Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Characterization of Poly(allyl methacrylate) Obtained by Free Radical Initiator

Tuğba Kantav Vardarel[a]; Selda Keskn[a]; Al Usanmaz[a]
[a] Department of Chemistry and Polymer Science and Technology, Middle East Technical University, Ankara, Turkey

To cite this Article Vardarel, Tuğba Kantav , Keskn, Selda and Usanmaz, Al(2008) 'Synthesis and Characterization of Poly(allyl methacrylate) Obtained by Free Radical Initiator', Journal of Macromolecular Science, Part A, 45: 4, 302 — 311
To link to this Article: DOI: 10.1080/10601320701863783
URL: http://dx.doi.org/10.1080/10601320701863783

Journal of Macromolecular Science®, *Part A: Pure and Applied Chemistry* (2008) **45**, 302–311

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701863783

Synthesis and Characterization of Poly(allyl methacrylate) Obtained by Free Radical Initiator

TUĞBA KANTAV VARDARELİ, SELDA KESKİN, and ALİ USANMAZ

Department of Chemistry and Polymer Science and Technology, Middle East Technical University, Ankara, Turkey

Received August, 2007, Accepted September, 2007

Allyl methacrylate was polymerized in CCl_4 solution by α,α'-azoisobutyronitrile at 50, 60, and 70°C. The kinetic curves were auto-accelarated types at 60 and 70°C, but almost linear at 50°C. Arrhenius activation energy was 77.5 kJ/mol. The polymer was insoluble in common organic solvents. It was characterized by FT-IR, NMR, DSC, TGA and XPS methods. About 98–99% of allyl side groups were remained as pendant even after completion of the polymerization. The spectroscopic and thermal results showed that polymerization is not a cyclopolymerization type, but may have end group cyclization. The high molecular weight is the main cause of a polymer being insoluble even in the early stage of the polymerization. Molecular weight of 1.1×10^6 for a soluble polymer fraction was measured by light scattering method. The Tg of polymer was 94°C, and after curing at 150–200°C, increased to 211°C. The thermal pyrolysis of polymer at about 350°C gave an anhydride by linkage type degradation, and side group cyclization. The XPS analysis showed the presence of radical fragments of AIBN (initiator) and CCl_4 (solvent) associated with oligomers.

Keywords: allyl methacrylate; solution polymerization; TGA-FT-IR; NMR; XPS

1 Introduction

The polymerization of allyl methacrylate, AMA was reported in the 1940's (1–3). The kinetics of polymerization was studied by a chemical free radical initiator decomposed thermally or by UV. Higgins and Weale (4) reported the free radical polymerization kinetics of AMA and suggested the cyclopolymerization that gives five- and/or six-membered lactones based on their IR results. They also pointed out that the solvent molecules terminate the allyl radical preventing crosslinking, and as a result, the polymer is soluble. The anionic polymerization of AMA is reported (5, 6) to give a linear polymer with molecular weights up to $1–2 \times 10^4$. It was suggested that the anionic initiator was effective for the vinyl groups, but does not respond to the allyl groups. However, this argument is not supported by further experimental results. The kinetics and mechanism of AMA polymerization have been studied extensively by Matsumoto and coworkers (7–11) using the free radical initiator. Matsumoto (7) proposed cyclopolymerization with the formation of lactones, which is contradicted by their NMR spectrum. Heatley et al. (12) also pointed this contradiction by Matsumoto when characterizing the polymer obtained by free radical homo and copolymerization of AMA using NMR for characterization. Matsumoto (8, 9, 11) reported in his later works that the gel formation was due to the crosslinking and calculated the therotical degree of crosslinking (8). Hirano et al. (13) studied stereoregularity of oligo(AMA) by ^{13}C-NMR and showed the heterotactic nature of the polymer chain. The polymerization of AMA by the ATRP method (14–17) is reported to give a polymer with the molecular weight smaller than 2×10^4 and a polydispersity index (Pd) close to one (14). However, Paris and de la Fuente (15, 16) reported Pd values up to 5 due to the gel formation. They claimed the formation of lactones from the FT-IR results. Nagelsdiek et al. (17) demonstrated that the gel formation is due to the degree of polymerization rather than crosslinking by allyl groups. Thus, all the reported works about PAMA are concentrated on the possibility of crosslinking and/or cyclopolymerization with a contribution of allyl groups. The suggested evidences are based mainly on the solubility properties, IR and NMR spectral data. However, for the effective commercial application of this monomer, the kinetics and mechanism of polymerization and the properties of polymer need to be studied in detail.

The aim of this study is to clarify the mechanism of the AMA polymerization and verify the possible formation of crosslinking and/or cyclopolymerization by allyl groups to give lactones. In the previous work (18), it was shown that the cyclization is not observed for the radiation induced

---

Address correspondence to: Ali Usanmaz, Department of Chemistry and Polymer Science and Technology, Middle East Technical University, Ankara, Turkey. Tel.: 90-312-210322; Fax: 90-312-2101280; E-mail: usanmaz@metu.edu.tr

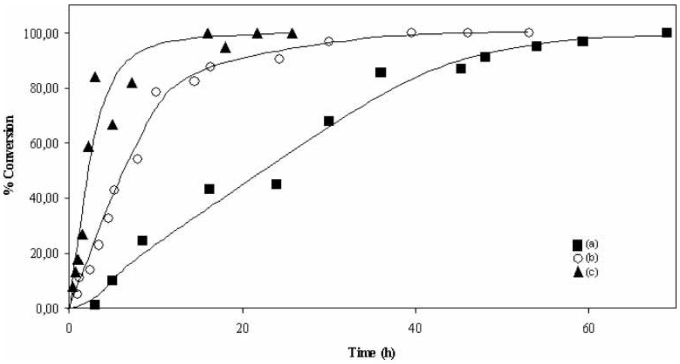


Fig. 1. Solution polymerization of AMA under vacuum by AIBN at (a) 50, (b) 60, and (c) 70°C.

polymerization of AMA. Only about 1–2% of the allyl group was consumed during the reaction which could be used in the end group cyclization or limited extent of crosslinking. The gel formation is mostly due to the high molecular weight of the polymer, but not the crosslinking due to the allyl groups as suggested in most of the published papers. In this work, the polymerization is carried out by a chemical free radical initiator and the polymer chain characterized by FT-IR, NMR, XPS analysis and thermal investigations. This provides more evidence related to the role of the allyl groups in crosslinking and lactones formation. The XPS analysis and detailed thermal degradation of PAMA will be reported for the first time in this work. The thermal degradation by MS and TGA analysis is already reported (19).

2 Experimental

2.1 Materials

Allyl methacrylate, AMA (Aldrich) was purified via distillation. α,α'-Azoisobutyronitrile, AIBN (Merck), carbon-tetrachloride (Merck), methanol (Riedel-de Haën), dichloromethane (Lab-Scan), toluene (Merck) were all of spectroscopic grade and used without further purification.

2.2 Methods

The NMR spectra were taken on a Bruker Ultrashield Digital NMR Spektrometer at 400 MHz and a Bruker Biospin High Resolution Digital 300 MHz NMR Spectrometer using

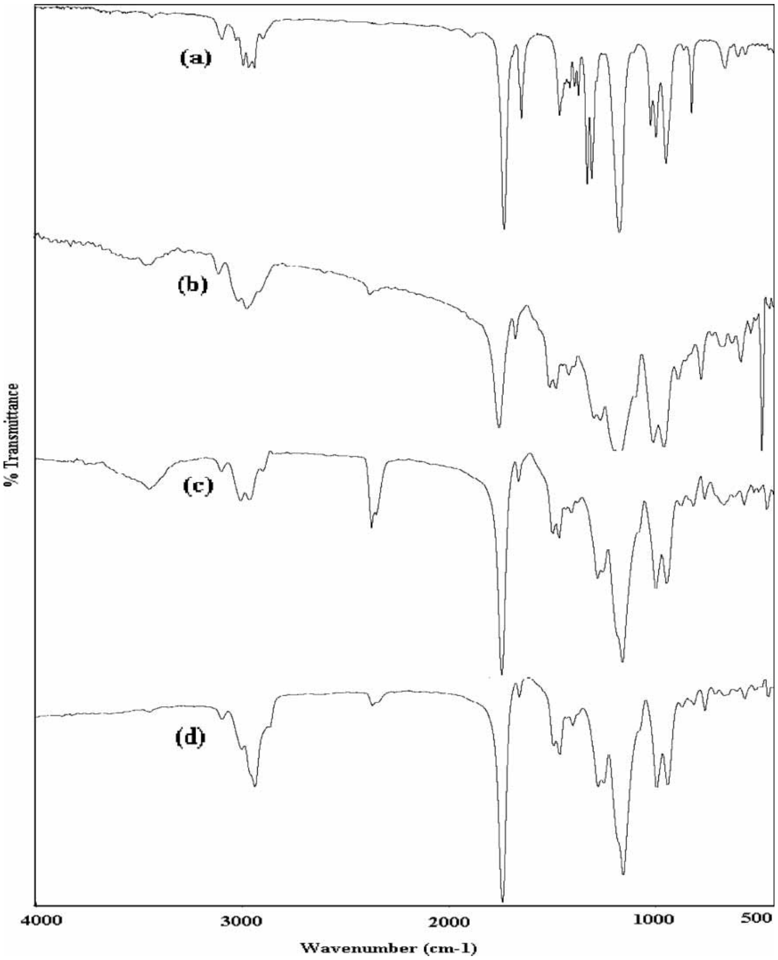


Fig. 2. FT-IR spectrum of (a) AMA and soluble PAMA fraction from conversion of (b) 10%, (c) 45%, and (d) 79%.

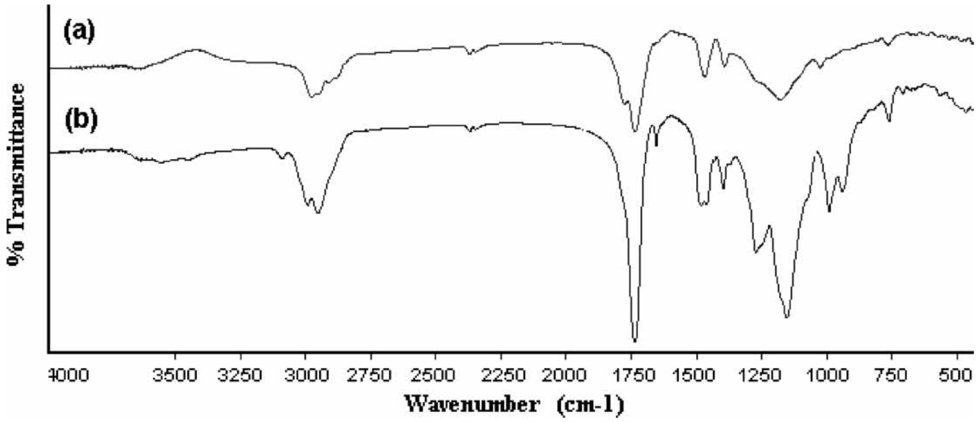


Fig. 3. FT-IR spectrum of residual PAMA pretreated at (a) 280 and (b) 350°C.

d-chloroform as solvent. The solid state NMR was a Bruker Superconducting FT-NMR Spectrometer Avance TM 300 MHz WB with a 4 mm MAS probe. The FT-IR spectra were taken on a Perkin-Elmer Spectrum-1 FT-IR Spectrometer and on a Bruker Vertex 70 ATR-FT-IR Spectrometer using KBr pellets. The DSC thermograms were taken on a TA-DSC 910S differential scanning calorimeter with a heating rate of 5°C/min in the temperature range of 25–350°C under nitrogen gas atmosphere. TGA-FT-IR (Perkin-Elmer Pyris 1 TGA and spectrum 1 FT-IR Spectrometer) thermogram was taken under nitrogen gas atmosphere in a temperature range of 30–800°C with a heating rate of 5°C/min. The X-ray Photoelectron Spectroscopy, XPS spectrum was taken on Specs XPS using 200 W MgKα (1253.6 eV) and a pressure of 10^{-9} torr.

2.3 Procedure

For the polymerization of AMA under vacuum; 2 ml (15 mmol) AMA, 5 mg (0.03 mmol) AIBN, and 4 ml CCl_4 were placed in a Pyrex tube, which was degassed via three freeze-pump-thaw cycles on the high vacuum system. The tube under vacuum was

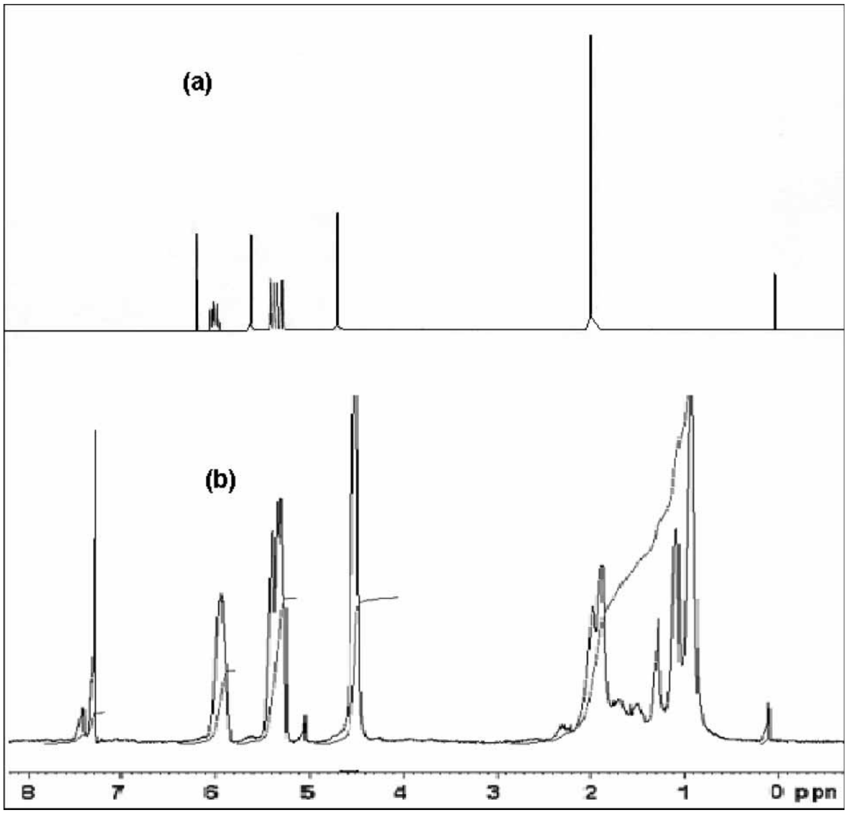


Fig. 4. ^{1}H-NMR spectrum of (a) AMA and (b) PAMA.

sealed by a flame and placed in an oil bath at 50, 60, and 70°C, respectively for the desired period. They were then broken open; the polymer was precipitated by excess methanol, filtered and dried under vacuum at 40°C to a constant weight. Conversions were calculated gravimetrically. The soluble fraction of polymer was extracted with toluene.

For thermal pyrolysis, the polymer samples were heated in evacuated test tubes at (a) 280 and (b) 350°C to a constant weight. The FT-IR of residual polymer, after removal of volatile degraded fragments, was recorded.

3 Results and Discussion

3.1 Polymerization of Allyl Methacrylate, AMA

The percent conversion-time plot for the solution polymerization of AMA by AIBN under vacuum at (a) 50, (b) 60, and (c) 70°C is given in Figure 1. The polymerization rate increased with an increase of temperature. The polymer obtained is partially soluble at lower conversions. The insoluble fraction increased with conversion, reaching to 100%.

The FT-IR and NMR results in the previous work (18, 19) showed that even at 100% conversion the allyl groups have contributed to the crosslinking and/or cyclization at the extent of about 1–2% total allyl groups. Therefore, it was suggested that the insoluble nature of the polymer is mostly due to the high molecular weight, which is also in agreement with the results of Nagelsdiek et al. (17). The measured molecular weights of several soluble fractions at different conversions, by the light scattering method were in the order of 10^6. The results will be published separately for the solution properties of soluble polymer fractions.

The Arrhenius activation energy of the solution polymerization, calculated from initial rate constants (lnk vs. 1/T plot) of kinetic curves in Figure 1, was 77.5 kJ/mol.

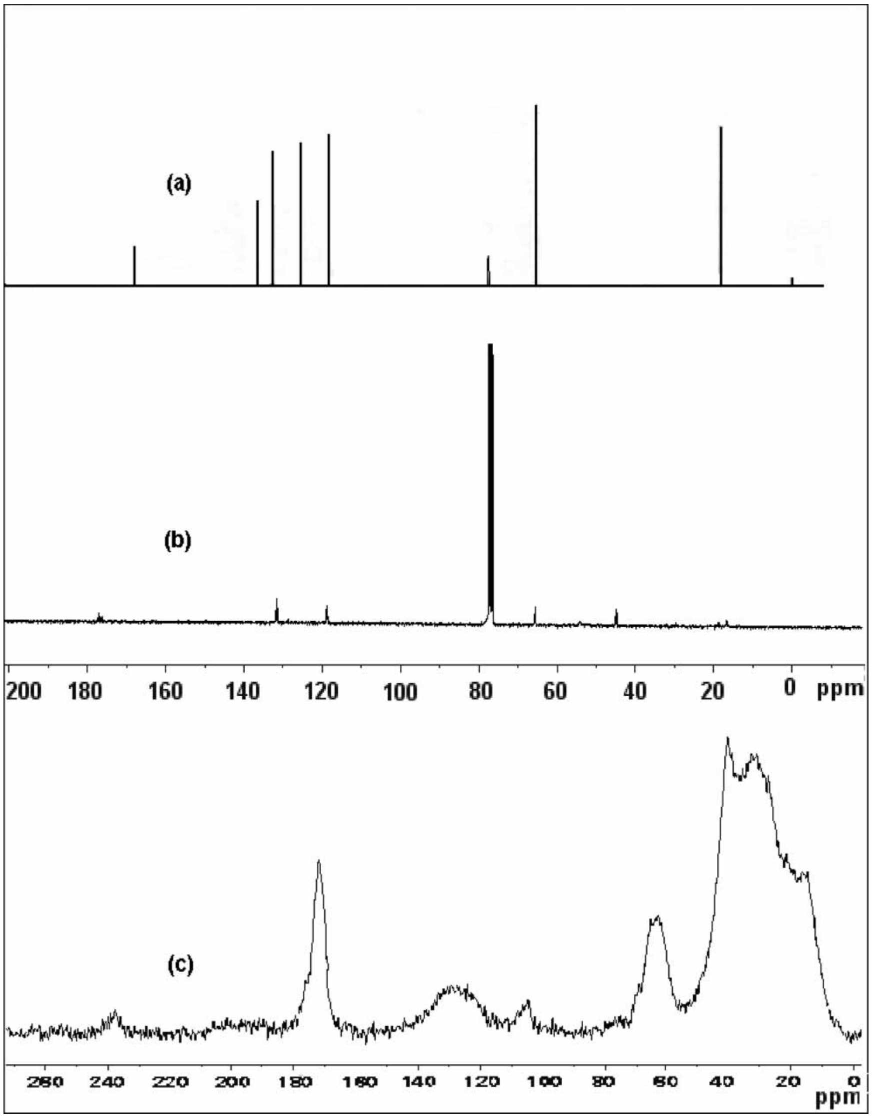


Fig. 5. ^{13}C-NMR spectrum of (a) AMA, (b) PAMA, and (c) PAMA pretreated at 350°C.

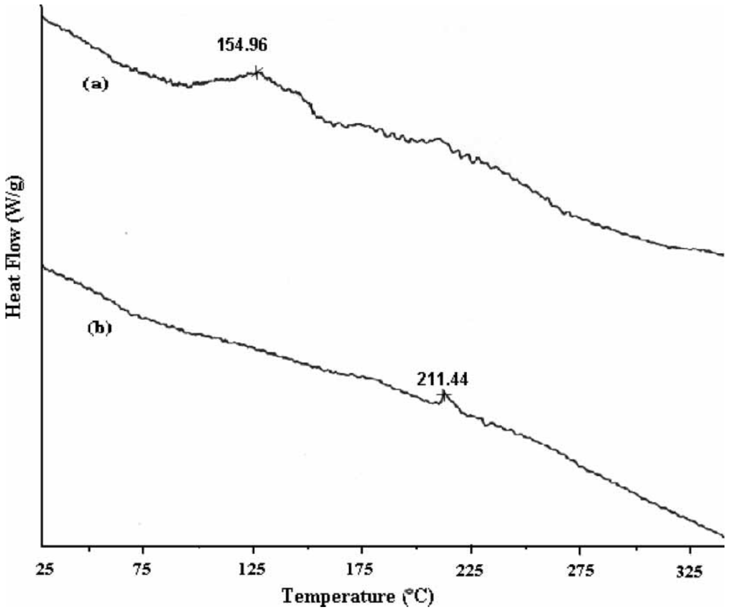


Fig. 6. DSC thermogram of soluble fraction of PAMA (a) first run and (b) second run.

3.2 *FT-IR Investigation*

The FT-IR spectra of AMA and PAMA obtained at different conversions are given in Figure 2. Peak assignments are as follows; for AMA (Figure 4a): ═CH at 3087.9 and 3019.2 cm^{-1}; C-H in CH_3 at 2985.2 and 2960.8 cm^{-1}; C-H in CH_2 at 2930.7 cm^{-1}; C-H in OCH_2 at 2890.8 cm^{-1}; C═O (ester) at 1722.6 cm^{-1}; C═C in vinyl and allyl groups at 1638.5 cm^{-1}; CH_2 at 1453.6, 1403.6 cm^{-1}; CH_3 at 1379.9–1297.6 cm^{-1}; ester C-O at 1164.4 and 1013 cm^{-1}; CH═C for allyl at 986 and 937.9 cm^{-1} and for vinyl at 814.4 cm^{-1}.

In the spectrum of 10% conversion PAMA (Figure 2b) the allyl peaks observed at 3087.3, 1648.5, and 981.2 cm^{-1} retain their positions with a decrease of intensity due to the vinyl group disappearance. The specific vinyl peak at 814.4 cm^{-1} disappeared completely. The peak for the -CN in the initiator was observed at 2350–2360 cm^{-1}. The solvent C-Cl peak is at 750 cm^{-1}. Since the molecular weight of the polymer is very high, the end groups cannot be detected in FT-IR spectra. Therefore, the presence of -CN peak is most probably due to the oligomers with initiator ending, which were documented in MS (19) characterization. The same modifications are also observed for the polymers from 45% (Figure 2c) and 79% (Figure 2d) conversions. The main difference observed is in the relative intensity of peaks as conversion increased.

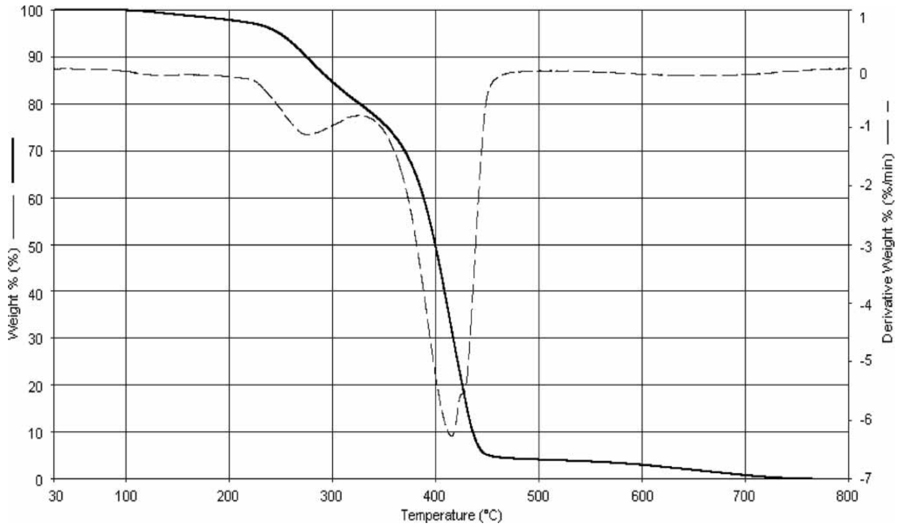


Fig. 7. TGA themogram of insoluble fraction PAMA.

The lactones and anhydride peaks (20) at 1750–1850 cm^{-1} were not observed in the FT-IR spectrum in this work. Thus, either these groups are not present in the polymer chain at all or they are in very small quantities for the resolution power of FT-IR. If the molecular weight of polymer is small, the end vinyl groups due to the termination by disproportionation could also be observed in the FT-IR spectrum and they might also form lactones by the end group cyclization. Most probably, that is what Higgins and Weale (4) observed for the low molecular weight chains in their observation.

The polymer sample was thermally treated at different temperatures to observe possible side group cyclization. The FT-IR spectrum of residual PAMA pretreated at (a) 280 and (b) 350°C is given in Figure 3. The allyl peaks after thermal treatment at 280°C (Figure 3a) retained their position with a decrease in intensity, but after 350°C treatment (Figure 3b) the allyl groups almost disappeared and the anhydride and/or lactones carbonyl peak appeared at 1771.5 cm^{-1}.

3.3 NMR Investigation

^{1}H-NMR spectrum of AMA and PAMA are given in Figure 4. Peak assignments are as follows; for AMA (Figure 4a): $-C\mathbf{H}_3$ peak is at 1.96 ppm; $-OC\mathbf{H}_2-$ at 4.64 ppm (triplet); $-CH{=}C\mathbf{H}H-$ at 5.21–5.24 ppm (doublet); $-CH{=}CH\mathbf{H}-$ at 5.31–5.35 ppm (doublet); $-C\mathbf{H}_2{=}C(CH_3)-$ at 5.56 and 6.12 ppm; $-C\mathbf{H}{=}CH_2-$ at 5.90–6.0 ppm (octet). The solvent (DMSO) is at 2.42 ppm. For PAMA (Figure 4b), the $-C\mathbf{H}_3$ peak shifted to 0.9–1.07 ppm after opening of vinyl group; $-C\mathbf{H}_3$ from initiator at 1.27 ppm; the peaks of vinyl hydrogens in AMA after opening are shifted to 1.87–1.96 ppm; the $-OC\mathbf{H}_2-$ peak is at 4.49 ppm; the peak of allyl groups are at 5.29–5.39 ppm for $=C\mathbf{H}_2-$ and 5.94 ppm for $-C\mathbf{H}=$, which are not much different from that of monomer. The peak at 7.3 ppm in the spectrum of PAMA corresponds to the solvent (chloroform). The results showed that allyl groups remained as pendant in the polymer chain, while the vinyl double bond is opened. If five- or/and six-member lactones

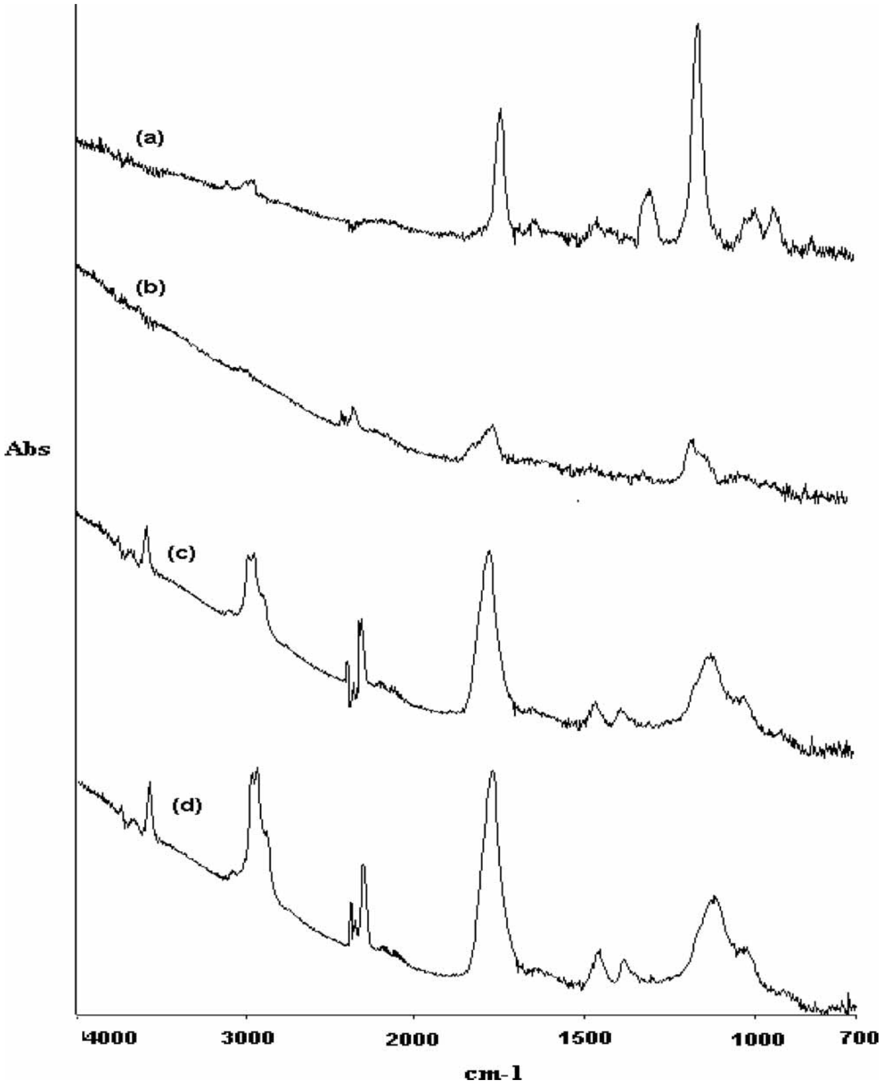


Fig. 8. FT-IR spectrum of degraded PAMA fragments from TGA at (a) 270, (b) 350, (c) 400, and (d) 420°C.

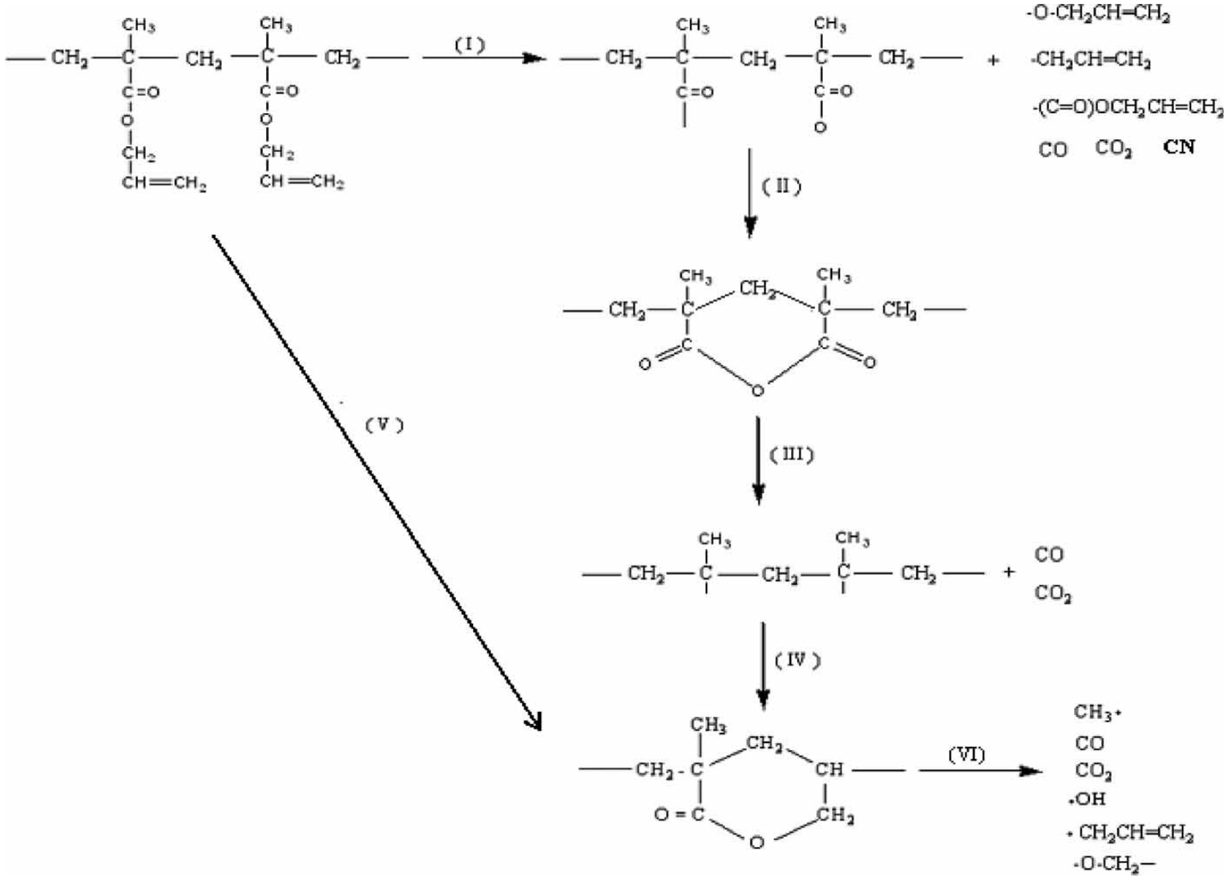
were present, the proton peaks would be at 2.07, 4.14, 4.39 ppm (quartet); for anhydride peaks at 1.52, 1.54, and 1.79 ppm (multiplet) which do not exist in the spectrum (Figure 4b). Therefore, there are no observable lactones or anhydride groups in the polymer chain.

^{13}C-NMR spectrum of AMA and PAMA are given in Figure 5. Peak assignments are as follows; for AMA (Figure 7a): $-\mathbf{CH_3}$ peak is at 18.3 ppm; $-O\mathbf{C}H_2-$ at 65.3 ppm; $-CH{=}\mathbf{C}H_2-$ at 117.9 ppm; $-\mathbf{C}H_2{=}C(CH_3)-$ at 125.5 ppm; $-\mathbf{C}H{=}CH_2-$ at 132.5 ppm; $-CH_2{=}\mathbf{C}(CH_3)-$ at 136.5 ppm; $\mathbf{C}{=}O$ at 166.9 ppm; solvent $\mathbf{C}DCl_3$ at 77 ppm (triplet). For PAMA (Figure 5b), the $-\mathbf{CH_3}$ peak is at 18.7 ppm; C from initiator, $(CH_\mathbf{3})_2\mathbf{C}(CN)-$ at 16.8 ppm; $(CH_\mathbf{3})_2C(\mathbf{C}N)-$ at 119.0 ppm; $-CH_2-\mathbf{C}(CH_3)-$ at 30.0 ppm; $-\mathbf{C}H_2-C(CH_3)-$ at 44.9 ppm; $-O\mathbf{C}H_2-$ at 65.6 ppm; $-CH{=}\mathbf{C}H_2-$ at 118.9 ppm; $-\mathbf{C}H{=}CH_2-$ at 131.6 ppm; $-\mathbf{C}{=}O$ at 177 ppm (triplet); solvent $\mathbf{C}DCl_3$ at 77 ppm (quartet). The results showed that polymerization proceeded on the vinyl group with the initiator at the end of the polymer chain or/and oligomers. The five- and/or six-member lactones peaks should appear at about 40.2, 42.4, 58, 70.1 ppm and anhydrides at 40.0, 36.1, 32.1 ppm. However, these peaks are not observed in the spectrum in Figure 5b. Therefore, during the polymerization, considerable amounts of lactones or anhydrides are not formed. The quartet nature of chloroform peak, which is normally triplet, at 77 ppm is due to the presence of $-CCl_3$ from solvent in the oligomers. The presence of -CN and solvent -Cl is in agreement with MS data (19) for the presence of oligomers.

In order to understand the formation of lactones and/or anhydrides better, the solid state ^{13}C-NMR spectrum of PAMA pretreated at 350°C is also given in Figure 5c. In this spectrum, the peaks observed in Figure 4b for the allyl groups became broader. The peaks of anhydride at 32.6, 36.1 and 40.1 ppm appeared in the spectrum. The broad peak at 240 ppm indicates the formation of anhydrides. Since the peaks are very broad, conclusive remarks cannot be made for the presence of lactones.

3.4 *Thermal Investigation*

The DSC thermogram of insoluble PAMA did not give a Tg value (18), which is a common property of polyacrylates. The detail study is reported for PMMA (21). The thermogram of soluble fraction is given in Figure 6. A broad endothermic peak (100–160°C) centered at 135°C (Figure 6a) is due to the curing (further polymerization or crosslinking). The other peaks corresponding to Tg values are not very distinct in this thermogram. However, the derivative of the



Sch. 1. Fragmentation of PAMA at temperature range of 220–340°C.

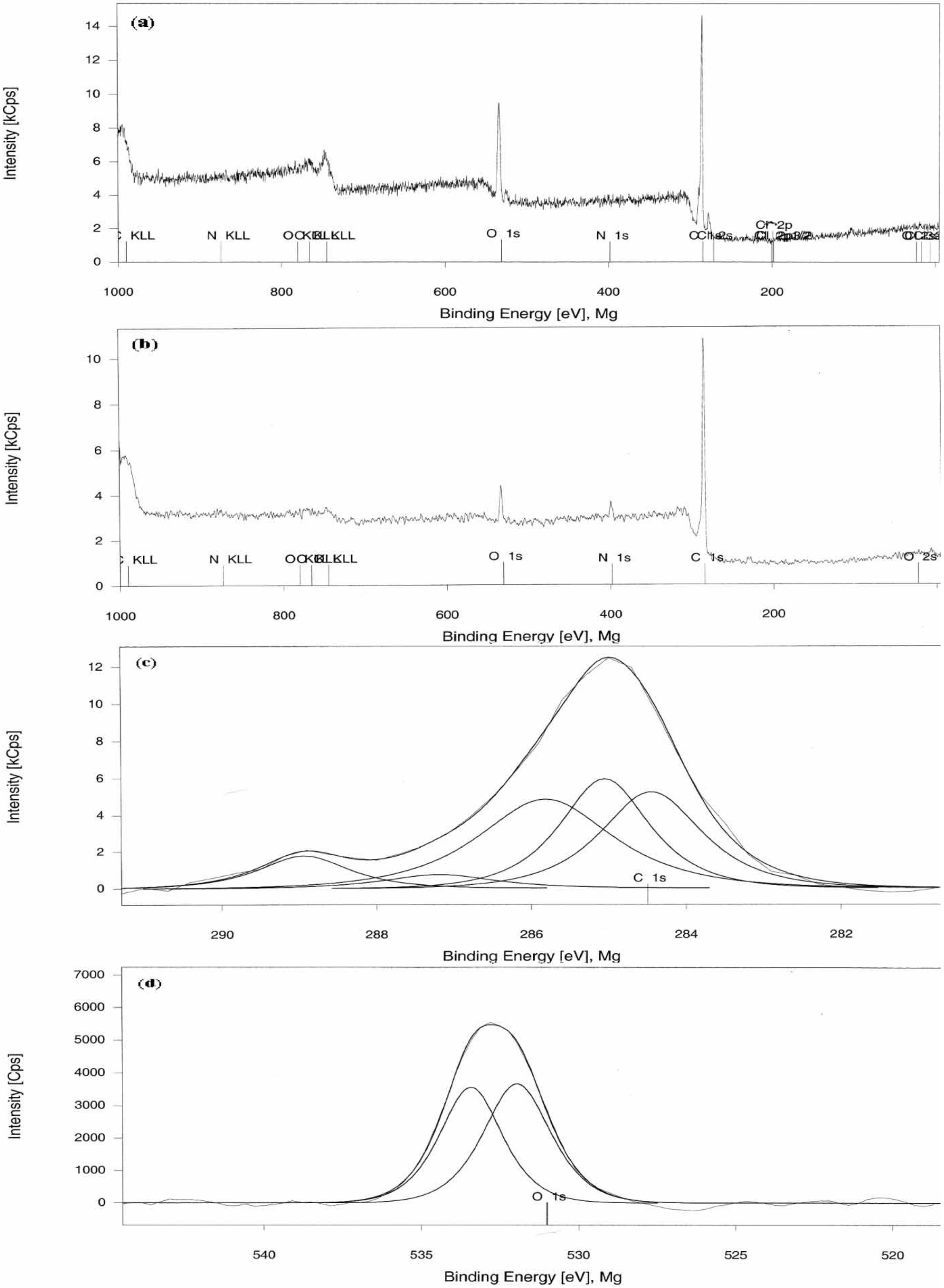


Fig. 9. XPS spectrum of PAMA (a) before, (b) after thermal treatment at 350°C and peak fitting (c) C 1s and (d) O1s before thermal treatment.

Table 1. The assignment of atomic eV to XPS peaks for PAMA

	1	2	3	4	5	Atomic %
Poly(allyl methacrylate)						
C 1s (eV)	285.00	285.82	288.94	287.19	284.45	77.3
O 1s (eV)	531.93	533.39				21.2
N 1s (eV)	398.37					1.1
Cl 2p (eV)	200.14					0.4
Poly(allyl methacrylate)-thermally treated at 350°C						
C 1s (eV)	285.00	285.77	288.27	287.14	284.35	75.9
O 1s (eV)	532.08	533.49				21.3
N 1s (eV)	399.07					2.8

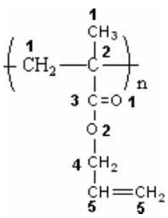
thermogram curve showed two Tg values at about 94 and 211°C. In order to understand the nature of endothermic peak, a second run was taken (Figure 6b). The endothermic peak disappeared and a Tg is observed from derivative at 211°C. Therefore, the polymer has a Tg value of about 94°C and after thermal curing increased to 211°C. Therefore, polymer was cured at 100–160°C, but still had T_g at higher temperature (211°C). However, the insoluble samples obtained by radiation and solution polymerization did not have T_g (18).

The TGA thermogram of soluble PAMA was reported before (19) and that of the insoluble fraction is given in Figure 7. The FT-IR spectra of degraded fragments from TGA at (a) 270, (b) 350, (c) 400, and (d) 420°C are given in Figure 8. The TGA thermogram showed a two-stage degradation. The first stage (220–340°C) is the linkage type degradation (fragmentation I and II in Scheme 1) and the products are CO, CO_2, CN, $-CH_2-CH{=}CH_2$, $-O-CH_2-CH{=}CH_2$, $-C({=}O)-O-CH_2-CH{=}CH_2$ and anhydride (Figure 8a and b). The results are in agreement with that of FT-IR spectrum given in Figure 3. In the second-stage (350–500°C), thermal degradation was the depolymerization type and further anhydride degradation is observed (fragmentation III). The main fragmentation products are that of monomer. The end group cyclization forms lactones, which degraded to monomer fragments (fragmentation IV, V and VI). The monomer molecule is not observed in the FT-IR spectrum of fragments contradicted to PMMA. Therefore, the monomer is thermally unstable and easily fragmented. This was in agreement with data from MS (19). The only reported work published for thermal degradation of PAMA and its copolymers with MMA is that of Zulfigar et al. (22, 23). However, the experimental setup and results are different from that in this work.

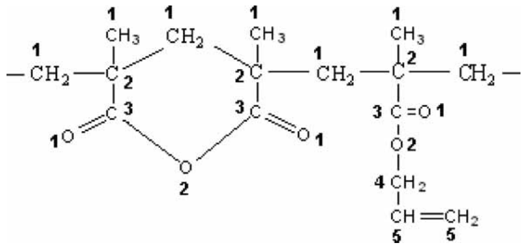
3.5 *X-Ray Photoelectron Spectroscopy (XPS) Investigation*

In order to verify the presence of initiator and solvent fragments in the polymer, the detailed surface analysis of PAMA (a) before and (b) after thermal treatment at 350°C were carried out by XPS (Figure 9). The PAMA gave high amounts of anhydride at around 350°C. Therefore, the XPS results should be in agreement with other methods discussed above. The peak fitting was done by the SpecLab program and the data are given in Table 1 based on the assigned atomic numbers in Schemes 2 and 3.

The fragments of initiator and solvent observed in spectroscopic measurements were also found from XPS. The atomic percent of N 1s was 1.1 and increased to 2.8 after thermal treatment at 350°C. The degradation at 350°C is a linkage type with the evolution of pendant allyl group fragments. Therefore, the amount of C and O are decreased, but not that of N. Therefore, this causes a theoretical overall increase in the atomic percent of N. This was also observed in the NMR and FT-IR spectra. Similarly, the atomic percent of Cl 2p was 0.4 before and did not appear within the resolution power of XPS analysis (above 0.1 atomic %) after thermal treatment. Loosely bonded Cl is removed by volatilization with thermal treatment. Similar results were observed in Figure 3 where the intensity of C-Cl peak at 752 cm^{-1} decreased with a temperature increase to 350°C. The atomic percentage (Table 1) in the



Sch. 2. (before thermal treatment).



Sch. 3. (after thermal treatment).

polymer chain is in agreement with the calculated values. The peak fitting for C 1s (Figure 9c) and for O 1s (Figure 9d) showed the expected binding energy values of C_1, C_5 and O_1, O_2. After thermal treatment, the changes in positions and percentages are in agreement with the anhydride formation as shown in Scheme 3. The presence of allyl group (-CH═CH$_2$) at 284.45 eV with the expected atomic % (Scheme 2) shows that allyl groups are retained during the polymerization. However, after thermal treatment (Scheme 3), the atomic % decreased in accordance. Thus, XPS analysis does not give data for the lactones formation which is in agreement with the other experimental findings in this work.

4 Conclusions

AMA is an important commercial acrylate monomer and its polymer PAMA can be used as a valuable biomaterial (24) such as in dental and bone cement applications. However, the reported date for the kinetic and mechanism of polymerization leaves many unanswered questions about the characterization of polymer. Therefore, the application of this polymer is not valued as it should be. The formation of lactones, anhydride and crosslinking by allyl groups is very contrary to the published data. The polymer has not been synthesized in a solvent (CCl_4) that is an important radical transfer agent. The FT-IR and NMR results in this work clearly proved that there is no considerable formation of lactones and anhydrides during the polymerization. On the contrary, the allyl groups are retained as pendant after polymerization. The NMR results showed that only about 1–2% of allyl groups were exhausted during the polymerization reaction. Even for the soluble fractions, the molecular weight of polymer obtained was in the order of 0^6. Therefore, for the insoluble fractions, the molecular weight will be much higher.

Characterization of the polymer chain was also investigated by thermal properties. The Tg after annealing increased from 94 to 211°C. The TGA degradation gave thermal behavior of the polymer resulting with anhydride formation. This has not been reported before. These properties were also supported by chemical analysis with XPS.

5 References

1. Blout, E.R. and Ostberg, B.E. (1946) *J. Polym. Sci.*, **1**, 230–238.
2. Cohen, S.G., Ostberg, B.E., Sparrow, D.B. and Blout, E.R. (1948) *J. Polym. Sci.*, **3**, 264–282.
3. Cohen, S.G. and Sparrow, D.B. (1948) *J. Polym. Sci.*, **3**, 693–703.
4. Higgins, J.P.J. and Weale, K.E. (1967) *J. Polym. Sci.: Part A-1*, **6**, 3007–3013.
5. D'alelio, G.F. and Hoffend, T.R. (1967) *J. Polym. Sci.: Part A-1*, **5**, 323–337.
6. Zhang, H. and Ruckenstein, E. (1997) *J. Polym. Sci.: Part A: Polym. Chem.*, **35**, 2901–2906.
7. Matsumoto, A., Ishido, H. and Oiwa, M. (1982) *J. Polym. Sci.: Polym. Chem. Ed.*, **20**, 3207–3217.
8. Matsumoto, A., Asai, S. and Aota, H. (2000) *Macromol. Chem. Phys.*, **201**, 2735–2741.
9. Matsumoto, A., Asai, S., Shimizu, S. and Aota, H. (2000) *Eur. Polym. J.*, **38**, 863–868.
10. Matsumoto, A. (2002) *Macromol. Symp.*, **179**, 141–152.
11. Matsumoto, A., Fujihashi, M. and Aota, H. (2003) *Eur. Polym. J.*, **39**, 2023–2027.
12. Heatley, F., Lovell, P.A. and McDonald, J. (1992) *Eur. Polym. J.*, **29**, 255–268.
13. Hirano, T., Kitayama, T., Cao, J. and Hatada, K. (2000) *Polym. J.*, **32**, 961–969.
14. Mennicken, M., Nagelsdiek, R., Keul, H. and Höcker, H. (2004) *Macromol. Chem. Phys.*, **205**, 2429–2437.
15. Paris, R. and de la Fuente, J.L. (2005) *J. Polym. Sci.: Part A: Polym. Chem.*, **43**, 2395–2406.
16. Paris, R. and de la Fuente, J.L. (2005) *J. Polym. Sci.: Part A: Polym. Chem.*, **43**, 6247–6261.
17. Nagelsdiek, R., Mennicken, M., Maier, B., Keul, H. and Höcker, H. (2004) *Macromolecules*, **37**, 8923–8932.
18. Vardareli, K.T. and Usanmaz, A. (2007) *J. Appl. Polym. Sci.*, **104**, 1076–1083.
19. Vardareli, T.K., Keskin, S. and Usanmaz, A. (2006) *J. Macromol. Sci.-Part A: Pure and Appl. Chem.*, **43**, 1569–1581.
20. Rzaev, Z.M.O., Akovalı, G. and Salamova, Ü. (1998) *J. Polym. Sci.: Part A: Polym. Chem.*, **36**, 1501–1508.
21. Usanmaz, A., Türker, F., Doğan, A. and Akkaş, N. (1998) *J. Appl. Polym. Sci.*, **65**, 1409–1417.
22. Zulfigar, A., Pirach, A. and Masud, K. (1996) *Polym. Degrad. Stab.*, **52**, 89–93.
23. Zulfigar, A., Pirach, A., Masud, K. and McNeill, I.C. (1997) *Polym. Degrad. Stab.*, **55**, 257–263.
24. Moszner, N. and Salz, U. (2001) *Prog. Polym. Sci.*, **26**, 535–576.