetic acid, AA: Acetic acid, M: Methanol O: Oxime, H:Hydrazone, +: soluble, +-: partially soluble, -: insoluble,S: swelling, * soluble at high temperature.

Polyvinylpyrolidone is soluble in water as well as in various solvents. The reason is, PVP has functional groups both hydrophilic and hydrophobic in character, thus, intermolecular interactions with various solvents are possible.

Polyacrolein is soluble in formic acid, DMF, DMSO and pyridine around 180^{o}C.

However polyacrolein are usually insoluble in water and many organic solvents, probably because of the existence of cyclic –C-O-C structure in the main chain. However it can be expected that copolymerization and/or chemical modification of the aldehyde groups can cause an increase in solubility, in many organic solvents, but did not. Particularly, results indicated that modification of copolymers did not considerably effect the in solubility behavior.

The copolymers have limited solubility in DMSO, in contrast to the readily soluble NVP and polyacrolein.

The poly(acrolein-co-vinylpyrrolidone) copolymers can only be dissolved efficiently in trichloroacetic acid at 180^{o}C, and partly soluble in aprotic polar solvents, such as DMF, DMSO and pyridine around 180^{o}C as well.

5. CONCLUSIONS

- The free radical copolymerization of N- vinylpyrrolidone (NVP) with acrolein at different feed ratios as carried out by using potassium persulfate ($K_2S_2O_8$), as an initiator in water at 65°C.

- The conversions of monomer mixtures to polymers were obtained in actual mole ratio (58/42, 62/38 and 74/26) at 65°C and for various time periods. The maximum conversions were obtained as 23%, 19% and 31% respectively, in 192 h.

- The copolymer composition was determined from the elemental analysis and FT-IR analysis of the copolymer. The reactivity ratio values were derived from the Fineman Ross (FR), Kelen Tüdos (KT), Extended Kelen Tüdos (E-KT), Mayo Lewis (M-L), and PREVM methods. The reactivity ratios values obtained by elemental analysis data results were compared with the data of FT-IR analysis. The reactivity ratios of acrolein and NVP were found as; $r_{1=}$ 0.44 and r_2= -0.082 (FR), $r_{1=}$ 0.47 and r_2= -0.065 (KT), $r_{1=}$ 0.46 and r_2= -0.064 (E-KT), $r_{1=}$ 0.49 and r_2= -0.065 (M-L), $r_{1=}$ 0.49 and r_2= -0.049 (PREVM). The values obtained in the linearization methods were in agreement with those of the nonlinear method. The 95% joint confidence limits confirmed that E-KT, KT and M-L more reliable. Also reactivity ratios were found by using FT-IR analysis data results were obtained by using data $r_{1=}$ 0.36 and r_2= -0.077 (FR), $r_{1=}$ 0.41 and r_2= -0.031 (KT), $r_{1=}$ 0.41 and r_2= -0.033 (E-KT), $r_{1=}$ 0.36 and r_2= -0.0010 (M-L), $r_{1=}$ 0.46 and r_2= 0.004 (PREVM).

These results indicated that the reactivity ratio of acrolein was greater than NVP. The higher value of acrolein confirmed the higher reactivity of acrolein than NVP.

- The carbonyl groups of Acrolein/ NVP copolymers A74/NVP26, A58/NVP42 and A62/NVP38 were modified by hydroxylamine and phenylhydrazone. It was found by elemental analysis that content of modification of copolymers at different reaction times, were close to each other. The maximum degree of modifications by hydroxylamine was obtained as 35%, 50% and 73% respectively, in 168 h. The maximum degree of modifications by phenylhydrazone was obtained as 27%, 30% and 39% respectively, in 168 h. The degree modifications of copolymers could be directly related to the free aldehyde group in copolymer, thus the degree of modification of copolymer A74/NVP26 was higher than the other of copolymers.

- The degree modification of the phenylhydrazone modified copolymers was much lower than oxime modified copolymers. These results arose from difficulty of the incorporation of phenylhydrazine molecules in to the copolymer, which was caused by larger size of phenylhydazine.

- FT-IR spectra reveal that PVP shows a strong C=O absorption peak from the amide group of the polymer at 1654 cm^{-1} and polyacrolein represents a strong C=O absorption peak from the aldehyde group of the polymer at 1720cm^{-1}. After copolymerization acrolein C=O absorption peak and C=O of NVP overlapped.

The FTIR spectra of phenylhydrazone derivative of copolymers gave the absorption peak at 1650 cm^{-1} which was due to C=N stretching band of the hydrazone group, 2900 cm^{-1} aliphatic (-CH$_2$-) regions, 1600 cm^{-1} (C=C) for aromatic ring of phenyl group. There were absorption bands in the 3450 cm^{-1} (-OH), 2940 cm^{-1} (-CH$_2$-), 900 cm^{-1} (-N-O-) regions in the FT-IR spectra after oxime modification of copolymers.

- The homopolymer, copolymer and their derivatives were evaluated by high-resolution ^{1}H and ^{13}C NMR spectra. The polyacrolein ^{1}H NMR spectra consisted of three groups of peaks: The first peak at 9.3 ppm represented CHO (aldehyde proton), the second peak 6.3 and 5.0 ppm belonged to ether group protons, the third broad peak between 1.30 with 2.05 ppm belonged to backbone protons of repeating units. The –CH-N- proton of VP appeared at 3.5 ppm. The chemical shifts assignments for the copolymer were based on the chemical shifts observed for the respective homopolymers. The peak at 7.2 ppm aromatic proton (-CH-), 7.0 ppm (-NHPh-) was observed in phenylhydrazone modified copolymers. The peak at 10.2 ppm being assigned to the (-NOH-) was observed in ^{1}H NMR spectra of oxime modified copolymers. Two characteristic peaks (210 ppm CHO in aldehyde group of acrolein unit, 175 ppm C=O in NVP unit) could be identified in the ^{13}C NMR spectra of the copolymers.

- Thermal stabilities of pristine and modified copolymers were also investigated by TGA method. Two maxima were observed for the thermal degradation of copolymers. Initial weight loss of about 20%, of the original weight between 140-340^{o}C which is assigned to the loss of aldehyde groups, the second stage of thermal degradation about 450^{o}C is attributed to the loss of NVP groups and the main chain polymer degradation.

- DSC thermogram of copolymers and their modified represented no significant glass transition temperature.

- Polyacrolein is soluble in formic acid, DMF, DMSO and pyridine around 180^{o}C. But polyacrolein are usually insoluble in water and many organic solvents, propably because of the existence of cyclic –C-O-C structure on the main chain. However it can be expected that copolymerization and/or chemical modification of the aldehyde groups can cause an increase in solubility, in many organic solvents. but did not. Particularly, results indicated that modification of copolymers did not considerably effect in the solubility behavior of.

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