POLYMERIZATION AND CHARACTERIZATION
OF
N-VINYL-2-PYRROLIDONE

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ŞULE ALTINSOY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
POLYMER SCIENCE AND TECHNOLOGY

SEPTEMBER 2009

Approval of the thesis:

POLYMERIZATION AND CHARACTERIZATION
OF
N-VINYL-2-PYRROLIDONE

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ABSTRACT

POLYMERIZATION AND CHARACTERIZATION OF N-VINYL-2-PYRROLIDONE

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September 2009, 62 pages

N-vinyl-2-pyrrolidone, NVP, was polymerized by γ-radiation in the presence of atmospheric oxygen and under vacuum at different periods. Polymerization also conducted by using chemical initiator, α, α'-Azoisobutyronitrile, AIBN, in bulk at different temperatures and times. The activation energy for polymerization was found from Arrhenius plot as 31,8 kJ/mol. By using the Fox-Flory equation $T_{g,\infty}$ and k values calculated for each polymerization methods. The polymer obtained was white gel type. The different types of polymer obtained were investigated by FT-IR, ^{1}H-NMR and ^{13}C-NMR, DSC, TGA and viscosity measurement methods. According to the FT-IR and NMR results, the polymerizations proceeded via vinyl group. As expected, solution viscosity measurements and DSC results showed that the glass transition temperature of polymer increases with increasing molecular weight.

Keywords: PVP, gamma radiation, free radicalic polymerization, characterization.

ÖZ

N-VİNİL-2-PİROLİDONE POLİMERLEŞTİRİLMESİ VE KARAKTERİZASYONU

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Yüksek Lisans, Polimer Bilimi ve Teknolojisi Bölümü

Tez Yöneticisi: Prof. Dr. Ali Usanmaz

Eylül 2009, 62 sayfa

N-vinil-2-pirolidon, NVP, atmosfer varlığında ve vakum altında γ-radyasyonuyla değişen zaman aralıklarıyla polimerleştirildi. Ayrıca, polimerleştirme kimyasal başlatıcı, α, α'-Azoisobutironitril, AIBN, kullanılarak farklı sıcaklıklarda ve periyotlarda balk olarak gerçekleştirildi. Polimerleşme için aktivasyon enerjisi Arrhenius grafiğinden 31,8 kJ/mol olarak bulundu. Fox-Flory denklemi kullanılarak her polimerleştirme tekniğinde elde edilen polimerler için $T_{g,\infty}$ ve K değerleri hesaplandı. Elde edilen polimerler beyaz ve kırılgan jel tipindeydi. Polimerlerin karakterizasyonu FT-IR, ^{1}H-NMR and ^{13}C-NMR, DSC, TGA ve viskozite ölçüm metotları ile yapıldı. FT-IR ve NMR sonuçlarına göre, polimerleşmenin vinil grubu üzerinden gerçekleştiği görüldü. Viskozite ve DSC sonuçları, bilindiği üzere polimerlerin camsı geçiş noktası artışının molekül ağırlığının artmasına bağlı olduğunu gösterdi.

Anahtar Kelimeler: PVP, gama radyasyon, serbest radikal polimerleştirmesi, karakterizasyon.

to the existence

ACKNOWLEDGEMENT

I would like to express my warmest gratitude to all who gave me the possibility to complete this thesis.

I am greateful to my supervisor Prof. Dr. Ali Usanmaz for his tremendous support and enabling me to take this Project.

I am indepted to my lab mates. Only with the help and assistance of Elif Vargün and advice of such scholars, it is possible to complete my experiments. I would like to thank to Selin Kozanoğlu for her invaluable hints and helps, Selda Keskin for her stimulating sugesstions, guidance, valued feedbacks and Bengi Aran for her encouragement and advice. Also, I would like to tank to Çiğdem Zeytin Derin for her supports.

I am also exteremely appraciative of the Chemistry Department and Central Laboratory staff for their help.

I would like to give an expression of appreciation for people who never accepting less than my best effort.

I would like to give my heartfelt thanks to my family for their love, support, interest and help.

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INTRODUCTION

1.1 N-VINYL-2-PYRROLIDONE

N-vinyl-2-pyrrolidone, NVP, is a yellowish heterocyclic, reactive vinyl monomer. The monomer contains an amide group on the substituents similar to acrylamides, the nitrogen is directly attached to the vinyl group, and thus the vinyl group is not conjugated with the carbonyl group unlike acrylamides (Figure 1).

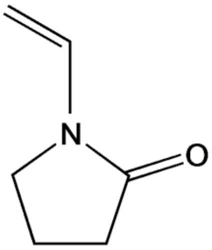


Figure 1 Structure of NVP

The properties of high polarity, low toxicity, water solubility, chemical stability and pseudo-cationic activity of NVP are imparted to its homopolymers and copolymers. The physical properties of NVP are given in Table 1.

Table 1 Physical properties of NVP

Property	Value
Boiling range, °C at 13 mbar	90 – 92
Melting point, °C	13.6
Density at 20 °C, g/ml	1.043
Flash point, °C	95
Viscosity at 20 °C, mPa.s	2.4

1.2 POLY(N-VINYL-2-PYRROLIDONE)

Poly(N-vinyl-2-pyrrolidone) PVP, PNVP, povidone, polyvidone, Luvitec®, Collidone®, Plasdone®, is a vinylic polymer.

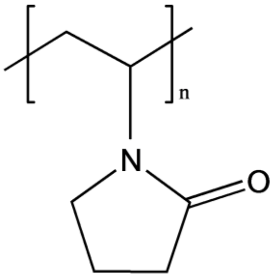


Figure 2 Structure of poly(N-vinyl-2-pyrrolidone)

PVP is a white, hydrophilic powder with a weak odor. In contrast to most polymers, solubility of PVP is a special property [1, 2, 3, 4]. The reason for this is, the polymer has hydrophilic as well as hydrophobic functional groups and therefore interactions with various solvents are possible. It is a polymer with a high solubilizing ability, due to the amide groups. Amide groups can solve small molecules by forming hydrogen bonds. It is insoluble in the less polar organic solvents as it can be seen from Table 2 [5].

PVP provides a remarkable combination of properties such as protection, adhesiveness [6], absorbency, solubilization, and condensation; its special features are excellent solubility, biological compatibility [7-11], and transparency [12]. PVP was an early plasma and blood volume extender [13, 14]. It is used extensively in pharmaceutical tablets [15-22] as soluble drug carriers [14]. Its complex with iodine is a germicide. It is used as a component in cosmetics, hair shampoos, and sprays and is a stabilizing agent for beer [23].

Hydrogels based on PVP [24] have been applied successfully as local dressings on wound treatments, such as burns, skin's ulceration. Furthermore, a hydrogel dressing prevents the wound from microbial contamination, inhibits the loss of body fluids, provides free flow of oxygen to the wound, and generally accelerates the healing process [25-27]. This is due to their high water content and soft consistency that is similar to natural tissue and also the polymer gels have a very low modulus of elasticity, and therefore cause minimal mechanical irritation [28].

The polymer is very stable in a wide temperature and pH range, which is due to the polyethylene polymer backbone. The solubility of PVP makes it good as a coating or as an additive to coatings as it can be blended with many polymers, in particular with polyacrylics. PVP can react by physical interaction with hydrogen dipolar links. Therefore, its low migration and crosslinkability give importance for manufacturing. Therefore, coated materials with this polymer can be used as medical devices intended for either transient or permanent implant in the human body [26].

Table 2 Solubility of PVP in various solvents [5]

Soluble in		**Insoluble in**
Water	Ethylenediamine	Ethyl acetate
Methanol	Di(ethylene glycol)	Acetone
Ethanol	Proplylene glycol	Dioxane
Propanol	1,4-Butanediol	Diethylether
Butanol	Glycerol	Pentane
Cyclohexanol	N-Vinylpyrrolidone	Cyclohexane
Chloroform	Triethanolamine	Carbon tetrachloride
Dichloromethane	Formic acid	Light petroleum
1,2-Dichloroethane	Propionic acid	Xylene
N-Metylpyrrolidone	Ethylenediamine	Mineral oil

Water-soluble polymers can be classified into two large groups; polyelectrolyte and neutral water-soluble polymers. Polyelectrolytes are soluble due to their charges and latters are soluble because of the hydrogen bonds with water [29].

Because of the differences in requirements, which polymers have to meet for these diverse applications, three types of PVP are offered, namely homopolymers, copolymers and crosslinked PVP [30,31].

1.2.1 Literature Survey

White et al. investigated the free radical bulk polymerization of NVP with an NVP-based crosslinker. The enthalpies of polymerization and rates of polymerization were determined for the polymerization at various temperatures [32, 33].

Haaf et al. obtained PVP by free-radical polymerization in solution [34, 35]. Molecular weight of the polymer was determined by the gel permeation chromatography, GPC. As a result, PVP having molecular weights (M_w) from 2500 to 1 million were obtained. According to this study, high molecular weight polymers have higher Tg values than the lower molecular weight polymers [5].

The oligomerization of NVP was performed in the presence of AIBN as radical initiator in solution at 80 °C by Ferruti et al. Viscosimetric measurements conducted for obtained oligomer of the PVP. However, molecular weights could not be calculated because of the low intrinsic viscosities of the samples [14].

Luo et al. synthesised low molecular weight of PVP by free-radical polymerization in solution. The degassed solution was polymerized at 85 °C for 24 h. Viscosity-average molecular weight (M_v) of the polymer was determined [36].

Solution polymerization of NVP by AIBN at 60 °C for 0,5 h studied by Ray et al. Gravimetrically 100% polymers were obtained and characterized by ^{1}H-NMR. GPC results showed that, polymers having low polydispersity indexes (PDI □ 1,1) and relatively low molecular weight polymers (Mn □ 15 000) were obtained [37].

Breitenbach experimented the effect of the impurities of PVP on polymerization and studied the polymerization of NVP in the presence and in the absence of AIBN as initiator. This study showed that the highly purified sample gives no thermal polymerization at 140 °C [38].

An investigation of atom transfer radical polymerization (ATRP) of NVP by using different initiators and catalyst at room temperature was carried out by Xiaoju et al. The resultant polymer had high conversion of up to 65% in 3 h and a narrow molecular weight distribution between 1.2 and 1.3 obtained [31].

Darwis et al. tried polymerization of NVP by gamma radiation. They investigated the effects of irradiation dose on the conversion of NVP with various concentration of aqueous solution. Results showed that the conversion of monomer to polymer was almost 100% at a dose of 2 kGy. [8, 39, 40, 41].

Gabor et al. conducted a study for molecular weight determination of PVP by viscosity methods [42, 43].

1.3 POLYMERIZATION OF N-VINYLPYRROLIDONE

NVP monomer polymerizes under free-radical conditions via bulk, solution, and suspension methods.

1.3.1 Free Radical Polymerization

In free radical polymerization, the radical attacks one monomer, and the electron migrates to another part of the molecule. This newly formed radical attacks another monomer and the process is repeated by the addition of large number of monomers. Free radical chain polymerization includes initiation, propagation and termination steps.

1.3.1.1 Initiation

In this step, AIBN, the initiator (I), dissociates to radical (R•) as shown in Figure 3.

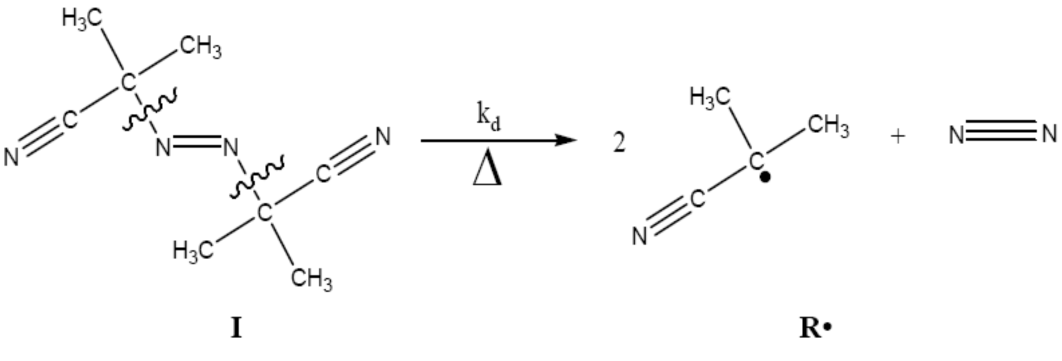
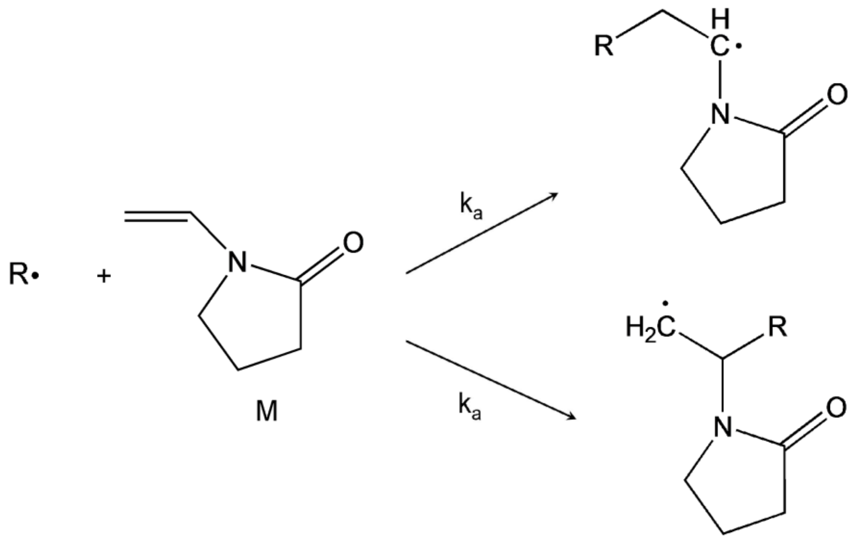


Figure 3 Dissociation of AIBN

After the generation of free radical, (R•) from an initiator, it attacks the monomer molecule NVP, (M) to form RM•. There are two possible models of addition:



(I)

(II)

Figure 4 Addition of NVP to the free radical

In free radical reactions, the reaction favored which produce more stable product. Therefore, radical (I) is favored for this reaction. Because radical (I) can be stabilized by the resonance effects of the substituent. Moreover, radical (I) is less sterically hindered compared to radical (II) [44].

1.3.1.2 Propagation

In the propagation step, series of reactions are involved in which the free radical at the end of the growing polymer reacts with the monomer to increase the length of the chain. More monomer units are added as in Figure 5.

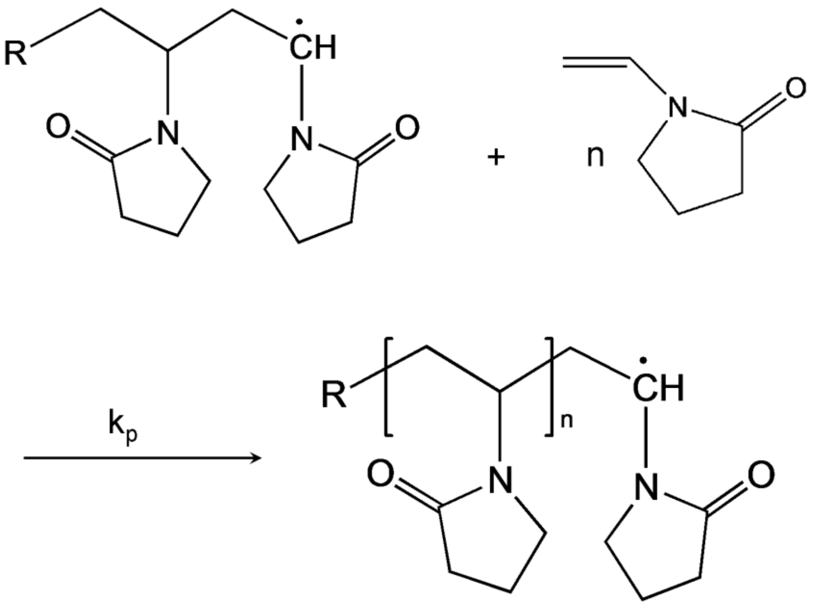
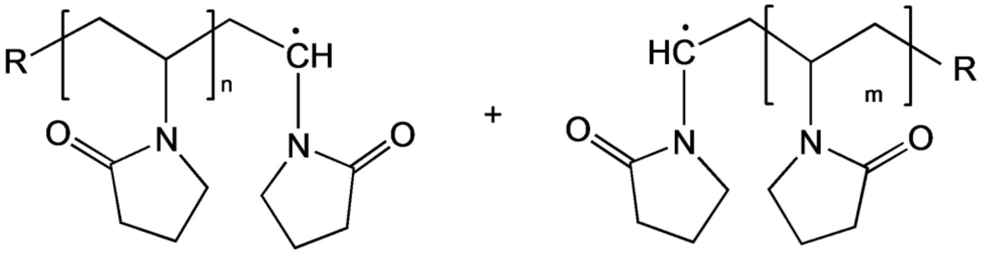


Figure 5 Growth of the polymer chain

1.3.1.3 Termination

In theory, the propagation reaction could continue until the supply of monomers is exhausted. However, most often the growth of a polymer chain is stopped by the termination reaction. Termination typically occurs in two ways: combination and disproportionation. Combination occurs when the growth of polymer is stopped by free electrons from two growing chains that join and form a single chain as shown in Figure 6.



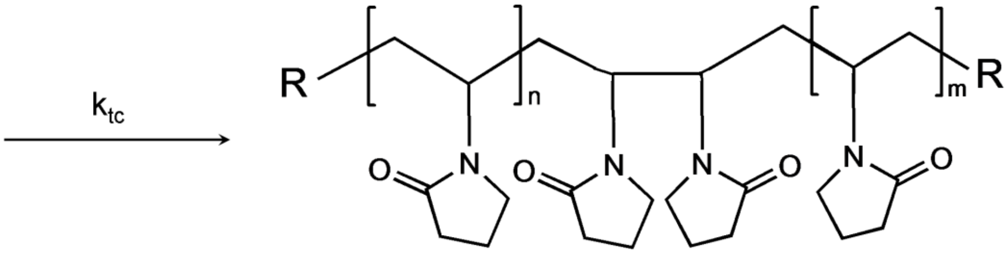
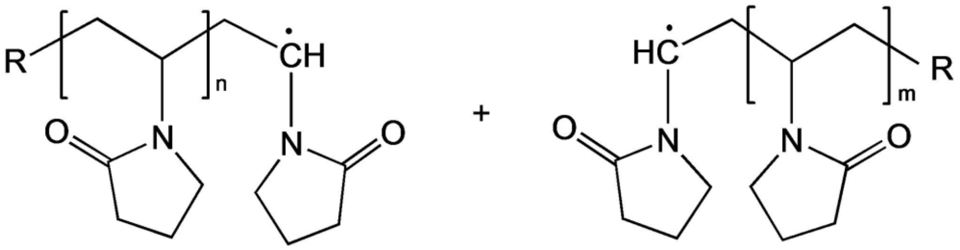


Figure 6 Combination of growing chains

Disproportionation stops the propagation reaction when a free radical transfers a hydrogen atom from an active chain. A carbon-carbon double bond takes the place of the missing hydrogen as indicated in Figure 7.



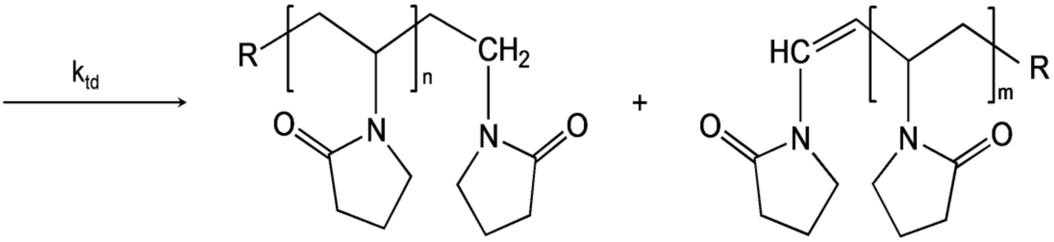


Figure 7 Disproportionation of PVP

1.3.2 Kinetics of Free Radical Polymerization

The rates of the three steps in free radical polymerization can be determined in terms of the concentrations of the species involved and the rate constants.

Initiation:

$$I \xrightarrow{k_d} 2R\bullet$$
$$R\bullet + M \xrightarrow{k_a} RM\bullet \qquad \textbf{(1)}$$

The rate determining step is the dissociation of the initiator and the rate of initiation is given by equation (2).

$$R_i = 2fk_d\,[I] = d[R\bullet]/dt \qquad \textbf{(2)}$$

where R_i is the rate of initiation, k_d is the dissociation rate constant, is the concentration of the initiator, and f is the initiator efficiency. Initiator efficiency, f is the fraction of radicals formed by equation (1) [44].

Propagation:

For the propagation stage, subsequent propagation steps are generalized in one reaction, as follows:

$$M_n\bullet + M \xrightarrow{k_p} M_{n+1}\bullet \qquad \textbf{(3)}$$

The radical reactivity is independent of the size of the growing polymer. Therefore a single rate constant is assumed to apply to subsequent steps. Major consumption of monomer is involved in the propagation stage, so the rate of monomer loss can be explained in term of rate of propagation:

$$R_p = k_p [M\bullet][M] = -d [M] / dt \qquad \textbf{(4)}$$

where k_p is the propagation rate constant.

Termination: Termination of the two chains occurs by combination or disproportionation (5).

$$\begin{aligned} M_n\bullet + M_m\bullet &\xrightarrow{k_{tc}} M_{n+m}\bullet \\ M_n\bullet + M_m\bullet &\xrightarrow{k_{td}} M_n + M_m \end{aligned} \qquad \textbf{(5)}$$

The overall rate of termination is given by equation (6).

$$R_t = 2\ k_{tc} [M\bullet] [M\bullet] + 2\ k_{td} [M\bullet] [M\bullet] = 2\ k_t [M\bullet]^2 \qquad \textbf{(6)}$$

where k_t is the overall rate constant for termination and is given by

$$k_t = k_{tc} + k_{td} \qquad \textbf{(7)}$$

At steady-state conditions rate of initiation and termination are equal, thus resulting in a steady-state concentration of free radicals, and so $R_i = R_t$ as in equation (8).

$$2f\ k_d [I] = 2\ k_t [M\bullet]^2 \qquad \textbf{(8)}$$

So the steady state total concentration of all radical species is given by

$$[M\bullet] = (f\ k_d [I] / k_t)^{1/2} \qquad \textbf{(9)}$$

Substituting equation (9) into (4) will give general rate expression:

$$R_p = -d\,[M] / dt = k_p\,[M]\,[I]^{1/2}(f\,k_d / k_t)^{1/2} \tag{10}$$

In the early stages of the polymerization, if the initiator efficiency is too high, the overall rate of polymerization is proportional to the square root of the initiator concentration. Moreover, it is proportional to the first power of the monomer concentration if f is independent of [M]. If the efficiency is very low, f might be proportional to [M], leading R_p proportional to $[M]^{3/2}$ [44].

1.4 MOLECULAR WEIGHT DETERMINATION

The molecular weights of polymers were measured by solution viscosity methods.

1.4.1 Solution Viscosity Measurement

Viscosities of different concentrations of polymer solutions were measured with methanol as a solvent at 30 °C by using Ubbelohde glass viscometer. In viscosity method, the time taken for the solution to flow through the capillary is compared with the time for a pure solvent. The flow time for the solvent is t_0 and that of solution is t, the relative viscosity, η_r,is

$$\eta_r = \frac{t}{t_0} \tag{11}$$

The specific viscosity, ηsp, in terms of ηr, is

$$\eta_{sp} = \eta_r - 1 = \frac{t - t_0}{t_0} \tag{12}$$

Reduced viscosity, ηred, is defined as

$$\eta_{red} = \frac{\eta_{sp}}{c} \tag{13}$$

The viscosity data as a function of concentration are extrapolated to infinite dilution by means of the Huggins (14) or Kraemer (15) equation [44].

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k'' \eta^2 c \qquad \textbf{(14)}$$

$$\frac{\ln \eta_{rel}}{c} = [\eta] + k'' \eta^2 c \qquad \textbf{(15)}$$

The intrinsic viscosity, [η], is determined by taking the following limit:

$$[\eta] = \lim_{c \to 0} [(\eta - \eta_0) / \eta_0 c] \qquad \textbf{(16)}$$

The value of [η] may be found experimentally from the intercept of the graph of $[(\eta-\eta_0) / \eta_0 c]$ versus c or ln ηrel / c versus c.

Relative molecular weight can be determined by using Mark Houwink equation:

$$[\eta] = KM^a \qquad \textbf{(17)}$$

$$\log [\eta] = \log K + a \log M \qquad \textbf{(18)}$$

In equations (17) and (18), K and a are constants which are dependent on the solvent, the type of the polymer and the temperature.

1.5 AIM OF THIS STUDY

This study was aimed to polymerize N-vinyl-2-pyrrolidone by γ-radiation in bulk in the presence of atmospheric oxygen and under vacuum. The different characterization methods were employed to investigate the properties of obtained polymers. Also, the monomer was polymerized by chemical initiator in bulk, AIBN, at different temperatures for different time periods. The obtained polymers were characterized to understand the effect of the temperature and the time on % conversion. Furthermore, the polymers obtained by different conditions were investigated by viscosity measurement methods and calculated molecular weights were used to see the relationship between glass transition temperature and molecular weight of the polymer.

CHAPTER 2

EXPERIMENTAL

2.1 MATERIALS

2.1.1 Monomer

N-vinyl-2-pyrrolidone (Merck) was used as a monomer. The monomer was distilled under vacuum in order to remove inhibitor.

2.1.2 Initiator

α, α'-Azoisobutyronitrile, AIBN (Merck) was used as initiator for free radical bulk polymerization of NVP without further purification. Structure of AIBN is shown in Figure 8.

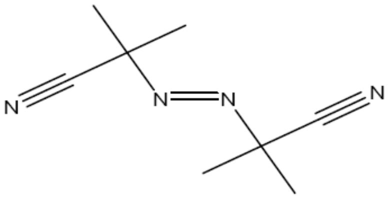


Figure 8 Initiator (AIBN)

2.1.3 Solvents

Ethanol (Merck), diethyl ether (Riedel de-Haen), methanol (Merck) and THF (Merck) were used.

2.2 INSTRUMENTATION

2.2.1 Polymerization Tubes

The polymerization tubes (Pyrex) were 1-3 cm in diameter and 10 cm in length. The open ends of the tubes were attached to another tube of smaller diameter, which allows to be connected to the vacuum line.

2.2.2 High Vacuum System

The polymerization tubes were evacuated at pressure of 10^{-4} to 10^{-5} mmHg for about 5-6 hours.

2.2.3 ^{60}Co γ–Ray Source

The gamma radiation source was ^{60}Co Gamma-cell 220 of Atomic Energy of Canada Ltd. Co. Dose rate of the source was 1551 Gy/day which corresponds dose rate of 64,63 Gy/hours.

2.2.4 Viscometer

Viscosities of different concentrations of polymer solutions were measured with methanol as a solvent at 30 °C by using Ubbelohde glass viscometer.

2.2.5 Oil Bath

Polymerization was carried out in a Memmert oil bath at different temperatures.

2.2.6 Vacuum Drying Oven

The polymer was dried to constant weight under vacuum drying oven, Labart DZF 6030A Model.

2.2.7 Fourier Transform Infrared Resonance (FTIR) Spectroscopy

Infrared spectra of monomer and the polymer were taken from KBr pellets by using Perkin Elmer Spectrum-One FT-IR Spectrometer. The data was processed by the OMNIC computer program.

2.2.8 Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H-NMR and ^{13}C-NMR spectra of the NVP and PVP were recorded on a Bruker DPX 400. Deuterated water was used as the solvent, and tetramethyl silane (TMS) served as the internal standard.

2.2.9 Differential Scanning Calorimeter (DSC)

Thermal properties of the monomer and polymer were analyzed by using Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910 S and Perkin Elmer

Diamond DSC. All the measurements were done under N_2 atmosphere in a temperature range of 25 ºC to 300 ºC with 10 ºC/min heating rate.

2.2.10 Thermogravimetric Analysis (TGA)

PVP was characterized by Perkin Elmer Pyris 1 TGA & Spectrum 1 FT-IR Spectrometer. Thermograms were recorded under N_2 atmosphere in a temperature range of 25 ºC to 800 ºC with 5 ºC/min heating rate.

2.3 EXPERIMENTAL PROCEDURE

2.3.1 Radiation Induced Bulk Polymerization of NVP at Open Atmosphere

2 ml (18,7 mmol) portions of distilled NVP were placed in Pyrex tubes and were sealed by flame. The tubes were put into the gamma radiation source. After reaching the desired irradiation period they were broken open. The materials were dissolved in ethanol and polymer precipitated with excess diethyl ether to remove unreacted monomer, separated by filtration, dried under vacuum at 40 °C to a constant weight. Conversions were calculated gravimetrically by equation 19.

$$\% \text{ Conversion} = \frac{\text{Polymer Mass}}{\text{Monomer Mass}} x100 \qquad \textbf{(19)}$$

2.3.2 Radiation Induced Bulk Polymerization of NVP Under Vacuum

In vacuum tubes, 2 ml portions of distilled NVP were placed and high vacuum system was applied about 6 hours at 10^{-4} to 10^{-6} mmHg. The tubes were degassed by three freeze-vacuum-thaw cycles in order to remove the atmospheric oxygen. The tubes were put into the gamma radiation source at room temperature. After reaching the desired irradiation period they were broken open. The tubes were sealed by flame. The rest of procedure was the same as 2.3.1.

2.3.3 Free Radical Polymerization by AIBN Under Vacuum

The stock solution of 100 ml (936 mmol) monomer and 145 mg (169 mmol) AIBN was prepared. High vacuum system with the same procedure as 2.3.2 was applied to the the vacuum tubes containing 2 ml of this solution, afterwards they were heated in an oil bath thermostated at 50 °C, 60 °C, 70 °C respectively and polymerized at different time periods. After reaching the desired period they were broken open. The rest of procedure was the same as 2.3.1.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 POLYMERIZATION OF NVP

3.1.1 Radiation Induced Bulk Polymerization of NVP

The radiation induced bulk polymerization of NVP in the presence of atmospheric oxygen and under vacuum was carried out at room temperature and percent conversions were calculated. The results are tabulated in Table 3 - 4 and plotted in Figure 9 - 10. The kinetic curve of the polymerization of NVP in the atmospheric oxygen is S-shape type and the polymerization showed an autoaccelaration mechanism. After all the oxygen is consumed, the monomer was polymerized. In the case of polymerization under vacuum, the percent conversion changed linearly up to about 90%. The polymer obtained was white in color and in the form of gel.

Table 3 Radiation induced polymerization of NVP in the presence of atmospheric oxygen.

Time (Hours)	Total Dose (kGy)	Conversion (%)	ln[M_0/M]	[η] x 10^{-3} (dl/g)	Mv x 10^3 (g/mol)
6,0	0,39	6,450	0,067	093,5	10,33
12	0,76	11,97	0,128	106,0	12,53
15	0,97	12,40	0,132	121,1	15,37
18	1,16	53,66	0,769	206,6	34,97
20	1,29	76,37	1,443	218,6	38,14
21	1,36	91,85	2,507	220,3	38,60
23	1,89	93,67	2,760	236,2	42,96
24	1,55	94,31	2,867	238,9	43,73
25	1,62	93,04	2,665	237,0	43,19

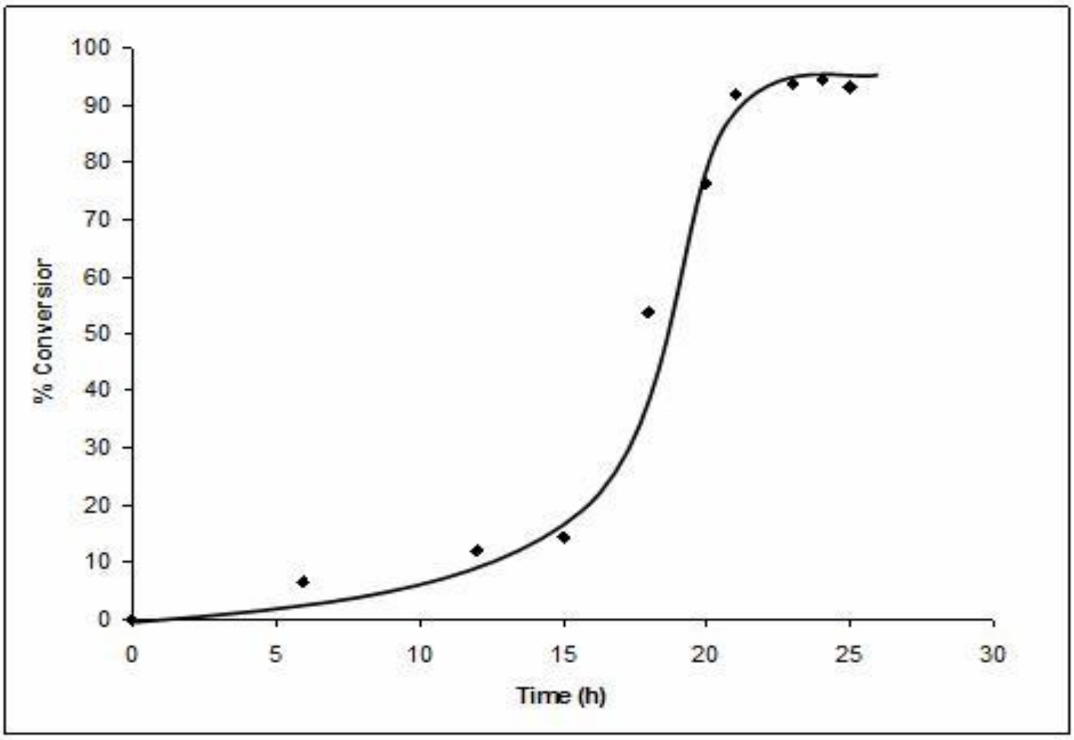


Figure 9 The percent conversion vs. time graph for radiation induced polymerization of NVP in the presence of atmospheric oxygen.

Table 4 Radiation induced polymerization of NVP under vacuum.

Time (Hours)	**Total Dose (kGy)**	**Conversion (%)**	**ln[M_0/M]**	**[η] x 10^{-3} (dl/g)**	**Mv x 10^3 (g/mol)**
5	0,32	13,58	0,146	226,9	40,39
6	0,39	23,59	0,269	233,0	42,08
10	0,65	46,98	0,635	237,1	43,22
11	0,71	60,13	0,919	235,4	42,76
12	0,76	58,33	0,875	230,2	41,30
15	0,97	80,61	1,640	241,8	44,55
17	1,10	88,81	2,190	223,6	39,49
18	1,16	87,89	2,111	235,6	42,80

Table 4 (Continued)

Time (Hours)	Total Dose (kGy)	Conversion (%)	ln[M_0/M]	[η] x 10^{-3} (dl/g)	Mv x 10^3 (g/mol)
20	1,29	93,21	2,689	250,3	46,98
21	1,36	98,16	3,995	252,5	47,62
23	1,49	96,03	3,226	248,4	46,43
26	1,68	94,73	2,943	239,1	43,78

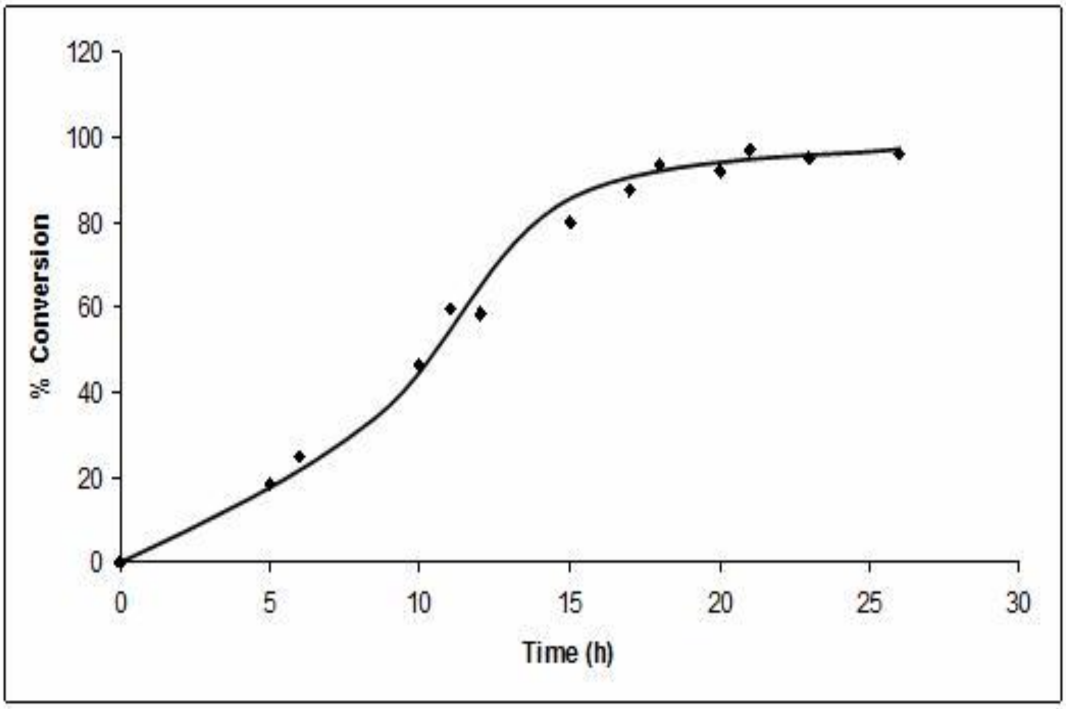


Figure 10 The percent conversion vs. time graph for radiation induced polymerization of NVP under vacuum.

3.1.2 Bulk Polymerization of NVP via Chemical Initiatior

The bulk polymerization of NVP with initiator under vacuum at different temperatures was carried out and percent conversions were calculated gravimetrically. The results are tabulated in the Table 5, 6, 7 and plotted in Figure 11, 12 and 13. In the kinetic curve, the percent conversion reached linearly up to about 90%. The conversion was reached to about 90% at 50 °C in 5 h, at 60°C in

4,5 h, and at 70°C in 4 h. This showed that the polymerization rate increased with the increasing of temperature.

Table 5 Polymerization of NVP by AIBN at 50 °C.

Time (Hours)	**Conversion (%)**	**ln[M_0/M]**	**[η] x 10^{-3} (dl/g)**	**Mv x 10^3 (g/mol)**
0,25	1,490	0,015	115,2	14,24
0,5	5,950	0,061	109,4	13,15
1	22,46	0,254	218,1	38,01
2	36,24	0,450	230,7	41,44
3	52,11	0,736	232,3	41,88
4	72,92	1,306	220,0	38,52
5	90,07	2,309	216,1	37,47
8	94,21	2,849	237,3	43,27
13	99,99	9,210	240,2	44,09
15	98,12	3,974	214,5	37,05
23	95,60	3,124	239,4	43,86

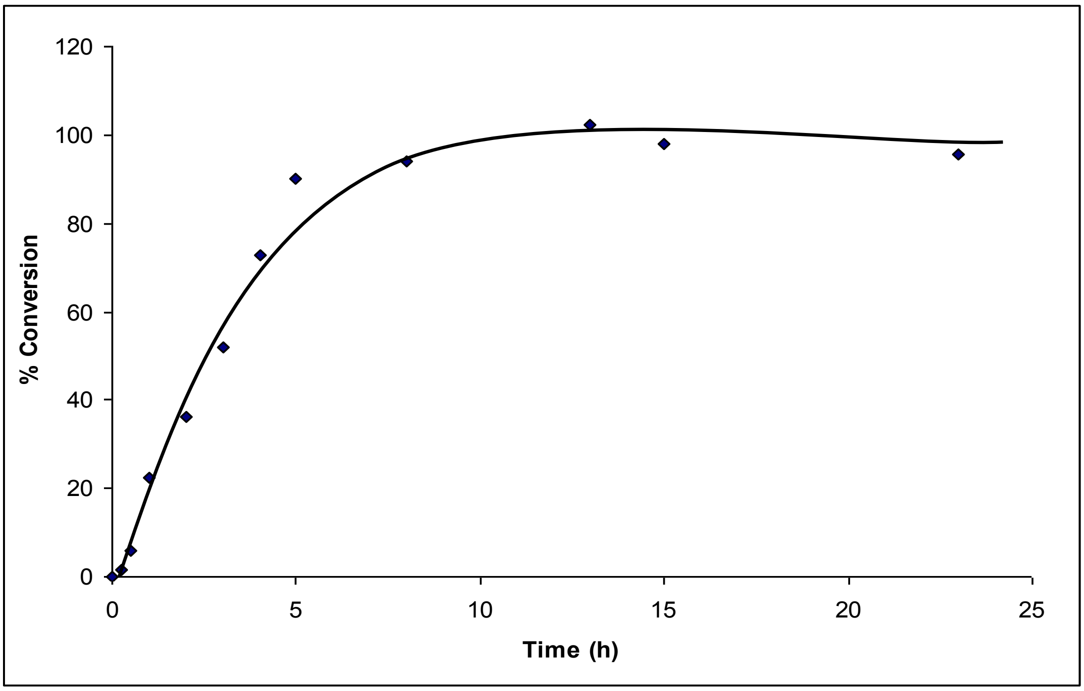


Figure 11 The percent conversion vs. time graph for polymerization of NVP by AIBN at 50 °C.

Table 6 Polymerization of NVP by AIBN at 60 °C.

Time (Hours)	Conversion (%)	ln[M_0/M]	[η] x 10^{-3} (dl/g)	Mv x 10^3 (g/mol)
0,083	4,340	0,044	130,8	17,31
0,25	9,120	0,096	214,0	36,92
0,5	17,99	0,198	231,5	41,66
1,0	41,63	0,538	223,9	39,58
1,5	56,30	0,828	227,3	40,50
2,0	74,69	1,374	230,7	41,44
3,0	84,53	1,866	223,5	39,47
3,5	90,62	2,367	248,0	46,32
4,5	90,29	2,332	223,2	39,39
6,0	96,72	3,417	228,4	40,81
7,0	97,27	3,601	248,4	46,43

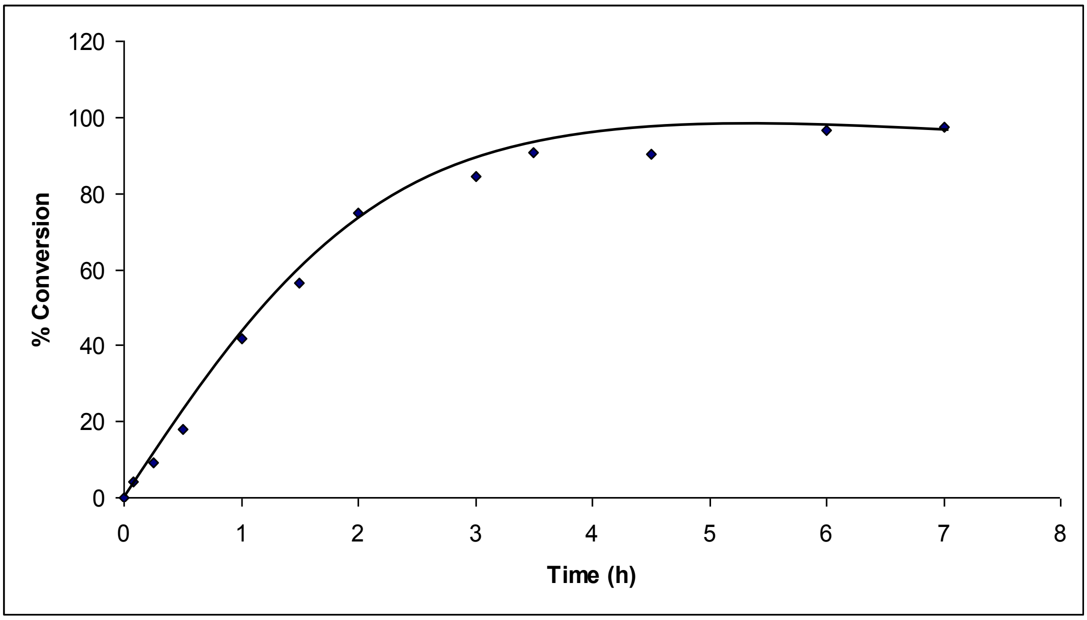


Figure 12 The percent conversion vs. time graph for polymerization of NVP by AIBN at 60 °C.

Table 7 Polymerization of NVP by AIBN at 70 °C.

Time (Hours)	**Conversion (%)**	**ln[M_0/M]**	**[η] x 10^{-3} (dl/g)**	**Mv x 10^3 (g/mol)**
0,017	4,250	0,043	212,1	36,41
0,033	4,190	0,043	217,5	37,85
0,050	5,630	0,058	220,6	38,68
0,083	9,870	0,104	234,8	42,58
0,117	71,44	1,253	233,1	42,10
0,167	71,14	1,243	220,9	38,76
0,250	76,49	1,448	206,8	35,02
0,500	77,97	1,513	234,3	42,44
1,00	87,23	2,058	235,1	42,66
2,00	88,00	2,120	238,6	43,64
3,00	88,61	2,172	246,3	45,83
4,00	89,62	2,265	237,6	43,36
5,00	91,92	2,516	239,0	43,76
7,50	88,76	2,186	250,1	46,92
8,50	92,70	2,617	226,3	40,23

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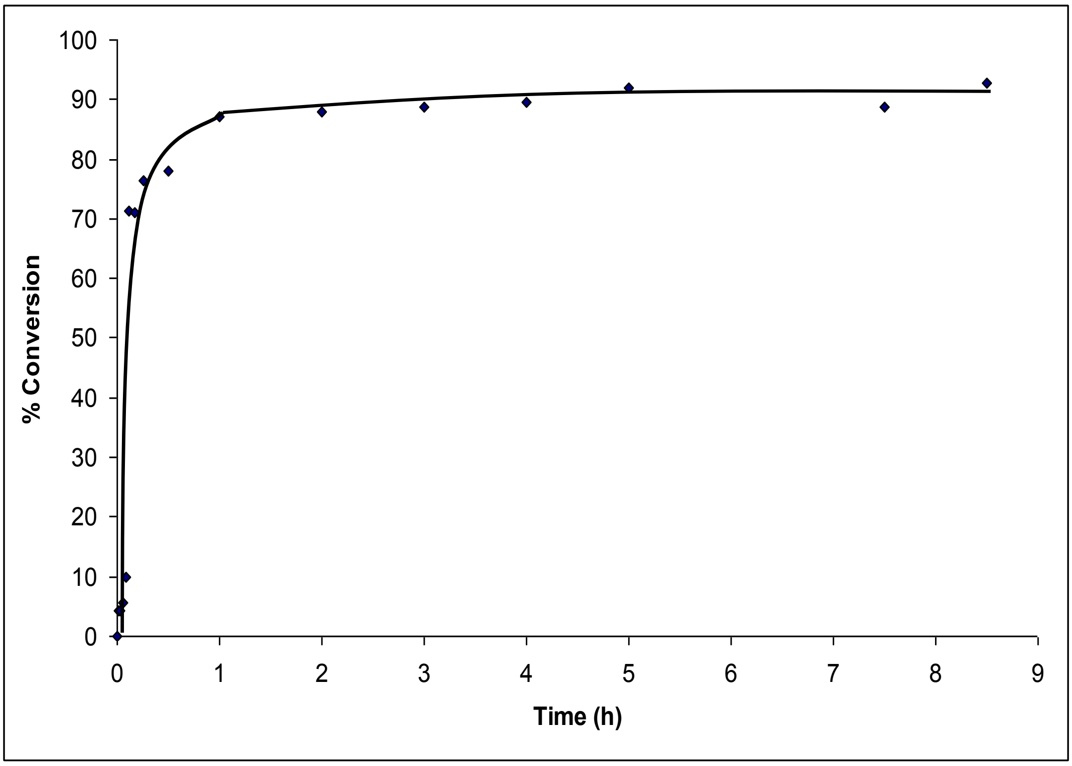


Figure 13 The percent conversion vs. time graph for polymerization of NVP by AIBN at 70 °C.

In order to observe the differences of the polymerization of NVP at these three different temperatures, the percent conversion versus time graphs are shown in Figure 14.

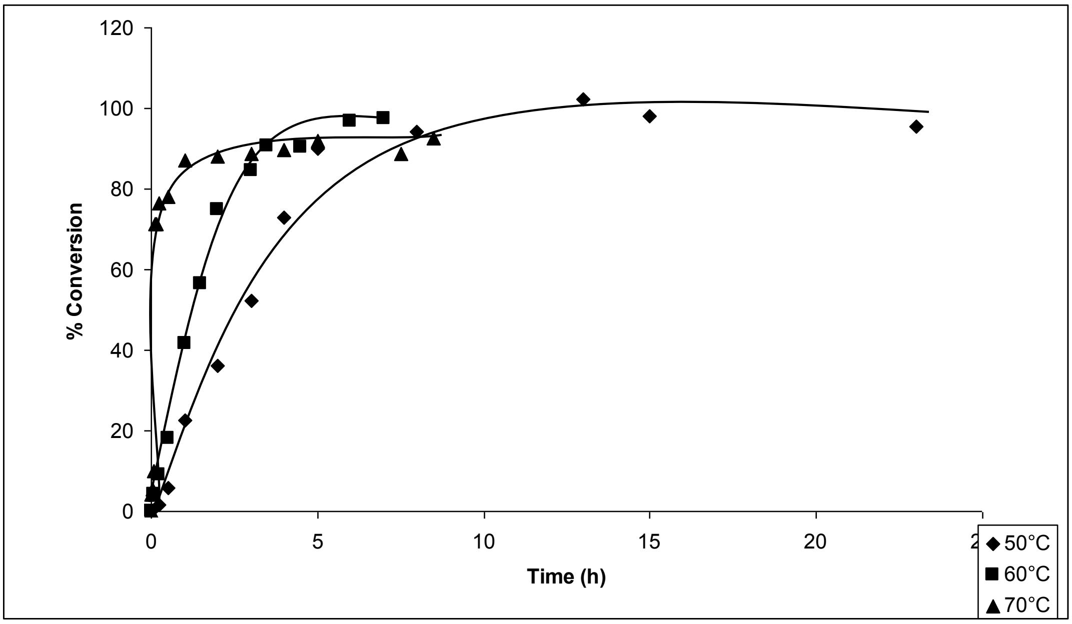


Figure 14 The percent conversion vs. time graph for polymerization of NVP by AIBN at 50 °C, 60 °C and 70 °C.

Activation energy of polymerization was calculated from Arrhenius plot using rate constant for each of temperature of polymerization. The rate constants were calculated by application of kinetic equation (20) [44].

$$\ln\frac{[M_0]}{[M]} = k[I]^{1/2}t \qquad \textbf{(20)}$$

$\ln[M_0/M]$ values were plotted against time and plots were illustrated in Figure 15, 16, 17. Slopes were calculated from straight lines for each of polymerization temperature studied.

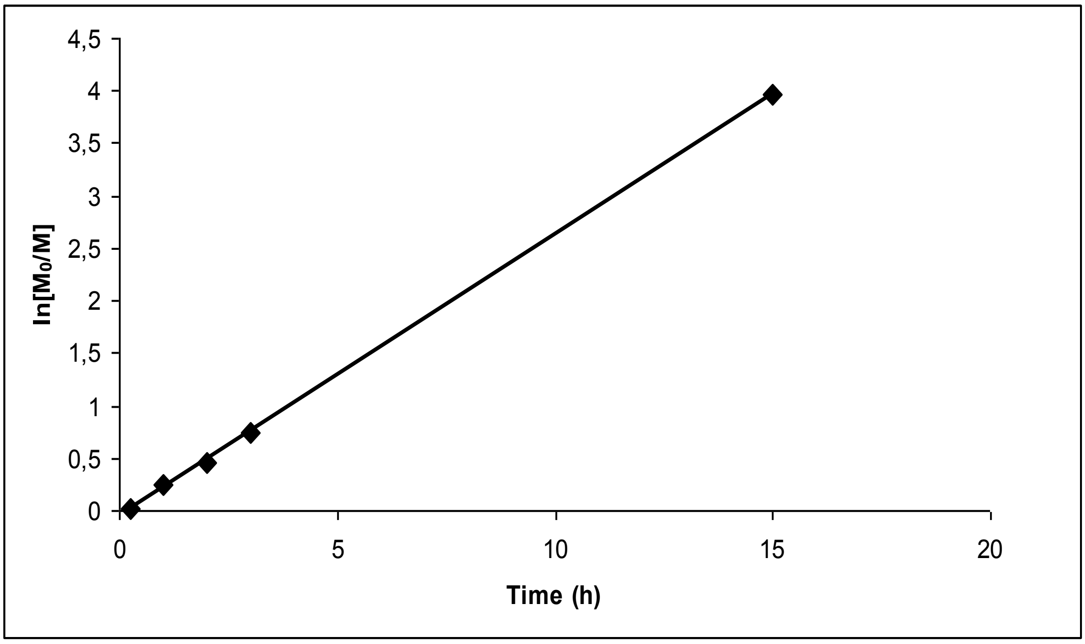


Figure 15 The plot of ln[M_0/M] vs. time for polymerization of NVP by AIBN at 50°C.

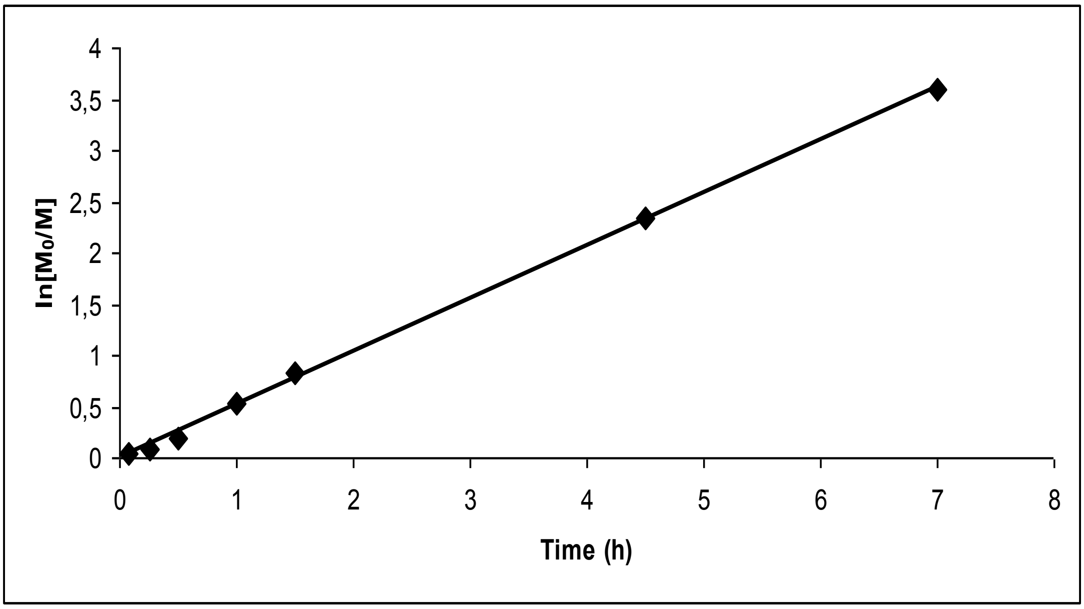


Figure 16 The plot of ln[M_0/M] vs. time for polymerization of NVP by AIBN at 60°C.

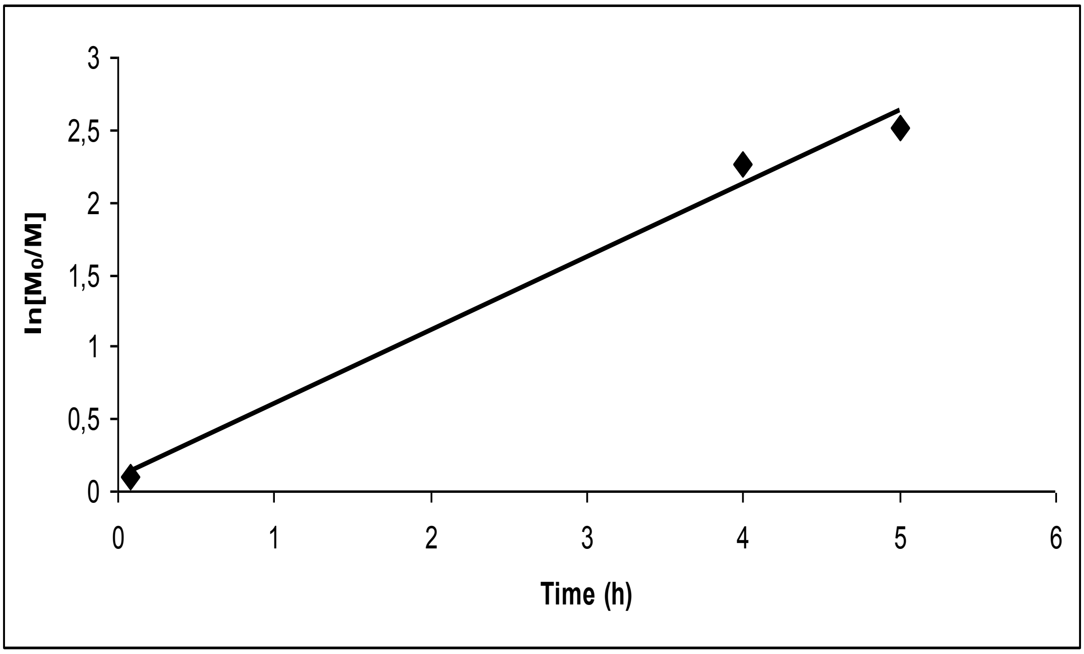


Figure 17 The plot of ln[M_0/M] vs. time for polymerization of NVP by AIBN at 70°C.

In the rate equation (20) the $[I]^{1/2}$ is constant, therefore overall rate constant will be

$$k = k\,[I]^{1/2} \qquad \textbf{(21)}$$

which is the slope of a straight line obtained by plotting ln [M_0]/[M] against time. The obtained k values from Figure 15-17 were given in Table 8. Activation energy of polymerization was calculated from Arrhenius equation:

$$k=Ae^{-Ea/RT} \qquad \textbf{(22)}$$

Taking the natural logarithm of both sides of the Arrhenius equation gives:

$$\ln k = \ln A+\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \qquad \textbf{(23)}$$

The reaction rate constans for different temperatures are tabulated in Table 8 and the natural logarithm of rate constant against 1/T was plotted in Figure 18. The slope of straight line obtained was equal to $-E_a/R$ and activation energy, E_a calculated from slope is 31,8 kJ/mol.

Table 8 Reaction rate constants for free radical bulk polymerization of NVP at different temperatures.

T (K)	1/T (K^{-1})	k=slope (h^{-1})	lnk
323	0,00309	0,2682	-1,3160
333	0,00300	0,5176	-0,6586
343	0,00292	0,5078	-0,6777

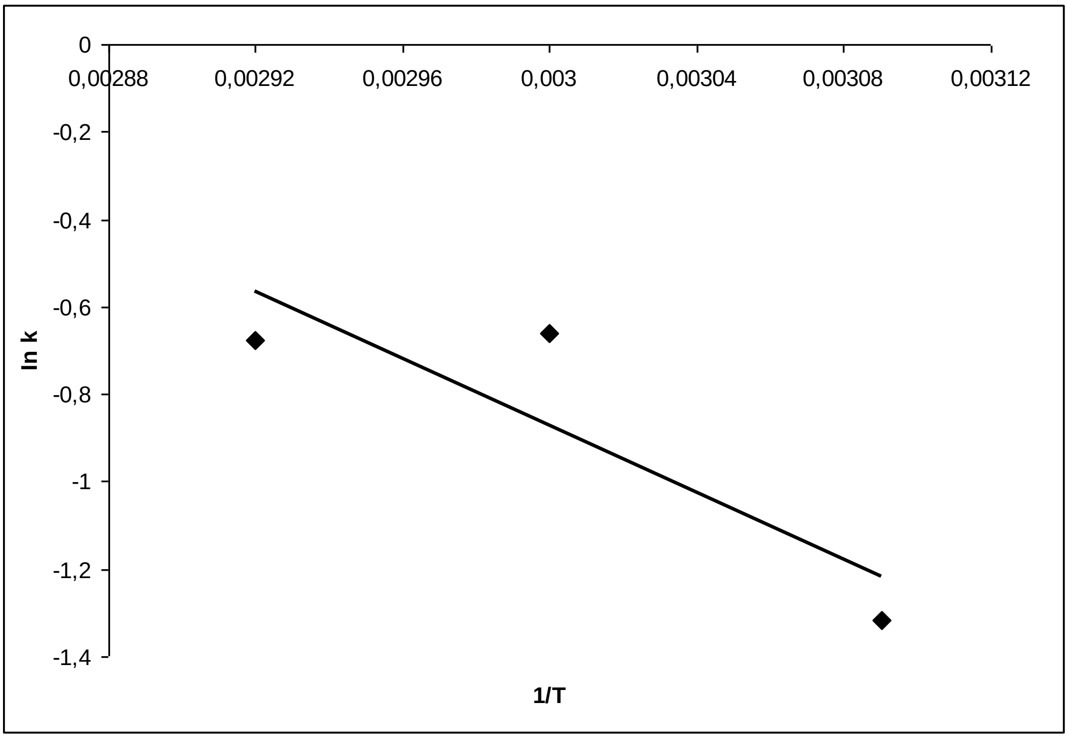


Figure 18 ln k vs. 1/T

3.2 CHARACTERIZATION OF PVP

3.2.1 FT-IR Investigation

The FT-IR spectrum for NVP and PVP in the region of 500-4000 cm^{-1} are shown in Figure 19 and 20 respectively. The peak assignments are tabulated in Table 9. Conversion increase of the polymers obtained under different temperatures did not induced any substantial change in the FT-IR spectra.

Table 9 The peak assignments for the FT-IR spectra of NVP and PVP.

Functional Group	**Wavenumber (cm^{-1})**	
	NVP	**PVP**
N-H stretching	3360	3360
Aliphatic C-H stretching	2950, 2850	2950, 2850
C=O stretching	1700	1650
C-N stretching, bending	1490	1490
$-CH_2$ -(sp^2) stretching	1460	1460
C=C	1650	-
=CH stretching	3160	-
-CH bending	1280	1280
$=CH_2$	980	-
O-H	3500	3430
C-C ring	844	844
N-C=O bend, ring def.	640	640

There is an apparent absorption peak at 1650 cm^{-1} in the spectrum of PVP and NVP. This is the absorption peak of amide (I), which is a stretching vibration absorption band formed by the combination of >C=O and C-N. Because it is a combination, the peak is lower than that of the absorption peak of pure >C=O (1750-1700 cm^{-1}) in the spectrum of the PVP. The nonbonding electron pair on the nitrogen can lower the frequency. Furthermore the negative shift arise from the intermolecular bond (such as hydrogen bond) formed by the carbonyl group.

Two very strong bands were observed for pure liquid NVP in the IR spectrum; the first is a C=C bond stretching vibration at 1650 cm^{-1}, corresponding to olefinic (C=C) stretching. The absorption peak of pure >C=O at 1700 cm^{-1}. Strong peaks in the range 800–1000 cm^{-1} corresponding to the stretching mode of vinyl double bonds (=CH and =CH$_2$) were also recorded. The peak of C-N stretching vibration was observed at 1490 cm^{-1}. Furthermore, the peak at 3360 cm^{-1} is assigned to N-H stretching vibration. After the polymerization of NVP the peaks belong to double bond in the spectrum of monomer were completely disappeared.

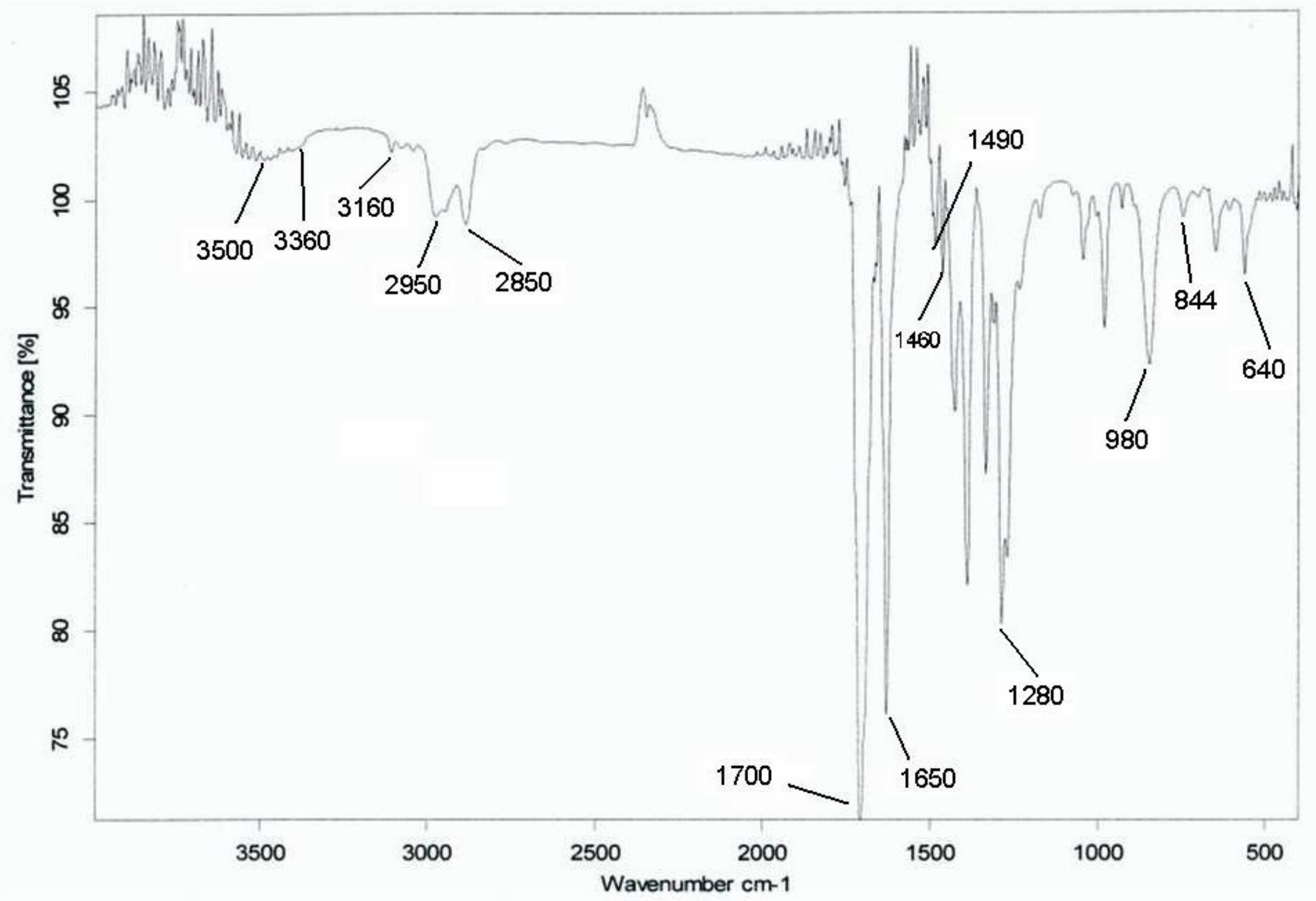


Figure 19 FT-IR spectrum of NVP

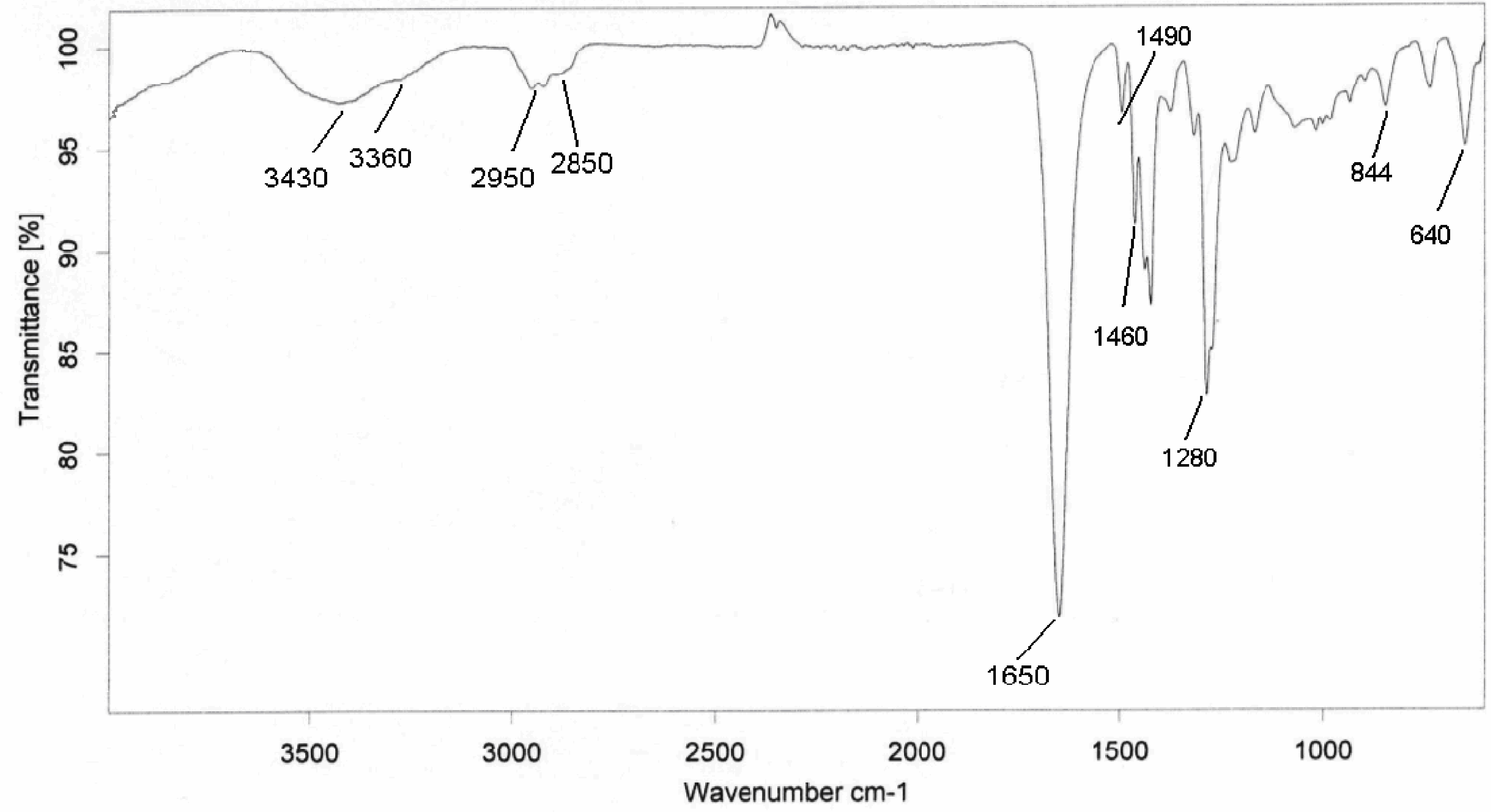


Figure 20 FT-IR spectrum of PVP

3.2.2 NMR Investigation

^{1}H-NMR spectra of NVP and PVP are given in Figure 21 and 22, respectively, and the peak assignments are tabulated in Table 10 and 11. In the ^{1}H-NMR spectrum of NVP (Figure 22), seven different peaks were observed. The assigned protons are shown in formula of monomer.

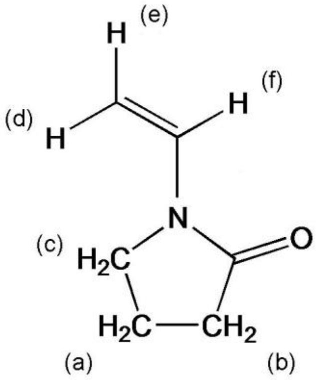


Table 10 The peak assignements of ^{1}H-NMR spectrum of NVP.

Proton Type	**Shift (ppm)**
H_a	2,10
H_b	2,50
H_c	3,55
H_d	4,56
H_e	4,60
H_f	6,90
d-H_2O	4,70

In the ^{1}H-NMR spectrum of NVP (Figure 21), the protons (H_a) for methylene group, (2 H, -CH_2- of the ring) which is appear at 2,10 ppm. The peaks for CH_2 groups close to C=O, (H_b), and N, (H_c) are observed at 2,50 and 3,55 ppm. The peaks at 4,56, 4,60 and 6,90 ppm correspond to the protons of the vinyl group. The reason of high chemical shift, (6,90 ppm) of the proton, (H_f) in the vinyl group is the presence of –N–C=O group in geminal position. The peak observed at 4,70 comes from the solvent, deuterated water.

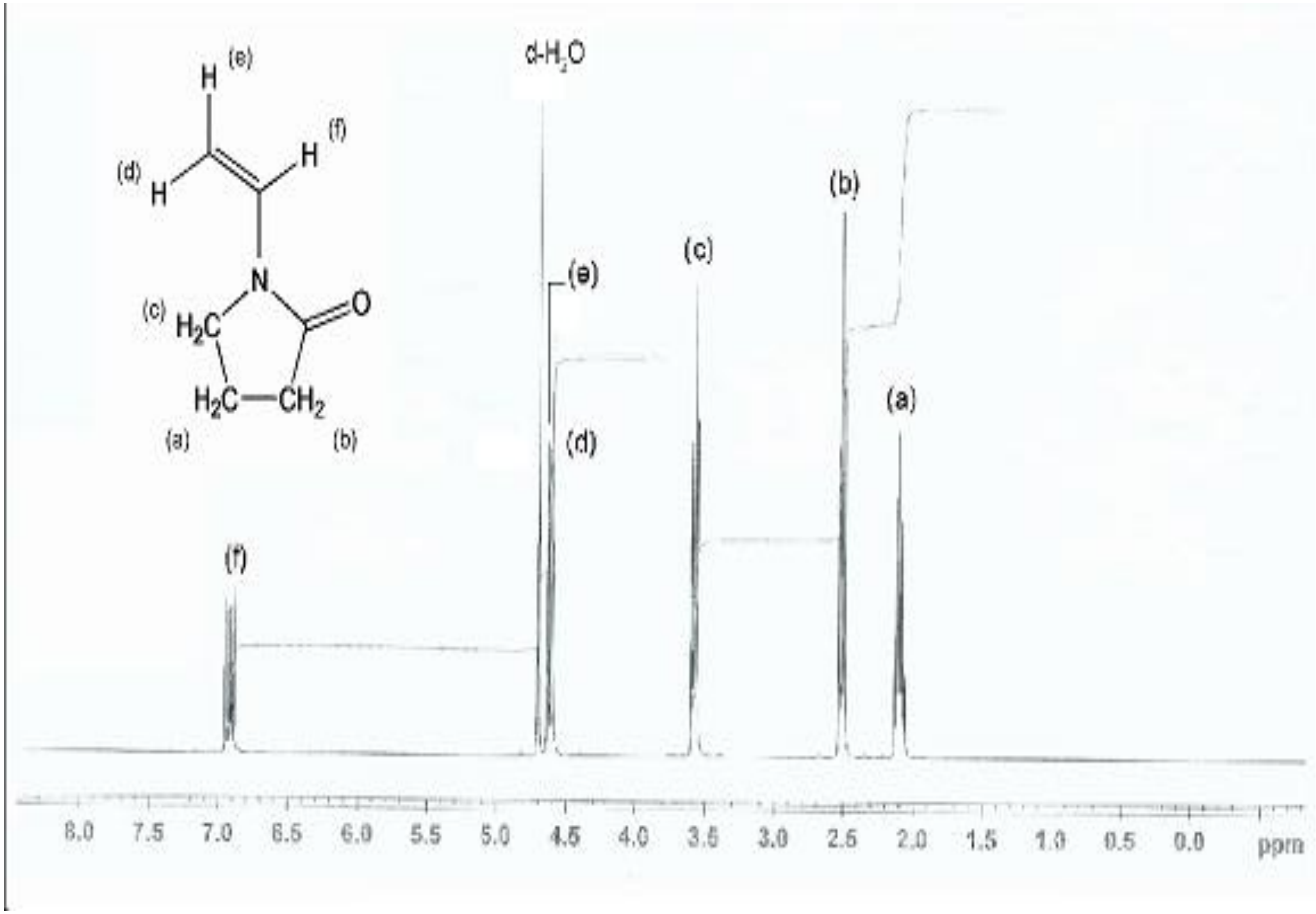


Figure 21 The ^{1}H-NMR spectrum of NVP.

In the ^{1}H-NMR spectrum of PVP (Figure 22), six different peaks were observed. The assigned protons are shown in formula of polymer and the peak assignments are tabulated in Table 11.

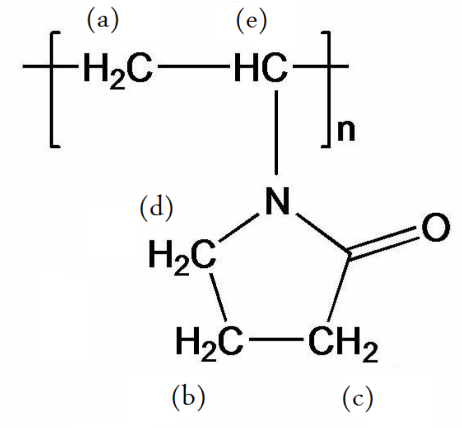


Table 11 The peak assignements of ^{1}H-NMR spectrum of PVP.

Proton Type	**Shift (ppm)**
H_a	1,4 - 1,9
H_b	2,0
H_c	2,2 – 2,6
H_d	3,3
H_e	3,5 – 3,9
d-H_2O	4,7

In the ^{1}H-NMR spectrum of PVP (Figure 22), very small change was observed in the chemical shifts of methylene protons, (H_a, H_b and H_c) in the ring. However the peaks of the polymer became broader. Moreover the peaks that belong to vinyl group disappeared. The peak observed at 4,70 comes from the solvent, deuterated water as the same as monomer spectrum. The ^{1}H-NMR spectrum of PVP exhibited peaks at 3,5 – 3,9 ppm (1H, −NCH−), 3,3 ppm (2H, $-NCH_2-$), 2,2 -2,6 ppm (2H, $-COCH_2-$) and 2,0 ppm (2H, $-CH_2-$ of the ring) and 1,4 – 1,9 ppm (2H, $-CH_2-$ of the backbone).

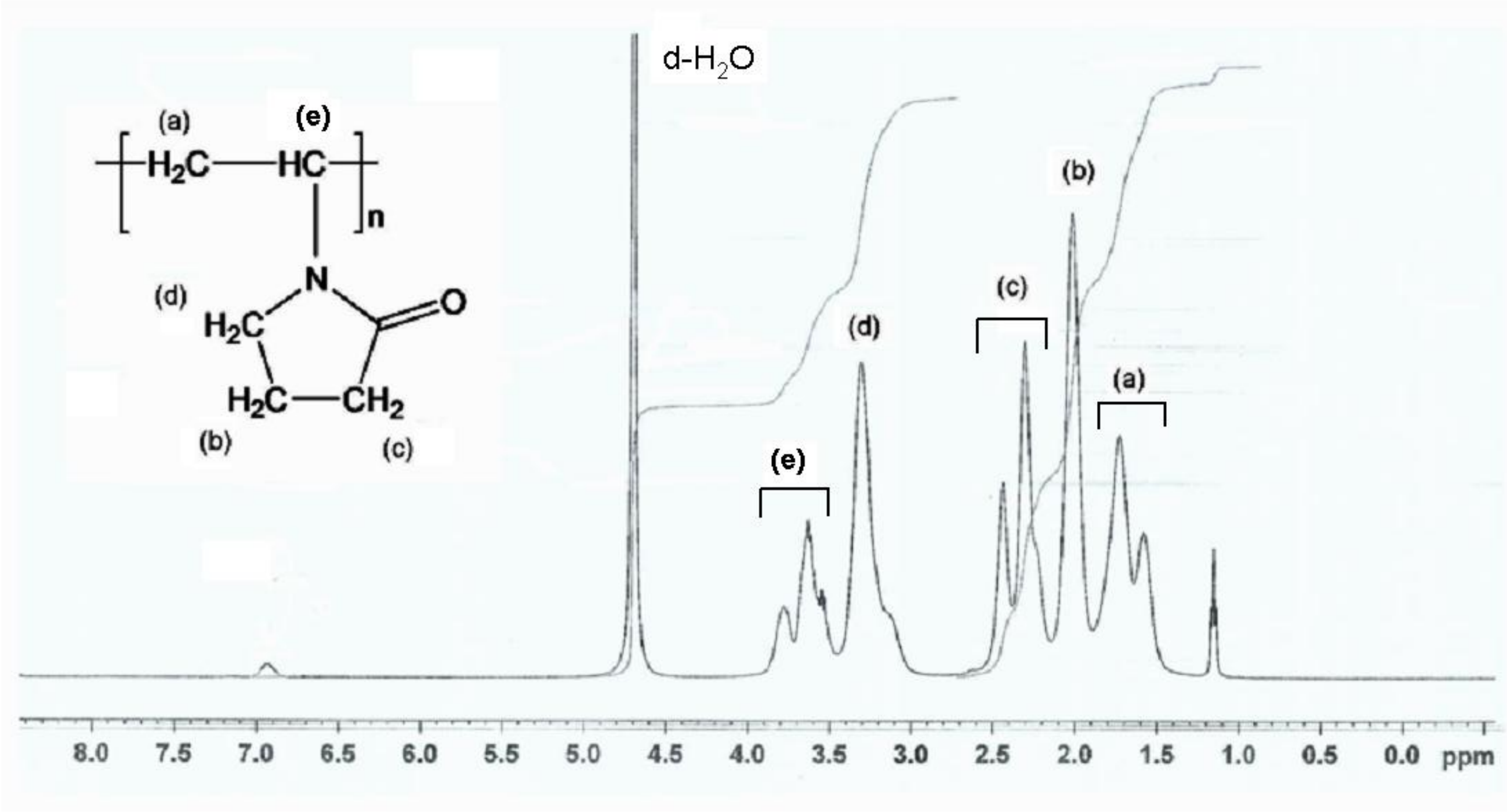


Figure 22 The ^{1}H-NMR spectrum of PVP.

^{13}C-NMR spectra of NVP and PVP are given in Figure 23 and Figure 24, respectively and the peak assignments are tabulated in Table 12 and Table 13. In the ^{13}C-NMR spectrum of NVP (Figure 23), six different peaks were observed. The assigned carbons are shown in formula of monomer.

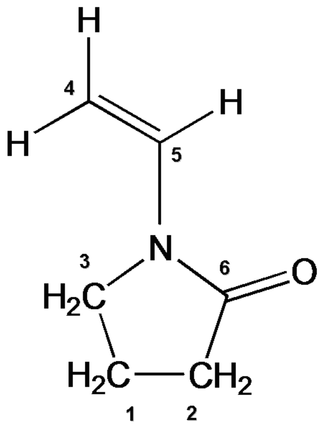


Table 12 The peak assignements of ^{13}C-NMR spectrum of NVP.

Carbon Type	Shift (ppm)
C_1	17
C_2	31
C_3	43
C_4	97
C_5	128
C_6	177

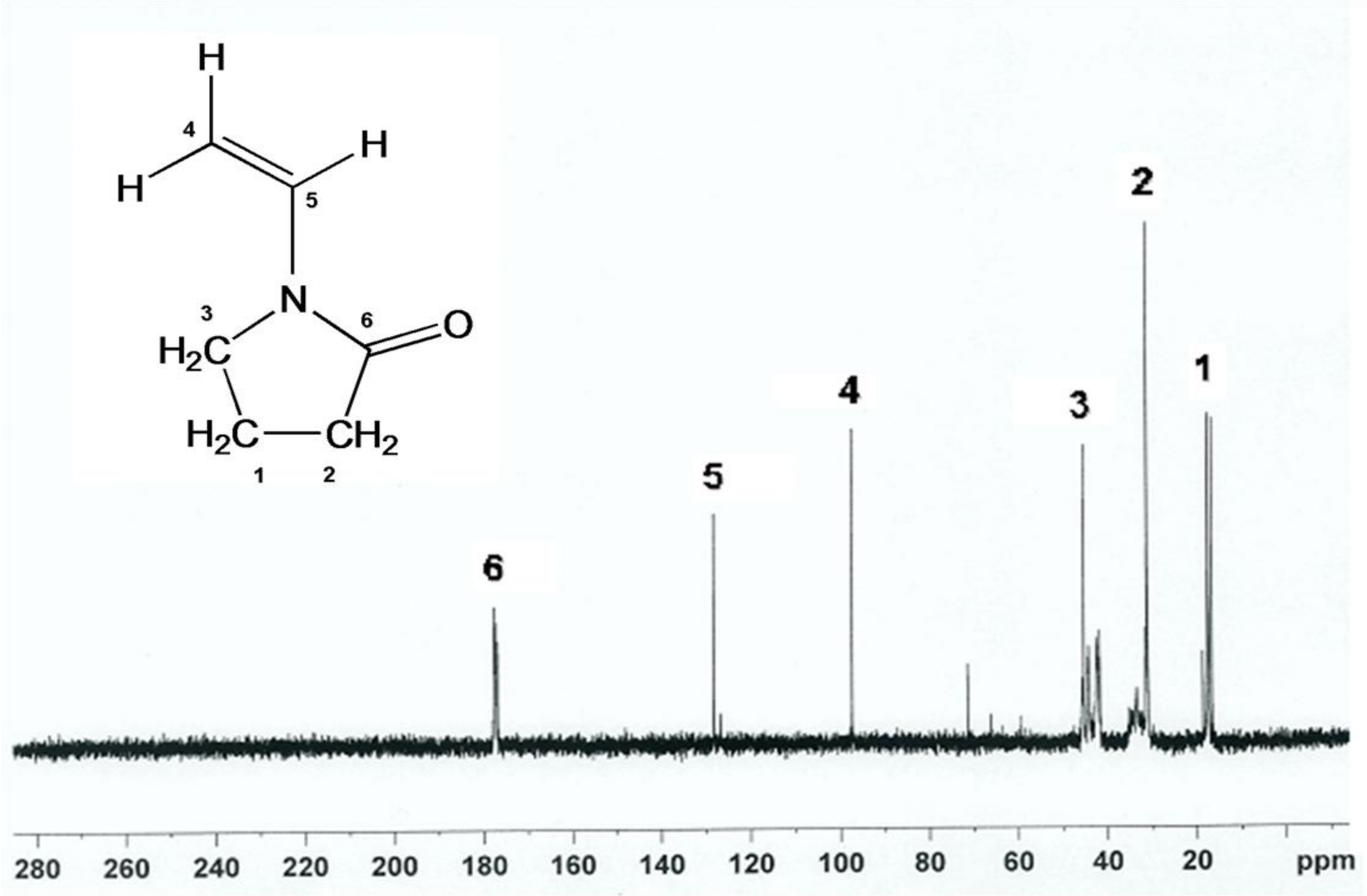
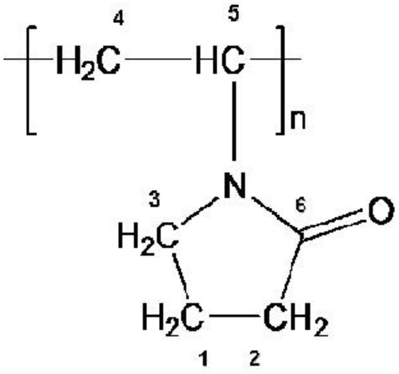


Figure 23 ^{13}C-NMR spectrum of NVP.

The ^{13}C-NMR spectrum of monomer (Figure 23), exhibited peak at 17 ppm for the C atom in the methylene groups ($–CH_2$). The peaks at 31 ppm and 43 ppm correspond to the signal of carbon atoms in methylene groups near −C=O− and −NCH−. The peaks of vinyl carbons were observed at 97 ppm and 128 ppm. The signal at 177 ppm showed the presence of carbonyl group (C=O) in the polymer. The peak at 71 ppm is due to the solvent heavy water.

In the ^{13}C-NMR spectrum of PVP (Figure 24), some of the peaks changed their position when compared with the spectrum of the monomer. The assigned protons are shown in formula of polymer and the peak assignments are tabulated in Table 13. In the ^{13}C-NMR spectrum of PVP the CH_2 peaks in the spectrum of the monomer did not change their position, but the intensity of the peaks became smaller and the peaks became broader in the spectrum of the polymer. These changes might be results from the conformational changes of the polymerized molecules.



The carbonyl peak appeared at 177 ppm in the spectrum of the PVP. The peaks that belong to vinyl group changed their position in the spectrum of the polymer. The peaks at 97 ppm (CH_2=) and 128 ppm (−NCH=) in the monomer spectrum, shifted to 42 ppm ($−CH_2−$) and 48 ppm (−NCH−) in the spectrum of the polymer.

Table 13 The peak assignements of ^{13}C-NMR spectrum of PVP.

Carbon Type	**Shift (ppm)**
C_1	17
C_2	32
C_3	46
C_4	42
C_5	48
C_6	177

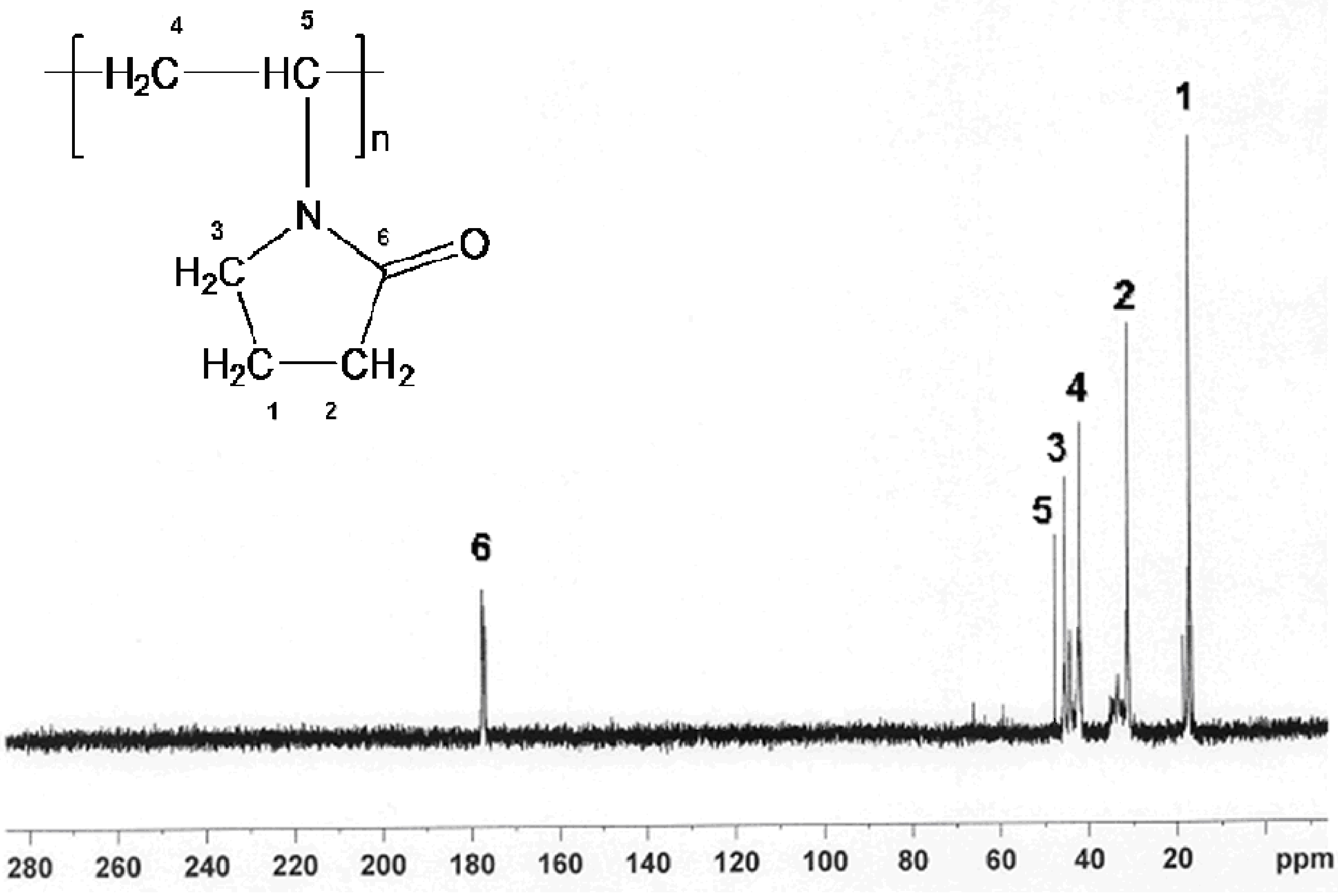


Figure 24 ^{13}C-NMR spectrum of PVP

3.2.3 Molecular Weight Investigation

The molecular weight determination of polymer was carried out by solution viscosity methods.

In order to calculate the molecular weight of the polymers having different conversion, solution viscosity method was applied. The intrinsic viscosity values were obtained from the program written by Prof. Dr. Osman Yılmaz [45].

The intrinsic viscosity values and viscosity average molecular weight (M_v) are tabulated in Table 3, 4 and 5 for 50 °C, 60 °C and 70 °C.

Relative molecular weight can be determined by using Mark Houwink equation:

$$[\eta] = KM^{a} \tag{24}$$

$$\log [\eta] = \log K + a \log M \tag{25}$$

In equations 24 and 25, “K” and “a” are constants which are dependent on the solvent, the type of the polymer and the temperature. In literature for PVP $K\text{x}10^3$=23 ml/g and a=0,65 at 30 °C in methanol [46].

According to the obtained values, regular trend could not be achieved from intrinsic viscosity measurements with respect to % conversion or time of polymerization. This could be due to the complex relation of solvent and polymer chain.

3.2.4 DSC Investigation

The DSC measurements were carried out at a heating rate of 10 °C/min under nitrogen atmosphere in the temperature range 25-300 °C. The DSC thermograms of PVP samples polymerized by gamma radiation and free radical polymerization by AIBN at 50 °C with having different percent conversions are given in Figures 25-33.

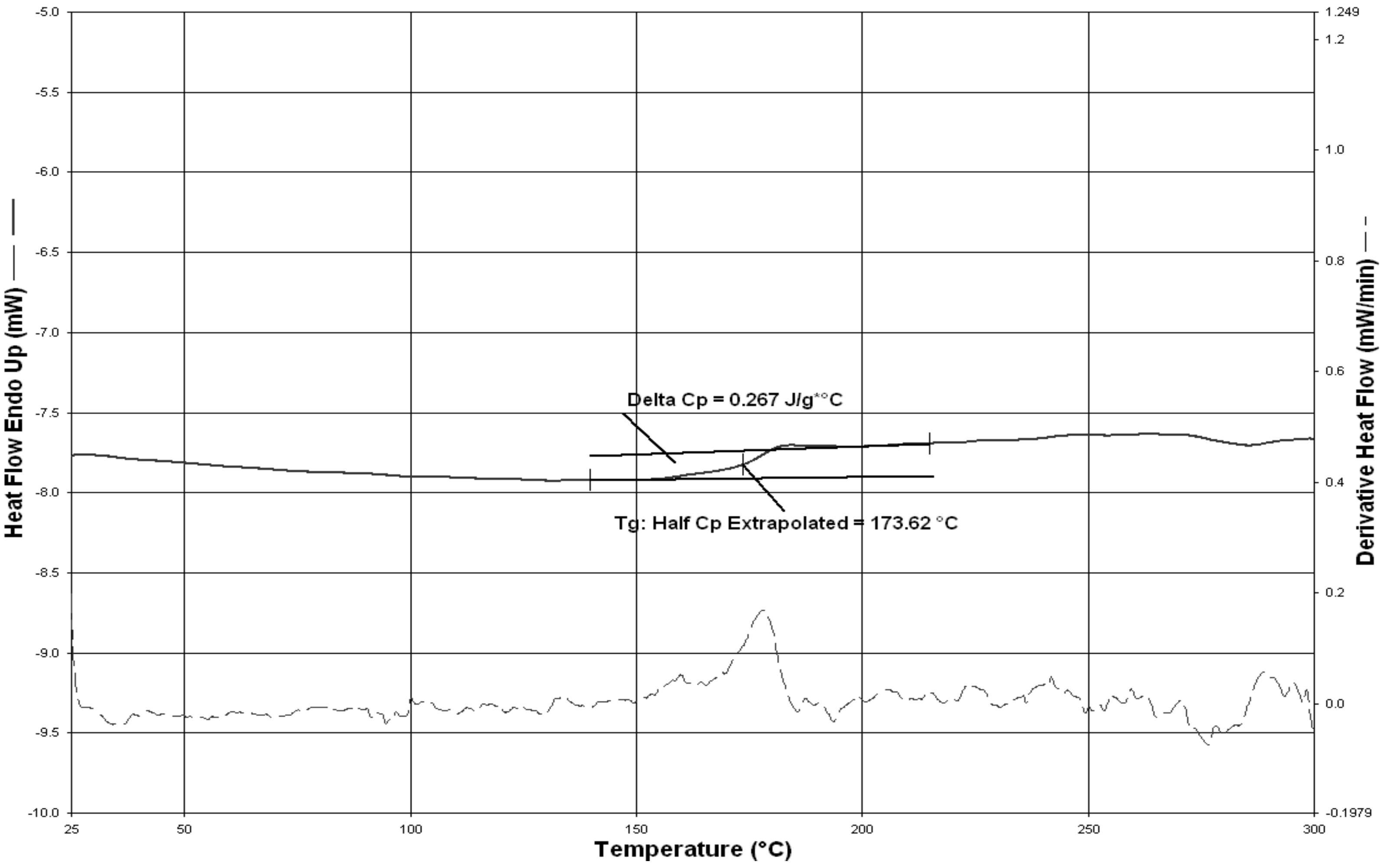


Figure 25 DSC thermogram of the PVP (γ-radiation at open atmosphere, 12 % conversion).

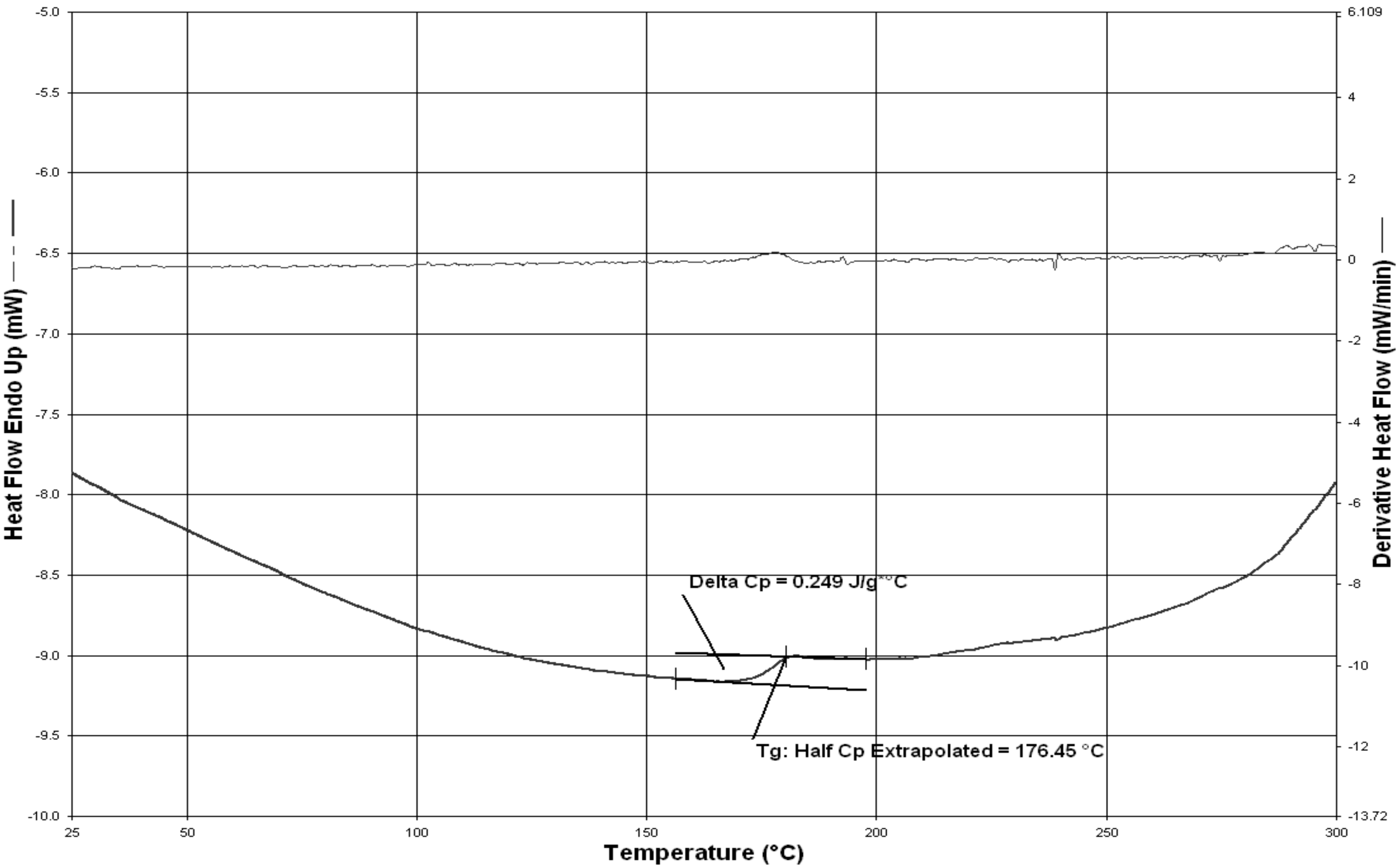


Figure 26 DSC thermogram of the PVP (γ-radiation at open atmosphere, 54 % conversion).

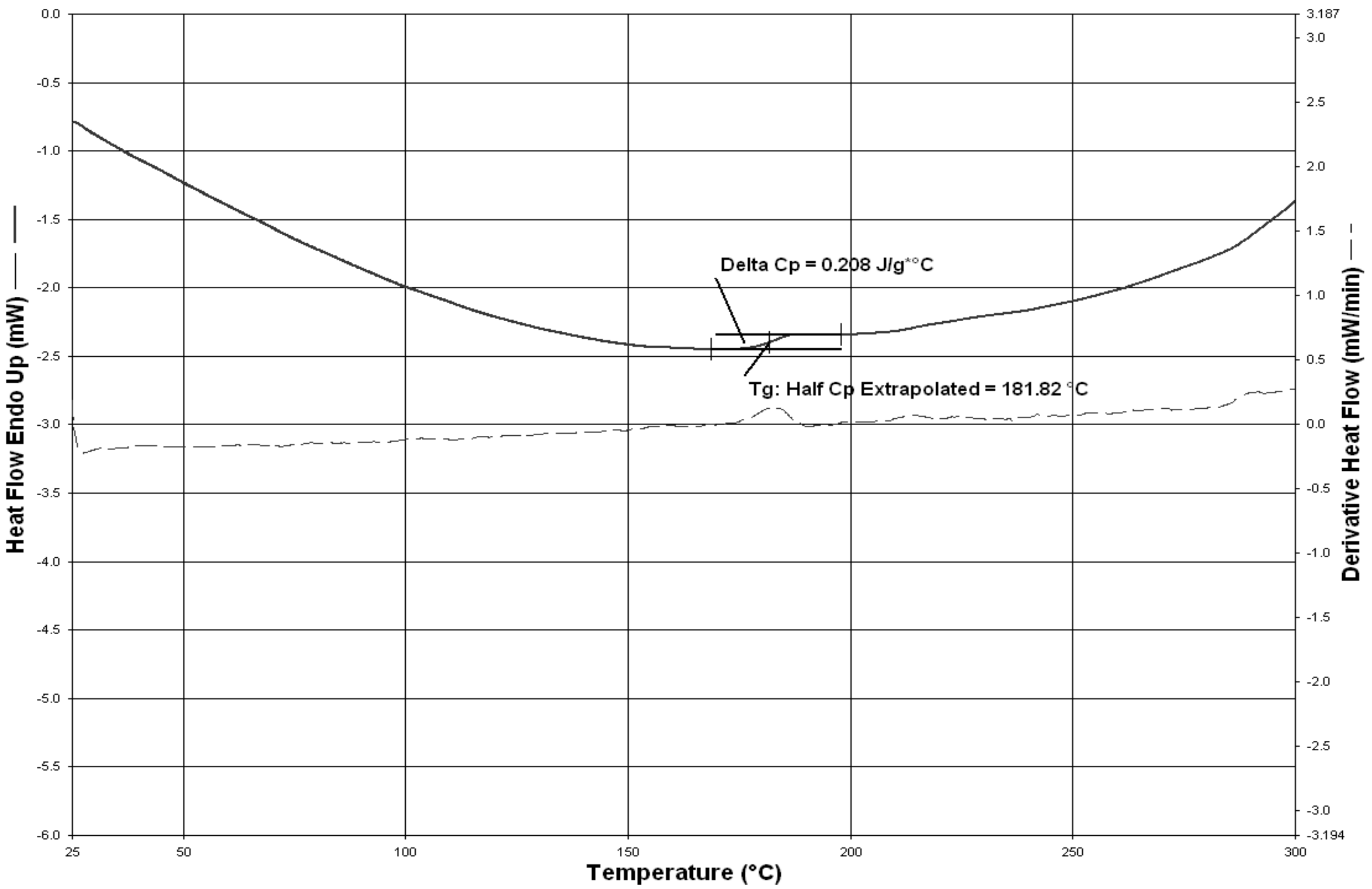


Figure 27 DSC thermogram of the PVP (γ-radiation at open atmosphere, 94 % conversion).

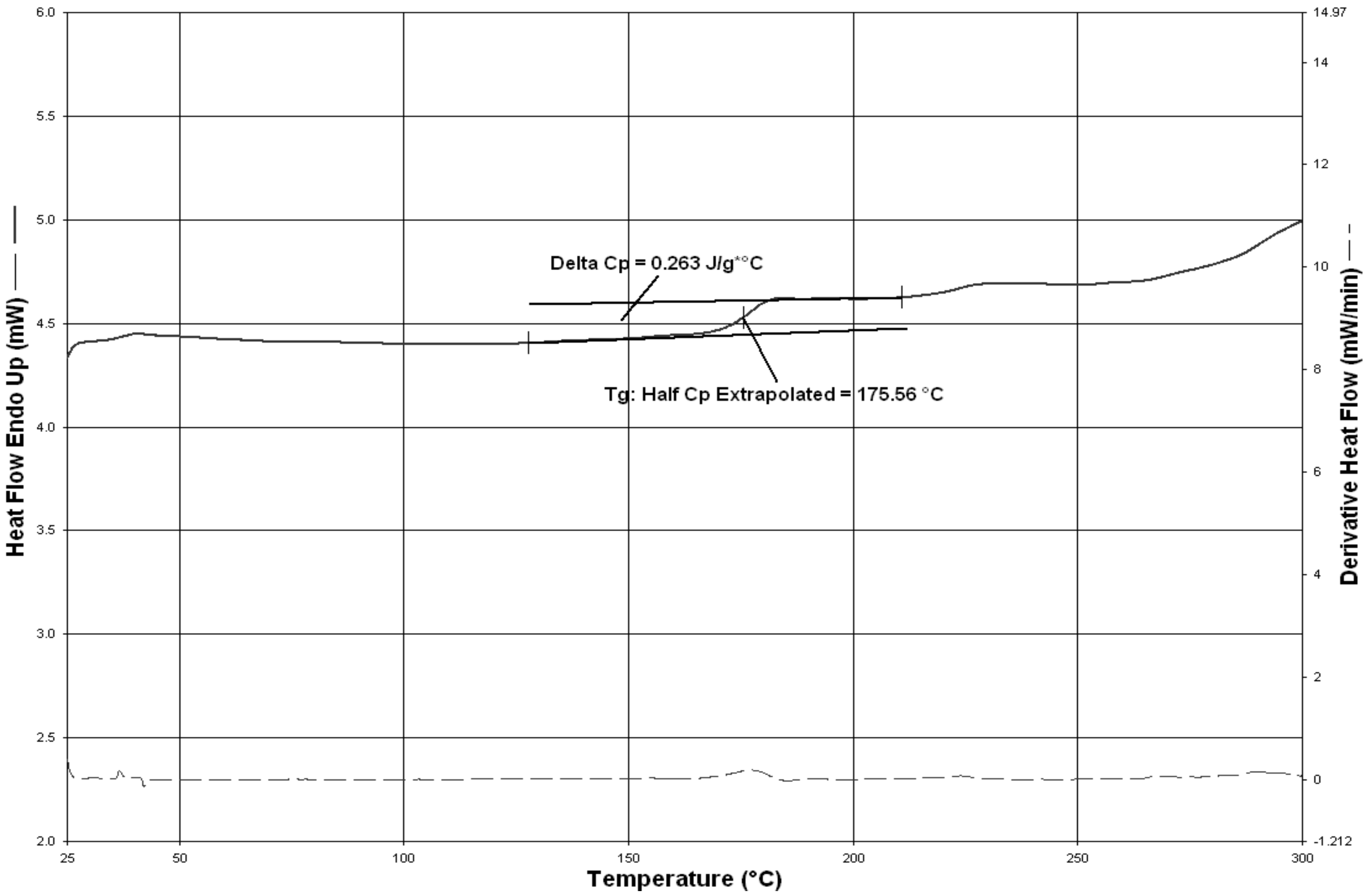


Figure 28 DSC thermogram of the PVP (γ-radiation under vacuum, 14 % conversion).

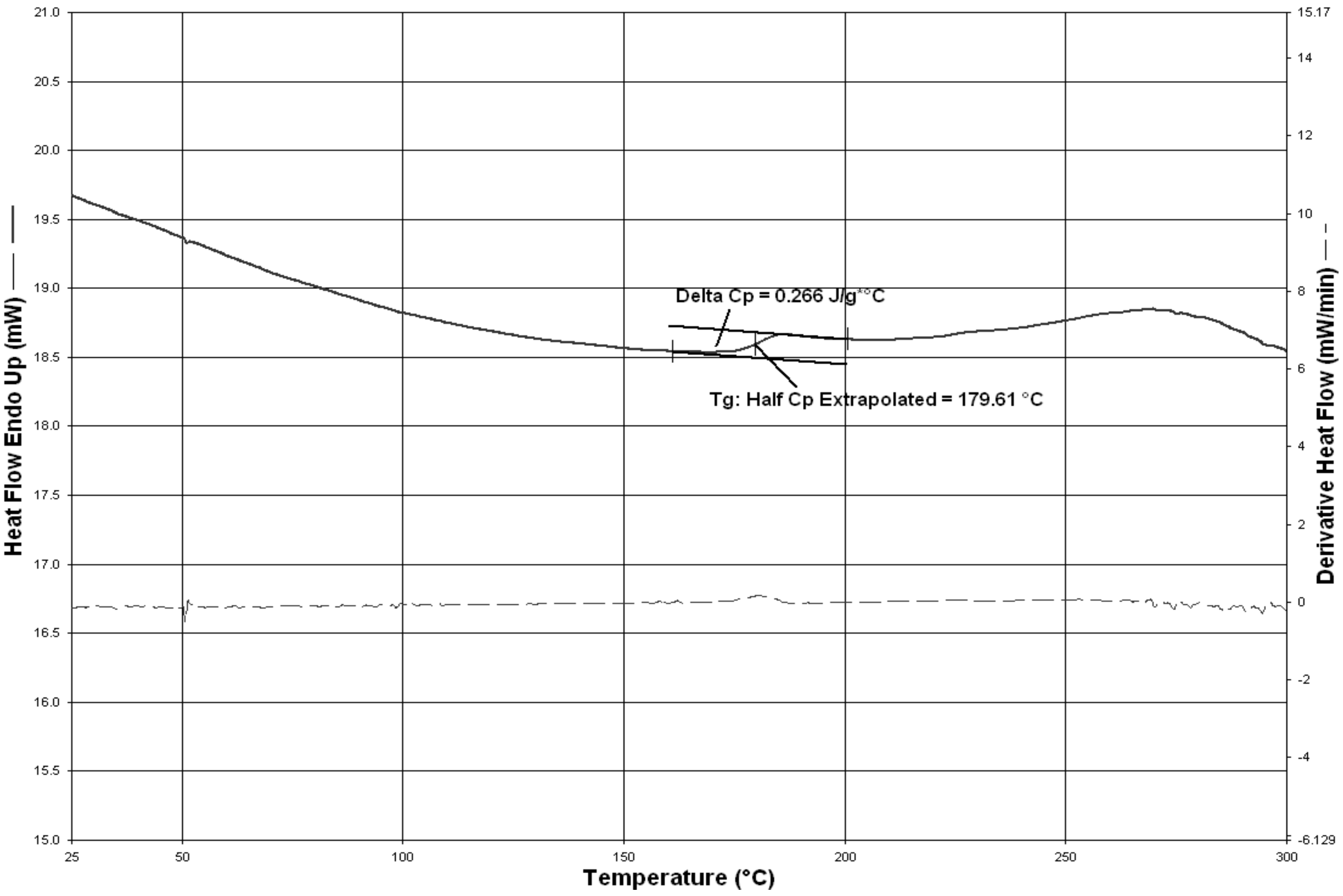


Figure 29 DSC thermogram of the PVP (γ-radiation under vacuum, 47 % conversion).

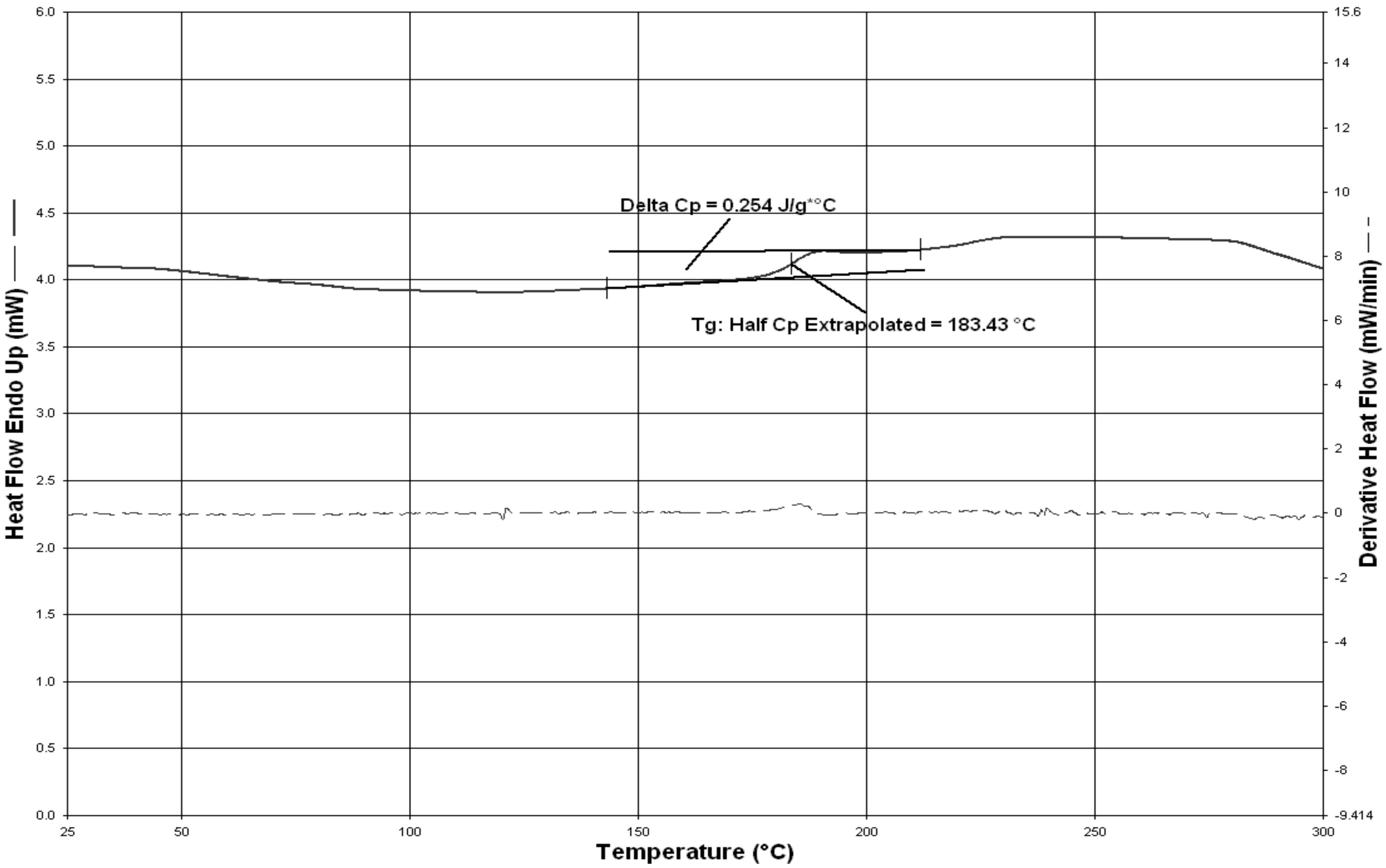


Figure 30 DSC thermogram of the PVP (γ-radiation under vacuum, 93 % conversion)

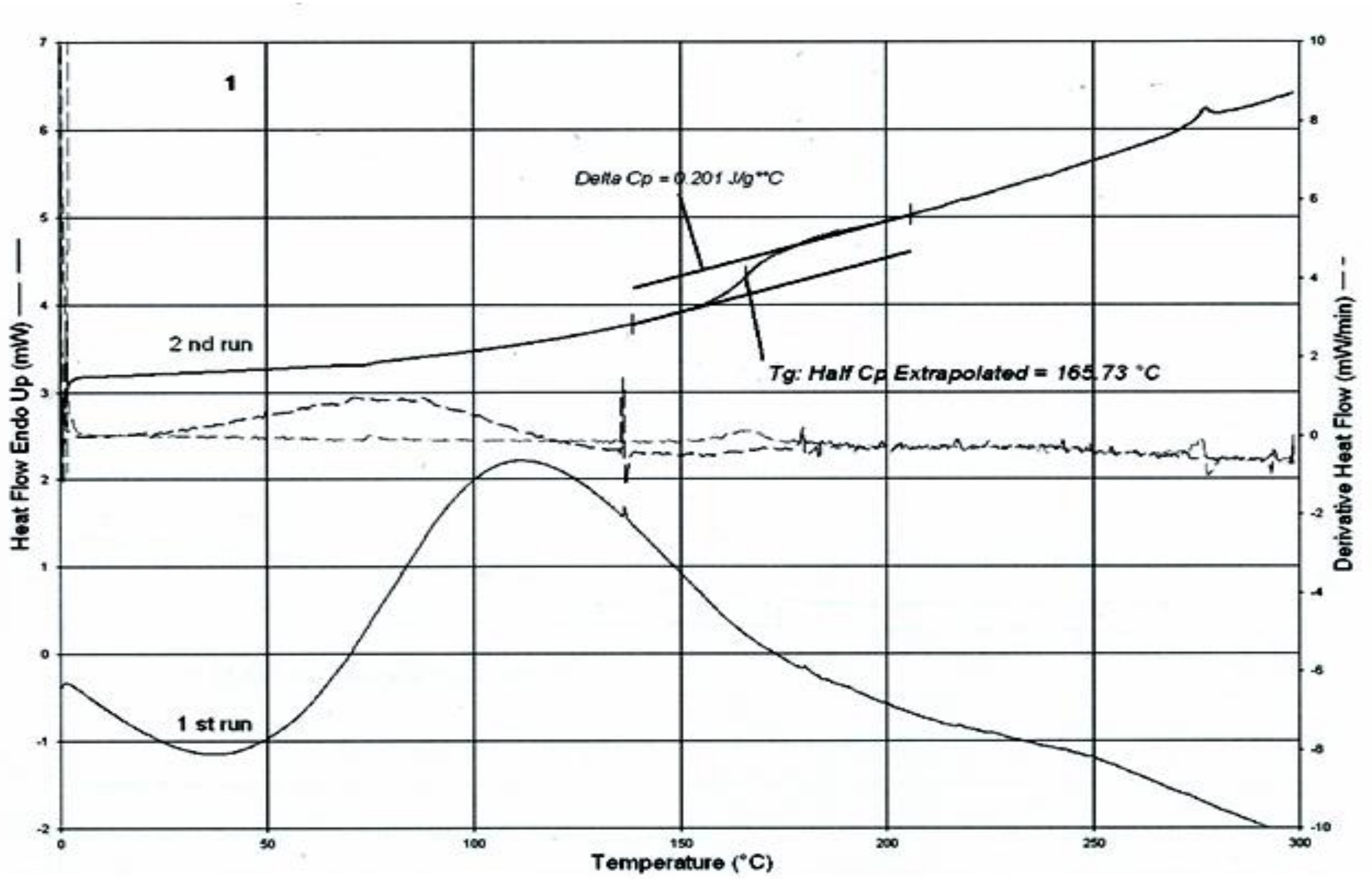


Figure 31 DSC thermogram of the PVP (by AIBN, 36 % conversion).

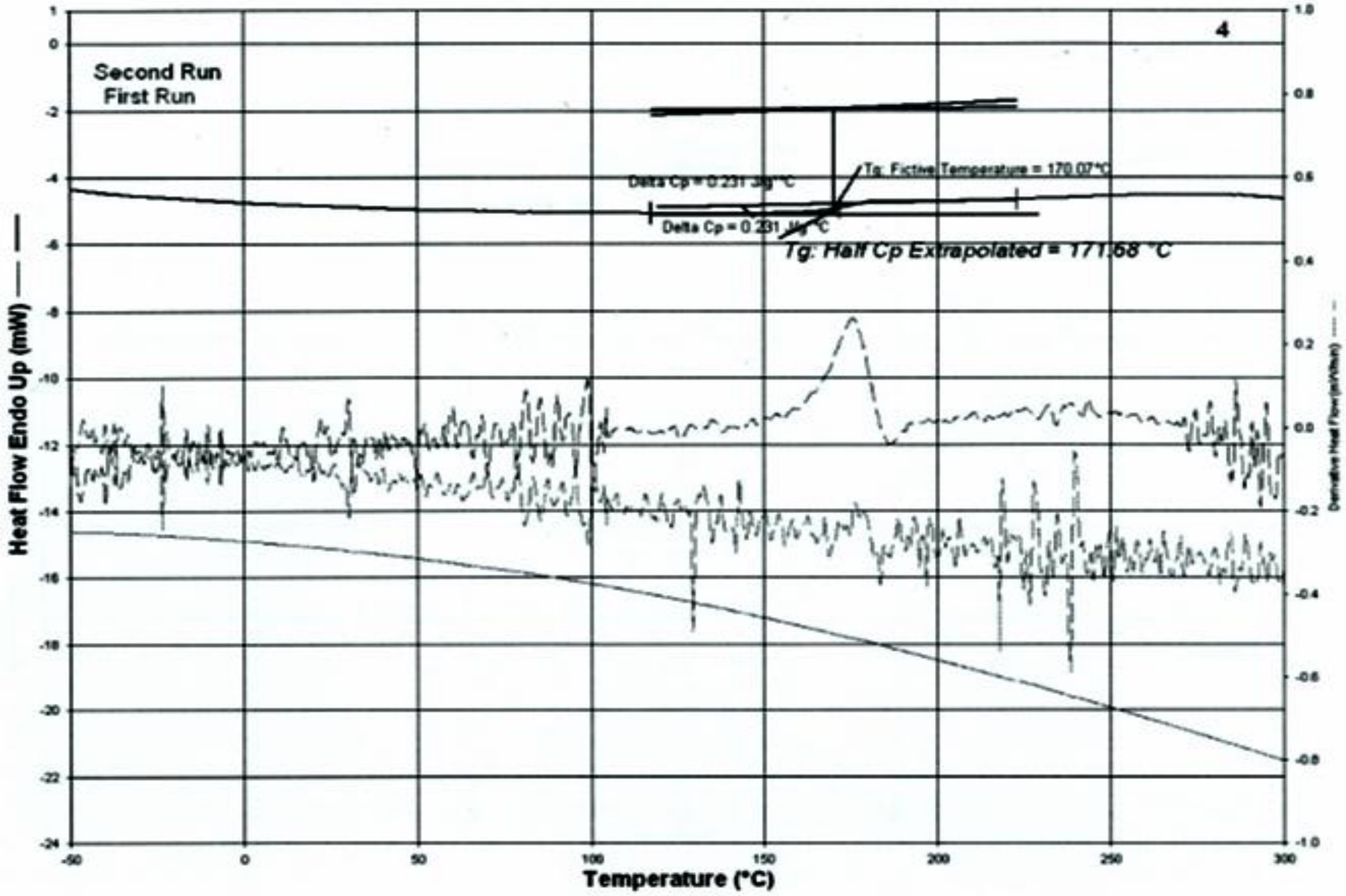


Figure 32 DSC thermogram of the PVP (by AIBN, 73 % conversion).

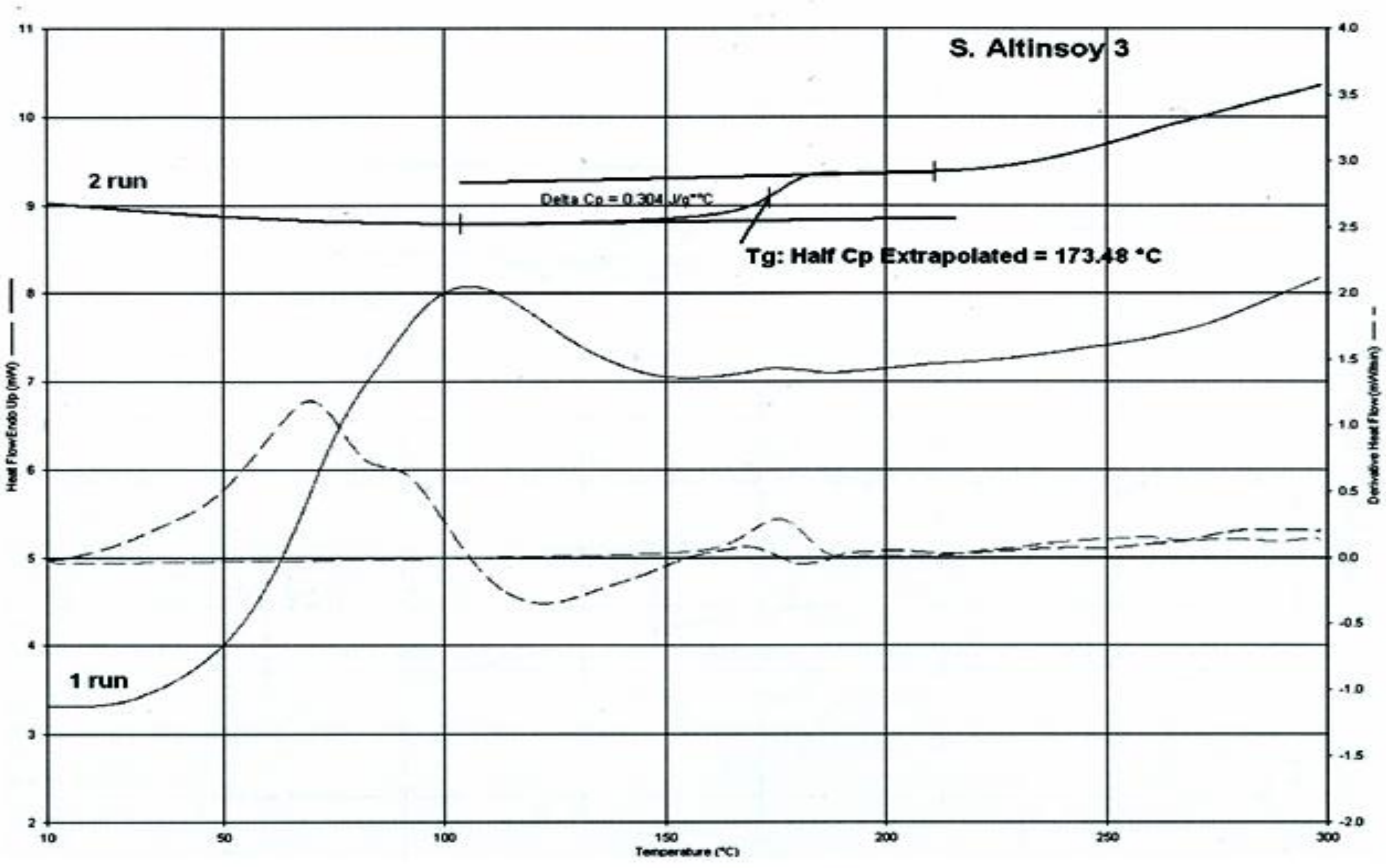


Figure 33 DSC thermogram of the PVP (by AIBN, 94 % conversion).

The value of T_g would be influenced by the formation of the hydrogen bond, which would retard the movement of polymer segment and result in an increase of T_g. The increase of the molecular weight of the sample may also affect the T_g value of the PVP samples.

The relation of the T_g and the molecular weight is approximated by Fox-Flory equation (44):

$$T_g = T_{g,\infty} - K / M \qquad \textbf{(26)}$$

where $T_{g,\infty}$ is the glass transition temperature of a linear chain of infinite molecular weight and K is a constant depending on the nature of the polymer. The molecular weights were calculated from the viscosity measurement in terms of Mv. The results are tabulated in Table 14, 15 and 16 and the T_g is plotted against reciprocal of molecular weight in Figure 34-36. From intercept of the straight line, $T_{g,\infty}$ and K are obtained from the slopes. The obtained values are tabulated in Table 17.

Table 14 Some of the T_g and M_v values of polymers obtained by γ -radiation at open atmosphere.

Time (Hours)	Conversion (%)	T_g (°C)	M_v (g/mol)
15	12,40	173,62	15374,3
18	53,66	176,45	34970,0
24	94,31	181,82	43727,2

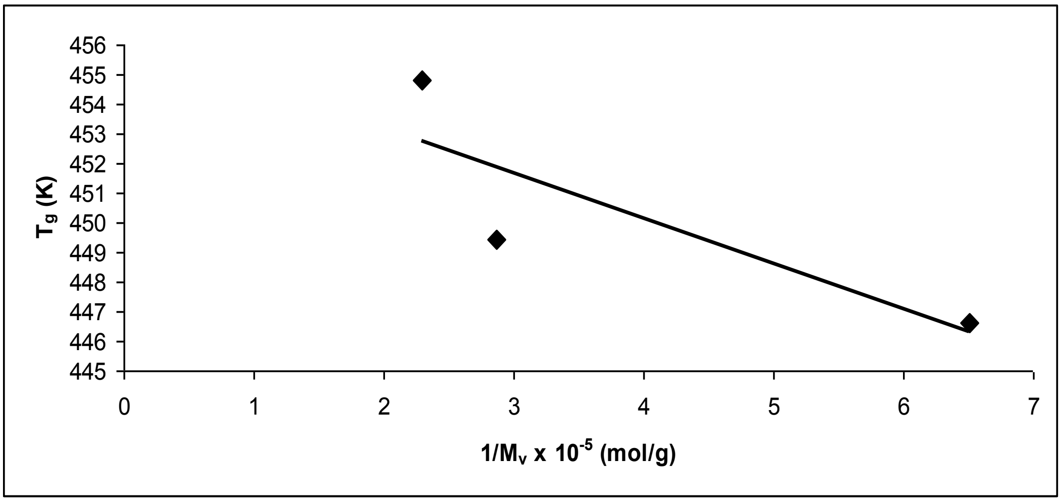


Figure 34 T_g vs reciprocal M_v values of polymers obtained by γ-radiation at open atmosphere.

Table 15 Some of the T_g and M_v values of polymers obtained by γ-radiation under vacuum.

Time (Hours)	Conversion (%)	T_g (°C)	M_v (g/mol)
5	13,58	175,56	40394,1
10	46,98	179,51	43221,3
20	93,21	183,43	46978,3

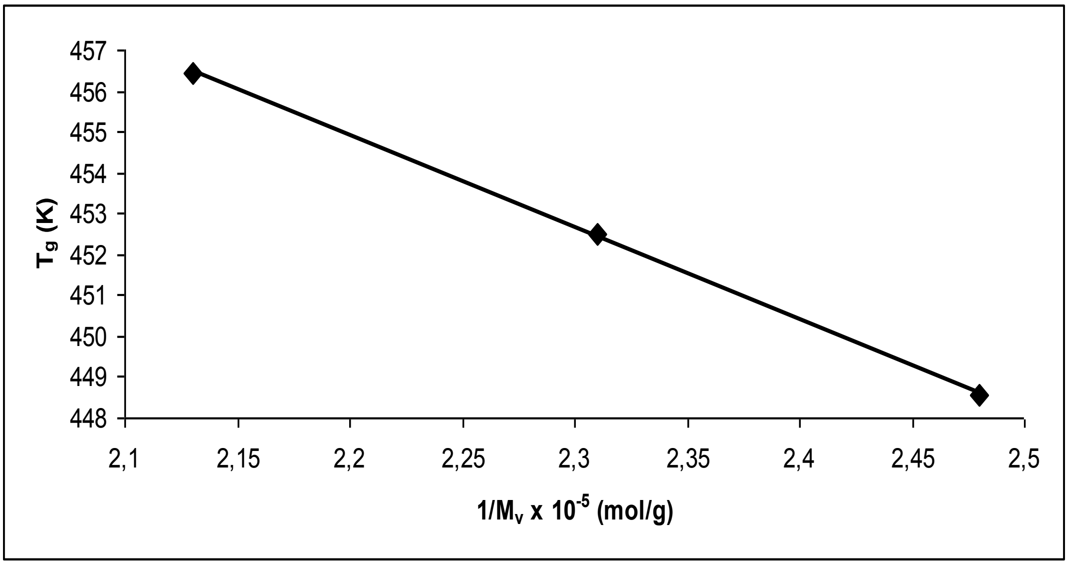


Figure 35 T_g vs reciprocal M_v values of polymers obtained by γ-radiation under vacuum.

Table 16 Some of the T_g and M_v values of polymers obtained by polymerization by AIBN at 50 °C.

Time (Hours)	Conversion (%)	T_g (°C)	M_v (g/mol)
0,5	5,950	165,73	13149,4
4	72,92	171,68	38519,8
8	94,21	173,48	43277,4

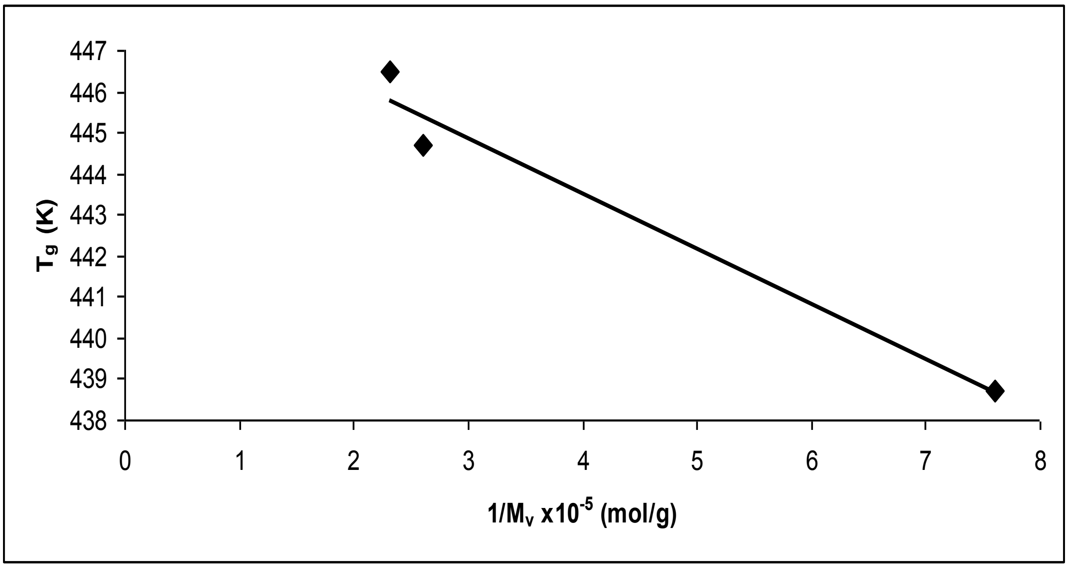


Figure 36 T_g vs reciprocal M_v values of polymers obtained by polymerization by AIBN at 50 °C.

Table 17 T_g and K values of polymers obtained by different methods of polymerization.

Polymerization by	**$T_{g,\infty}$ (K)**	**K x 10^5 (K g mol^{-1})**
γ-ray at open atm.	456,2	1,53
γ-ray under vacuum	504,4	22,5
AIBN at 50 °C	448,9	1,34

According to the results, the polymers obtained by the γ-ray under vacuum has the highest $T_{g,\infty}$ and thus the K value. This is caused by the high molecular weight polymers which are obtained under vacuum by γ-radiation.

3.2.5 TGA Investigation

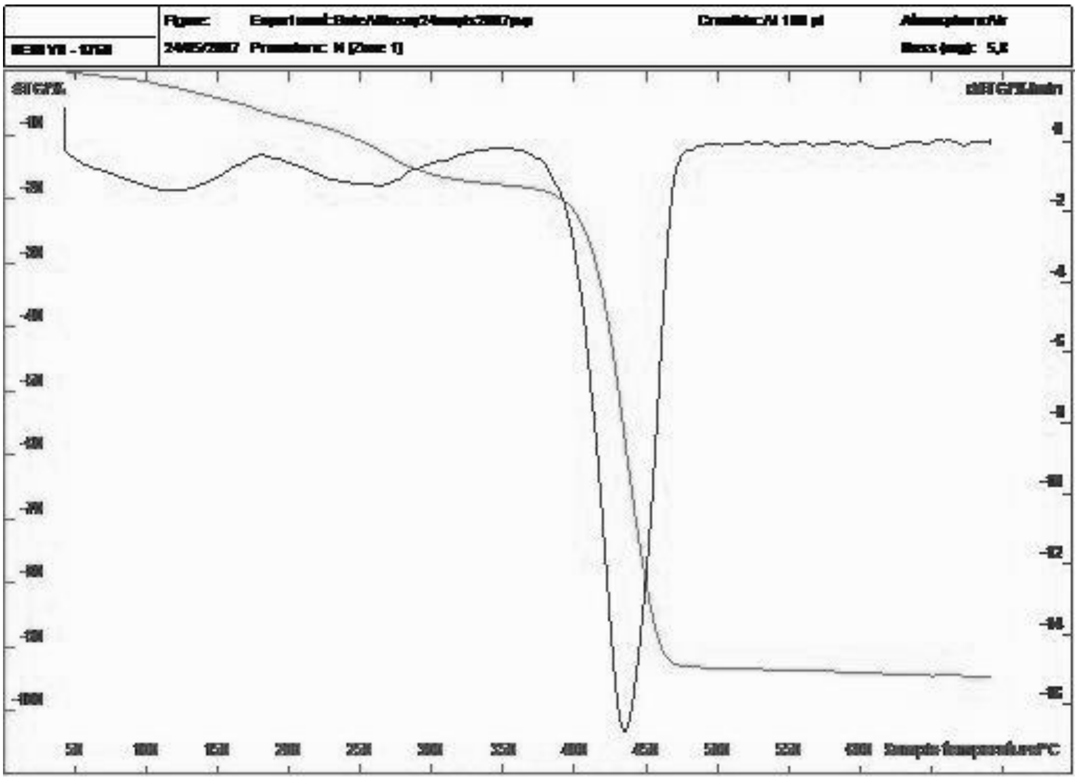


Figure 37 TGA thermogram of PVP obtained by AIBN at 50 °C.

All the thermograms of the PVP samples obtained by different polymerization conditions were the same. As a sample, PVP obtained by AIBN at 50 °C is given in Figure 37. The thermogram indicates a single-stage decomposition reaction. Removing of solvent from the sample is observed in the range from 50°C to 180°C. Depolymerization starts at about 400°C and continues to 460°C. High decomposition temperature of PVP shows high thermal stability of the polymer. According to data, 94% of the sample is consumed.

CHAPTER 4

CONCLUSIONS

Whitin the limitations of this study following conclusions can be drawned:

1. All synthesized polymer was white in color and hydrophilic gel type.

2. The % conversion versus time curves at open atmosphere showed an autoacceleration mechanism.

3. Polymerizations carried out at open atmosphere showed an induction period of as a result of inhibition of oxygen.

4. The percent conversion increased with polymerization time.

5. From Arrhenius plot activation energy of polymerization by AIBN at different temperatures was calculated as 31,8 kJ/mol.

6. $T_{g,\infty}$ and K values were calculated for each polymerization methods. As expected, results showed that the glass transition temperature of polymer increases with increasing molecular weight.

7. FT-IR and NMR results showed that polymerization proceeded via carbon-carbon double bond without any change in the ring. Also, the chemical structure of polymers obtained under different polymerization conditions were the same and did not change with conversion.

8. The TGA thermogram showed that thermal degradation of polymer is in the form of depolymerization.

REFERENCES

1. Molyneux, P., The Physical Chemistry and Pharmaceutical Applications of Polyvinylpyrrolidone, Proceedings of the International Symposium on Povidone, April 17-20, Lexington, U.S.A., 1-19, 1983.

2. Sanner, A., Straub, F., Tschang, C.H., Chemistry, Structure and Properties of Polyvinylpyrrolidone, 20-38.

3. Malawer, E.G., DeVasto, J.K., Frankoski, S.P., Montana, A.J., Aqueous Size Exclusion Chromatography of Polyvinylpyrrolidone: The Chromatographic Method, 503-517.

4. Ranucci, E., Spagnoli, G., Sartore, L., Bignotti, F., Ferruti, P., Synthesis and Molecular Weight Characterization of End-Functionalized N-vinyl-2-pyrrolidone Oligomers, Macromoecules, Chem. Phys. (196) 763-774, 1995.

5. Haaf, F., Sanner, A., Straub, F., Polymers of N-Vinylpyrrolidone: Synthesis, characterization and Uses, Polymer Journal (17) 143-152, 1985.

6. Zhongqing, H., Zhicheng, Z., Guixi, Z., Weijun, L., Complex-Radical Terpolymerization of Styrene, Maleic Anhydride, and N-Vinylpyrrolidone via γ-Ray Radiation: Synthesis, Characterization, and Micellization, Polymer (46) 12711-12715, 2005.

7. Kantoğlu, Ö., Şen, M., Çaykara, T., Güven, O., Synthesis and Application of N-Vinyl-2-Pyrrolidone Based Hydrogels Containing mono-, di- and tri-protic Acid Moieties, Macromolecules, (199), 273-279, 1998.

8. Guven, O., Sen, M., Preparation and Charaterization of Poly(N-Vinylpyrrolidone) Hydrogels, Polymer, (32) 2491, 1991.

9. Benamer, S., Mahlous, M., Boukrif, A., Mansouri, B., You, S.L., Synthesis and Characterisation of Hydrogels Based on Poly(Vinylpyrrolidone), Nuclear Instruments and Methods in Physics Research B (248) 284-290, 2006.

10. Can, H.K., Synthesis of Persulfate Containing Poly(N-Vinyl-2-Pyrrolidone) (PVP) Hydrogels in Aqueous Solutions by ɣ-Induced Radiation, Radiation Physics and Chemistry (72) 703-710, 2005.

11. Jianguo, W., Ma, Z., Han, M., Hong, J., Wang, G., Poly(N-Vinyl-2-Pyrrolidone) Cluster-Assembled Nanostructure Films Prepared by Low Energy Cluster Beam Deposition, Solis State Communications (121) 251-256 ,2002.

12. Huang, K.S., Lee, E.C., Chang, Y.S., Synthesis and Characterization of Soluble Hybrids of Poly(vinyl pyrrolidone) or Its Copolymer, Journal of Applied Polymer Science (100) 2164-2170, 2006.

13. Huang, K.S., Hsiao, C.N., Nien Y.H., Lin J.M., Synthesis, Characterization, and Application of PVP/PAM Copolymer, Journal of Applied Polymer Science (99) 2454-2459, 2006.

14. Ranucci, E., Spagnoli, G., Sartore, L., Bignotti, F., Ferruti, P., Synthesis and Molecular Weight Characterization of End-Functionalized N-vinyl-2-pyrrolidone Oligomers, Macromoecules, Chem. Phys. (196) 763-774, 1995.

15. Zhang, H.L., Bai,T.C., Yan, G.B., Hu J., Solubility of Silybin in aqueous Poly(vinylpyrrolidone) Solution, Fluid Phase Equilibria (238) 186-192, 2005.

16. Bai T.C., Huang, C.G. Yao, W.W., Zhu, C.W., Viscosity B-Coefficients and Activation Free Energy of Viscous Flow for Hexanedioic Acid in Aqueous Polyvinylpyrrolidone Solution, Fluid Phase Equilibria (232) 171-181, 2005.

17. Tarassova, E., Aseyev, V., Tenhu, H., Klenin, S., Poly(vinyl pyrrolidone)—C70 complexes in aqueous solutions, Polymer (44)4863-4870, 2003.

18. Kırcı, B, Güner, A., Effect of Phenolic Cosolutes on the Main Parameters, Phase Separation and Theta Temperature of Dilute Aqueous Poly(Nvinyl-2-pyrrolidone) Solutions, European Polymer Journal (37) 361-365, 2001.

19. Abraham, G.A., Queiroz, A.A., Román, J.S., Hydrophilic Hybrid IPNs of Segmented Polyurethanes and Copolymers of Vinylpyrrolidone for Applications in Medicine, Biomaterials (22) 1971-1985, 2001.

20. Száraz, I., Forsling, W., A Spectroscopic Study of the Solvation of 1-Vinyl-2-Pyrrolidone and Poly(1-Vinyl-2-Pyrrolidone) in Different Solvents, Polymer (41) 4831-4839, 2000.

21. Sionkowska, O., Interaction of Collagen and Poly(Vinylpyrrolidone) in Blends, European Polymer Journal (39) 2135-2140, 2003.

22. Devine, D.M., Higginbotham, C.L., The synthesis of a Physically Crosslinked NVP Based Hydrogel, Polymer (44) 7851-7860, 2003.

23. Hsiao, C.N., Huang, K.S., Synthesis, Characterization, and Applications of Polyvinylpyrrolidone/SiO2 Hybrid Materials, Journal of Applied Polymer Science (96)1936-1942, 2005.

24. Muta, H., Ishida, K., Tamaki, E., satoh, M., An IR Study on Ion-Specific and Solvent-Specific Swelling of Poly(N-Vinyl-2-Pyrrolidone) Gel, Polymer (43) 103-110, 2002.

25. Şen, M., Avcı, E.N., Radiation Synthesis of Poly(N-Vinyl-2-Pyrrolidone)–κ-Carrageenan Hydrogels and Their Use in Wound Dressing Applications. I. Preliminary Laboratory Tests, Journal of Biomedical Materials Res. (74A) 187-196, 2005.

26. Jin, s., Liu, M., Zhang, F., Chen, C., Niu, A., Synthesis and Characterization of pH-Sensitivity Semi-IPN Hydrogel Based on Hydrogen Bond Between Poly(N-Vinylpyrrolidone) and Poly(Acrylic Acid), Polymer (47) 1526-1532, 2006.

27. Nguyen, V., Yoshida, W., Jou, J.D., Cohen, Y., Kinetics of Free-Radical Graft Polymerization of 1-Vinyl-2-Pyrrolidone onto Silica, Journal of Polymer Science Part A: Polym. Chem. (40) 26-42, 2002.

28. Park, K.R., Nho, Y.C., Preparation and Characterization by Radiation of Hydrogels of PVA and PVP Containing Aloe Vera, Journal of Polymer Science (91) 1612-1618, 2004.

29. Sedlařík, V., Saha, N., Kuřitka, I., Sáha, P., Characterization of Polymeric Biocomposite Based on Poly(vinyl alcohol) and Poly(vinyl pyrrolidone), Polymer Composite (27) 147-152, 2006.

30. Water-Soluble Polymers” in EPSE 2nd Ed., Vol. 17, pp. 730–784, by C. L. McCormick, University of Southern Mississippi; J. Bock and D. N. Schulz, Exxon Research.

31. Lu, X., Gong, S., Meng, L., Li, C., Yang, S., Zhang, L., Controllable Synthesis of Poly(*N*-vinylpyrrolidone) and Its Block Copolymers by Atom Transfer Radical Polymerization, Polymer (48) 2835-2842, 2007.

32. White, L.A., Hoyle, C.E., Jonsson, S., Mathias, L.J., Bulk Free-Radical Photopolymerizations of 1-Vinyl-2-Pyrrolidinone and Its Derivatives, Journal of Polymer Science Part A: Polym. Chem. (40) 694-706, 2002.

33. Wan, D., Satoh, K., Kamigaito, M., Okamoto, Y., Xanthate-Mediated Radical Polymerization of N-Vinylpyrrolidone in Fluoroalcohols for Simultaneous Control of Molecular Weight and Tacticity, Macromolecules (38) 10397-10405, 2005.

34. Polyvinylpyrrolidone Excipients for Pharmaceuticals, Springer Berlin Heidelberg, 5-124, 2005.

35. Liu, Z., and Rimmer, S., Studies on the Free Radical Polymerization of N-Vinylpyrrolidinone in 3-Methylbutan-2-one, Macromolecules (35) 1200-1207, 2002.

36. Luo, L., Ranger, M., Lessard, D.G., Garrec, D., Gori, S., Leroux, J.C., Rimmer, S., Smith, D., Novel Amphiphilic Diblock Copolymer of Low Molecular Weight Poly(N-vinylpyrrolidone)-block-poly(D,L-lactide): Synthesis, Characterization, and Micellization, Macromolecules (37) 4008-4013, 2004.

37. Ray, B., Kotani, M., Yamago, S., Highly Controlled Synthesis of Poly(N-vinylpyrrolidone) and Its Block Copolymers by Organostibine-Mediated Living Radical Polymerization, Macromolecules (39), 5259-5265, 2006.

38. Breitenbach, J.W., Polymerization and Polymers of N-Vinylpyrrolidone, Journal of Polymer Science (23) 949-953, 1957.

39. Darwis, D., Hilmy, N., Hardiningsih, L., Erlinda, T., Poly(N-vinylpyrrolidone) hydrogels: 1.Radiation Polymerization and Crosslinking of N-vinylpyrrolidone, 2002.

40. Mondino, A.V., Effect of Gamma-Radiation in Vinylpyrrolidone, Journal of Radioanalytical and Nuclear Chemistry (254) 395-396, 2002.

41. Ulanski, P., Rosiak, J.M., The Use of Radiation Technique in the Synthesis of Polymeric Nanogels, Nuclear Instruments and Methods in Physics Research B (151) 356-360, 1999.

42. Levy, G.B., Frank, H. P., Determination of molecular weight of polyvinylpyrrolidone, Journal of Polymer Science (17) 234-247, 1955.

43. Kreft, K., Kozamernik, B., Urleb, U., Qualitative Determination of Polyvinylpyrrolidone Type by Near-Infrared Spectrometry, International Journal of Pharmaceutics (177) 1-6, 1999.

44. Billmeyer, F. W., Textbook of Polymer Chemistry, Interscience Publisher, New York, Chapter 21, 1961.

45. Prof. Dr. Osman Yılmaz (Personal Communication).

46. Brandrup, J., Immergut, E.H., Polymer Handbook, Wiley-Interscience publication, New York, 3rd Edition, 1989.