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Solid State Polymerization of N-vinylcaprolactam via Gamma Irradiation and Characterization

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In this study, N-vinylcaprolactam was polymerized via gamma irradiation in the solid state. The polymerization was carried out at room temperature both under vacuum and open to atmosphere. The polymerization mechanism showed auto acceleration and the rate of polymerization was higher in the presence of oxygen. Complete conversion was obtained under vacuum conditions and 90% conversion was obtained in the case of polymerization open to atmosphere. The polymers were characterized by FTIR, NMR, DSC, TGA, GPC, X-ray diffraction and mass spectrometry tests. FTIR and NMR results showed that polymerization proceeded through the vinyl groups and caprolactam is pendant group. DSC results showed that the polymer obtained could be polymerized further or crosslinked by heat treatment. The Tg value for the polymer obtained from radiation induced polymerization was about 135°C and increased to 174.6°C after thermal treatment. Molecular weights of some polymer samples were measured by GPC. X-ray diffraction studies showed that the monomer structure was retained up to about 86% conversion of monomer to polymer. The chain structure of the polymer was confirmed by mass spectroscopy results.

Keywords: Solid state, polymerization, gamma, irradiation, N-vinylcaprolactam, poly(N- vinylcaprolactam), characterization

1 Introduction

The polymerization by radiation can be initiated either by a radical or an ion. Although radiation produces ions and excited molecules as a primary act, most of the polymerization reactions studied have been found to proceed by a radical mechanism (1).

The solid state polymerization was reported for the first time by Schmitz and Lawton in 1951 (2). The crystal structure effect and mechanism of radiation induced solid state polymerization of acrylamide was well documented by Usanmaz (3). Usanmaz and Melad (4) polymerized 3-aminocrotonamide via radiation in solid state. Polymerization by a condensation mechanism with evolution of $(2n-1)NH_3$ molecules for each 2n monomer molecules. The polymer formed was similar in crystal structure to that of monomer. Thus, it gives a topotactic polymerization by condensation.

The mechanism of polymerization is greatly influenced by monomer crystal geometry in the solid state. The change in the crystal structure most probably orients the molecules in more favorable arrangements for polymerization of allylthiourea (5). The effect of oxygen on the polymerization of allylthiourea was investigated by Usanmaz and Y lmaz (5). The accelerating effect of oxygen was clear at conversions above 40%. This suggests that the crystal structure becomes distorted with the formation of polymer to allow easier diffusion of oxygen.

N-Vinylcaprolactam, NVCL, monomer contains (6) hyrophilic cylic amide (caprolactam) attached to vinyl group by nitrogen. In the case of addition polymerization, the vinyl group is used for polymerization and caprolactam becomes pendant group, the polymer backbone is vinyl type. The presence of side lactam group makes the polymer very valuable for bioapplication. If the condensation polymerization is carried out, the caprolactam ring is opened and nylon type polymer is obtained. The side group in this polymer chain will be a vinyl group. After applications such as drawing into fiber, the side vinyl group can be used for crosslinking to improve the mechanical strength of polymer. The polymer can be used as an engineering polymer.

The crystal structure of monomer was reported by Tishchenko et al. (7). The compound is water soluble with a low critical temperature of 36–37°C. The crystals are triclinic with 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 ant the space group is P1. The molecule exhibits a chair conformation. The amide and vinyl groups are

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approximately coplanar. The charge distribution calculated (8) indicates the increase reactivity of the terminal C atom ($CH_2 =$) in vinyl group, which promotes the polymerization reaction given polymer chain as follows:

$$\left(\!\!-CH_2\!\!-\!\!-CH\!-\!\right)_n$$
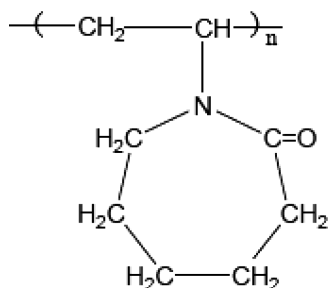
The kinetics of N-vinylcaprolactam polymerization has not been reported in the literature. However, due to the interesting and unique solution properties, the solution properties have been studied intensively. In the poly(N-vinylcaprolactam), (PVCL), chain, nitrogen is directly attached to the hydrophobic carbon-carbon backbone chain (9). Therefore, the hydrolysis of PVCL does not produce low molecular weight amines. The appropriate balance of hydrophobicity and hydrophilicity within the polymer chain is the reason for unusual properties of polymer. Cheng et al. (10) reported the polymerization of NVCL by radiation in water. The effects of radiation dose and total dose on the viscosity of polymer obtained and low critical solution temperature were studied. It was shown that the polymer obtained via irradiation (dose rate range of 2–14 Gy/min and total dose greater than 2 kGy) has good temperature sensitivity and uniformity. PVCL is a nonionic synthetic polymer soluble in water and also exhibit thermosensitive properties in an aqueous solutions. The relation of temperature-solubility of PVCL was reported in 1968 (11). When the aqueous solutions are heated, phase separations are observed in the range of 32–38°C (12); a low temperature transition (lower critical solution temperature, LCST) at 32°C is attributed to a micro segregation of hydrophobic domains and a higher temperature transition around 38°C, corresponding to the gel volume collapse itself. Therefore, this polymer is considered to be suitable materials for novel biotechnological applications such as in drug delivery, bioseparation, diagnostics, etc. (10).

The radiation graft polymerization of N-vinylcaprolactam onto polypropylene films was studied by Kudryavtsev et al. (13). 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 studied and it was shown that the modified polymers of polypropylene with grafted poly(N- vinylcaprolactam) chains exhibited thermoresponsive properties.

Kirsh and Yanul (8) studied structural transformations and water associate interactions in poly-N-vinylcaprolactam-water system and it was shown that (i) the conformation type of a side seven-member ring deduced by quantum-chemical calculations is the chair; (ii) the main chain of PVCL prepared by usual radical polymerization has syndiotactic structure; (iii) the calculation of charge distribution on a C=O oxygen atom in the analogue of PVCL chain link gives the large electron density value being -0.362, (iv) the addition of water to PVCL changes Tg from 147°C (dry polymer) to $-17/-38$°C at N (number of water molecules per unit) being 2.6/8.0. Phase and conformational behavior of PVCL was studied as a function of polymer concentration, NaCl concentration and sodium dodecyl sulfate concentration (14). Microgel particles produced by using NVCL and poly(ethylene glycol) diacrylate or N,N$_0$-methylenebisacrylamide were synthesized and the influence of concentration and type of crosslinker on polymerization kinetics and colloidal characteristics were studied (15).

In this study, N-vinylcaprolactam was polymerized in solid state via gamma irradiation. The polymerization was carried out in vacuum and open to atmosphere conditions to observe the effect of oxygen on polymerization mechanism. The kinetics of polymerization has been investigated. Polymer obtained was characterized via FTIR, NMR, DSC, TGA, GPC, XRD and mass spectrometry tests. X-ray diffraction pattern of powder monomer and monomer-polymer mixtures after irradiation were obtained and the changes in crystal structure of monomer was investigated. The indexing of diffraction of data was done by using the reported cell parameter data given in literature (7).

2 Experimental

2.1 Materials and Methods

N-vinylcaprolactam (Aldrich) was purified by recrystallization in hexane. Technical grade diethylether (Riedel de-Haen) and benzene (Baker Analyzed) were purified by distillation. Deionised water was obtained in our laboratory.

Gammacell 220 model radiation source (AECL, Canada) with the dose rate of 87.8 Gy/h was used for the irradiations. Infrared Spectra of monomer and polymers obtained from KBr pellets by using Perkin Elmer Spectrum 1 FTIR Spectrometer. The DSC tests were carried out on Thermal Analyst 2000 Differential Scanning Calorimeter 910 S under N_2 atmosphere in the temperature range of -50 to 300°C with heating rate of 10°C/min. TGA studies was carried out via Dupont 951 Thermogravimetric Analyzer and thermograms were recorded under N_2 atmosphere in the temperature range of 30°C to 900°C with 5°C/min heating rate. Bruker Ultrashield 400 MHz Digital NMR was used for the NMR spectrums.
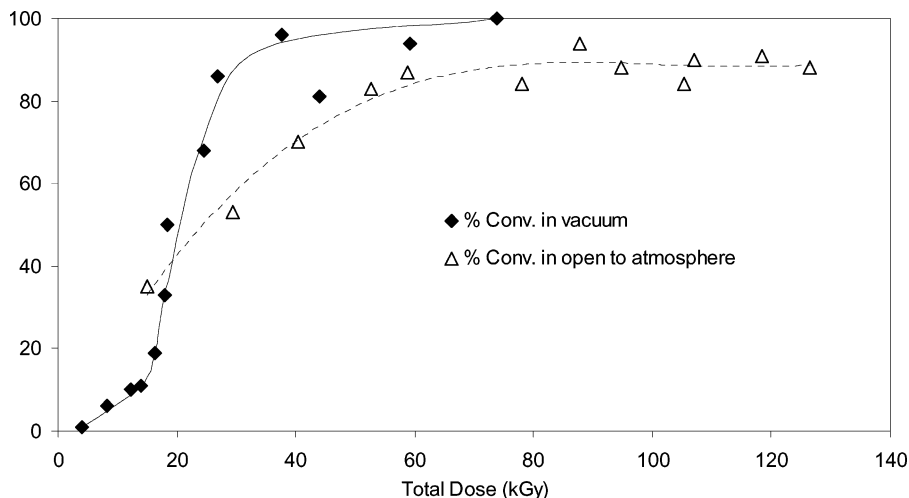
Fig. 1. Conversion vs. dose for the solid state polymerization in vacuum and open to atmosphere.

Molecular weight determination of several poly (vinylcaprolactam) samples was carried out by GPC on a PL-GPC 220 integrated GPC system. X-Ray powder diffraction patterns (XRD) were taken by using Rigaku Miniflex with Cu (Kα 30 kV, 15 mA, λ = 1,54178 A$^\circ$) radiation. Direct insertion probe pyrolysis mass spectrometry (DP-MS) system used for the thermal analyzes consists of 5973 HP quadruple mass spectrometer coupled to JHP SIS direct insertion probe pyrolysis system. This system provides fast scanning, self-tuning of experimental parameters and wide mass range. Mass spectra of the products was recorded at a scan rate of 2 scan/s in the mass range of 10–800 amu.

The solid state polymerization of N-vinylcaprolactam initiated by gamma rays was carried out under vacuum and in atmospheric air at room temperature. About 3–5 g of monomer sample was put into the Pyrex glass tube and connected to the high vacuum system, evacuated at 10^{-4}—10^{-5} mmHg for about 6 h. The tube was sealed by flame and irradiated in gamma source for desired period of time at room temperature. For the polymerization in open to atmosphere condition, samples were placed in to the tubes, sealed without evacuation and irradiated in radition source. After the irradiation period, the tubes were break open, samples were dissolved in a small amount of benzene and the polymer precipated in diethylether. The polymer was filtered and dried to constant weight. The percent conversion of the monomer to the polymer was calculated gravimetrically.

water and common organic solvents. The polymer is very hygroscopic and absorb water in air. The change of percent conversion with total dose of irradiation under vacuum and open to atmosephere condititons are given in Figure 1. The polymerization in vacuum condititon showed a S-type behaviour. The initial rate is almost linear up to 10–12% conversion, then increases to high rate showing an auto accelaritation mechanism. The polymerization reaches 100% conversion. The initial rate of polymerization is much higher for polymerization in open atmosphere conditions compared to polymerization under vacuum. The polymer obtained in open atmosphere conditions were soluble in ether. But from vacuum condition were not. The seperation of polymer from monomer was very difficult. The percent polymer could not be safely obtained for lower conversions in open atmosphere polymerization. However, the auto accelaration behaviour was not observed and the limiting conversion was about 90% in open atmosphere polymerization. The initial rate was linear up to about 70% conversion. Around the limiting coversion the data scattering is also higher in this case. This is due to the termination of polymer chains in the presence of oxygen and formation of low molecular weight oligomers in the presence of oxygen. The low molecular weight (tellomers and oligomers) polymers can not be seperated by precipitation method.

The molecular weights of four polymer samples were carried out by GPC and given in Table 1. They were in the

3 Results and Discussions

3.1 Solid State Polymerization of N-Vinylcaprolactam

The radiation induced solid state polymerization of N-vinylcaprolactam gave gel type white polymer soluble in

Table 1. Results obtained from the GPC measurements

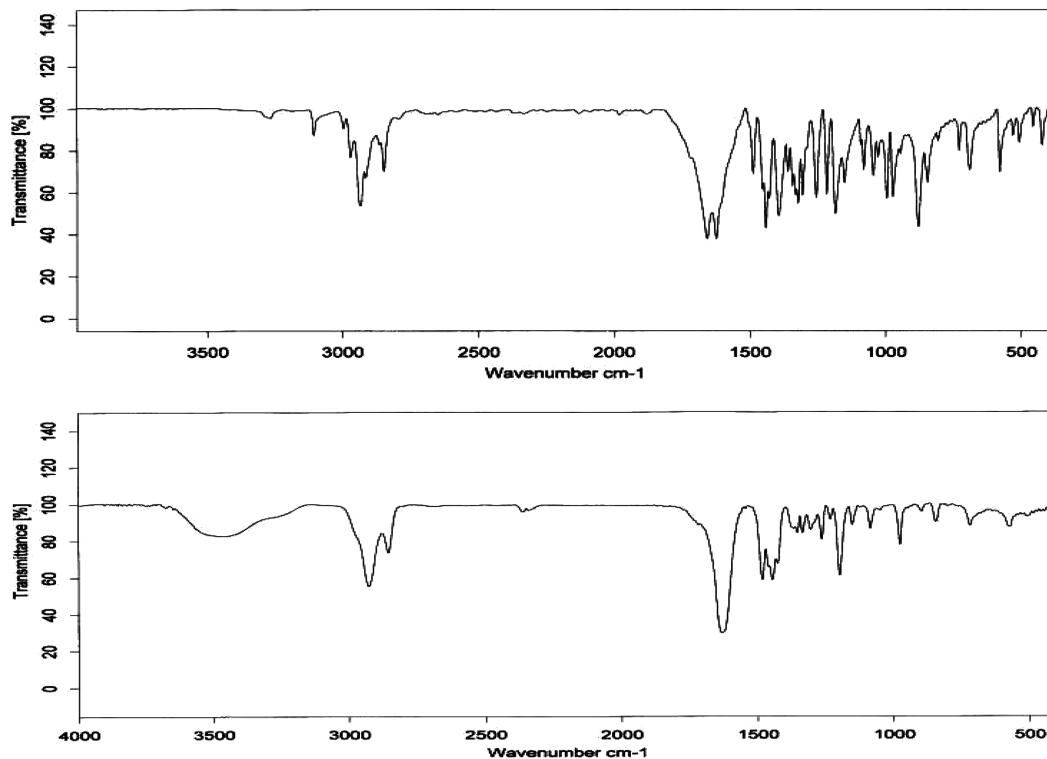| Sample	Mw	Mn	Mz	Mp	Dispersity Index
PVCL 1	115,700	23,480	1,522,000	39,550	4.93
PVCL 2	13,260	176	102,800	2,031	75.34
PVCL 3	69,730	69,680	69,790	69,450	1.0
PVCL 4	83,830	81,430	87,220	81,870	1.03

Fig. 2. FTIR spectrum of (a) NVCL, (b) PVCL.

range of 13,000–116,000 and the dispersity index of polymers with molecular weight around 70,000 is 1. However the dispersity index for lower molecular weight is very high (about 75). This is related to the high fraction of oligomers.

3.2 FTIR Analysis

The FTIR spectra of monomer and polymer are given in Figure 2. In the FTIR spectrum of NVCL (Figure 2a), the characteristic carbonyl peak (C=O) is at 1657 cm^{-1}.
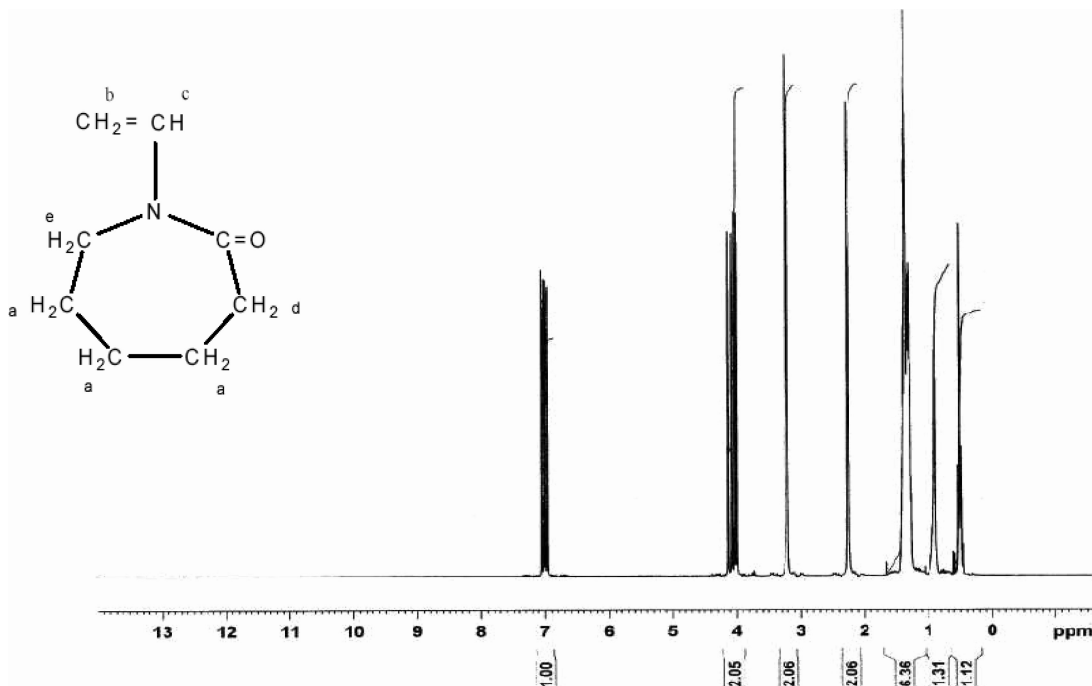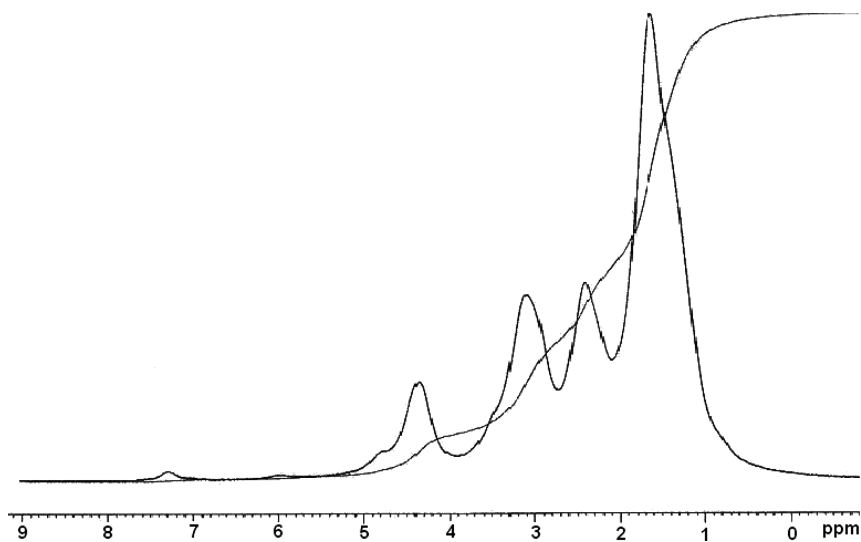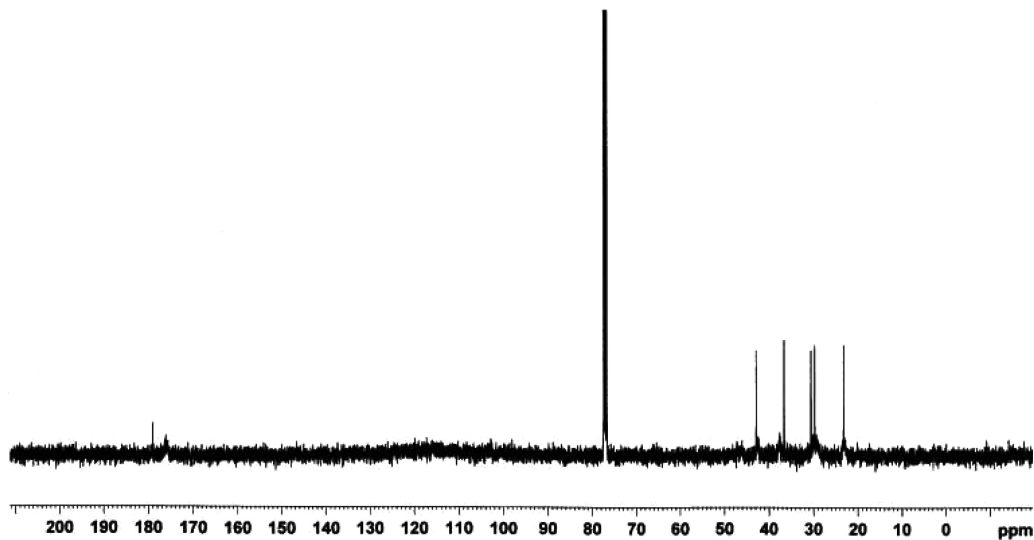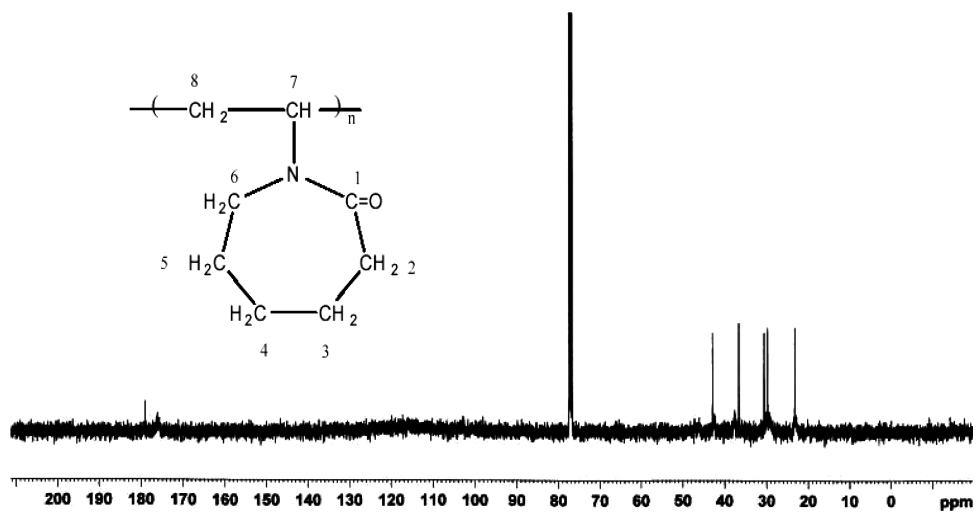

Fig. 3. ^{1}H-NMR Spectrum of NVCL.

Fig. 4. ^{1}H-NMR Spectrum of PVCL.

Fig. 5. ^{13}C-NMR spectrum for NVCL.

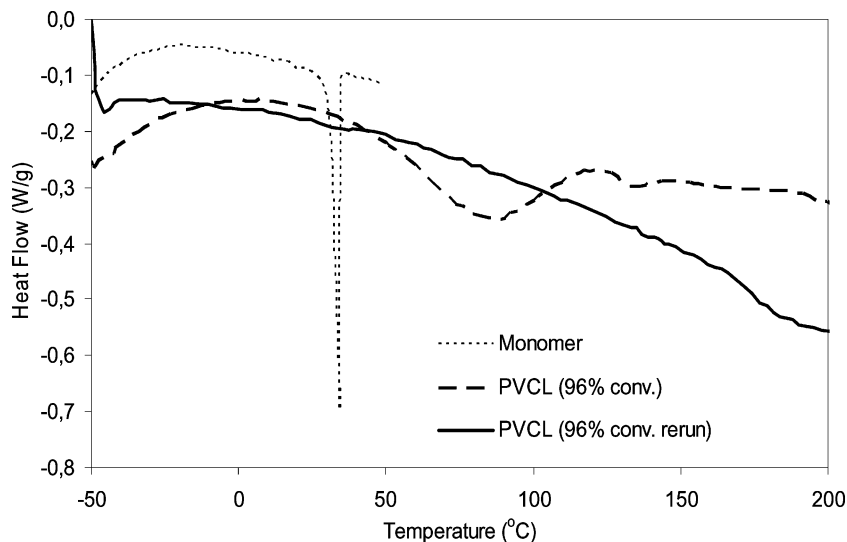**Fig. 6.** ^{13}C-NMR spectrum for PVCL.

Fig. 7. DSC thermograms for the monomer (NVCL) and the polymer (PVCL).

The peaks for the C=C was observed at 1624 cm^{-1} and at 939 cm^{-1}. The peaks in the 2935 and 2850 cm^{-1} correspond to the aliphatic C-H stretching. The -CH$_2$- peaks are at 1440–1300 cm^{-1}. C-N stretching vibrations are at 1255–1045 cm^{-1}. In the spectrum of PVCL (Figure 2b), C=O bond stretching at 1630 cm^{-1} becomes broader and peak of double bond (-C=C-) near C=O peak disappeared. The aliphatic C-H stretching was observed at 2928 and 2856 cm^{-1}. The vinyl, CH$_2$ =CH- peak in the spectrum of monomer at 939 cm^{-1} is not observed in the spectrum of PVCL. The other vinyl peak at 1624 cm^{-1} is replaced with shifted C=O peak. The CH$_2$ peaks are at about 1443 cm^{-1}. Peaks belong to double bond were completely disappeared. The peaks of C-N stretching vibration at 1255–1045 cm^{-1} in the monomer spectrum showed changes in intensity and position in the spectrum of polymer. This might be due to changes in conformation of side group and resonance structures. This can also be observed in the region of
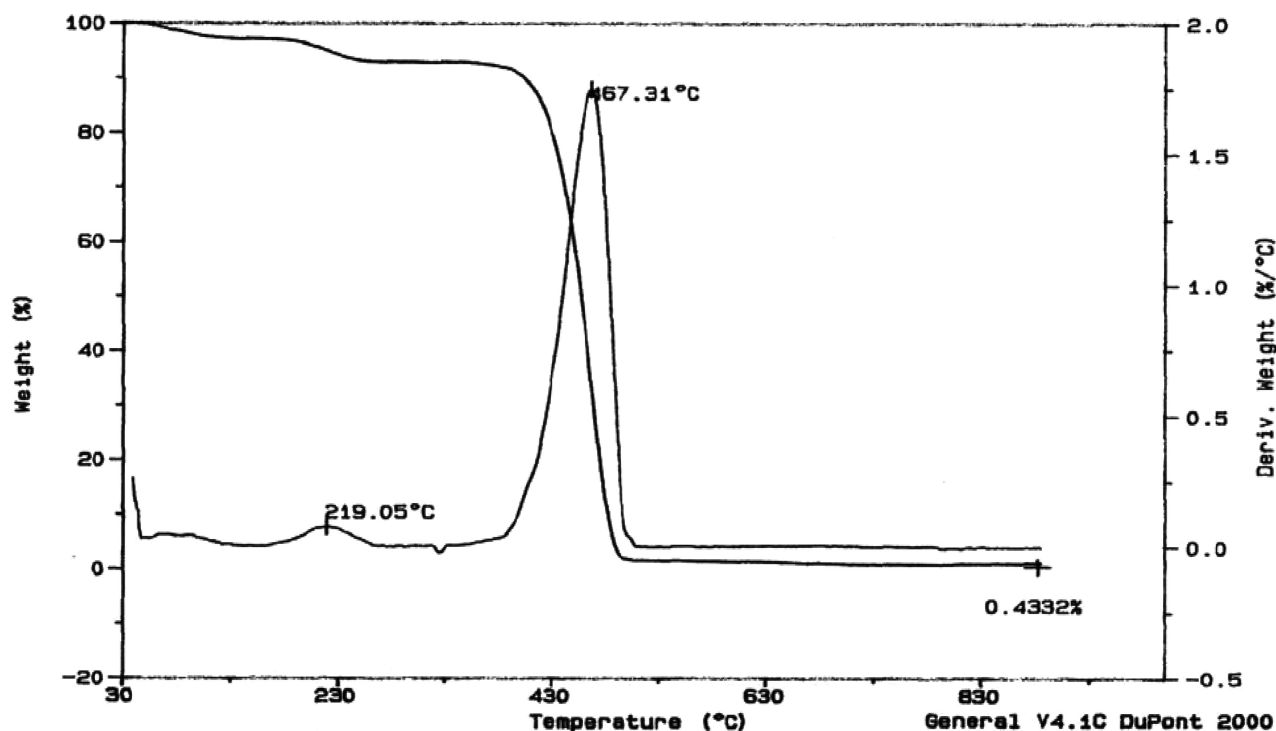
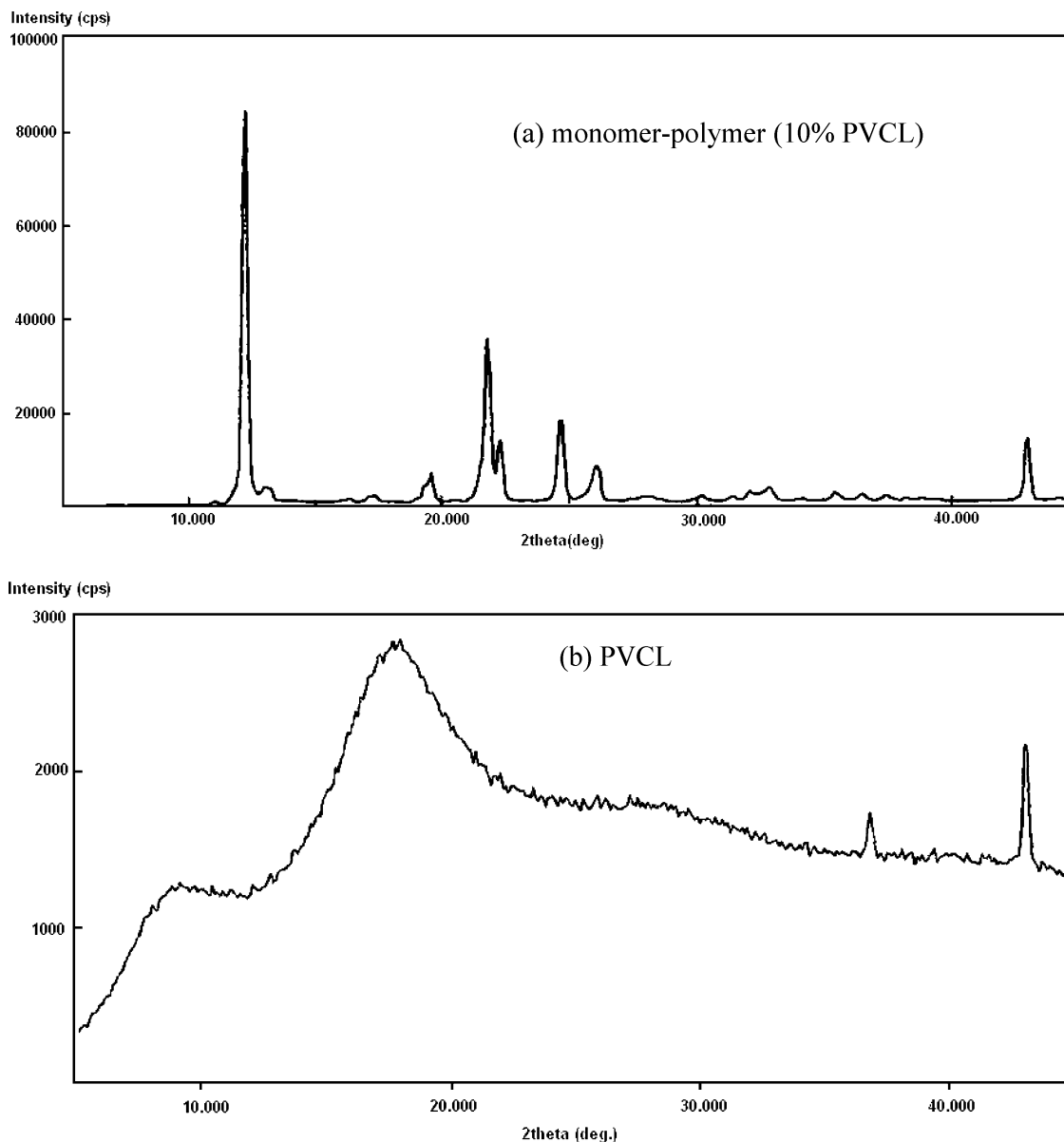

Fig. 8. TGA thermogram of PVCL.

Fig. 9. X-Ray spectrum of (a) monomer-polymer (10% PVCL) mixture, (b) PVCL.

$3900–3300 \, cm^{-1}$, where new peaks corresponding to the O-H and N-H are observed in the spectrum of polymer. The sharpness of the peaks in polymer spectrum showed regularity in polymer molecular chain. It can be concluded from IR spectra investigation that polymer was successfully obtained and the polymerization proceeds by carbon-carbon double bond opening.

3.3 NMR Analysis

The ^{1}H-NMR and ^{13}C-NMR spectras of N-vinylcaprolactam monomer and polymer were taken. The monomer peaks in the ^{1}H-NMR spectrum and the assignments are given in Figure 3. The vinyl group corresponding to b and c are in the 4.0 and 4.13 ppm, respectively. The CH$_2$ groups in the ring as shown with "a" are equivalent and appears at 1.35 ppm. The CH$_2$ groups close to C=O, and N are at 2. 3 and 3.2 ppm, respectively. These peaks show some changes in the spectrum of polymer as given in Figure 4. The vinyl peaks are not completely disappeared upon polymerization but becomes much broader. These peaks correspond to the chain end vinyl groups and also indicates the presence of oligomers in the polymer samples. When the molecular weight is small, the end group analysis can easily be observed in the NMR spectrum. The other peaks of monomer become much broader in the spectrum of polymer. This is due to the changes in the chair conformation of lactam group in the molecule after changing of intermolecular distance with polymerization.
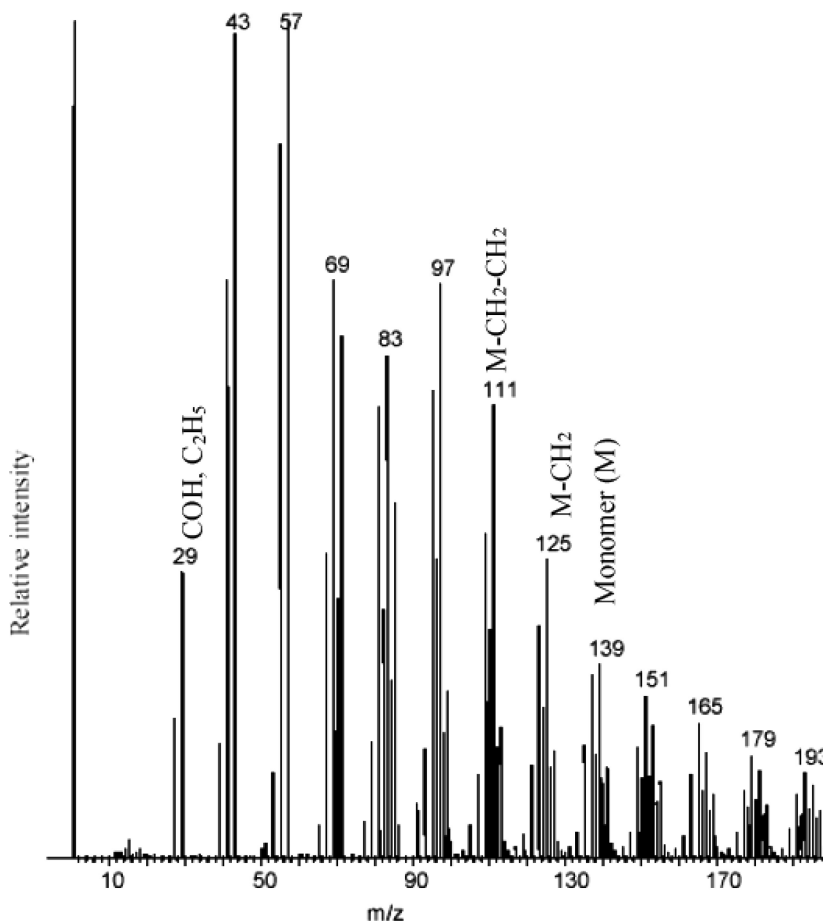
Fig. 10. Mass spectrum of NVCL.

The NVCL peaks in the ^{13}C-NMR spectrum and the assignments are given in Figure 5. Similar spectrum of PVCL and the assignments are given in Figure 6. The $CH_2 =$ at 92.4 ppm in the spectrum of monomer was not observed in the spectrum of the polymer. Moreover, the methylene peak at 132 ppm in the monomer spectrum was not observed in the spectrum of the polymer. These changes are due to the changes in the conformation of molecules upon polymerization.

3.4 Thermal Analysis

The DSC thermograms of monomer and the polymer are given in Figure 7. There is an endothermic peak at 34.3°C corresponding to the melting point of the monomer. The thermogram is recorded in the temperature range of −50°C to 50°C and no other peaks were observed. In the thermogram of the polymer, there is a broad peak at about 85°C and a less probable peak at about 135°C, which can be the Tg value. The sample was cooled and the thermogram of the same sample was taken again (second run). The peak at 85°C disappeared and a new peak of Tg was observed at about 174.6°C. Therefore, at about 85°C, further

polymerization of small molecular weight fractions or crosslinking took place. The higher Tg compared to Tg observed before rerun of the thermogram at about 135°C is due to the increase of molecular weight.

Thermogravimetric analysis of polymer was carried out under nitrogen atmosphere from room temperature up to 900°C. The thermogram is given in Figure 8. The decrease in weight starts at about 60°C and continues up to about 200°C by about 3%. The second range is maximized at 290°C. After about 383°C, the weight decrease is very sharp and reaches zero percent. The first decomposition corresponds to adsorb water and then crystalline water. The main decomposition maximized at 467°C. The sharp decrease of weight shows that the degradation of polymer is in the form of depolymerization.

3.5 X-RAY Analysis

The powder X-Ray spectrum of monomer has very sharp peaks with very high intensity. The indexing of peaks were done with cell parameters reported by Tishchenko et al. (7) as a = 8.170(4) A, b = 8.094(4) A, c = 6.799(4) A, $\alpha = 99.92(1)^0$, $\beta = 88.89(1)^0$, $\gamma = 115.30(1)^0$. The most intense peak is due to 010 reflection. The next most intense
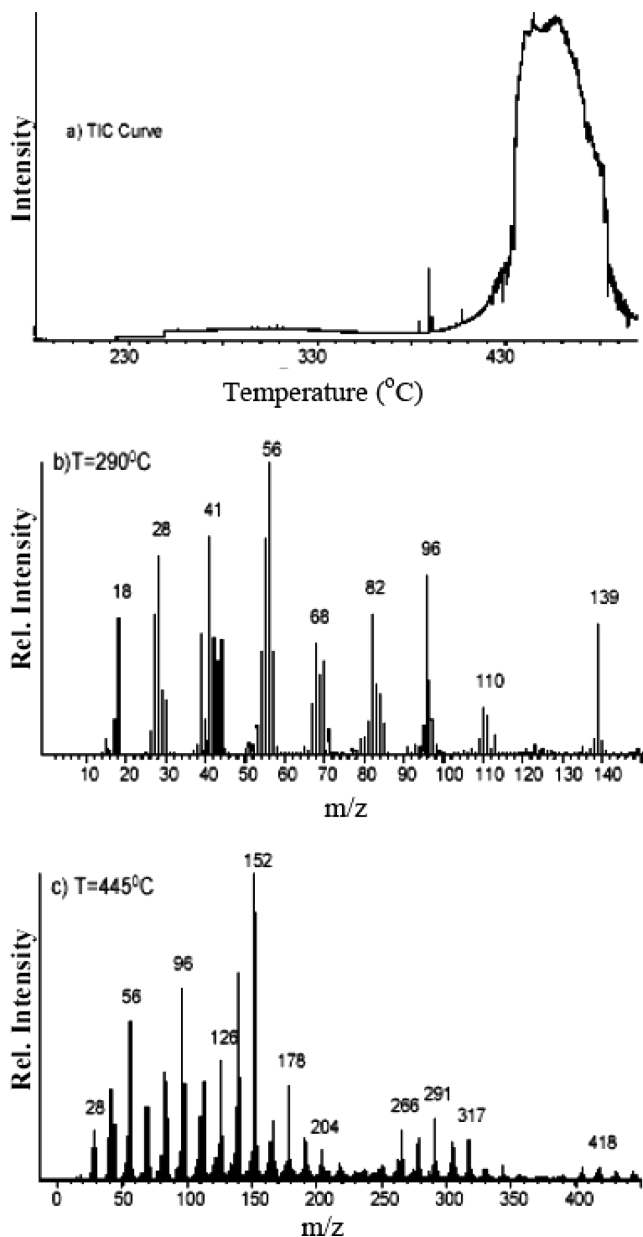
Fig. 11. Mass spectrum of PVCL.

peak is at 020. Thus, the monomer is aligned in the b-crystallographic axis direction.

The mechanism of polymerization was investigated via X-ray powder pattern of monomer polymer mixtures after irradiation with different conversions in order to understand the change in monomer structure during polymerization. The spectrum of monomer polymer mixtures for 1% conversion to polymerwere taken and the intense peak (010) in the spectrum of monomer retained its position, however, in this case, the next intense peak was not at 020. The relative intensity of this peak in the monomer spectrum was 69%, but in this spectrum, it was only 11%. Instead of the peak at 020, the intensity of 210 peak, which was 11% in the spectrum of monomer, reached to 36% in this spectra.

Other peaks which were weak in the monomer spectrum but become more intense in this spectrum are 021 and 211. Therefore, polymerization most probably proceeds in the direction of 011.

In the X-ray powder spectrum of the monomer polymer mixture for 10% conversion to polymer (Figure 9a), the intensity of peaks are relatively decreased compared to that of the monomer. However the most intense peak was still 010. The next intense peaks were in a similar position as that of the sample after 1% conversion. The X-ray powder spectrum of monomer polymer mixture for 50% conversion to polymer shows many differences compared to other spectrums. There is a large decrease in the intensity of monomer peaks and a broad peak corresponding to polymer appears in the spectrum. The intensity of 010 peak is no more than the most intense peak (67% intensity). The most intense peak now is 220 (100% intensity). It was only about 12% in the spectrum of monomer. This shows that even at this percent conversion, the monomer retains most of its characteristic structure. However, the polymer also shows crystalline structure with the appearance of new peaks. Thus, the polymer obtained at 50% conversion has a relatively high percent of crystallinity.

The X-ray powder spectrum of monomer polymer mixture for 86% conversion shows a typical appearance of low percent crystalline polymer. There are some background peaks of the monomer also in the spectrum. The structure of the monomer almost completely disappeared in the spectrum. When the polymer is separated from the monomer, the X-ray spectrum showed the same pattern. X-ray powder spectrum of polymer is given in Figure 9b.

3.6 Mass Spectral Analysis

The mass spectrum of the monomer is given in Figure 10 with the corresponding peak assignments, the monomer peaks were quite intense. Moreover, there were some high mass peaks indicating presence of oligomers. The base peak was at m/z = 57 Da due to $N=COHCH_2$ indicating that McLafferty rearrangement reaction was the main dissociation pathway during ionization. The second intense peak was at m/z = 43 Da due to $N=COH$. Other intense peaks were at m/z = 41,69, 71, 83 and 97 due to C_3H_5; $C_3H_6CH=CH_2$, $CH_2=CH-N=CH_2$; $N=C(OH)(CH_2)_2$; $CH_2=CH-N(CO)(CH_2)_2$; $C=O(CH_2)_3CH=CH_2$, respectively.

Total ion-current (TIC), the variation of total ion yield as a function of temperature and the pyrolysis mass spectra of the polymer at 290°C and at 445°C are shown in Figure 11. It can be seen from the Figure 11 that the main decomposition occurred above 430°C in accordance with the TGA. The base peak in the mass spectrum recorded at 290°C is at m/z = 56 Da due to $(CH_2)_5$. The highest mass fragment was monomer. Evolution of the water was also detected around this temperature range. At the final stage of pyrolysis, the base peak was at m/z = 152 Da due to

M+CH. However, the monomer yield was also quite intense. The data indicated cleavage of side groups from the low molecular weight oligomers. The loss of side groups probably occurred mainly during the ionization processes inside the mass spectrometer. Thus, it could be concluded that the thermal degradation occurs by random cleavages of the polymer backbone in a single yielding mainly monomer and low molecular weight oligomers.

However, in order to be sure about the thermal degradation processes taking place, the single ion pyrograms and the variation of intensity of a single product ion as a function of temperature were also studied. It was seen that besides H_2O, monomer and dissociation products, the monomer, thermal decomposition mainly occured in the final stage of pyrolysis.

4 Conclusions

The following conclusion were obtained from this study:

1. The rate of polymerization was higher in open to air condititon and complete conversion was obtained in vacuum that of open to atmosphere condititon was 90%.
2. Polymer obtained was gel type soluble in water and most common organic solvents.
3. FTIR and NMR results showed that polymerization proceeded by opening of vinyl group.
4. X-Ray analysis showed that the crystal structure of monomer retained its identity up to about 86% conversion. The polymer was amorphous but showed some polymer chain regularity and chain orientation up to a certain extend.

5. Mass spectrum analysis of monomer and polymer gave the fragments compatible with a vinyl group backbone chain and lactam as side group.

References

1. Charlesby, A., Atomic Radiation and Polymers, Pergamon Press: New York, 1960.
2. Schmitz, J.V., and Lawton, E.J. (1951) *Science*, 113(2947), 718.
3. Usanmaz, A., (1997) *Turk. J. Chem.*, 21(4), 304–312.
4. Usanmaz A., and Melad, O.K. (1996) *J. Polym. Sci., Part A., Polym. Chem.*, 34(6), 1087–1093.
5. Usanmaz, A., and Y lmaz, E. (1987) *J. Macromolecular Sci., Part A* 24(5), 479–491.
6. Nasimova, I.R., Evlanova, N.F., Makhaeva, E.E. and Khokhlov, A.R. (2001) *Journ. of Applied Polymer Sci.*, 81(12), 2838–2842.
7. Tishchenko, G.N., Zhukhlistova, N.E., and Kirsh, Yu E. (1997) *Crystallography Reports*, 42(4), 626–630.
8. Kirsh, Yu E., Yanul, N.A., and Kalninsh, K.K. (1999) *Eur. Polym. Journ.*, 35, 305–316.
9. Lau, A.C.W., and Wu, C. (1999) *Macromolecules*, 32(3), 581–584.
10. Cheng, S.C., Feng, W., Pashikin II, Yuan, L.H, Deng, H.C., and Zhou, Y. (2002) *Radiation Physics and Chemistry*, 63(3), 517–519.
11. Solomon, O.F., Corciovei, M., Ciuta, I., and Boghina, C. (1968) *J. Appl. Pol. Sci.*, 12(8), 1835–1842.
12. Anufrieva, E.V., Gromova, R.A., Kirsh, Yu E., Yanul, N.A., Krakovyak, M.G., Lushchik V.B., Pautov V.D., and Sheveleva TV. (2001) Eur. Polym. J. 37(2), 323–328.
13. Kudryavtsev, Val. N., Kabanov, V. Ya., Yanul, N.A., and Kedik, S.A. (2003) *High Energy Chemistry*, 37(6), 382–388.
14. Dubovik, A.S., Makhaeva, E.E., Grinberg, V.Y., and Khokhlov, A.R. (2005) *Macromol. Chem. Phys.*, 206, 915–928.
15. Imaz, A., and Forcada, J. (2008) *Journ. of Polym. Sci.: Part A: Polym. Chem.*, 46, 2766–2627.