POLYMERIZATION AND CHARACTERIZATION
OF
N-VINYLCAPROLACTAM

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ABSTRACT

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OF
N-VINYLCAPROLACTAM

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Poly(N-vinylcaprolactam), PNVCL, is a nonionic, nontoxic, water soluble, thermally sensitive and biocompatible polymer. It contains hydrophilic carboxylic and amide groups with hydrophobic carbon-carbon backbone chain so its hydrolysis does not produce small amide compounds which are often not desired for biomedical applications. Moreover PNVCL possesses lower critical solution temperature, (LCST) in the range of physiological temperature (32-34 ^{o}C). These properties make the polymer suitable for use in some biotechnology applications such as implantation of artificial organs and tissues, purification of enzymes, proteins and living cells, and in drug release systems.

In this study PNVCL was synthesized by free radical polymerization with solution technique. Polymerization was done at different temperatures for different time periods in an oil bath. The activation energy for polymerization was found from Arrhenius plot as 108.4 kJ/mol. Polymer was characterized by FT-IR, ^{1}H-NMR and

^{13}C-NMR, DSC, TGA and XRD techniques. FT-IR and NMR measurements confirmed that the polymerization proceeded through the vinyl group.

Keywords: N-vinylcaprolactam, Solution polymerization, Lower critical solution temperature, Characterization

ÖZ

N-VİNİLKAPROLAKTAM POLİMERLEŞTİRİLMESİ VE KARAKTERİZASYONU

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Poli(N-Vinilkaprolaktam), PNVCL, iyonik olmayan, zehirsiz, suda çözünen, ısıya duyarlı ve biyolojik olarak uyumlu bir polimerdir. Hidrofilik karboksilik ve amid gruplarıyla hidrofobik karbon-karbon temel zinciri içermektedir. Bu yüzden hidrolize uğraması biomedikal uygulamalar için istenmeyen küçük amid bileşimlerini oluşturmaz. Poli(N-Vinilkaprolaktam) fizyolojik sıcaklık aralığında (32 ^{o}C -34 ^{o}C), en düşük kritik çözelti sıcaklığına (LCST) sahiptir. Bu özellikler polimerin bioteknolojide yapay organ ve kas emplantasyonunda, enzim, protein ve canlı hücrelerin temizlenmesinde ve ilaç salınım sistemlerinde kullanılmasını uygun kılar.

Bu çalışmada PNVCL serbest radikal polimerleşmesiyle, çözelti tekniğiyle polimerleştirilmiştir. Polimerleştirme farklı sıcaklıklarda ve farklı zaman aralıklarında yağ banyosunda yapılmıştır. Polimerleşme için aktivasyon enerjisi Arrhenius grafiğinden 108,4 kJ/mol olarak bulunmuştur. Polimerin karakterizasyonu FT-IR, ^{1}H-NMR ve ^{13}C-NMR, DSC, TGA ve XRD teknikleri ile yapılmıştır. FT-IR ve NMR teknikleri ile yapılan analizler polimerleşmenin vinil grubu üzerinden yürüdüğünü doğrulamıştır.

Anahtar Kelimeler: N-vinilkaprolaktam, Çözelti polimerleşmesi, En düşük kritik çözelti sıcaklığı, Karakterizasyon

To my family

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INTRODUCTION

1.1 N-VINYLCAPROLACTAM

N-Vinylcaprolactam, NVCL, is a monomer with amphiphilic character which possesses hydrophilic carboxylic and amide group (lactam ring) where the amide group is connected to the hydrophobic vinyl group (Figure 1).

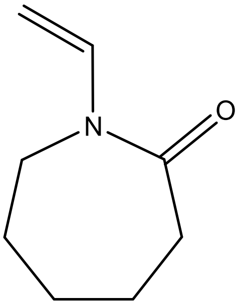

Figure 1 Structure of NVCL

Polymerization of NVCL occurs through the vinyl group by chain polymerization, so the polymer backbone is a vinyl type polymer.

Tishchenko et al. reported the crystal structure of monomer. The crystals are triclinic of cell parameters: a = 8.170(4) A°, b = 8.094(4) A°, c = 6.799(4) A°, α= 99.92(1)^0, β = 88.89(1)^0, γ = 115.30(1)^0. The space group of monomer is $P\bar{1}$ [1, 2].

NVCL contains a ring, which consists of six carbon atoms. So, it cannot be of the flat conformation. A seven-member NVCL ring includes the rigid amide group connected to the double bond therefore for this combination the "chair" conformation is the most favourable one [3]. Kirsch et al. reported the conformation type of NVCL by quantum-chemical method. Figure 2 illustrates the structure of NVCL determined by quantum-chemical method [3].

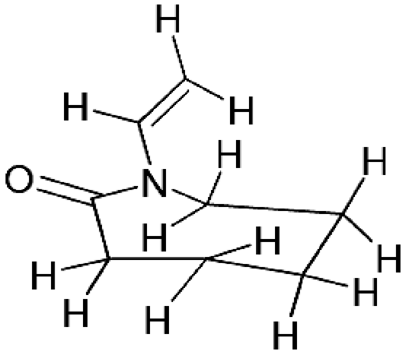

Figure 2 Structure of NVCL determined by quantum-chemical calculation [3]

Kirsch et al. confirmed the chair conformation of NVCL crystals by X-ray analysis, representing that two monomer rings are packed as if two chairs were placed on one another "seat-on-seat" with oppositely directed backs [3, 4]. Chair conformation of monomer is shown in Figure 3 [3].

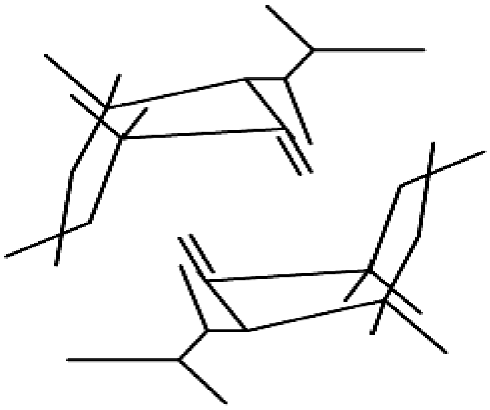

Figure 3 Structure of NVCL molecules in the crystal by X-ray analysis [3]

Physical properties of NVCL are given in Table 1.

Table 1 Physical properties of NVCL

Boiling Point, ^{o}C	128
Melting Point, ^{o}C	35
Specific Gravity, g/ml	1.029
Flash Point, ^{o}C	110
Appearance	White Crystals

NVCL is an organo-soluble amphiphilic compound. It is dissolved in both polar and non-polar organic substances, but is a poor-soluble substance in the aqueous ones. Hence, solvents such as benzene, hexane, isobutanol, isopropanol are used with free radical initiator for the solution polymerization of N-vinylcaprolactam [5].

1.2 POLY (N-VINYLCAPROLACTAM)

Poly (N-vinylcaprolactam), PNVCL, is a non-ionic, water-soluble, non-adhesive, nontoxic, thermo-sensitive and biocompatible polymer that belongs to the group of poly-N-vinylamide polymers (Figure 4) [6].

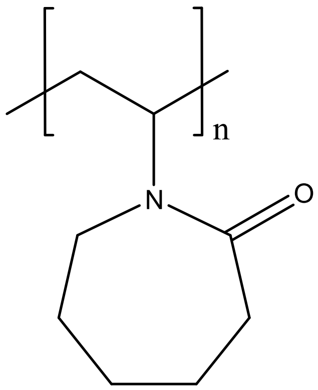

Figure 4 Poly (N-vinylcaprolactam)

PNVCL has a lower critical solution temperature (LCST) in aqueous medium. N-alkylated poly (acrylamides), methylcellulose, poly (methyl vinyl ether) and block co-polymers of ethylene oxide are other examples of polymers with LCST behavior. Among N-alkylated poly (acrylamides), poly (N-isopropylacrylamide), PNIPAM, is the most well studied polymer [5]. Both PNIPAM and PNVCL possess LCST in the range of physiological temperature (32-34 ^{o}C) [3, 7]. In this range of temperature PNVCL shows dissolution/precipitation transition in water which makes it applicable in biochemistry and medicine. Although both polymers are suitable for several applications, PNVCL is more biocompatible and applicable than PNIPAM. Both PNVCL and PNIPAM are water-soluble, non-ionic polymers and exhibit LCST at similar temperatures; however, they vary in the mechanisms and thermodynamics of the phase transitions [8, 9]. PNVCL has hydrophilic carboxylic and cyclic amide groups and hydrophobic carbon-carbon backbone chain. The amide group is directly connected to the hydrophobic carbon-carbon backbone chain, so hydrolysis of PNVCL will not produce small amide compound which is unwanted for biomedical applications such as implantation of artificial organs and tissues, purification of enzymes, proteins and living cells. Hydrolysis of PNVCL in strongly acidic conditions will produce a polymeric carboxylic acid and small toxic amide compounds will not form, like is the case with PNIPAM. Therefore PNVCL is a biocompatible polymer owing to its stability against hydrolysis [10, 11]. However, major disadvantage of PNVCL, is its non-biodegradable nature. PNVCL absorbs numerous organic compounds from water [10, 12]. Makhaeva et al. showed that owing to the hydrophobic interactions, charged surfactants bind to the PNVCL. As a result the polymer behaves as a polyelectrolyte, thus swelling the polymer coil [10, 13].

1.2.1 Thermosensitivity

Recently, water-soluble polymers have been extensively investigated due to their wide range of applications in medicine [14], biotechnology [15], ecology [16] and pharmacology [17]. They are stimuli-responsive polymers, which are able to respond to environmental changes, such as pH, temperature, ionic strength, and electric field [18, 19]. Separation of water-soluble polymers from their solutions upon heating is called a thermo-sensitive property [20]. Thermo-sensitive polymers dissolve in cold water, but collapse and precipitate with heating above a certain temperature. There is a phase transition temperature at which an abrupt change in conformation, solubility and hydrophilic-hydrophobic balance of the polymer occurs [21]. Polymers, which become soluble upon heating, have an upper critical solution temperature (UCST). Those polymers, which become insoluble and precipitate in solutions upon heating, possess a lower critical solution temperature (LCST) [22].

Thermo-sensitive amphiphilic water-soluble polymers are capable of self-organization in solutions upon heating. They have hydrophilic and hydrophobic compounds in their structure. Their capability of self organization is resulted from the intra and intermolecular hydrophobic attraction of the monomer units. Conformational coil-globule transition, micellization, liquid-liquid phase separation and gelation are the examples of self-organization in solutions of thermo-sensitive polymers [23].

Hydrogen bonding between the hydrophilic segments of the polymer chain and water molecules is effective at low temperatures [24]. When temperature is increased partial displacement of water from the polymer coil is observed. Displacement of water weakens the hydrogen bonds and increases interactions between the hydrophobic segments of the polymer macromolecules [23]. The polymers collapse, aggregate and phase separation occurs due to the intra and intermolecular hydrogen bonds between the hydrophobic parts of the polymer molecules. Hydrogen bonds are re-organized around the non-polar polymer. The polymers form a separate phase in solution and change their conformation from coil to globule (Figure 5) [23].

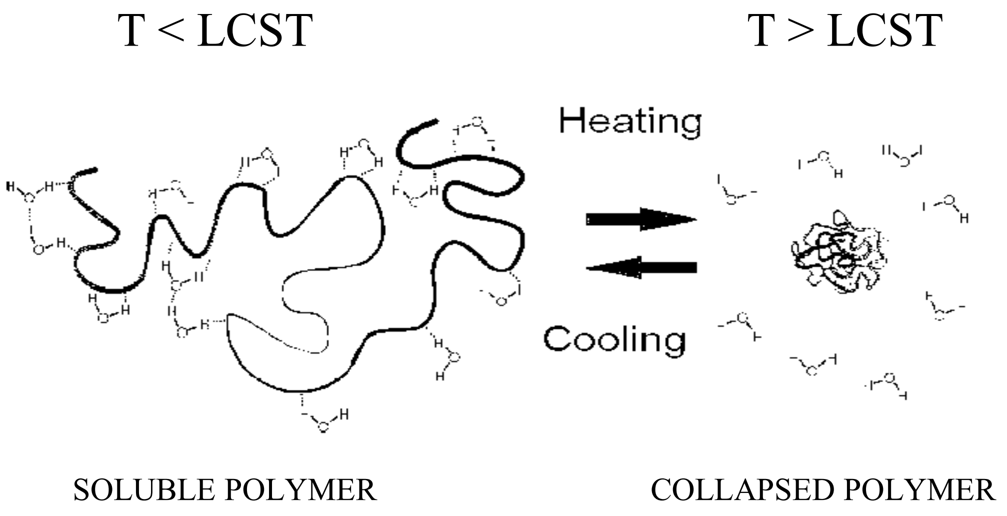

Figure 5 The effect of temperature on the thermo-sensitive polymer chain [22].

The LCST phenomenon is reversible, when the solution is cooled the thermo-sensitive polymers become soluble again.

LCST is sensitive to changes of polymer concentration, molecular weight of the polymer and composition of the solution. When the polymer chain length or polymer concentration is increased, the LCST of PNIPAM and PNVCL decreases [26, 27, 28]. In general, hydrophobic compounds decrease the LCST, whereas hydrophilic and charged compounds increase LCST of polymers due to the strong interactions between water and hydrophilic or charged groups [22]. When the amount of hydrophilic comonomer is too high, LCST disappears [27]. Salts are known to lower the LCST of PNIPAM and PNVCL [26, 8, 28, 29]. Moreover LCST of PNVCL is known to decrease by addition of small amount of alcohol [10]. Wu et al. reported presence of proteins, such as insulin and bovine serum albumin, has been found to increase the LCST of PNIPAM, due to the increased hydrophilicity of the polymer-protein complex [32]. Phase separation of PNVCL solutions upon heating is prevented by anionic surfactants. Anionic and cationic surfactants have been shown to bind to PNVCL due to hydrophobic interactions. PNVCL behaves as a polyelectrolyte upon binding of the surfactant which means the polymer coil swells. As the surfactant concentration increases, the transition temperature increases [8].

A gel is formed, when a polymer network is in contact with a liquid. The network starts to swell because of the thermodynamic compatibility of the polymer chains and solvent. According to the size of gels, there are microgels and macrogels. Macrogels form when concentration of monomers or initial polymer is large enough [33]. A microgel particle is a crosslinked colloidal particle which is swollen by a thermodynamically good solvent. Crosslinking of the temperature-sensitive polymer chains form colloidal particles. These colloidal particles undergo reversible volume change against temperature. The volume change against temperature is called volume phase transition temperature (VPTT) [34]. Hydrogels are crosslinked, hydrophilic and three-dimensional polymeric network structures that can take in large amounts of water. Hydrogels can contain a large volume of the solvent in the swollen state. Therefore, they have many application fields. Separation and filtration devices for small ions and large molecular weight macromolecules have been produced from these materials. For soft contact lenses and artificial lenses porous hydrogels have been used. Moreover, hydrogels are suitable for use in medicine, agriculture, food preparation and cosmetic industry [33].

Shostakovski et al. observed the thermo-sensitivity of PNVCL in 1957 [15]. LCST of PNVCL is in the physiological range of around 32°C. PNVCL finds a wide application in biomaterials. Although PNVCL has a long history, the first hydrogel based on PNVCL was reported only in 1996 [35]. Makhaeva et al. studied the different cross-linked systems based on PNVCL with different size and properties [13].

Lau reported that temperature of phase separation of PNVCL strongly depends on molecular weight of polymer [11]. Tager et al. showed for PNVCL with M_w = $5x10^5$g/mol, the change of the phase transition temperature from 32 ^oC to 34^oC depending on the concentration of the polymer in solution [36]. Meeussen et al. estimated the phase diagrams for polymers with different molecular weights. Moreover cloud point measurements and theoretical calculations were carried out [37].

Verbrugghe et al. reported thermo-sensitive property of PNVCL-g-PEO copolymers. According to this study it was concluded that a certain critical polymer concentration is needed for the polymers to form stable compounds [38].

Makhaeva et al. investigated the swelling behavior of linear copolymer PNVCL and methacrylic acid (MAA) as a function of pH and surfactant concentration by dynamic light scattering [39]. Tager et al. reported phase diagrams of PNVCL with different molecular weights and thermodynamic parameters for the mixing of water and the polymer [40].

Micro calorimetric study of PNVCL hydrogels have been carried by Mikheeva et al. According to this study it was seen that the gel system undergoes two successive cooperative transitions which are microsegregation and volume collapse [41].

Static and dynamic light scattering methods, especially dynamic light scattering (DLS), are very convenient techniques for measuring swelling of microgels. Wu et al. have measured static and dynamic light scattering of PNVCL and PNVCL gels [11, 42].

1.2.2 Literature Survey of PNVCL

PNVCL has many interesting properties which make it suitable for use in biotechnology and biomedicine. Recently, there has been a growing interest in temperature sensitive polymer PNVCL. Many authors have investigated different systems based on PNVCL. Several studies have been reported about the polymerization and properties of PNVCL.

Solomon et al. have studied the bulk polymerization of NVCL in the presence of different initiators in nitrogen or in air atmosphere [43]. The most effective initiator is 2, 2'- azobisisobutyronitrile (AIBN). In the temperature range from 60° to 80°C, high conversions of polymer is obtained by using low concentrations of AIBN. From experimental data, Solomon et al. have calculated $k_{70} = 0.07$; $k_{75} = 0.12$; $k_{80} = 0.19$ l/(mol·min). Moreover Solomon et al. obtained PNVCL by radical polymerization of NVCL in homogeneous solution [44, 45].

Eisele et al. reported polymerization of NVCL in benzene and water with AIBN. Redox initiating systems ($NaHSO_2$ + tert-butyl peroxide, NH_3, H_2O_2) were also tested by Eisele et al. [46].

Cheng et al. reported the polymerization of NVCL by radiation in water. The effects of radiation dose and total dose on the viscosity of polymer were studied [6].

Kudryavtsev et al. studied the radiation graft polymerization of N-vinylcaprolactam onto polypropylene films. The radiation graft polymerization was performed with preirradiation in air (peroxide method) or using a direct method in aqueous solutions and organic solvents. The effects of radiation dose, reaction time, monomer concentration, and homopolymerization inhibitor on the radiation graft polymerization were investigated [47].

Lozinsky et al. reported the polymerization of NVCL by emulsion polymerization using water as solvent and ammonium persulphate/tertiary amine redox initiator. The molecular weight and molecular weight distribution, their temperature-dependent solution behaviors and the thermodynamic parameters of phase segregation process of polymer have been studied by using SEC, DSC [5].

Laukkanen et al. synthesized PNVCL particles with varying surface charges and with different surface structures. The effectiveness of the stabilization in each particle was compared and the effects of electric charges and nonionic polymeric grafts on the thermal properties of the polymers were studied [11].

Narrowly distributed spherical PNVCL microgels prepared by precipitation polymerization in water using potassium persulpate/tertiary amine redox initiator have been studied by Gao et al. [48]. The effect of both anionic (sodium dodecyl sulfate, SDS) and cationic (N-dodecylpyridinium bromide, DPB) surfactants on the swelling and shrinking of the microgels were investigated by laser light scattering (LLS).

Laukkanen et al. prepared grafted PNVCL microgel particles by PEO segments [49]. Aseyev et al. analyzed the colloidal stability and characteristics of some homopolymers, including PNVCL [50]. Loos et al. prepared thermo-responsive hydrogels based on PNVCL and inorganic crosslinked silica phases [51]. Bronstein et al. studied the formation of core-shell PVNCL single-molecule nanostructures due to interaction of PNVCL with metal ions [52]. Van Durme et al. synthesized and characterized PNVCL-g-PEO copolymers [53, 54].

Kirsch and Yanul studied structural transformations and water associate interactions in PNVCL-water system. The chair conformation of PNVCL was determined by quantum-chemical calculations. According to their studies the main chain of PNVCL prepared by usual radical polymerization has syndiotactic structure. Moreover, the role of water molecules on T_g value was showed. According to this study, the addition of water to PNVCL changes T_g from 147 °C (dry polymer) to -17 °C/-38 °C at N (number of water molecules per unit) being 2.6/8.0 [3].

Chen et al. reported an amphiphilic diblock copolymer (PS-co-PNVCL) with PNVCL as a hydrophilic block and polystyrene as a hydrophobic block, which was prepared by reversible addition fragmentation chain transfer (RAFT) polymerization [55].

Shubo et al. synthesized PNVCL, PNVCL-dextrose and PNVCL-dextran copolymers. Solution properties of these compounds were measured by UV-Vis spectrophotometer and High Sensitive Differential Scanning Calorimeter (HSDSC). According to this study LCST of the graft copolymer of dextran and dextrose is lower than that of PNVCL. Moreover, thermo-responsive property of PNVCL and graft copolymers was confirmed [20].

1.3 POLYMERIZATION OF N-VINYLCAPROLACTAM

Polymerization of NVCL monomer is carried out in the presence of free radical polymerization initiators. PNVCL can be obtained by bulk, solution, emulsion and radiation polymerization of NVCL. The method which is also used in this work is summarized as follows:

1.3.1 Solution Polymerization

In solution polymerization the polymerization reaction is conducted in a suitable solvent. The presence of solvent provides reduction in viscosity. Therefore stirring is easier in solution polymerization than in bulk polymerization. Moreover heat transfer can be controlled easily by the solvent. Although solution polymerization has advantages, it has also some drawbacks. In this polymerization rate of reaction is limited, since the reaction temperature is limited by the boiling point of the solvent used. Solvents must be carefully chosen. For the polymerization of NVCL, using an organic solvent is suitable, but the organic solvent must be removed before any further processing of the polymer. Otherwise they may undergo chain-transfer reactions with the polymer which results in a limitation in the molecular weight of the product. The molecular weight of the polymer synthesized by solution polymerization depends on the type of the solvent, monomer and solvent ratio [56].

NVCL can be polymerized in an organic solvent or in water in the presence of free radical polymerization initiators. Bulk polymerization of NVCL is not efficient, because it is difficult to control the reaction mixture in this polymerization. As the polymerization proceeds the viscosity of reaction mixture increases rapidly. Therefore it is difficult to obtain complete mixing of the reaction mixture [57].

Polymerization of NVCL in water is not feasible due to the thermo-reversible solution behavior of the monomer. NVCL has a melting point of 34 °C. It is insoluble in cold water. However the polymer is soluble in cold water, but insoluble in water above the LCST. Therefore the polymerization of NVCL should be conducted at a temperature above the melting point of NVCL in the manner of an oil-in-water emulsion polymerization [57].

In order to polymerize NVCL, water-soluble polymerization-regulation solvents such as tetrahydrofuran, dioxane, methanol, ethanol, isopropanol, ethylene glycol, diethylene glycol and diethylene glycol dimethyl ether can be used [57].

1.3.2 Free Radical Polymerization

Free radical polymerization is the most common type of chain polymerization mechanism which is initiated by a free radical. A free radical is simply a molecule with an unpaired electron. Free radical is highly reactive. In order to gain an electron to form a pair it breaks the bond on another molecule by stealing an electron, leaving that molecule with an unpaired electron which is another free radical. Free radical is generated by the division of a molecule which is known as an initiator into two fragments along a single bond. The stability of a radical depends on the molecule's tendency to react with other compounds. An unstable radical will react with many different molecules. However a stable radical will not easily go in a reaction with other chemical substances. The stability of free radicals can vary widely depending on the properties of the molecule [58].

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.

1.3.2.1 Initiation

In the initiation step, first the initiator AIBN, (I) dissociates to radical, ($R^\bullet$) as shown in Figure 6.

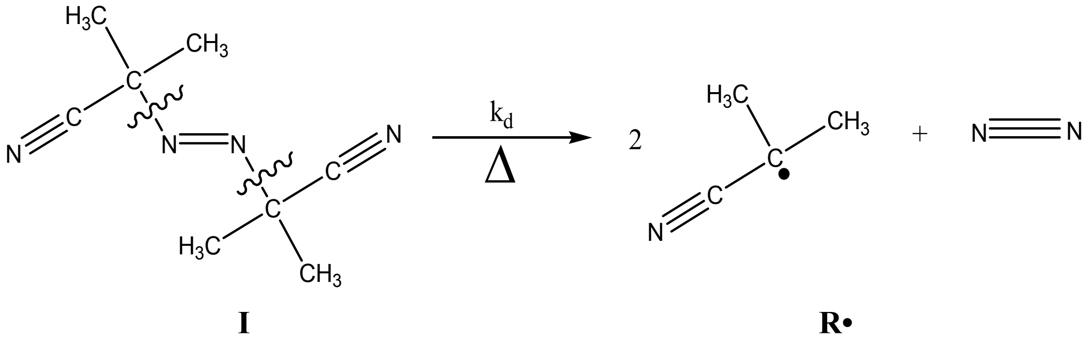

Figure 6 Dissociation of AIBN

After the generation of free radical, ($R^{\bullet}$) from an initiator, it attacks the monomer molecule NVCL, (M) to form $RM^{\bullet}$. There are two possible models of addition:

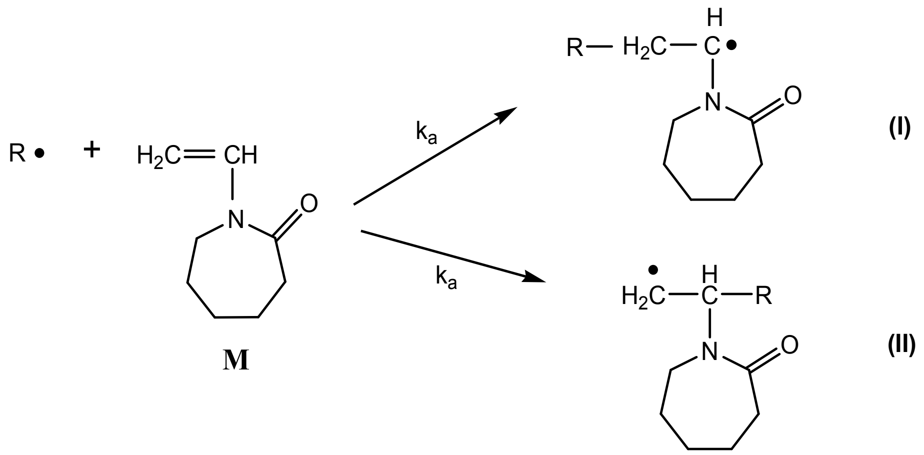

Figure 7 Addition of NVCL to the free radical

In free radical reactions, the reaction leading to more stable product will be favored. 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) [58].

1.3.2.2 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 8.

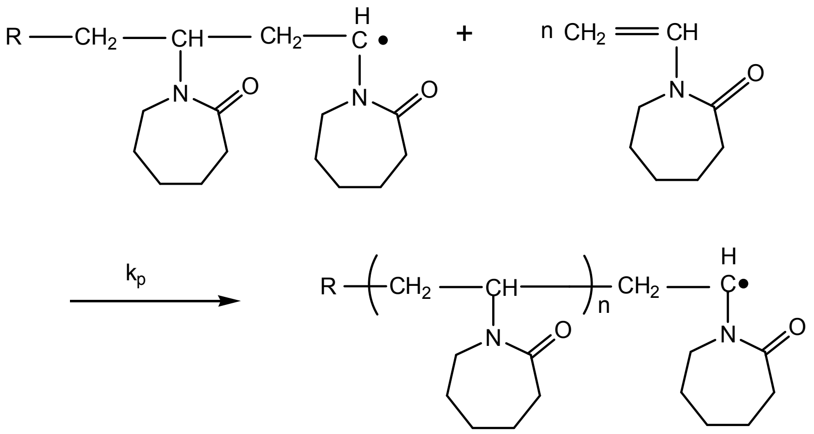

Figure 8 Growth of the Polymer Chain

1.3.2.3 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 9.

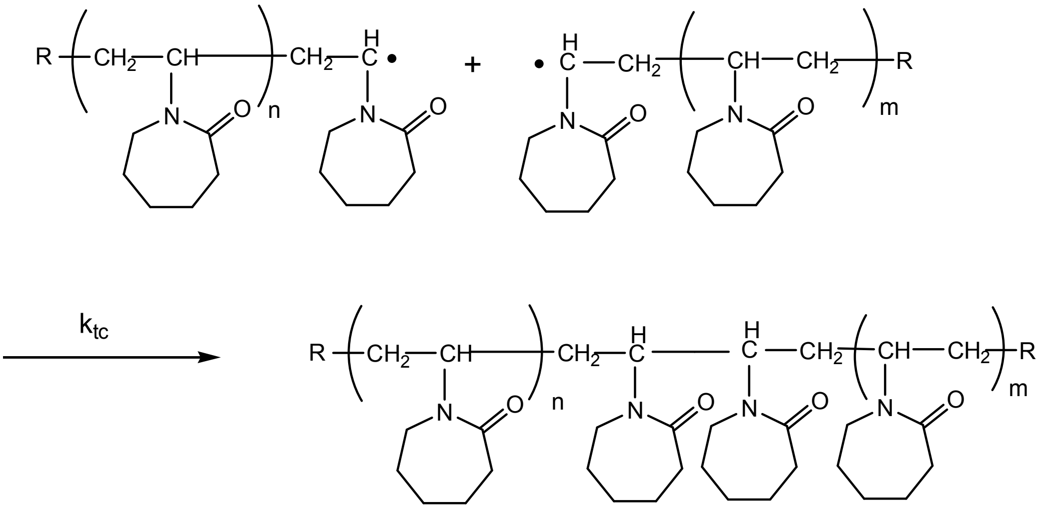

Figure 9 Combination of Growing Chains

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 10.

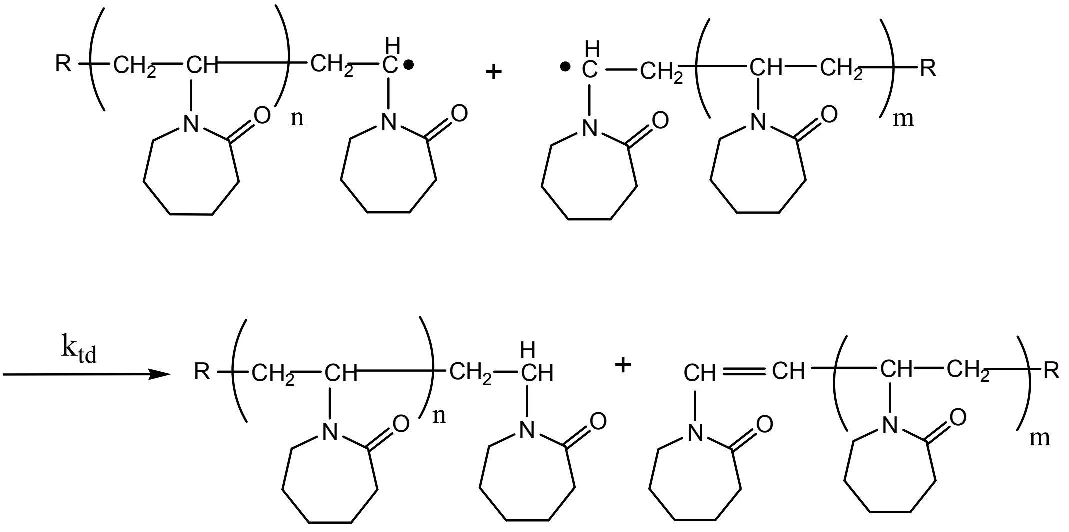

Figure 10 Disproportionation of PNVCL

1.3.3 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:

$$\begin{aligned} I &\xrightarrow{k_d} 2R\bullet \\ R + M &\xrightarrow{k_a} RM\bullet \end{aligned} \quad \textbf{(1)}$$

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

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

where R_i is the rate of initiation, k_d is the dissociation rate constant, [I] is the concentration of the initiator, and f is the initiator efficiency. Initiator efficiency, f is the fraction of radicals formed by equation (1) [58].

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) [54].

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

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

$$[M\bullet] = (f\ k_d\ [I]\ /\ k_t)^{½} \qquad \textbf{(9)}$$

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

$$R_p = -d\ [M]\ /\ d_t = k_p\ [M]\ [I]^{1/2}\ (f\ k_d\ /\ k_t)^{½} \qquad \textbf{(10)}$$

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 $[M]^{3/2}$ [58].

1.4 MOLECULAR WEIGHT DETERMINATION

The molecular weights of polymers were measured by GPC, light scattering and solution viscosity methods.

Solution Viscosity Measurement

Viscosities of different concentrations of polymer solutions were measured with toluene as a solvent at 25 ^{o}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, $\eta_{sp,}$ in terms of $\eta_{r,}$ is

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

Reduced viscosity, η_{red}, 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 [56].

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k'' \eta^2 c \tag{14}$$

$$\frac{\ln \eta_{rel}}{c} = [\eta] + k'' \eta^2 c \tag{15}$$

The intrinsic viscosity, $[\eta]$, is determined by taking the following limit:

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

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

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

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

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

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 X-RAY POWDER DIFFRACTOMETER

X-Ray powder diffraction pattern gives the following information:

- Identification of polymers
- Lateral ordering of polymeric chains
- Orientation of crystallites
- Crystalline size
- Crystalline content
- Unit cell data
- Determination of the point group
- Atomic positions within the unit cell

In order to index the powder X-ray pattern of a sample crystallized in triclinic unit cell, equation (19) was used:

$$d^{*2} = a^{*2}h^2 + b^{*2}k^2 + c^{*2}l^2 + 2a^*b^*hk\cos\gamma^* + 2a^*c^*hl\cos\beta^* + 2b^*c^*kl\cos\alpha^* \quad \textbf{(19)}$$

where h, k, l are Miller indices, a*, b*, c* are reciprocal cell edges and α*, β*, γ* reciprocal cell angles. If cell parameters are known the theoretical d^{*2} are calculated for different h, k, l combinations and compared to the experimentally calculated values which are obtained by equation (20):

$$d^{*2} = (2\sin\theta/\lambda)^2 \qquad \textbf{(20)}$$

where λ is X-ray wavelength and θ is Bragg reflection angle.

The indexing of diffraction data were done with cell parameters reported by Tishchenko et al. as $a = 8.170(4)$ A^{o}, $b = 8.094(4)$ A^{o}, $c = 6.799(4)$ A^{o}, $\alpha = 99.92(1)^{0}$, $\beta = 88.89(1)^{0}$ and $\gamma = 115.30(1)^{0}$ [1, 2].

1.6 APPLICATION FIELDS

PNVCL finds wide application in the area of biotechnology and biomedicine. When the solution temperature is increased or different denaturizing agents are present in water, enzyme activity decreases. In order to prevent this PNVCL can be used as a protein carrier in the polymer matrix with chemically bonded protein [59] or it can be used as one of the separate components in alginate based gel particles [23]. By using PNVCL, enzyme resists against thermo-deactivation. Moreover, enzyme immobilization has been achieved by PNVCL. PNVCL-based hydrogel has increased the stability of enzymes which protects the enzymes from denaturation by entrapment [60, 24, 42].

PNVCL is used in drug release systems. Drug release systems that can be controlled by stimuli external to the body may release the drug both rapidly and locally. Polymeric materials and structures offer interesting possibilities for such controlled drug delivery [61]. Moreover, selective determination of some opiate drugs in aqueous media has been achieved with the aid of PNVCL [62]. Recently, self-assembling thermo-sensitive containers prepared of thin films of PNVCL deposited onto porous support membranes have been studied for controlled delivery applications [63].

The PNVCL can be used as a matrix for producing solid pharmaceutical and cosmetic preparations with controlled release of active ingredients [64]. Commercially, PNVCL is available as a hair-fixative excipient by the trade name Luviskol® Plus by the BASF-company. Besides hair spray, cosmetic formulations of PNVCL include skin care cosmetics [65].

PNVCL is able to kinetically suppress hydrate crystallization. This provides commercial importance to the oil and gas industry [66]. The aqueous solutions of PNVCL can be used as assistants in the area of production, isolation and transportation of petroleum and natural gas [57].

PNVCL and its copolymers with poly (N-vinylpyrrolidone) are known under the trademarks Luvicap and Luvitec which can be used in coating, in producing of clays, paper, and textile [67].

PNVCL is used as a polymer additive in lubricant compositions, as a protective colloid and as a binder for nonwovens [57]. It can be also used as the additive in oil-in-water nano-emulsion for the thickening of the composition [68]. The aqueous solutions of PNVCL are used as textile printing adhesive, raw material for adhesives, detergent additive, clarifier in the beverage industry and as opacifier in automatic shading systems. Moreover, aqueous PNVCL solutions can be used as agrochemical assistants, for instance as structure improvers for arable soils and for coating seed, for slow release formulations of drugs and fertilizers and for waste water treatment. Besides being used as agrochemical assistants, aqueous solutions of PNVCL can be used in photo industry [57].

1.7 AIM OF THE STUDY

The aim of this study is to polymerize N-vinylcaprolactam by free radical polymerization with solution technique. N-vinylcaprolactam polymerization was studied with hexane as a solvent and 2, 2'-azobisisobutyronitrile as an initiator at 50 °C, 60 °C and 70 °C. The obtained polymer was characterized by spectroscopic, thermal and X-Ray diffraction methods. Molecular weight determination by Light scattering, GPC and solution viscosity methods gave information about the solution properties of polymer. To confirm the polymerization of NVCL, FT-IR and NMR spectroscopy measurements were carried out. By applying XRD method the crystal structure effect on free radical polymerization of N-vinylcaprolactam was investigated. The thermal properties of monomer and polymer were studied by using DSC and TGA.

Polymerization of NVCL was also studied by Polat in 2005 [2]. In that study NVCL was polymerized in solid state by irradiation and Polat reported the structure, molecular weight distribution and thermal properties of polymer by FTIR, NMR, Mass spectroscopy, GPC, Light scattering, DSC and X-Ray. However, in this study polymerization was carried out by solution polymerization in the presence of free radical initiator. This study showed that NVCL can be also polymerized without irradiation.

CHAPTER 2

EXPERIMENTAL

2.1 MATERIALS

2.1.1 Monomer

N-Vinylcaprolactam, NVCL (Aldrich) was used as a monomer (Figure 11).

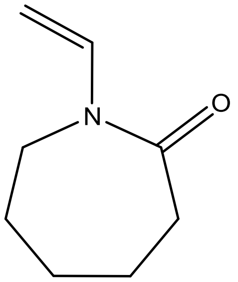

Figure 11 N-Vinylcaprolactam

N-Vinylcaprolactam was purified by recrystallization from hexane at room temperature. It was dissolved in hexane and the solution was filtered for several times. Purified solution was kept in the refrigerator to obtain pure NVCL crystals. When the crystals were reformed, the solvent was decanted and the purified NVCL was stored at 4 ^{o}C, since melting point of NVCL is 35 ^{o}C.

2.1.2 Initiator

α, α'-Azoisobutyronitrile, AIBN (Merck) was used as initiator for solution polymerization of NVCL without further purification. Structure of AIBN is shown in Figure 12.

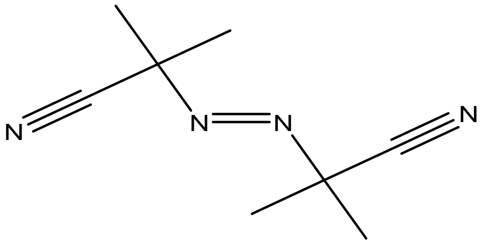

Figure 12 Initiator (AIBN)

2.1.3 Solvents

Hexane (Merck), diethyl ether (Riedel de-Haen) and toluene (Aldrich) were all reagent grades and used without further purification.

2.2 INSTRUMENTATION

2.2.1 Polymerization Tubes

The tubes used for the polymerization of NVCL were 1-3 cm in diameter, 12 cm in length Pyrex tubes.

2.2.2 Viscometer

Viscosities of different concentrations of polymer solutions were measured with toluene as a solvent at 25 ^{o}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.

2.2.3 Oil Bath

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

2.2.4 Vacuum Drying Oven

The polymer was dried to constant weight under vacuum drying oven, Labart DZF 6030A Model. The oven is micro computer controlled with timer.

2.2.5 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.

2.2.6 Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H and ^{13}C NMR spectra of the NVCL and PNVCL were recorded on a Bruker DPX 400. Deuterated chloroform ($CDCl_3$) was used as the solvent, and tetramethyl silane (TMS) served as the internal standard. Chemical shifts, δ were reported in ppm relative to $CHCl_3$ (^{1}H: δ=7.27), $CDCl_3$ (^{13}C: δ=77.0) as internal standards.

2.2.7 Dynamic Light Scattering

Molecular weight of samples was taken on Malvern CGS-3 Dynamic Light Scattering, DLS.

2.2.8 Gel Permeation Chromatography

For the molecular weight calculation of polymer samples, it is necessary to know the values of “a” and “K” constants in the Mark-Houwink equation. Therefore, the molecular weights of several polymer samples were measured by GPC using Polymer Laboratories PL-GPC 220. THF was used as a solvent in order to dissolve the polymer samples.

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. All the measurements were done under N_2 atmosphere in a temperature range of -100 ºC to 300 ºC with 10 ºC/min heating rate.

2.2.10 Thermogravimetric Analysis (TGA)

Thermal stability of PNVCL 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 -20 ºC to 800 ºC with 5ºC/min heating rate.

2.2.11 X-Ray Powder Diffractometer

X-Ray powder diffraction patterns (XRD) were taken by using Rigaku Miniflex with Cu (Kα 30 kV, 15 mA, λ=1.54178 A^{o}) radiation.

2.3 EXPERIMENTAL PROCEDURE

PNVCL was prepared by solution polymerization of NVCL in the presence of AIBN as an initiator. The stock solution was prepared from 10 g of NVCL, 50 ml of hexane and 0, 01 g of AIBN. 4 ml portions from this solution were placed in glass tubes and the tubes were sealed by flame without evacuation. The tubes were then immersed in an oil bath at 50 ºC, 60 ºC, 70 ºC and polymerized at different time periods. After the polymerization, the tubes were broken open. The polymer was precipitated with diethyl ether, filtered and dried in vacuum at 40 ºC to constant weight. The percent conversions were calculated gravimetrically by equation (21).

$$\% \text{ Conversion} = \frac{\text{Mass of Polymer}}{\text{Mass of Monomer}} \times 100 \qquad \textbf{(21)}$$

CHAPTER 3

RESULTS AND DISCUSSION

3.1 SOLUTION POLYMERIZATION OF NVCL

N-vinylcaprolactam was polymerized by free radical polymerization with solution technique. In solution polymerization of NVCL, hexane was used as a solvent, since both the initiator and monomer were soluble in it. Hexane has acceptable chain-transfer characteristics and suitable melting and boiling points for the conditions of the polymerization and subsequent solvent removal steps. Polymerization was carried out in an oil bath at 50 °C, 60 °C and 70 °C and % conversions were calculated. The obtained polymer was a white, powder type polymer. It was soluble in water and common organic solvents. It absorbs water in air.

The percent conversion versus time values for solution polymerization of monomer at 50 °C are given in Table 2 and the percent conversions are plotted against time in Figure 13.

Table 2 The percent conversion vs. time for solution polymerization of NVCL at 50^{o}C

Time (h)	**% Conversion**	**ln[M_0/M]**	**Intrinsic Viscosity (dl/g)**
12	6.5	0.06721	……………
24.5	15.3	0.16605	……………
51	40.7	0.52256	……………
72	49.5	0.6832	……………
90	63.5	1.00786	0.2393
96	66.1	1.08176	0.2412
114.5	71.2	1.24479	0.2433
120	65.8	1.07294	0.2844
145	71.2	1.24479	0.3055

Table 2 (Continued)

Time (h)	% Conversion	ln[M_0/M]	Intrinsic Viscosity (dl/g)
168	73.2	1.31677	0.2768
195	77.4	1.48722	0.2790
214	70.2	1.21066	0.2785
240	83.2	1.78379	0.2860
288	81.8	1.70375	0.2890
312	77.3	1.48281	0.2895
336	75.9	1.42296	0.2902
360	79.6	1.58964	0.2950

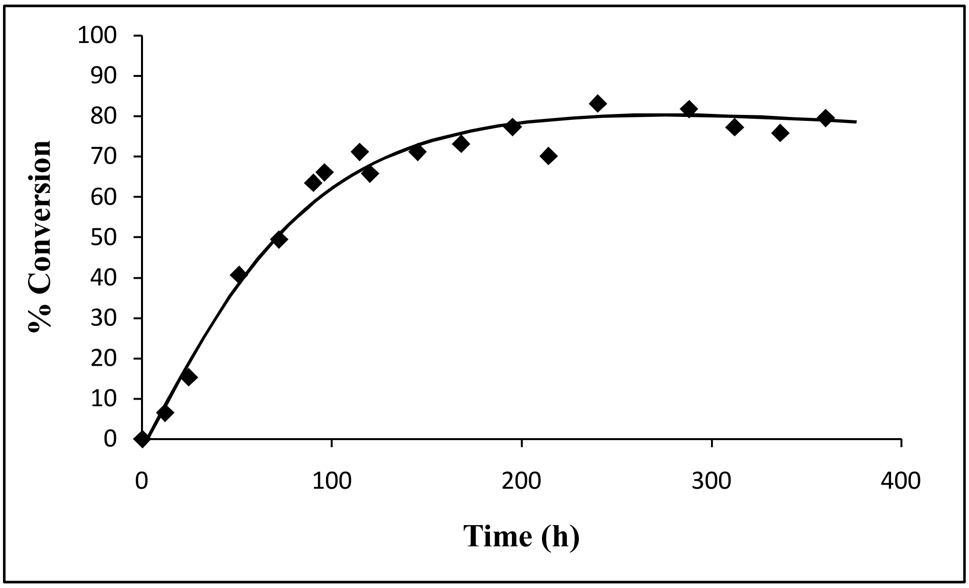

Figure 13 The percent conversion vs. time graph for solution polymerization of NVCL at 50°C

The percent conversion versus time values for solution polymerization of monomer at 60°C are given in Table 3 and the percent conversions are plotted against time in Figure 14.

Table 3 The percent conversion vs. time for solution polymerization of NVCL at 60 °C

Time (h)	**% Conversion**	**$\ln[M_0/M]$**	**Intrinsic Viscosity (dl/g)**
0.5	2.3	0.02327	……………
1	5.65	0.05816	……………
1.33	6.55	0.06774	……………
1.67	10.7	0.11317	……………
2	14.5	0.15665	……………
6	19.06	0.21146	……………
7	22.79	0.25864	……………
8	28.35	0.33338	……………
9	38.14	0.4803	……………
24	49.08	0.67491	……………
27	63.03	0.99506	0.3391
48	65.56	1.06595	0.1542
72	69.99	1.20364	0.3286
96	88.63	2.17419	0.2464
120	89.13	2.21916	0.2928
144	87.61	2.08828	0.1887
168	83.31	1.79036	0.0649
192	90.41	2.34445	0.2406
216	88.21	2.13792	0.295
240	88.38	2.15244	0.3145
264	88.09	2.12779	0.1757
288	89.46	2.24999	0.3479

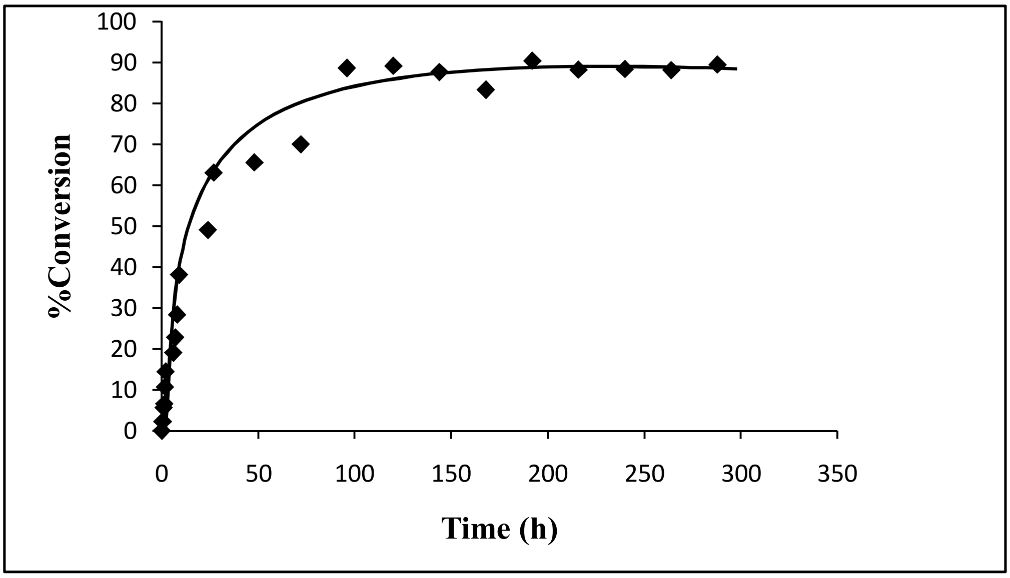

Figure 14 The percent conversion vs. time graph for solution polymerization of NVCL at 60°C

The percent conversion versus time values for solution polymerization of monomer at 70°C are given in Table 4 and the percent conversions are plotted against time in Figure 15.

Table 4 The percent conversion vs. time for solution polymerization of NVCL at 70°C

Time (h)	% Conversion	$\ln[M_0/M]$	Intrinsic Viscosity (dl/g)
0.33	3.23	0.03283	……………
0.66	6.39	0.06603	……………
1	10.24	0.10803	……………
1.33	13.29	0.1426	……………
1.66	15.9	0.17316	……………
2	19.16	0.2127	……………
4	41.93	0.54352	……………

Table 4 (Continued)

Time (h)	% Conversion	$\ln[M_0/M]$	Intrinsic Viscosity (dl/g)
6	40.38	0.51718	…………….
8	53.64	0.76873	…………….
10	63.1	0.99696	…………….
12	62.15	0.97154	…………….
24	70.3	1.21402	0.2809
48	81.06	1.66389	0.3644
72	79.79	1.59899	0.2532
78	80.06	1.61244	0.2948
93.5	79.46	1.5828	0.3179
96	76.8	1.46102	0.3336
120	79.36	1.57794	0.2989
144	77.6	1.49611	0.2387
168	78.9	1.5559	0.2688

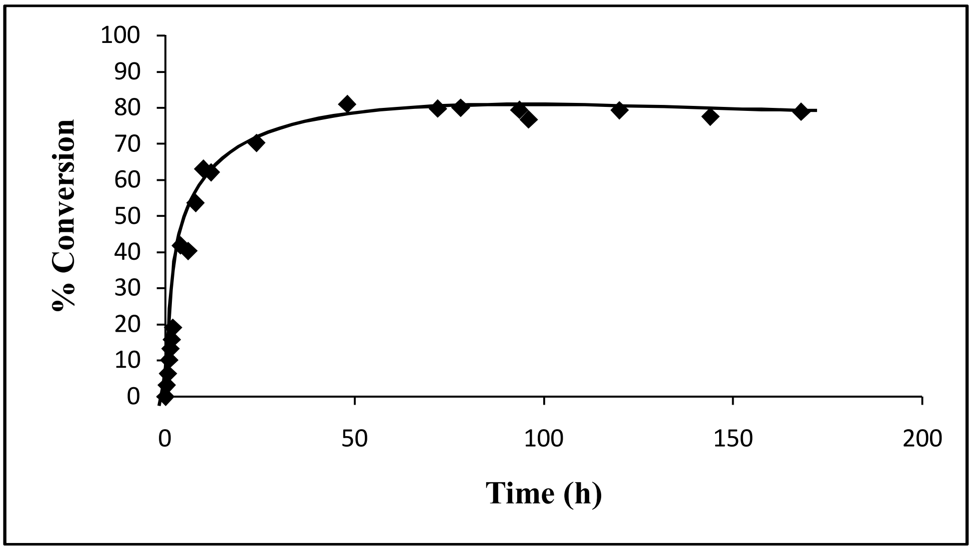

Figure 15 The percent conversion vs. time graph for solution polymerization of NVCL at 70°C

From the percent conversion versus time graphs for solution polymerization of NVCL at different time periods, it is seen that the percent conversion of NVCL increased with polymerization time. Moreover the same percent conversion was reached rapidly for higher temperature. For instance nearly 40% conversion was reached in 4 hours at 70 °C, 9 hours at 60 °C and 51 hours at 50 °C. However, 100% conversion was not reached for the three different temperatures. In solution polymerization, the percent conversion was reached to 83.2% at 50 °C, 90.41% at 60 °C and 81.06% at 70 °C. This is due to the nature of monomer and polymer. They are very dependent to the temperature and solvent, in addition to the conformation of growing chain. It can be observed much better from XRD investigation.

In order to observe the differences of the solution polymerization of NVCL at these three different temperatures, the percent conversion versus time graphs are shown in Figure 16.

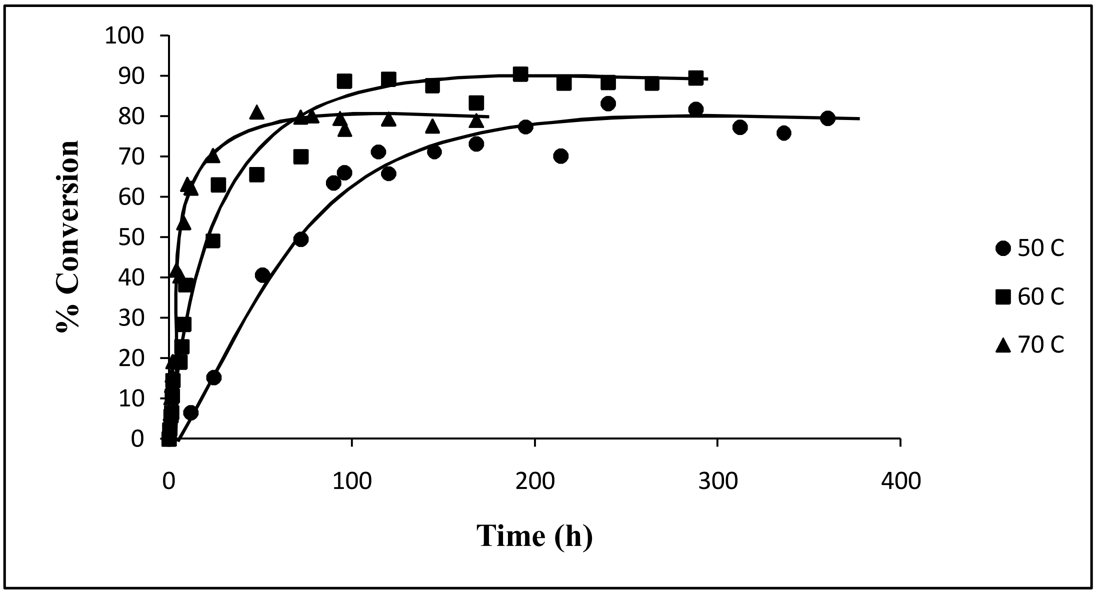

Figure 16 Comparison of the percent conversion vs. time graphs of NVCL at 50°C, 60°C and 70°C

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) [58].

$$\ln\frac{[M_0]}{[M]} = k[I]^{1/2}t \tag{20}$$

$\ln[M_0] / [M]$ values were plotted against time and plots were illustrated in Figure 17, 18 and 19. Slopes were calculated from straight lines for each of polymerization temperature studied.

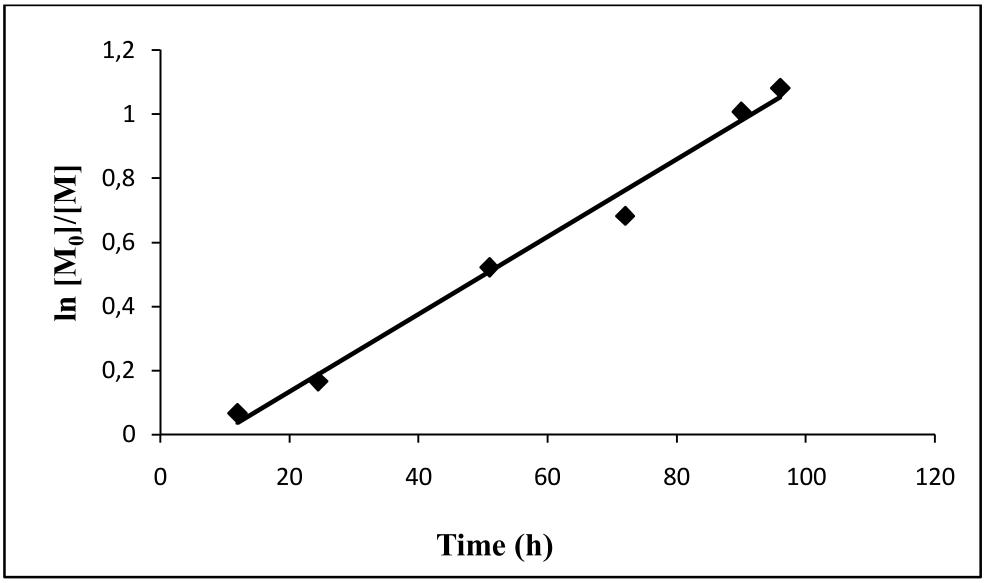

Figure 17 The plot of ln $[M_0]/[M]$ vs. time for solution polymerization of NVCL at 50°C

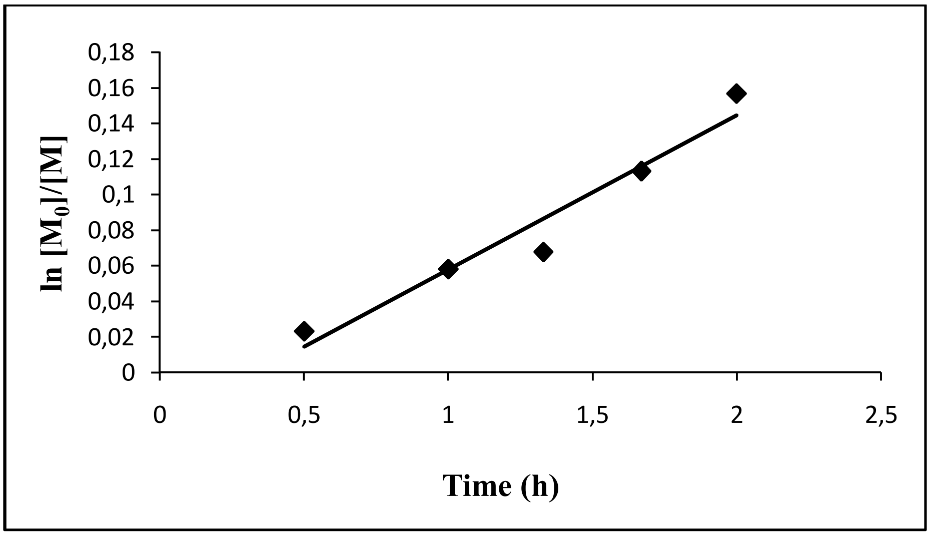

Figure 18 The plot of ln $[M_0]/[M]$ vs. time for solution polymerization of NVCL at 60°C

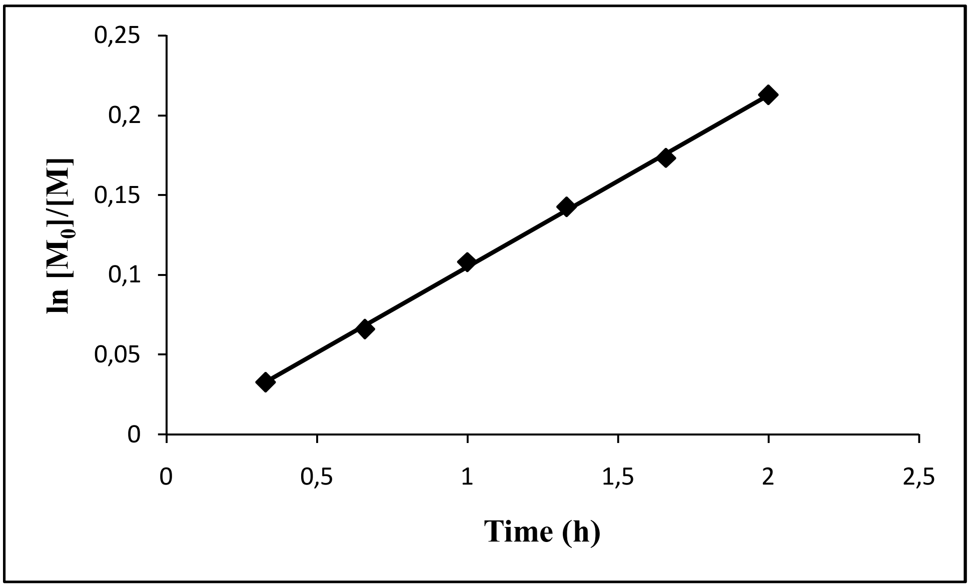

Figure 19 The plot of ln $[M_0]/[M]$ vs. time for solution polymerization of NVCL at 70°C

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.

Activation energy of polymerization was calculated from Arrhenius equation, equation (22) using rate constants for each of temperature of polymerization.

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

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

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

The natural logarithm of rate constant against 1/T was plotted in Figure 20. The slope of straight line obtained was equal to $-E_a/R$ and activation energy, E_a calculated from slope is 108.4 kJ/mol.

Table 5 Reaction rate constants for solution polymerization of NVCL at different temperatures.

T (K)	**1/T (K^{-1})**	**k=slope (h^{-1})**	**lnk**
323	0.00309	0.0121	-4.4145
333	0.00300	0.0865	-2.4476
343	0.00292	0.1075	-2.2303

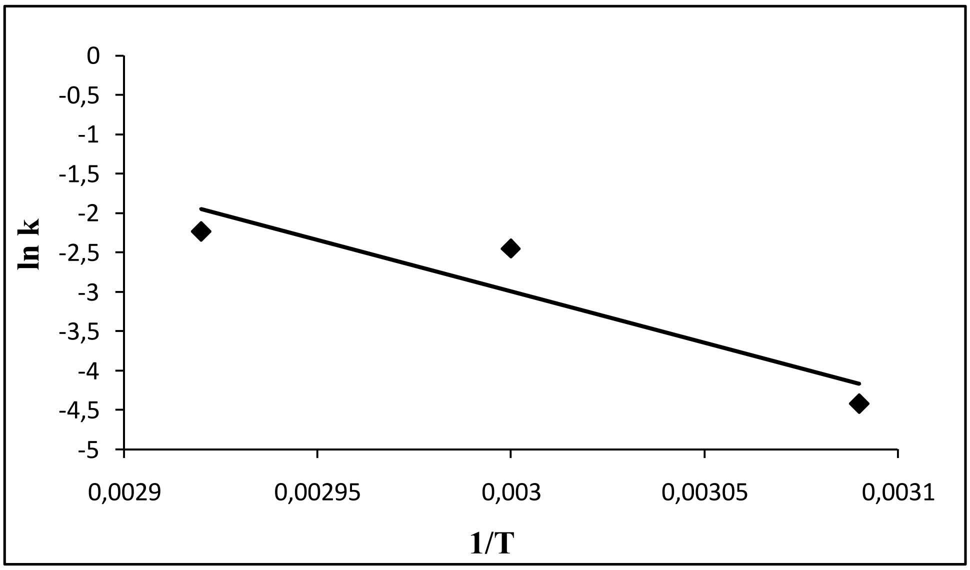

Figure 20 ln k vs. 1/T

3.2 MOLECULAR WEIGHT DETERMINATION

The molecular weight determination of polymer was carried out by GPC, Light scattering and solution viscosity methods. Although the polymer was soluble in THF, GPC method did not give any reasonable results and K and α values were not obtained. GPC chromatogram of the polymer for 88.63% conversion at 60 ^{o}C is given in Figure 21. The GPC chromatograms of polymers obtained under different temperatures were identical and they did not change with percent conversion. Moreover, the exact refractive index increment value of PNVCL in toluene at 25 ^{o}C could not be determined. Therefore, no result was obtained by Light scattering method. In order to observe the dependence of intrinsic viscosity on time and % conversion data, solution viscosity method was applied. The intrinsic viscosity values were obtained from the program written by Prof. Dr. Osman Yılmaz [69]. The intrinsic viscosity values, time and % conversion data are tabulated in Table 2, Table 3 and Table 4 for 50 ^{o}C, 60 ^{o}C and 70 ^{o}C. Solution viscosity measurement could not be applied to polymers which have low percent conversion, therefore in these tables the intrinsic viscosity values of these polymers are shown with dot.

There is no regular trend obtained from intrinsic viscosity measurements with respect to % conversion or time of polymerization. This is due to the complex relation of solvent and polymer chain.

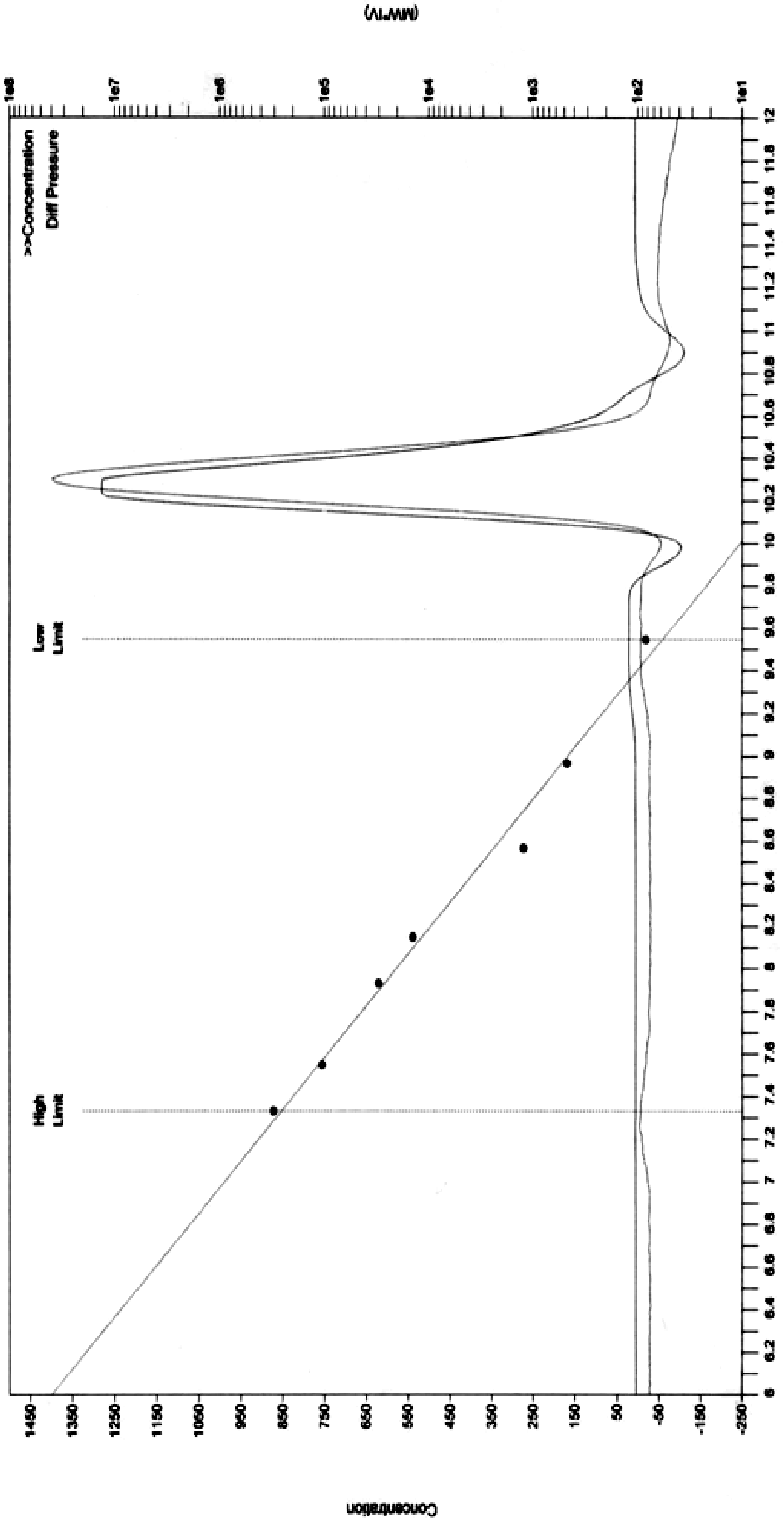

Figure 21 GPC Chromatogram of polymer for 88.63% conversion

3.3 FT-IR INVESTIGATION

The FT-IR spectrum for NVCL and PNVCL are shown in Figure 22 and Figure 23, respectively and the peak assignments are tabulated in Table 6. The FT-IR spectra of polymers obtained under different temperatures were identical and they did not change with percent conversion.

Table 6 The peak assignments for the FT-IR spectrum of NVCL and PNVCL

Functional Group	Shift (cm^{-1})	
	NVCL	**PNVCL**
N-H	3274	3274
Aliphatic C-H	2926, 2856	2926, 2856
C=O	1631	1631
C-N	1479	1479
$-CH_2-$	1441	1441
C=C	1659	-
=CH and $=CH_2$	3102, 994	-
O-H	-	3507

All amides show a carbonyl, (C=O) absorption band, known as the amide I band. The position of the amide I band depends on the degree of the hydrogen bonding and physical state of the compound [70]. In the IR spectrum of monomer (Figure 22), a characteristic carbonyl peak, (C=O stretching, amide I band) is at 1631 cm^{-1}. The peak for the C=C was observed at 1659 cm^{-1}. The peaks at 2926 cm^{-1} and 2856 cm^{-1} correspond to the aliphatic C-H stretching. The $-CH_2-$ peak is at 1441 cm^{-1}. The characteristic vinyl peaks, (=CH and $=CH_2$) were located at 3102 cm^{-1} and 994 cm^{-1}. The peak of C-N stretching vibration was observed at 1479 cm^{-1}. Furthermore, the peak at 3274 cm^{-1} is assigned to N-H stretching vibration.

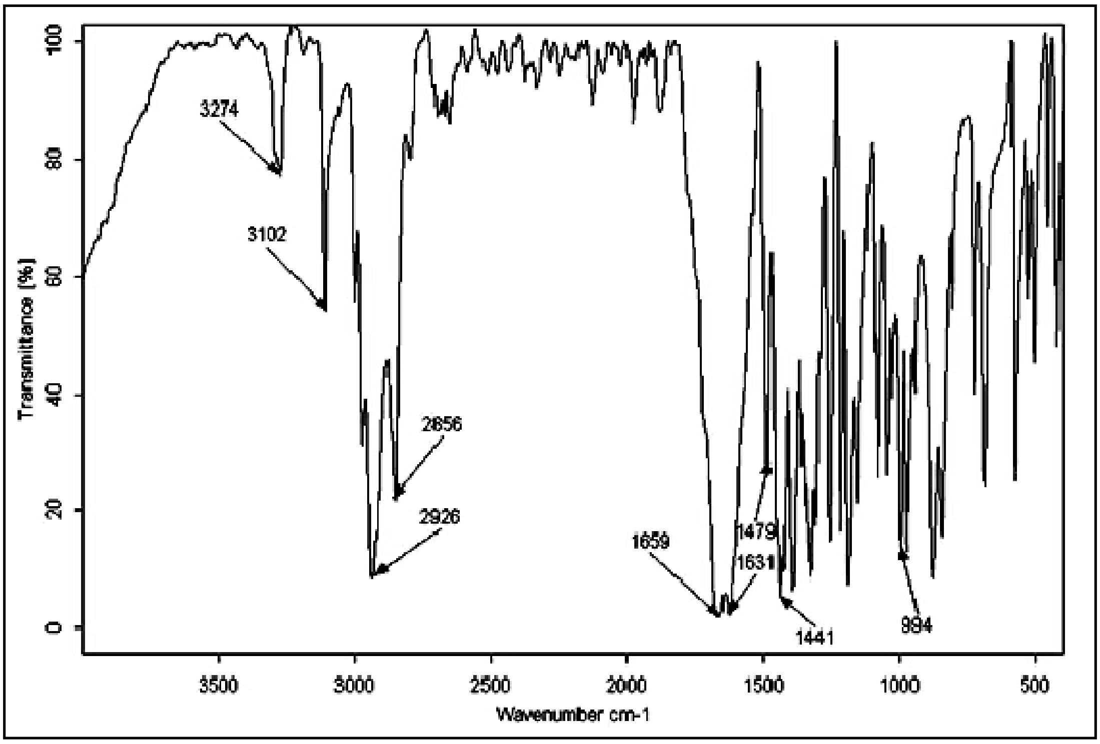

Figure 22 FT-IR Spectrum of NVCL

In the spectrum of PNVCL (Figure 23), carbonyl peak was observed at 1631 cm^{-1} as in the monomer. The peak of double bond observed in the spectrum of monomer at 1659 cm^{-1}, near C=O peak disappeared in the spectrum of polymer. The aliphatic C-H stretching peaks were located at 2926 cm^{-1} and 2856 cm^{-1}similar to the monomer. The -CH_2- peaks are at 1441 cm^{-1}. The vinyl peaks, (=CH and =CH_2) located in the spectrum of monomer at 3102 cm^{-1} and 994 cm^{-1}, disappeared in the spectrum of polymer. There is no change in the position of C-N stretching vibration peak (1479 cm^{-1}) in the polymer when it is compared with the monomer. Although location of the N-H stretching vibration peak (3274 cm^{-1}) did not change, it became broader in the spectrum of PNVCL. This might be due to the changes in the conformation of the molecules and interaction of molecules upon polymerization. Moreover new, broad peak was observed in the spectrum of the polymer at 3507 cm^{-1}, which corresponds to the O-H stretching. PNVCL absorbs moisture from the air easily.

This broad O-H stretching peak might be resulted from the absorption of water from the air.

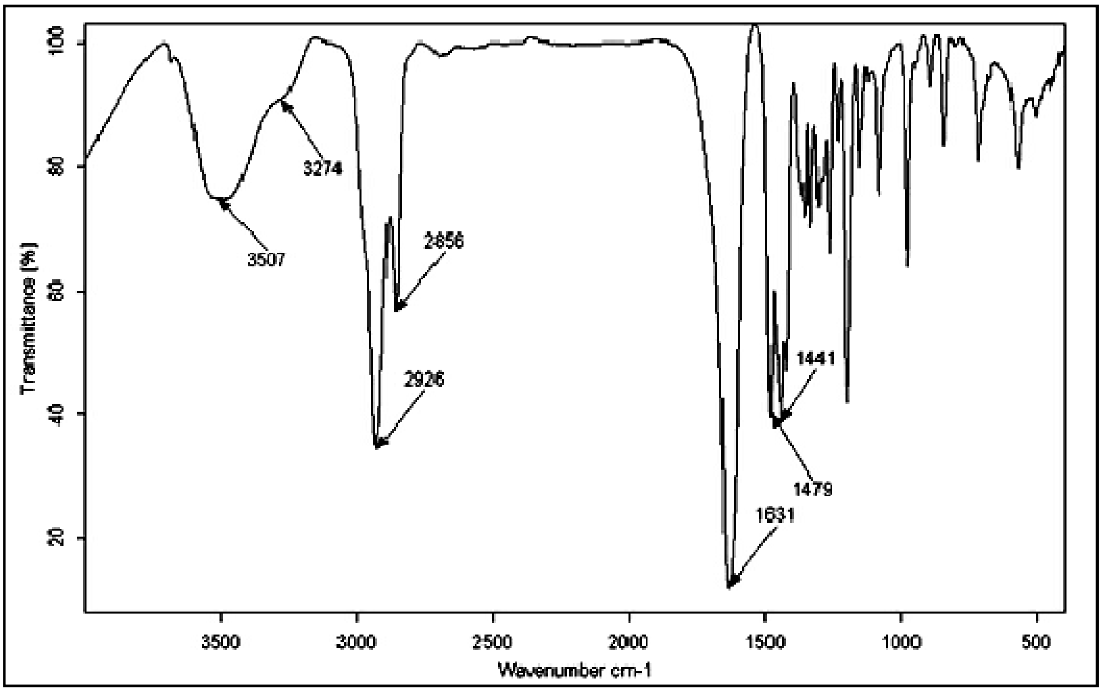

Figure 23 FT-IR Spectrum of PNVCL

After the polymerization of NVCL the peaks belong to double bond in the spectrum of monomer were completely disappeared. In order to confirm the polymerization of NVCL, FT-IR spectrum of the monomer and the polymer are shown in Figure 24.

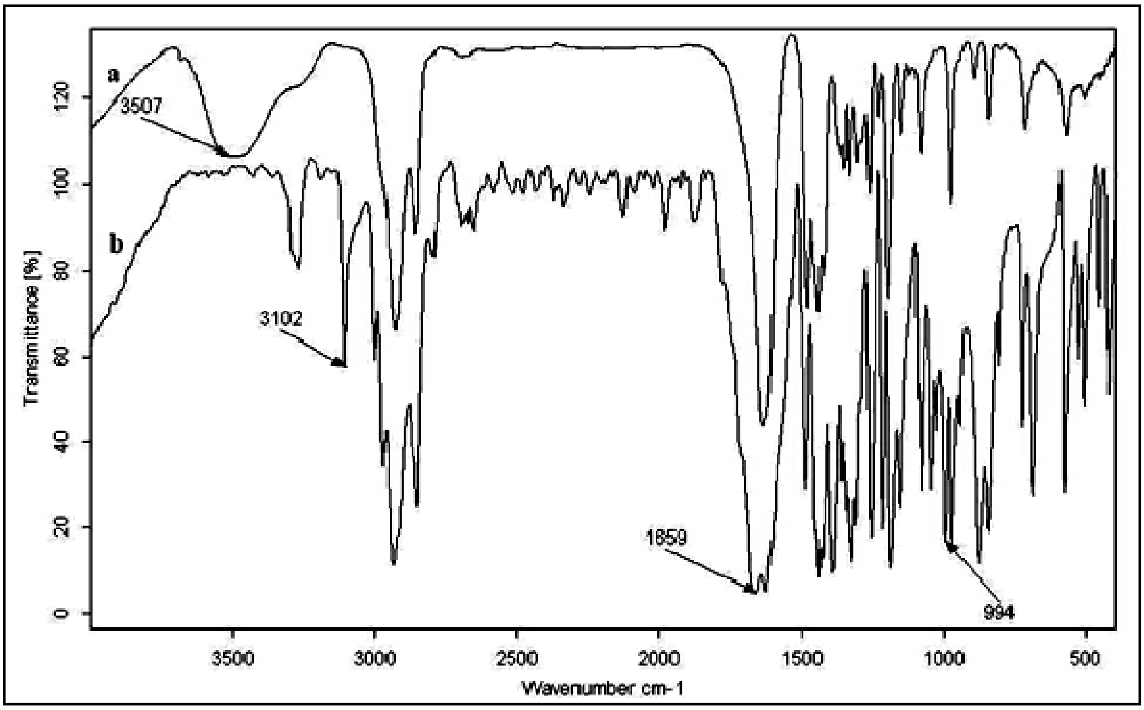

Figure 24 FT-IR Spectra of (a) PNVCL and (b) NVCL

It can be concluded from FT-IR spectra investigation that polymer was successfully achieved and the polymerization proceeds by carbon-carbon double bond opening without any change in the caprolactam ring. All the other polymer spectra resemble to the one shown in Figure 23.

3.4 NMR INVESTIGATION

^{1}H-NMR spectrum of NVCL and PNVCL are given in Figure 25 and Figure 26, respectively, and the peak assignments are tabulated in Table 7 and Table 8.

In the ^{1}H-NMR spectrum of NVCL (Figure 25), six different peaks were observed. The assigned protons are shown in formula of monomer and the peak assignments are tabulated in Table 7.

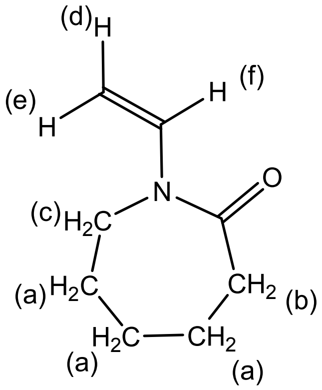

Table 7 The ^{1}H-NMR Spectrum of NVCL

Proton Type	Shift (ppm)	Group
H_a	1.3-1.6	methylene
H_b	2.4	methylene
H_c	3.4	methylene
H_d	4.18	ethylene
H_e	4.28	ethylene
H_f	7.17	ethylene
$CDCl_3$	7.25	-

In the ^{1}H-NMR spectrum of NVCL (Figure 25), the protons (H_a) for methylene group, (6 H, -CH_2- of the caprolactam ring) which are equivalent appear at 1.28-1.42 ppm. The peaks for CH_2 groups close to C=O, (H_b), and N, (H_c) are observed at 2.26 and 3.4 ppm. The peaks at 4.18, 4.28 and 7.17 ppm correspond to the protons of the vinyl group. The reason of high chemical shift, (7.17 ppm) of the proton, (H_f) in the vinyl group is the presence of –N–C=O group in geminal position.

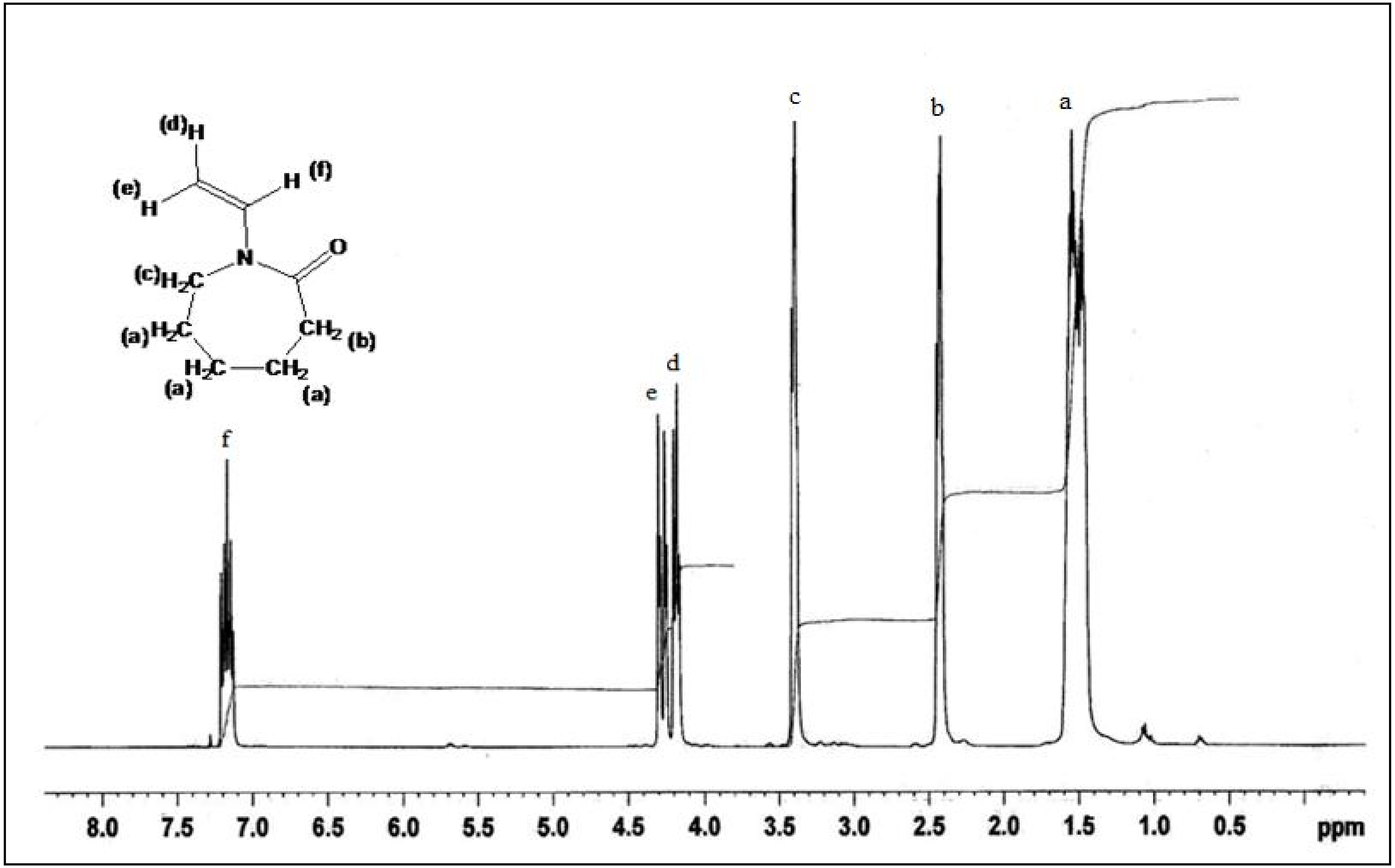

Figure 25 ^{1}H-NMR Spectrum of NVCL

In the ^1H-NMR spectrum of PNVCL (Figure 26), four different peaks were observed. The assigned protons are shown in formula of polymer and the peak assignments are tabulated in Table 8.

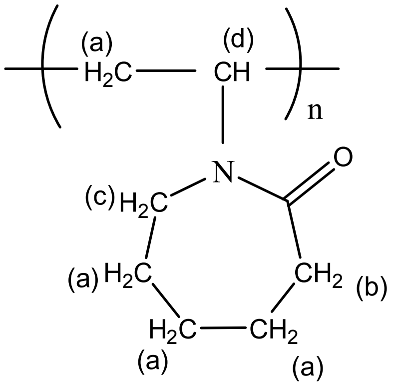

Table 8 The ^1H-NMR Spectrum of PNVCL

Proton Type	Shift (ppm)	Group
H_a	1.65	methylene
H_b	2.4	methylene
H_c	3.1	methylene
H_d	4.36	ethylene
$CDCl_3$	7.25	-

In the ^1H-NMR spectrum of PNVCL (Figure 26), 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. There is a small peak in the spectrum of the PNVCL at 7.29 ppm. This peak corresponds to the solvent, deuterated chloroform. The ^1H-NMR spectrum of PNVCL exhibited peaks at 4.36 ppm(1H, −NCH− of the α position), 3.1 ppm (2H, $-NCH_2-$), 2.4 ppm (2H, $-COCH_2-$) and 1.65 ppm (6H, $-CH_2-$ of the caprolactam ring, and 2H, $-CH_2-$ of the backbone).

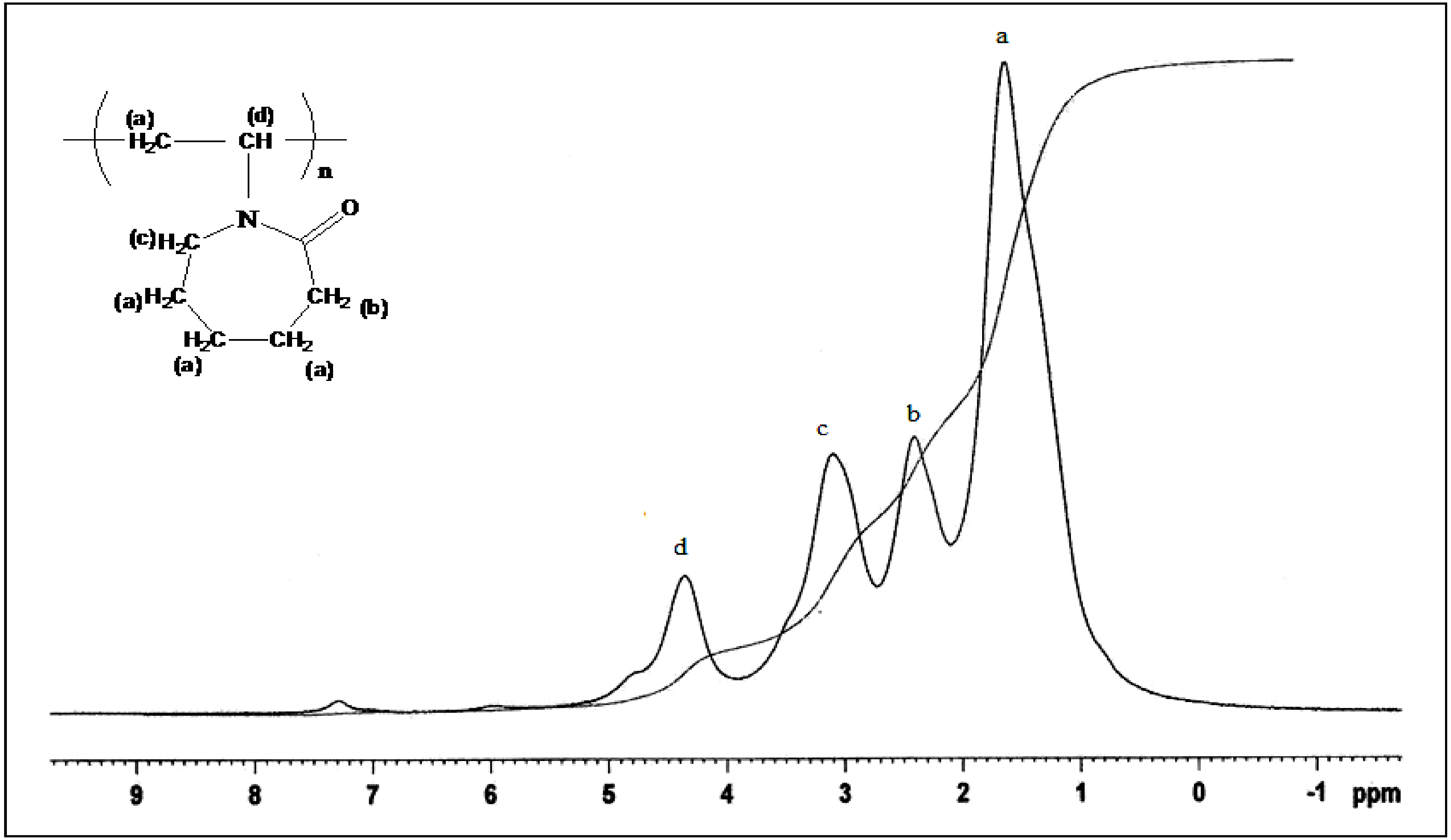

Figure 26 ^{1}H-NMR Spectrum of PNVCL

^{13}C-NMR spectrum of NVCL and PNVCL are given in Figure 27 and Figure 28, respectively and the peak assignments are tabulated in Table 9 .and Table 10.

In the ^{13}C-NMR spectrum of NVCL (Figure 27), eight different peaks were observed. The assigned carbons are shown in formula of monomer and the peak assignments are tabulated in Table 9.

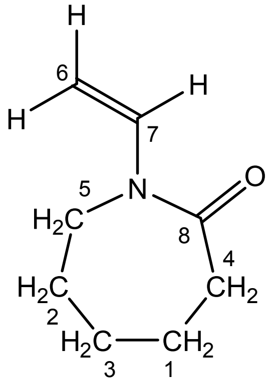

Table 9 ^{13}C-NMR Spectrum of NVCL

Carbon Type	Shift (ppm)	Group
C_1	24.7	methylene
C_2	28.5	methylene
C_3	30.6	methylene
C_4	38.4	methylene
C_5	45.3	methylene
C_6	93.8	ethylene
C_7	133.3	ethylene
C_8	175.4	amide
$CDCl_3$	78.8	-

The ^{13}C-NMR spectrum of monomer (Figure 27), exhibited peaks at 24.7 ppm, 28.5 ppm, and 30.6 ppm for the C atoms in the methylene groups (–CH_2). The peaks at

38.4 ppm and 45.3 ppm correspond to the signal of carbon atoms in methylene groups near −C=O− and −NCH−. The peaks of vinyl carbons were observed at 93.8 ppm and 133.3 ppm. The signal at 175.4 ppm showed the presence of carbonyl group (C=O) in the polymer. The peak at 78.8 ppm is due to the solvent chloroform.

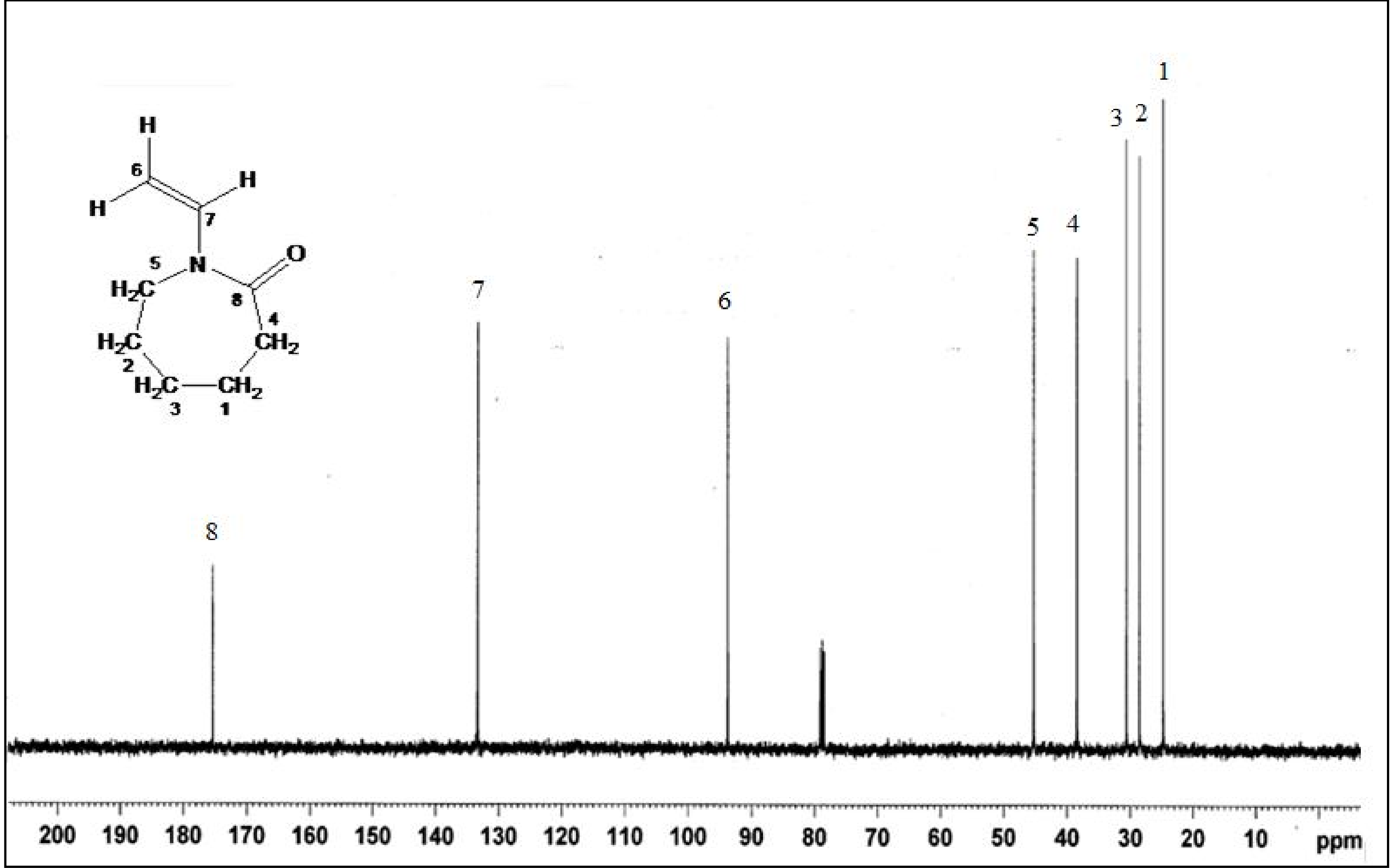

Figure 27 ^{13}C-NMR Spectrum of NVCL

In the ^{13}C-NMR spectrum of PNVCL (Figure 28), 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 10.

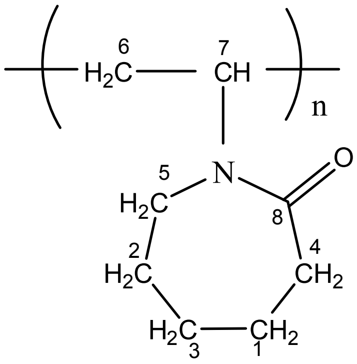

Table 10 ^{13}C-NMR Spectrum of PNVCL

Carbon Type	Shift (ppm)	Group
C_1	23.1	methylene
C_2	29.6	methylene
C_3	29.9	methylene
C_4	37.5	methylene
C_5	42.3	methylene
C_6	36.6	ethylene
C_7	46.2	ethylene
C_8	175.9	amide
$CDCl_3$	77.1	-

In the ^{13}C-NMR spectrum of PNVCL (Figure 28), 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 due to the changes in the conformation of molecules upon polymerization. The carbonyl peak appeared at 175.9 ppm in the spectrum of the PNVCL. The peaks that belong to vinyl group changed their position in the spectrum of the polymer. The peaks at 93.8 ppm (CH_2=) and 133.3 ppm (−NCH=) in the monomer spectrum, shifted to 36.6 ppm (−CH_2−) and 46.2 ppm (−NCH−) in the spectrum of the polymer.

It can be concluded from ^{1}H-NMR and^{13}C-NMR spectra investigations that polymer was successfully achieved and the polymerization proceeded by carbon-carbon double bond opening without any change in the caprolactam ring. All the other polymer spectra resemble to the ones shown in Figure 26 and Figure 28.

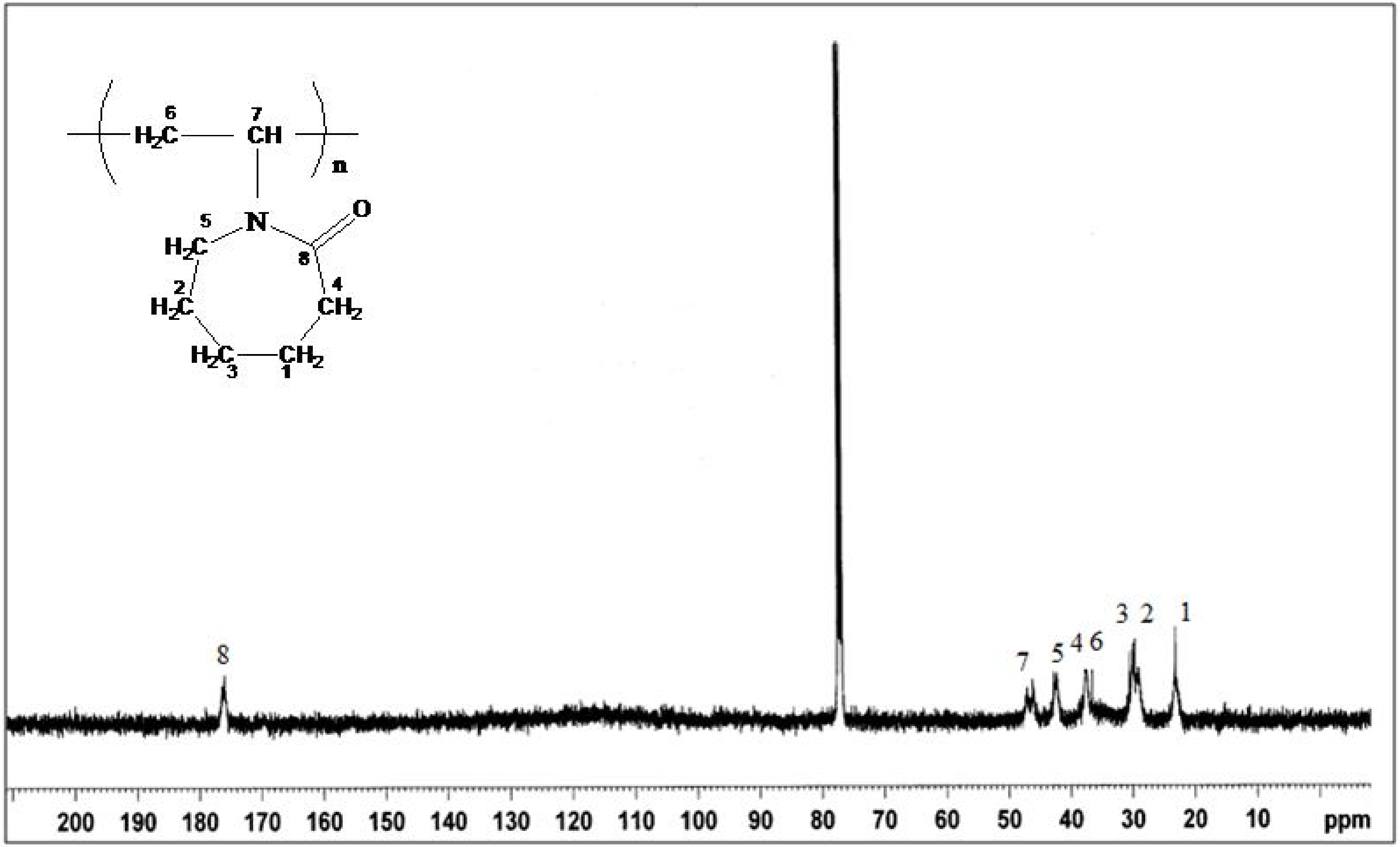

Figure 28 ^{13}C-NMR Spectrum of PNVCL

3.4 DSC INVESTIGATION

The DSC measurements were carried out at N_2 atmosphere by heating monomer in the temperature range of 25 °C to 80 °C and polymer with 89.46% conversion polymerized at 60 °C in the temperature range of –100 °C to 300 °C. The DSC thermogram of monomer and the polymer are given in Figure 29 and Figure 30, respectively. All the other polymer thermograms resemble to the ones shown in Figure 30.

Monomer has a melting peak at 37.3 °C and heat of fusion is 108.5 J/g. The melting peak of monomer is relatively broad. This broad peak shows that there might be some irregularity in the structure of the monomer.

The second derivative DSC thermogram of PNVCL is shown in Figure 31. From this thermogram it is seen that polymer has a T_g value at 1.8 °C. The DSC thermogram of polymer indicates that the polymer has a softening temperature at 68.8 °C. The softening peak is a peak for a polymer showing some structural regularity. This is in agreement with the X-Ray results.

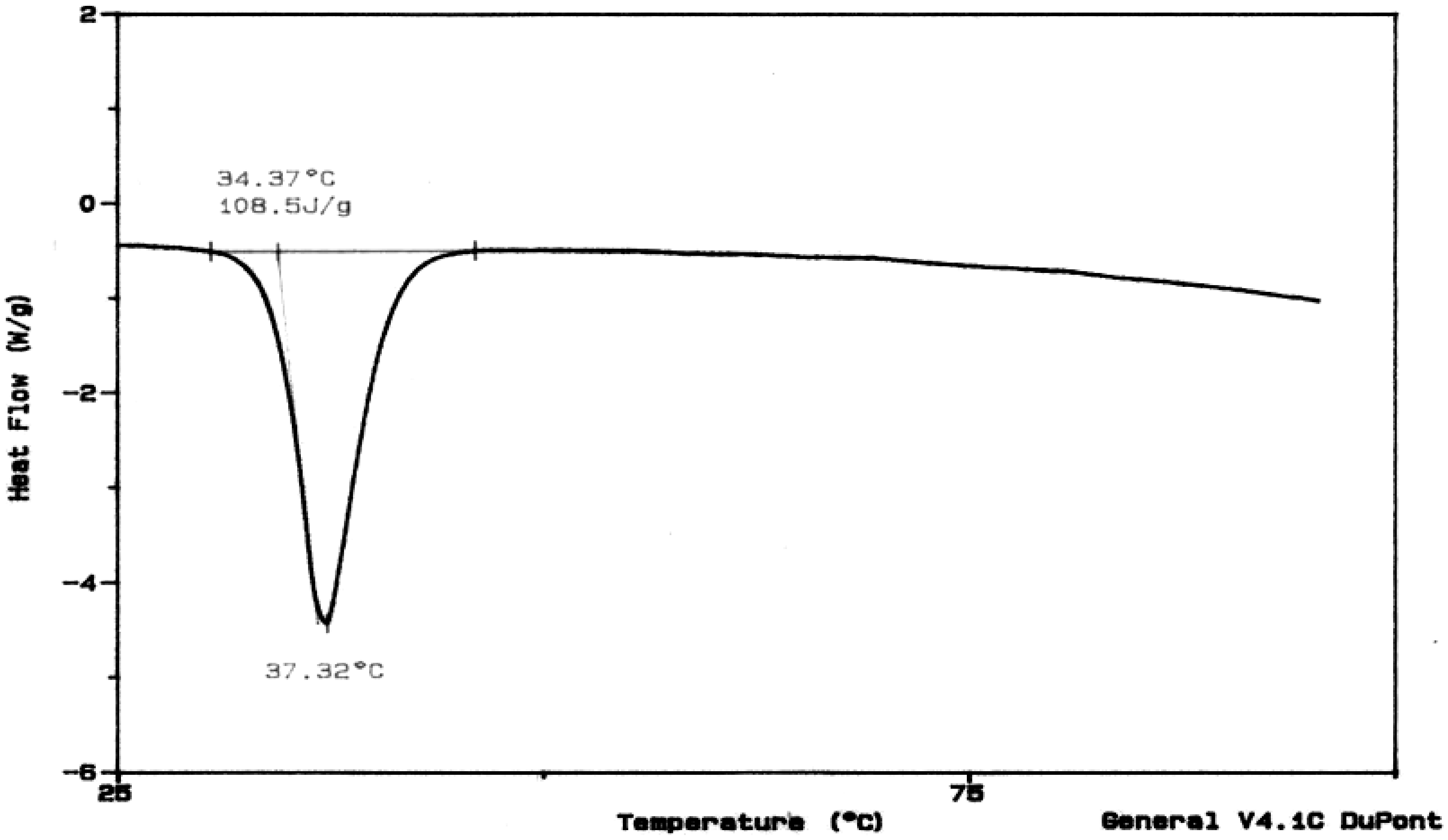

Figure 29 DSC Thermogram of NVCL

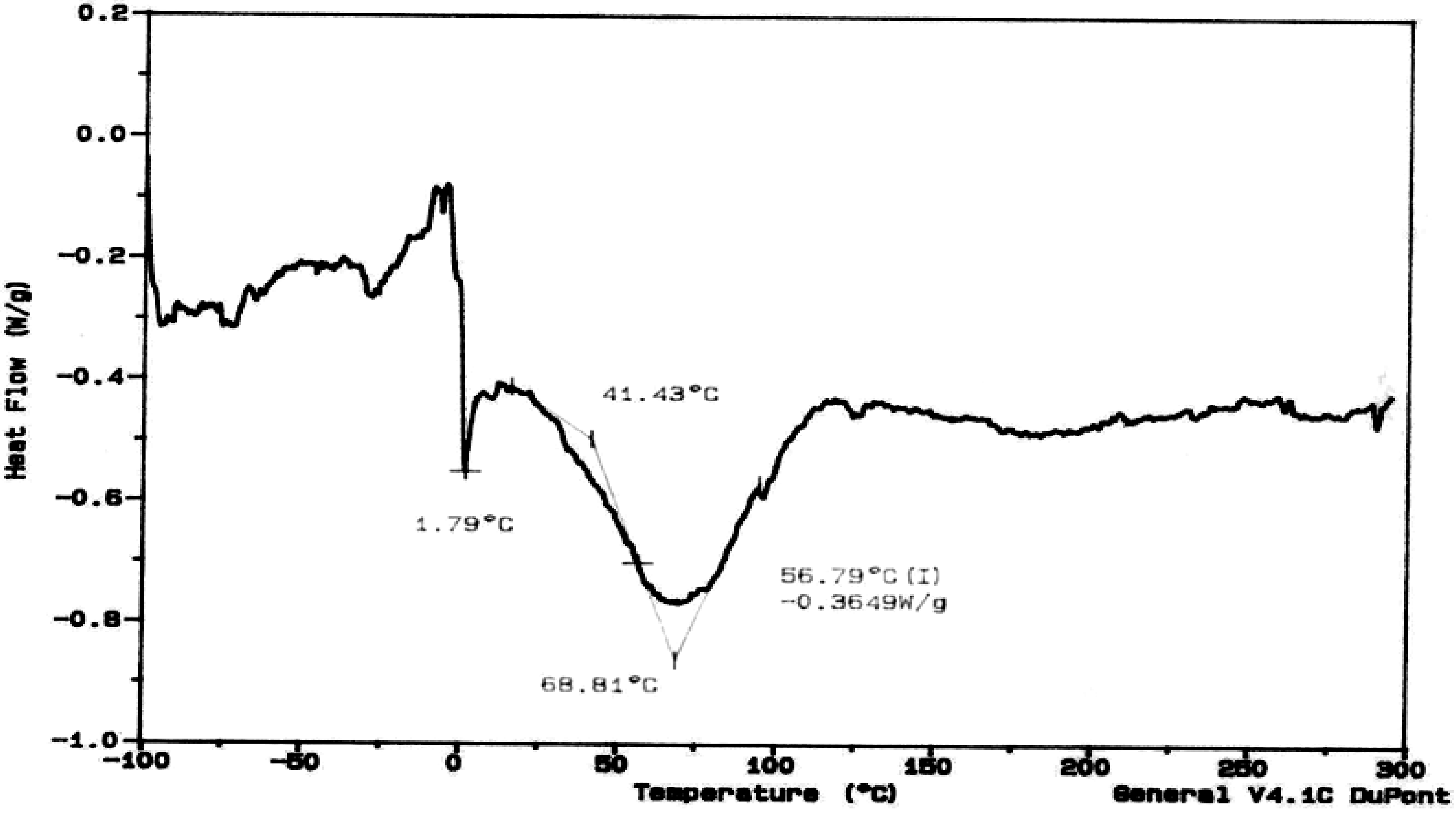

Figure 30 DSC Thermogram of PNVCL

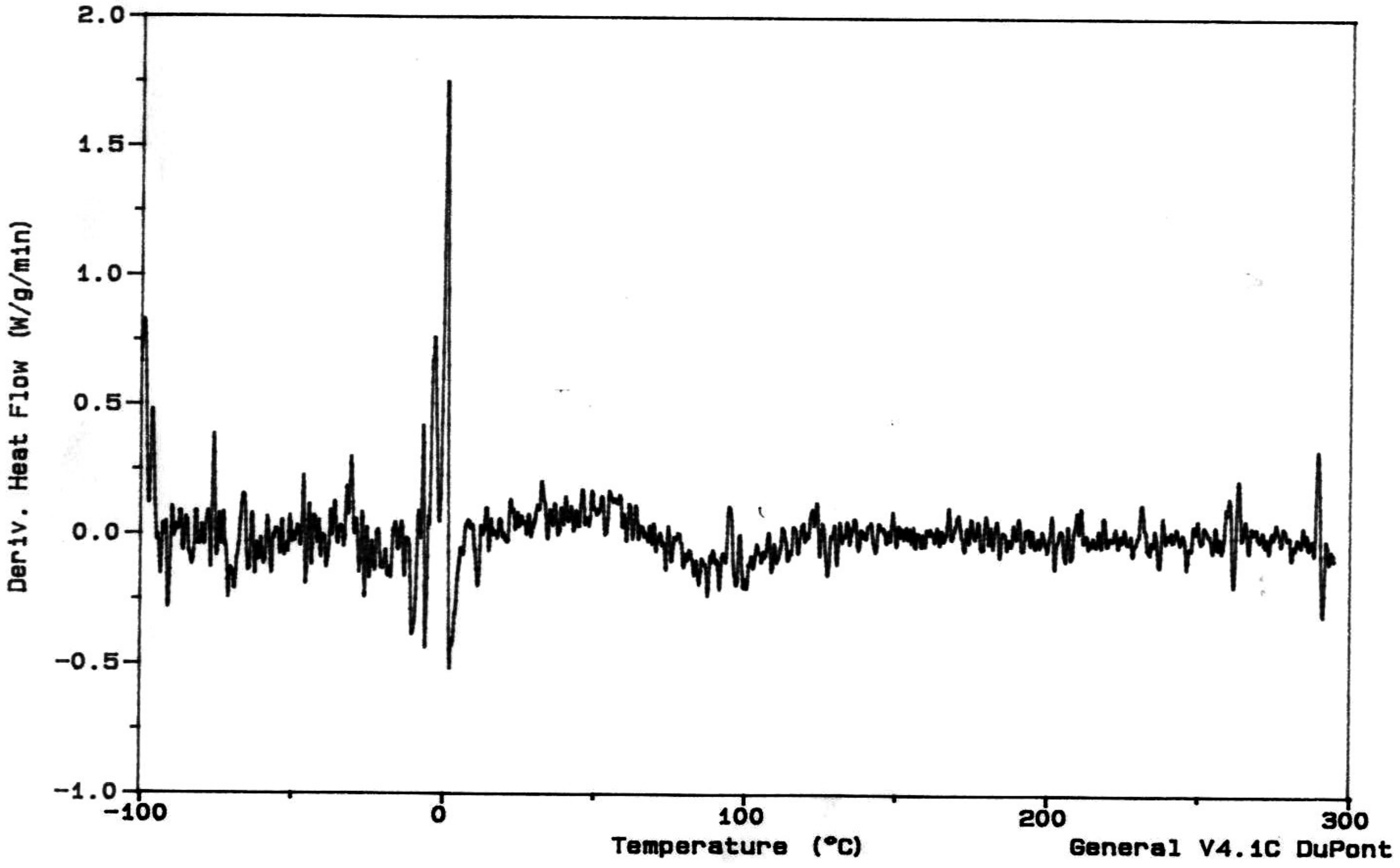

Figure 31 The second derivative DSC Thermogram of PNVCL

3.5 TGA INVESTIGATION

The thermal stability of PNVCL was also characterized by means of TGA from 20°C to 800°C under N_2 atmosphere as illustrated in Figure 32. According to the thermogram initial weight loss is resulted from the liberation of absorbed moisture. After about 380°C the weight decrease is very sharp and reaches to zero percent. The maximum weight loss rate temperature, seen from the thermogram is at about 430°C. The sharp loss of weight indicates that the thermal degradation of polymer is in the form of depolymerization.

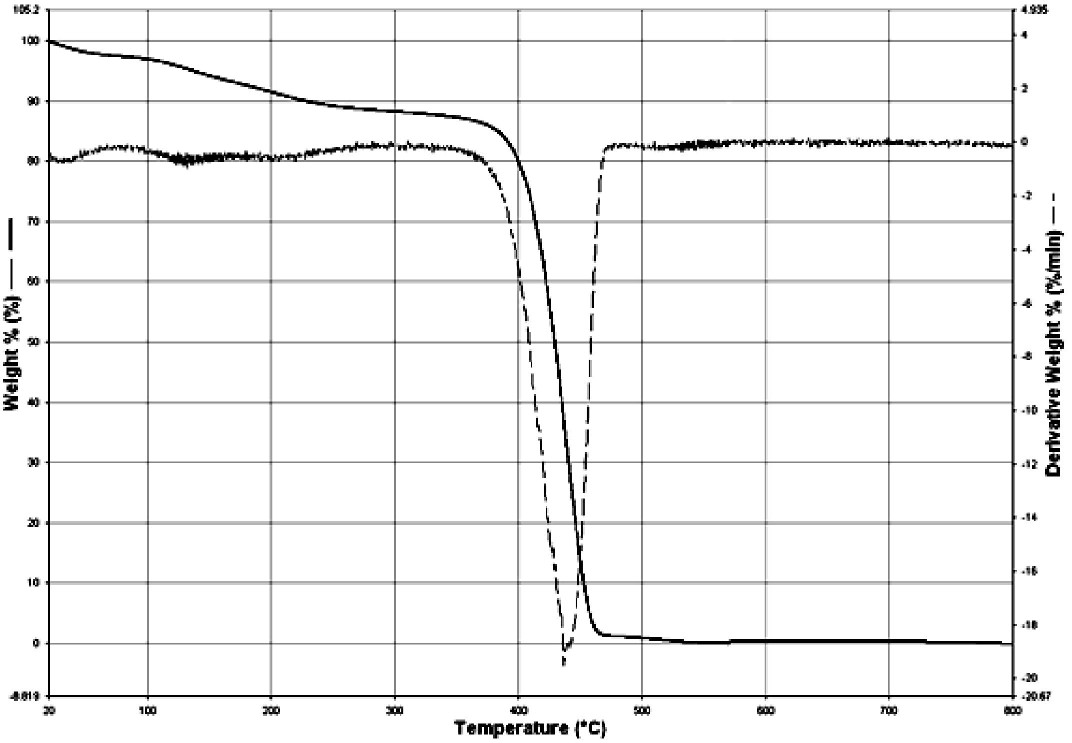

Figure 32 TGA Thermogram of PNVCL

3.6 X-RAY INVESTIGATION

The X-Ray powder pattern of NVCL is given in Figure 33. Crystal peaks of the monomer are given in Table 11. The structure was indexed using cell parameters: a = 8.170(4) A^o, b = 8.094(4) A^o, c = 6.799(4) A^o, α = 99.92(1)^0, β = 88.89(1)^0, γ = 115.30(1)^0 which were reported by Tishchenko et al. [1, 2]. The indexing is quite satisfactory.

The X-Ray powder pattern of monomer-polymer mixture for 49.08% conversion is given in Figure 34 and crystal peaks of this mixture are tabulated in Table 12. The strongest peak (I/I_0 = 100) for NVCL is at 2θ = 12.75^0. This peak shifts to 2θ = 16.55^0 for PNVCL. Although the polymer structure was also indexed satisfactorily with the same cell parameters, the most intense peak is $1\bar{1}0$ for the monomer and $0\bar{1}1$ for the polymer. Thus polymerization proceeded in the b-crystallographic axis direction. The polymerization is autotactic. The X-Ray powder pattern of monomer-polymer mixture for higher conversion (89.46%) is given in Figure 35. The polymer is generally amorphous, but still has regular orientation in b-crystallographic axis direction.

Table 11 X-Ray Analysis of NVCL

Peak No	**2θ**	**d-Value**	**Intensity**	**I/I_0**	**d-Calculated**	**h**	**k**	**l**
1	7.1	12.4396	61	1	………	–	–	–
2	7.55	11.6992	91	1	………	–	–	–
3	7.9	11.1816	72	1	………	–	–	–
4	11.2	7.8933	407	1	………	–	–	–
5	11.5	7.6881	1280	2	………	–	–	–
6	12.4	7.132	44121	69	7.1944	0	1	0
7	12.75	6.937	64272	100	6.8044	1	-1	0
8	13.4	6.602	413	1	6.6845	0	0	1
9	13.6	6.5053	952	2	………	–	–	–
10	16.7	5.3041	1113	2	5.381	0	-1	1
11	17.05	5.196	501	1	5.2684	1	-1	1
12	18.7	4.7411	261	1	………	–	–	–
13	19.95	4.4467	2166	4	4.3884	-1	1	1
14	20.75	4.2771	265	1	4.3105	1	1	0
15	20.95	4.2367	538	1	………	–	–	–
16	21.85	4.0642	1107	2	4.0605	-2	1	0
17	22.15	4.0098	20319	32	………	–	–	–
18	22.55	3.9396	1727	3	3.9699	1	-2	0
19	24.75	3.5941	14215	23	3.5972	0	2	0
20	25.1	3.5448	16408	26	………	–	–	–
21	26.2	3.3984	1443	3	3.4022	-2	2	0
22	26.5	3.3606	5437	9	3.3012	-2	1	1
23	28.15	3.1673	131	1	3.1842	1	-2	-1
24	28.3	3.1508	211	1	………	–	–	–
25	28.55	3.1238	307	1	………	–	–	–
26	29.0	3.0763	140	1	3.0667	1	0	2
27	30.4	2.9378	1074	2	2.9618	0	2	1
28	30.55	2.9237	663	2	………	–	–	–
29	31.7	2.8202	204	1	2.8274	2	1	0
30	32.75	2.7321	940	2	2.7452	2	-1	2
31	32.95	2.716	912	2	2.7069	-3	1	0
32	33.35	2.6844	838	2	2.6905	0	-2	2
33	34.3	2.6121	328	1	2.6161	-3	2	0
34	34.45	2.6011	375	1	………	–	–	–

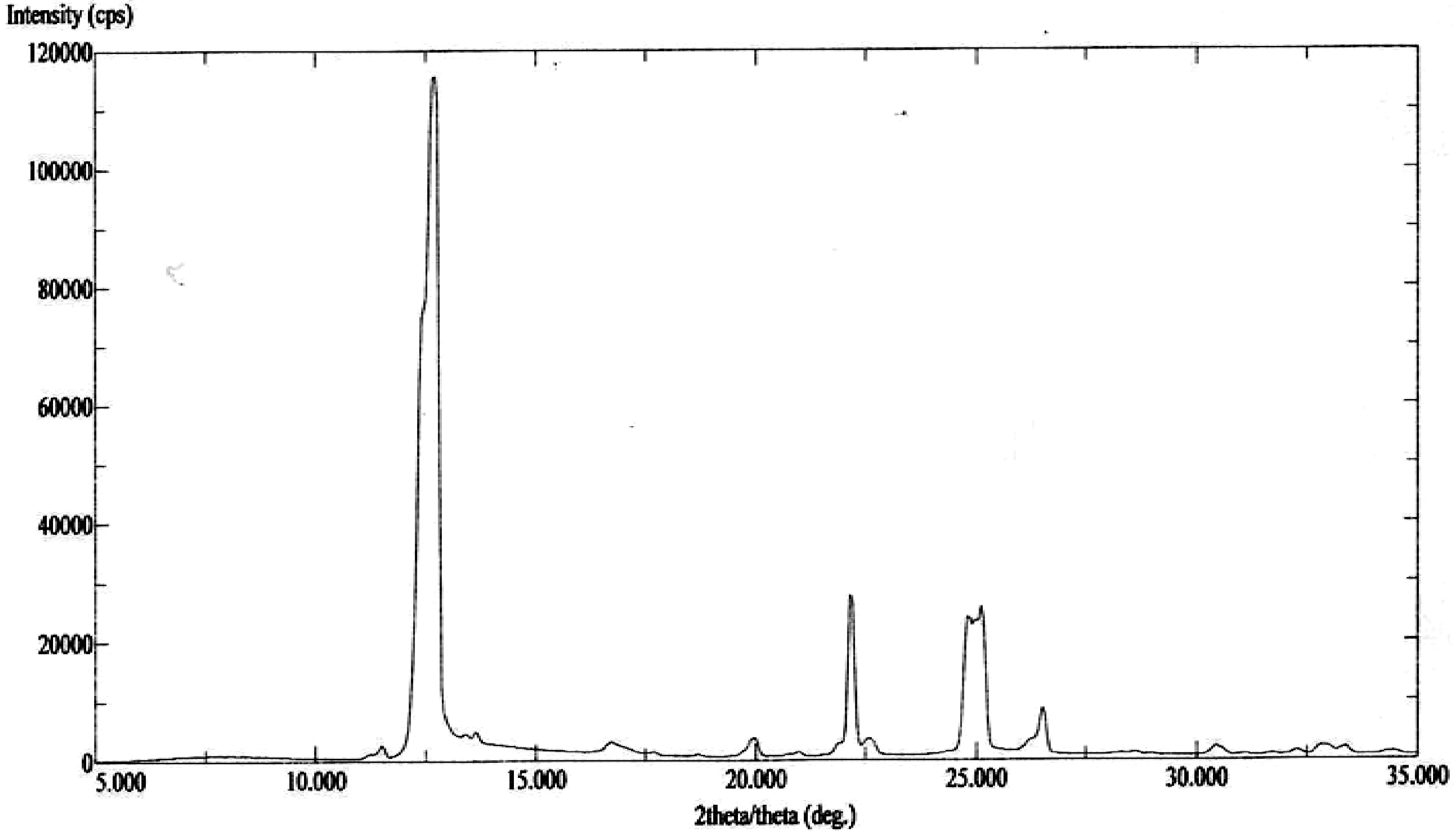

Figure 33 X-Ray Spectrum of NVCL

Table 12 X-Ray Analysis of monomer-polymer (49.08% conversion) mixture

Peak No	**2θ**	**d-Value**	**Intensity**	**I/I_0**	**d-Calculated**	**h**	**k**	**l**
1	13.7	6.4581	350	13	……….	–	–	–
2	16.55	5.3518	2911	100	5.381	0	-1	1
3	18.35	4.8307	61	3	4.9056	-1	0	1
4	25.2	3.531	687	24	3.5972	0	2	0
5	27.9	3.1951	63	3	3.2025	-2	0	1
6	28.35	3.1454	142	5	3.1842	1	-2	-1

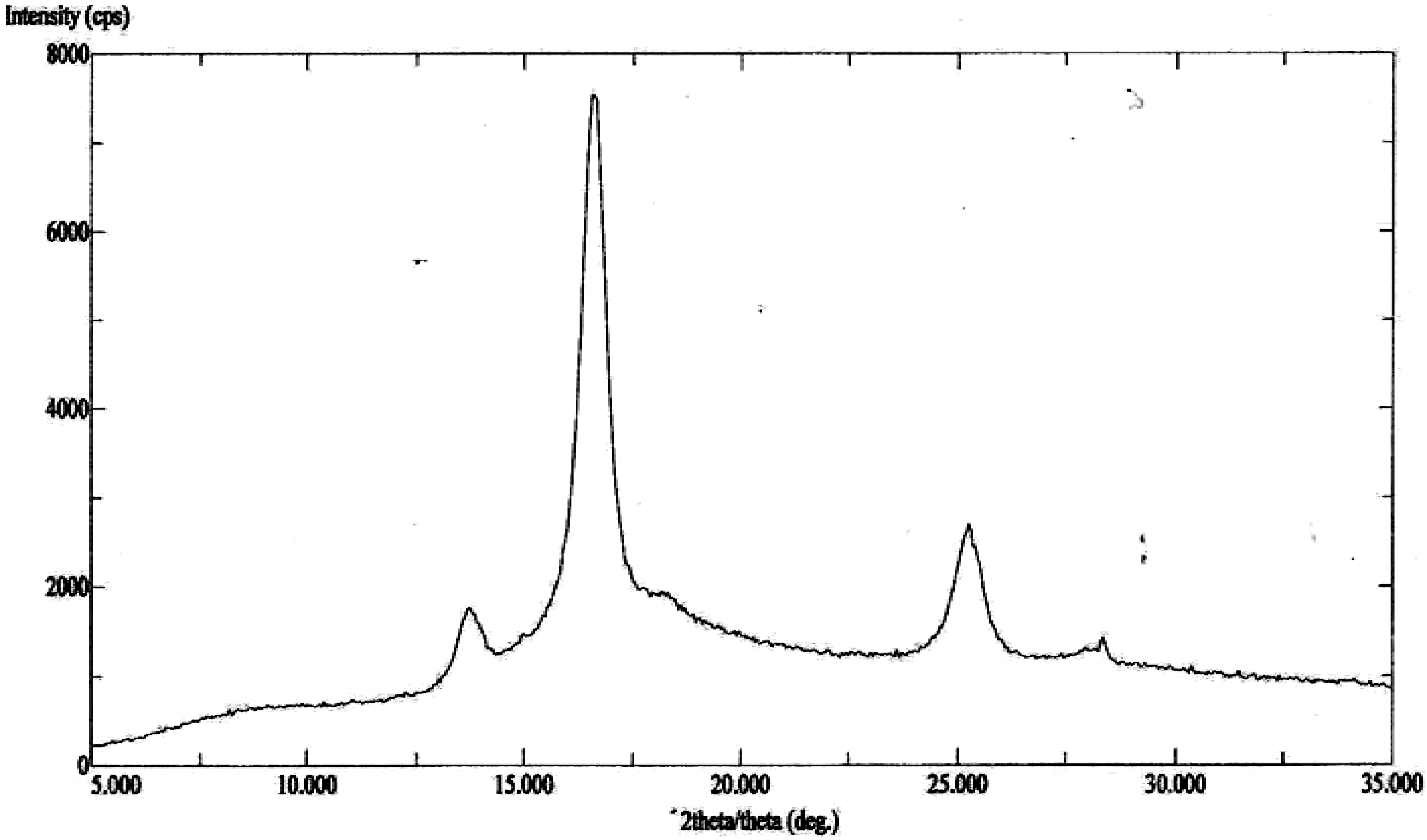

Figure 34 X-Ray Spectrum of monomer-polymer (49.08% conversion) mixture

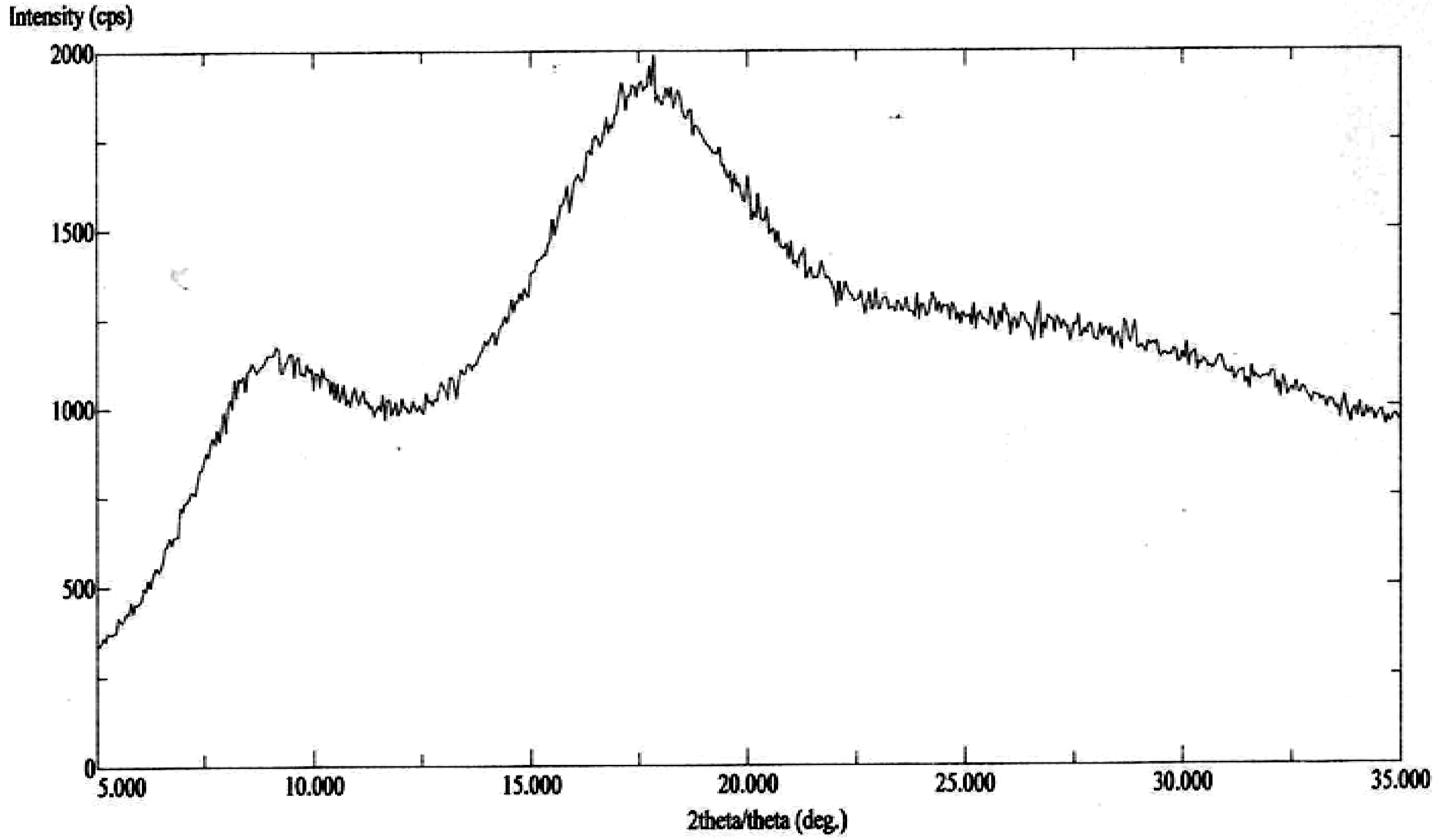

Figure 35 X-Ray Spectrum of monomer-polymer (89.46% conversion) mixture

CHAPTER 4

CONCLUSIONS

N-vinylcaprolactam was polymerized by free radical polymerization with solution technique at different temperatures of 50, 60 and 70 ^{o}C. From the results of experiments and investigations, the following conclusions can be made:

1) The synthesized polymer was a white, powder type polymer. It was soluble in water and common organic solvents. It absorbs water in air.

2) It was confirmed that PNVCL possess LCST in the range of physiological temperature (32 ^{o}C-34 ^{o}C). Below this temperature it is soluble, but when the temperature is raised phase separation occurs and the polymer precipitates.

3) The percent conversion vs. time graphs showed that the percent conversion of NVCL increased with polymerization time.

4) From Arrhenius plot activation energy of polymerization was calculated as 108.4 kJ/mol.

5) FT-IR and NMR results showed that polymerization takes place by opening of carbon-carbon double bond without any change in the caprolactam ring.

6) FT-IR investigations showed that, new peak was formed (O−H Stretching) in the spectrum of the polymer. This peak confirms the absorption of water by the polymer.

7) FT-IR and NMR results showed that after the polymerization of NVCL, shapes of the peaks in the spectra changed due to the changes in the conformation of the molecules and interaction of molecules upon polymerization.

8) The DSC thermogram of monomer confirmed that NVCL has a melting point at 37.3 ^{o}C. Moreover, the DSC thermogram of PNVCL showed that the polymer has a T_g value at 1.8 ^{o}C and softening temperature at 68.8 ^{o}C.

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

10) X-Ray powder pattern showed that the most intense peak is $1\bar{1}0$ for the monomer and $0\bar{1}1$ for the polymer. Thus polymerization proceeded in the b-crystallographic axis direction.

11) X-Ray powder pattern confirmed that the monomer has a crystal structure, and the polymer is generally amorphous, but still has regular orientation in b-crystallographic axis direction.

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