Synthesis and Characterization of Poly(allyl methacrylate) Obtained by γ-Radiation

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ABSTRACT: Allyl methacrylate was polymerized by γ-radiation under vacuum in solution and atom transfer radical polymerization (ATRP) methods and also in the presence of atmospheric oxygen in bulk. The kinetic curve is *S*-type with a longer induction period, because of the presence of oxygen, in bulk polymerization. The curve for the solution polymerization is almost linear with a short induction period. The rate started to decrease after about 60% conversion and reached to a limiting conversion of 100%. The polymerization by ARTP method using γ-radiation as initiator instead of conventional heating method gave a kinetic curve of linear character up to about limiting conversion of 100%. The polymers obtained were mostly gel type with linear chain fractions at lower conversions. The polymer characterizations were carried out by FTIR, differential scanning calorimetry, NMR, TGA, and XRD methods. The polymers were shown to proceed by the opening of vinyl groups. The allyl groups caused a limiting crosslinking, but 98–99% of the allyl groups are shown by FTIR and NMR, unchanged during the polymerization. The cyclic type polymer formation was not likely taking place. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1076–1083, 2007

Key words: degradation; gelation; NMR; TGA-FTIR; radiation polymerization

INTRODUCTION

Allyl methacrylate (AMA (I)) is a difunctional monomer with vinyl and allyl groups. The polymerization can be carried out on either of this two unsaturated groups as well as cyclization of them giving five- or six-membered lactone rings.

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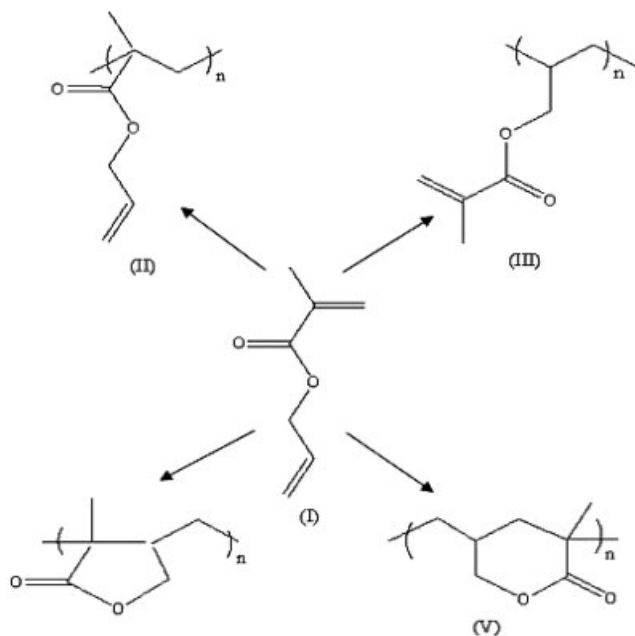
The polymerization of AMA have been reported by different techniques. The anionic polymerization[1,2] gives linear polymer soluble in most solvents. This type of polymerization was shown[2] to progress on vinyl groups giving poly(allyl methacrylate) (PAMA (II)), which has a molecular weight of about 10^4. Most of the reported free radical polymerization[3–10] gives insoluble gel-type polymers. However, Higgins and Weale[4] obtained soluble polymers when free radical polymerization was carried out in the solution. Free radical polymerization in bulk mostly gives crosslinking or/and cyclization (IV–V). Even though the cyclopolymerization is not definitely shown by experimental results, Matsumoto et al.[5] claimed the crosslinking to be due to the cyclic polymer formation. However, in later works,[7] he also reported that the crosslinking is mostly due to the contribution of allyl groups. The atom transfer radical polymerization (ATRP)[11,12] gives controlled molecular weight of soluble polymers type (II). According to Mennicken et al.,[11] the cyclic polymerization suggested by Matsumoto is not significant and the crosslinking is due to the partial contribution of pendant allyl groups. The spectroscopic evidences do not show the presence of lactone groups (IV and V). They also reported the copolymerization of AMA with other monomers. Liu et al.[13] reported that AMA in copolymer gives the linear polymer with its ally group as pendant. The reactivity ratios with other acrylates (e.g., MMA) are compared. The detailed kinetic of UV-peroxide induced polymerization of AMA is reported by Cohen et al.;[14] the polymer obtained

are partially soluble. The formation of polymer III type alone is not reported and the reactivity ratio is shown to be very small.[13] The microgel-like PAMA were synthesized by emulsion polymerization, which gives polymers with pendant allyl groups.[15]

In this work, the radiation induced polymerization of AMA under different conditions is studied. The types of polymer obtained will be investigated by different spectroscopic and thermal methods to clarify most of the questions that has not being answered in published researches. The effect of crosslinking and molecular weight on solubility will be tested. In the ATRP of AMA, initiation will be done by γ-radiation instead of heating at about 90°C. This type of polymerization has not been reported before. This work will explain most of the properties related to the polymerization conditions and also suggest some of the industrial or/and biomaterial use of PAMA.

EXPERIMENTAL

Materials

Allyl methacrylate (AMA, Aldrich) was purified via distillation, copper(I) chloride (CuCl, Riedel-de Haën), p-toluenesulfonyl chloride (Aldrich), 4,4′-dimethyl-2,2′-dipyridyl (Fluka), methanol (Riedel-de Haën), dichloromethane (CH_2Cl_2, Lab-Scan), carbontetrachloride (CCl_4, Merck), ethyl acetate (Merck), toluene (Merck) were all of spectroscopic grade and used without further purification.

Polymer characterization

The γ radiation source was Co-60 γ-cell 220 of Atomic Energy of Canada Ltd. Co. The dose rate was 0.014 Mrad/h The NMR spectra were taken on a Bruker Ultrashield Digital NMR spectrometer at 400 MHz and Bruker High Resolution Digital 300 MHz NMR Spectrometer. Deuterated chloroform ($CDCl_3$) was used as a solvent, and tetramethyl silane served as an internal standard. The solid state NMR used for insoluble polymer sample was Bruker Super Conducting FT-NMR Spectrometer, Avance TM 300 MHz WB with 4 mm MAS probe. The FTIR spectra were taken on a Perkin–Elmer Spectrum-1 FTIR Spectrometer using KBr pellets. The differential scanning calorimetry (DSC) thermograms of the samples were taken on a TA-DSC 910S DSC. The heating rate was 5°C/min in the temperature range of 25–350°C under nitrogen gas atmosphere. TGA-FTIR (Pyris-1 Perkin–Elmer) thermogram was taken under nitrogen in a temperature range of 25–500°C with a heating rate of 5°C/min.

Procedure

For the radiation-induced bulk polymerization in the presence of atmospheric oxygen, 2 mL (15 mmol) of AMA was placed in Pyrex tubes and were sealed by flame. The tubes were placed in the γ-radiation source for the desired period, and they were then broken open. The material was dissolved in CH_2Cl_2, polymer precipitated with excess methanol, separated by filtration, dried under vacuum at 40°C to a constant weight, and conversions were calculated gravimetrically.
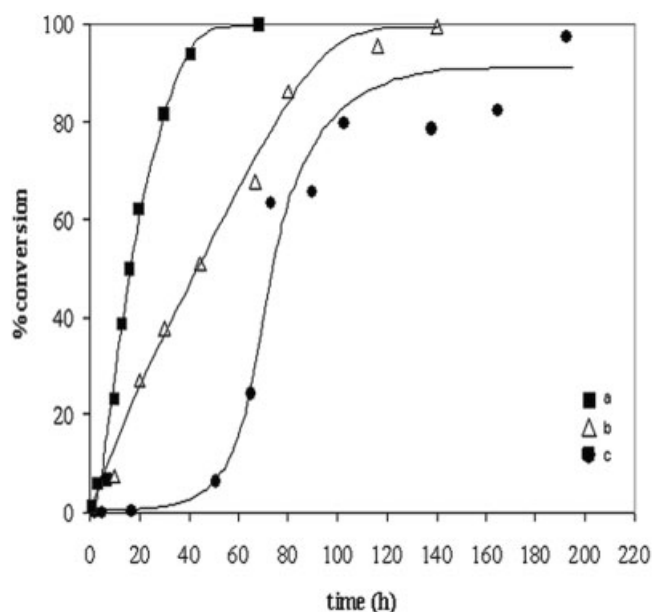
For the radiation-induced solution polymerization under vacuum, 2 mL (20 mmol) of CCl_4 and 2 mL (15 mmol) of AMA were placed in the Pyrex tubes, which were degassed via three freeze–pump–thaw cycles on the high vacuum system. The tubes under vacuum were sealed by flame and placed in the γ-radiation source for the desired period. After irradiation, they were broken open, polymer precipitated by the addition of excess methanol. The rest of the procedure was the same as bulk polymerization.

For the radiation induced ATRP under vacuum, 2 mL (15 mmol) of AMA, 15 mg (0.15 mmol) of CuCl, 55 mg (0.3 mmol) of 4,4′dimethyl-2,2′- dipyridyl, 28 mg (0.15 mmol) of p-toluenesulfonyl chloride, and 3 mL (28 mmol) of toluene were placed in Pyrex tubes. The rest of the experiment was the same as in solution polymerization. The polymer was cleared from copper and percent conversions were calculated gravimetrically.

RESULTS AND DISCUSSION

Polymerization of AMA

The kinetic curves for the polymerization of AMA by radiation (a) in CCl_4 solution under vacuum, (b) ATRP under vacuum, and (c) in bulk in the presence of atmospheric oxygen are given in Figure 1. In the

Figure 1 Radiation induced polymerization of AMA (a) in CCl_4 solution under vacuum, (b)ATRP under vacuum, and (c) in bulk in the presence of atmospheric oxygen.

radiation polymerization, the kinetic curve generally is in the S-shaped and the autoacceleration is observed. In this work, radiation induced polymerization under vacuum [Fig. 1(a)] was carried out in CCl_4 solution, which has a high chain transfer constant. The rate of polymerization was high and the curve obtained was almost linear up to limiting conversion. In the bulk polymerization, the tubes were sealed without removing O_2, which caused a considerable induction period [Fig. 1(c)]. The rate of polymerization then became almost the same as that of the solution polymerization. In the conventional ATRP method, the reactants are mixed and initiated thermally. However, most of the acrylic polymerization reactions are highly exothermic and the boiling points of monomers are relatively low (e.g., MMA boils at $100.8°C$). The high temperature will also start the polymerization and cause the crosslinking of polymer formed. To avoid the high temperature effect, in this work, ATRP method was initiated with radiation. The conversion [Fig. 1(b)] was almost linear with respect to time and it was different from radiation induced bulk polymerization, which usually gives autoacceleration kinetic. Therefore, the temperature did not interfere with the polymerization kinetic and the crosslinking caused by thermal curing is avoided. The polymer obtained had more soluble fractions when compared to that obtained for other methods. This showed that the molecular weight of the polymer obtained by the radiation induced polymerization of AMA was limited. However, the role of the complex used for the ATRP with that of radiation initiations has to be checked by more experiments. The polymers obtained by all of the polymerization methods carried out in this work were mostly insoluble, showing that molecular weight increased in early stage of polymerization. The contribution of crosslinking to the solubility will be checked further by spectroscopic investigation.

FTIR investigation

The FTIR spectra obtained for AMA and PAMA are shown in Figure 2. The spectra of polymers obtained under different conditions were identical. The peak assignment for the FTIR spectrum [Fig. 2(a)] of the AMA are as follows: $=CH$ at 3087.97 and 3019.24 cm^{-1}; C—H in CH_3 at 2985.26 and 2960.86 cm^{-1}; C—H in CH_2 at 2930.76 cm^{-1}; C—H in OCH_2 at 2890.81 cm^{-1}; characteristic carbonyl peak (C=O stretching) is at 1722.59 cm^{-1}; the C=C in vinyl and allyl groups at 1638.54 cm^{-1}; CH=C of ally at 986.00 and 937.92 cm^{-1} and of vinyl at 814.41 cm^{-1}; CH_2 at 1453.66 and 1403.67 cm^{-1}; CH_3 at 1379.93, 1361.71, 1318.80, and 1297.60 cm^{-1}; ester C—O peak at 1164.37 and 1013.05 cm^{-1}.

The FTIR spectra of polymers obtained by radiation under different conditions (Fig. 1) were identical

and they did not change with percent conversion. The peak assignment for the FTIR spectrum [Fig. 2(a)] of the PAMA are as follows: $=CH$ at 3087.40 cm^{-1}; C—H in CH_3 at 2988.24 cm^{-1}; C—H in CH_2 at 2940.42 cm^{-1}; C—H in OCH_2 as a shoulder on CH_2 peak at 2848.00 cm^{-1}; carbonyl peak (C=O stretching) is at 1728.83 cm^{-1}; C=C in allyl groups at 1647.52 cm^{-1}; CH_2 peak at 1471.64 cm^{-1}; CH_3 peak at 1389.86 and 1262.35 cm^{-1}; ester C—O peak at 1145.48 cm^{-1}; CH=C peak of allyl group at 982.18 and 930.76 cm^{-1}. The vinyl peak at 814.41 cm^{-1} is disappeared.

The FTIR result showed that polymerization proceeding on vinyl and allyl groups are not mainly involved in polymerization reaction. The insoluble nature of polymer is due to the high molecular weight and/or crosslinking at certain extent by some of the allyl groups. The presence of allyl group in the polymer spectra indicated that the ring formation on a large extent was not observed. If the ring formation takes place at a lower percentage, it cannot be observed in FTIR spectrum but can be predicted from the NMR results, which has higher resolution power. According to Zhang and Ruckenstein,[2] the ratio of absorption intensity for olefinic peak (at 1623 cm^{-1}) to that of carbonyl peak (at 1706 cm^{-1}) decreased to 50% after polymerization. This they show to be due to the loss of vinyl groups and retaining of all allyl groups upon polymerization. However, the FTIR peak intensity depends on the dipole moment of the bond, which is different for vinyl and allyl groups. Therefore, the direct contribution of vinyl and allyl group
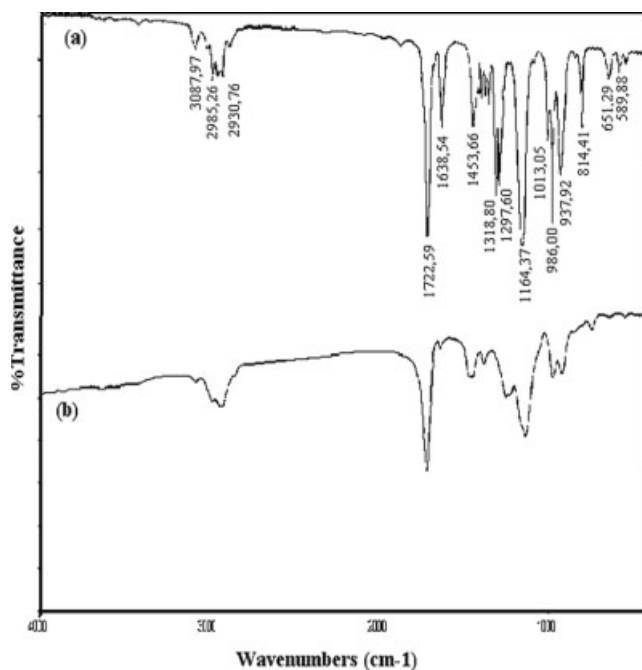
Figure 2 FTIR spectrum of (a) AMA and (b) PAMA (86% conversion).
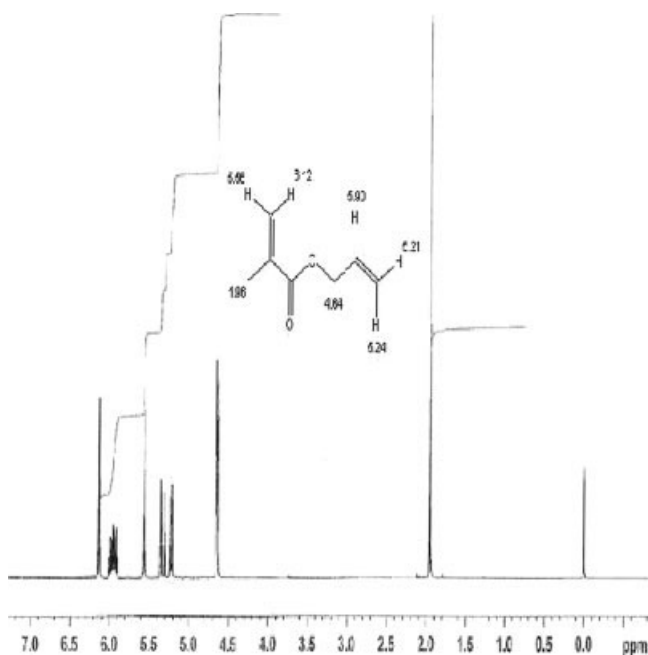
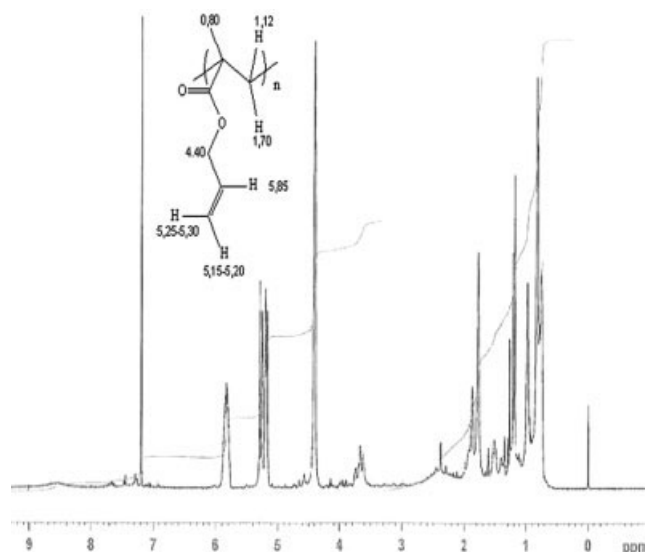**Figure 3** ¹H NMR spectrum of AMA (86% conversion).

absorbance intensities to the total absorbance is not one to one. In this work, it was observed that the corresponding ratio of the absorbance after polymerization decreased to about 25%. It was shown that[16] the insolubility of polyacrylates (e.g., PMMA) is highly dependent on the molecular weight of the polymer as well as crosslinking. Therefore, if the molecular weight of polyacrylate is low, some of the unreacted vinyl end groups (due to termination by disproportionation) can also be observed[17] in the polymer chain, which reflects in the intensity of the absorbance at 1623 cm⁻¹. The result reported by Zhang and Ruckenstein[2] is mostly due to the low-molecular-weight polymer (in the range of 10^4) obtained by living anionic polymerization method. According to Paris and de la Fuente,[10] the presence of a weak shoulder on the ester carbonyl peak (1730 cm⁻¹) at 1775 cm⁻¹ shows the presence of cyclization (lactones formation). However, the lactone peaks are usually more distinct at about 1800 cm⁻¹, which was not observed in the FTIR spectra in this work. It was shown that the ring formation is not observed by NMR, DSC, and TGA. Usually, the resolution power of FTIR is very low for the group abundance of less than about 5%. Therefore, to observe the lactones in FTIR spectrum, it should be more than 5% in the polymer chain, which is also not claimed by Paris and de la Fuente.[10]

NMR investigation

¹H NMR spectrum of AMA and PAMA are given in Figures 3 and 4, respectively. The NMR spectra of polymers similar to FTIR spectra for different poly-

merization conditions were identical. The peak assignments are made on the molecular formula of AMA and PAMA attached on the figures. It was observed that the vinyl groups of the AMA were opened (Fig. 4) during polymerization; the peaks of vinyl hydrogens in AMA (5.56 and 6.12 ppm, Fig. 3) were shifted to single C—C bond hydrogens (1.12 and 1.70 ppm, Fig. 4). The peak positions for most of the allyl groups (5.15–5.20, 5.25–5.30, and 5.85 ppm, Fig. 4) in AMA were not changed after polymerization. The hydrogen peak intensity calculations (Figs. 3 and 4) showed that about 98–99% of the allyl groups were retaining in the PAMA. About 1–2% allyl group were changed into crosslinking and/or lactones formation. This can be seen from the observed methylene peak of allyl group at 3.7 ppm in PAMA spectrum. The pendant allyl —CH₂ groups were in the range of 1.3–1.4 ppm as multiplet. Therefore, a very small amount of the allyl groups were involved in crosslinking. Since conversion for this polymer sample was about 86%, the crosslinking has a very limited contribution from allyl groups for the radiation-induced polymerization of AMA. The insolubility of polymer is therefore mostly due to the high molecular weight of PAMA as would be expected for most polyacrylates. The absence of any peak corresponding to the lactones in the NMR spectrum showed that the cyclo (IV and V) polymerization, under given polymerization conditions, was not taking place. The peak at 7.2 ppm in the spectrum of PAMA (Fig. 4) corresponds to solvent (chloroform).

¹³C NMR spectrum of AMA and PAMA are given in Figures 5 and 6, respectively. The peak assignments are made on the molecular formula of the AMA and PAMA attached on figures. The vinyl peaks in the spectrum of AMA (125.5 and 136.5 ppm,
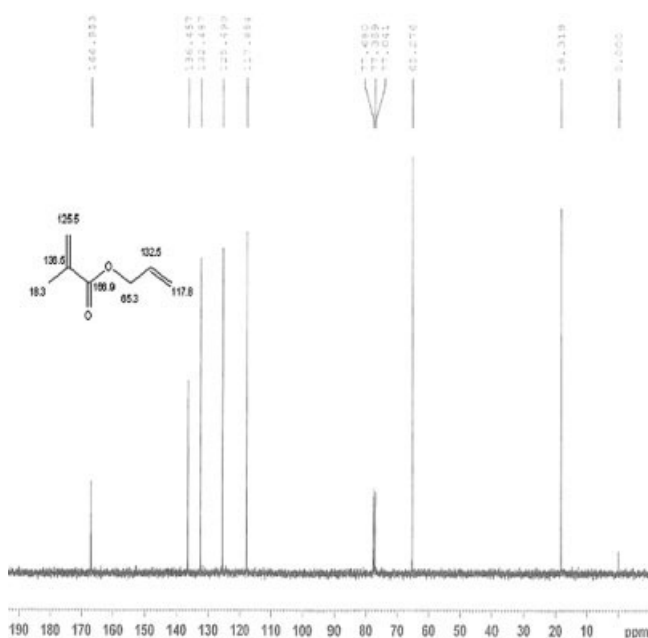

Figure 4 ¹H NMR spectrum of PAMA (86% conversion).

and giving crosslinking up to a certain extent. The opened carbons of allyl groups give very weak peaks at 80 ppm (—CH) and at 30 ppm (—CH₂). The peaks corresponding to five- or six-member lactones are not observed distinctly. Therefore, the formation of cyclic type polymer could not be predicted from ^{13}C NMR spectrum.

Thermal investigation

The DSC thermogram of (a₁) first run for polymer with 6.2% conversion, (a₂) second run for polymer with 6.2% conversion, (b₁) first run for polymer with 86.2% conversion, (b₂) second run for polymer with 86.2% conversion are given in Figure 7. The thermo-

Figure 7 The DSC thermogram of (a₁) first run for polymer with 6.2% conversion, (a₂) second run for polymer with 6.2% conversion, (b₁) first run for polymer with 86.2% conversion, (b₂) second run for polymer with 86.2% conversion.

Figure 5 ^{13}C NMR spectrum of AMA.

Fig. 5) were disappeared in the spectrum of PAMA (Fig. 6). Therefore, the vinyl bonds were opened during the polymerization. In the spectrum of PAMA (Fig. 6), they were shifted to the positions of 42.5 and 52.9 ppm, respectively. However, the peaks corresponding to the allyl group at 132.5 and 117 ppm in the spectrum of AMA are retaining their position with small shifts (130.1 and 116.2 ppm). This is in agreement with FTIR and ^{1}H NMR results that allyl group are not contributing to the polymerization process. Very small amounts of allyl group were opened
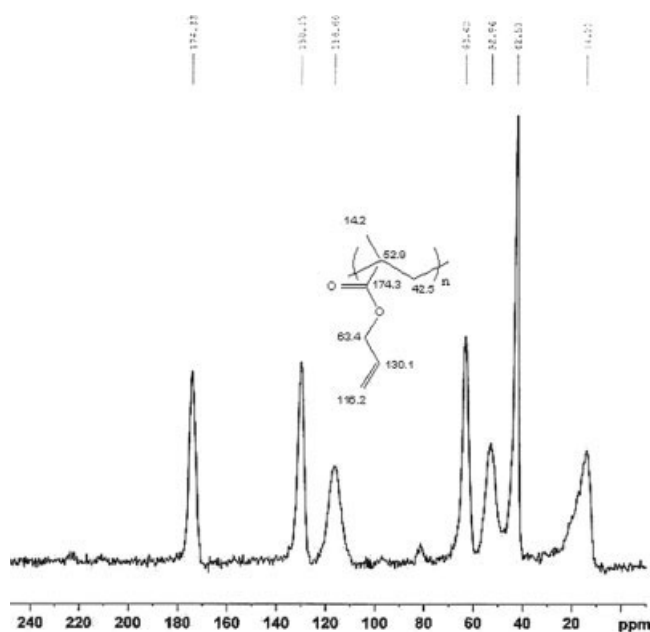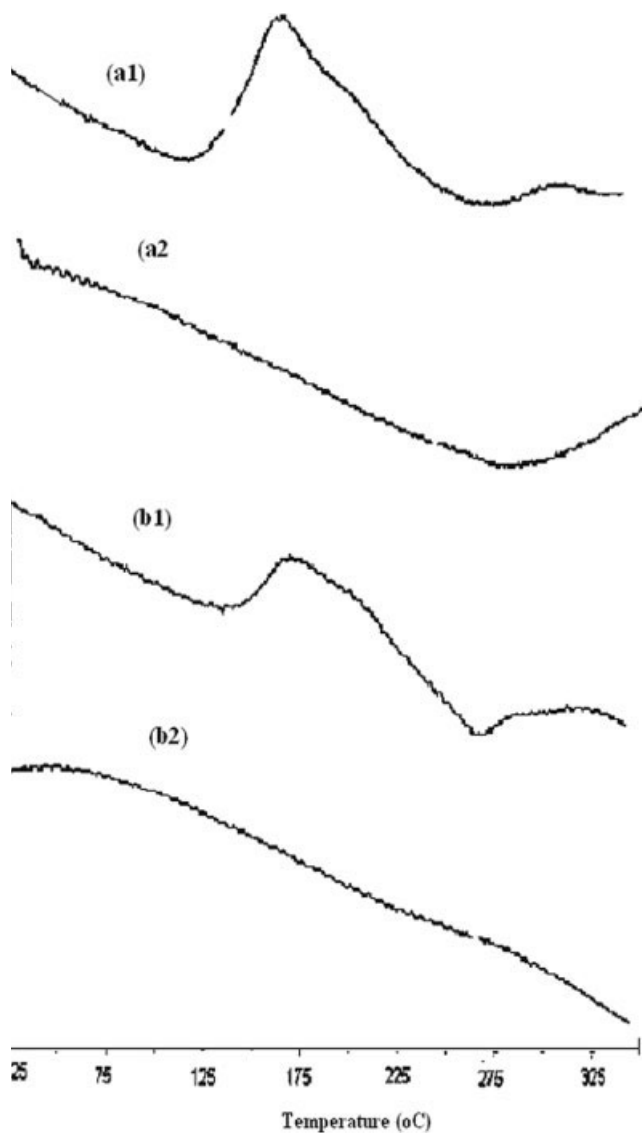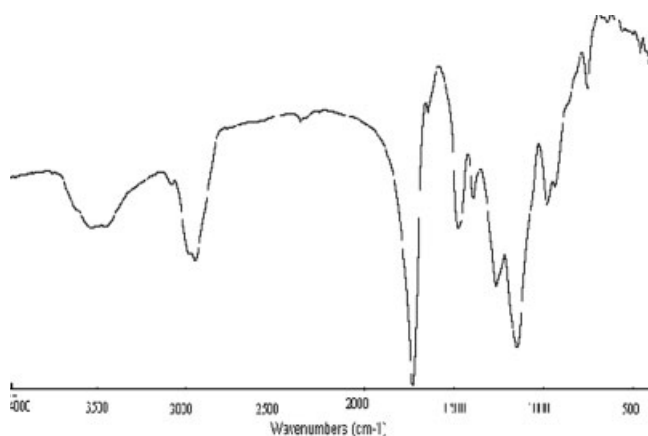

Figure 6 ^{13}C NMR spectrum of PAMA.

Figure 8 The FTIR spectrum of PAMA cured at 175°C for 24 h.


Figure 9 TGA themogram of PAMA.

grams for other polymer conversions were very similar to the given thermograms. In the first run thermogram [Fig. 7(a$_1$)], broad exothermic peak centered at about 175°C showed the curing (further polymerization and crosslinking) at around this temperature. The crosslinking is most probably due to the opening of some allyl groups. The T_g of polymer is overlapped by curing peak, and therefore could not be observed. In the second run [Fig. 7(a$_2$)], the thermogram did not show any peak. This is because of the completion of curing in the first run. The same results were also obtained for polymer with 86.2% conversion [Fig. 7(b)]. The results of DSC showed that opening of allyl group was not taking place even at very high conversions. Therefore, the insolubility of polymer in most solvents is due to the higher molecular weight that was observed at even very low conversions. The T_g of the polymer could not be observed. In the first run thermogram, it was covered with curing peak; in the second run, the polymer molecular weight is very high and T_g was not observed.[18] To understand the thermal behavior of PAMA better, samples of polymer were heated under vacuum at 125 and 175°C each for 24 h. The FTIR spectrum of the sample showed some changes after [Figs. 2(b) and 8] thermal treatment. The allyl peak at 1641.75 cm^{-1} became weaker and the new peak for hydroxyl group was observed. Therefore, after thermal treatment, some of the allyl groups are contributing to crosslinking and some were broken away by thermal degradation, leaving hydroxyl group (3500 cm^{-1}) and also carbonyl group (CO and CO_2 at about 2300 cm^{-1}). This has been clarified further by TGA investigation.

The TGA thermogram of PAMA is given in Figure 9. Up to 200°C, there is no decrease in the weight of the sample. Degradation started at 200°C and continued up to 250°C with a slower rate then increased and maximized at 266°C. Further degradation continued up to 313°C, maximizing at 409°C. Most of
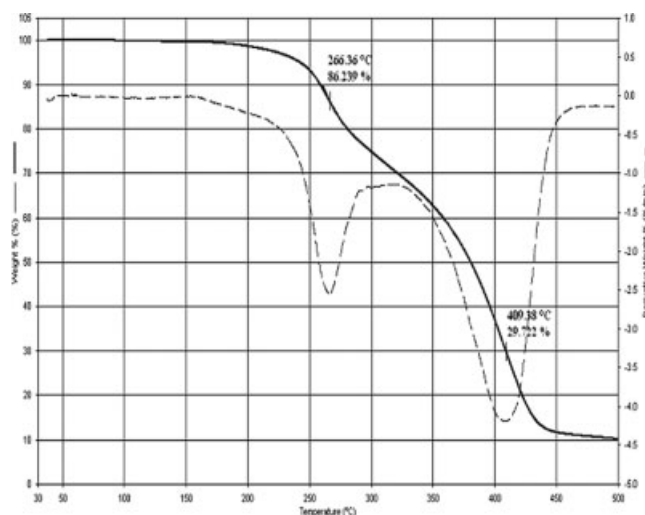
polyacrylates are degraded by depolymerization, which show a sharp drop in the thermogram curve, maximizing at about 450°C[16] for PHEA and 380°C for PMMA.[19] The FTIR spectra of degraded fragments at different temperatures were recorded and some are given in Figure 10. At early degradation stages, the degradation products were mostly CO, CO_2, and C—O—C. After about 200°C, allyl group
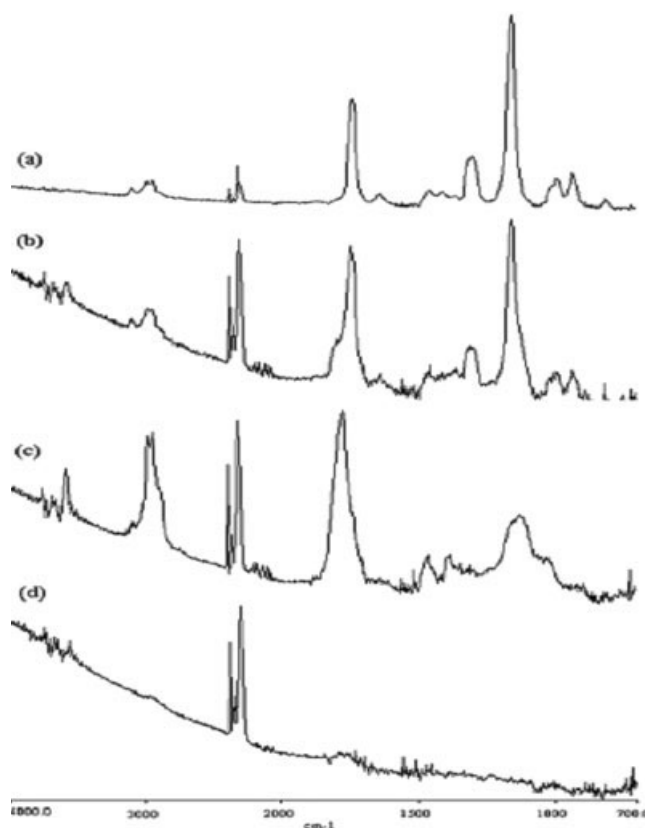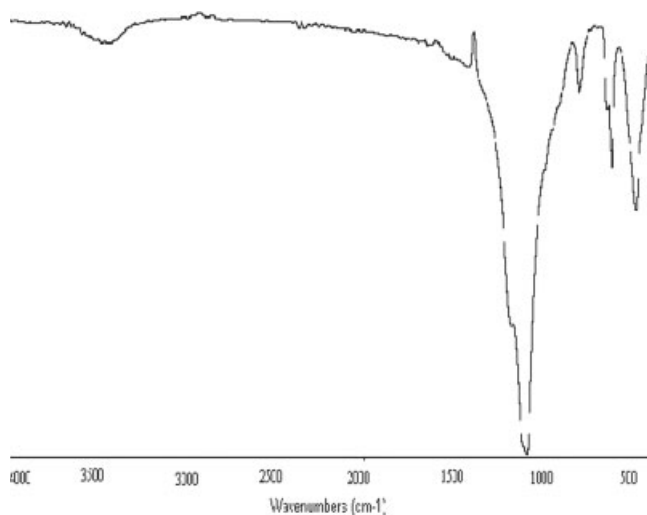

Figure 10 FTIR spectra of TGA degradation fragments of PAMA at (a) 253°C, (b) 313°C, (c) 399°C, and (d) 500°C.
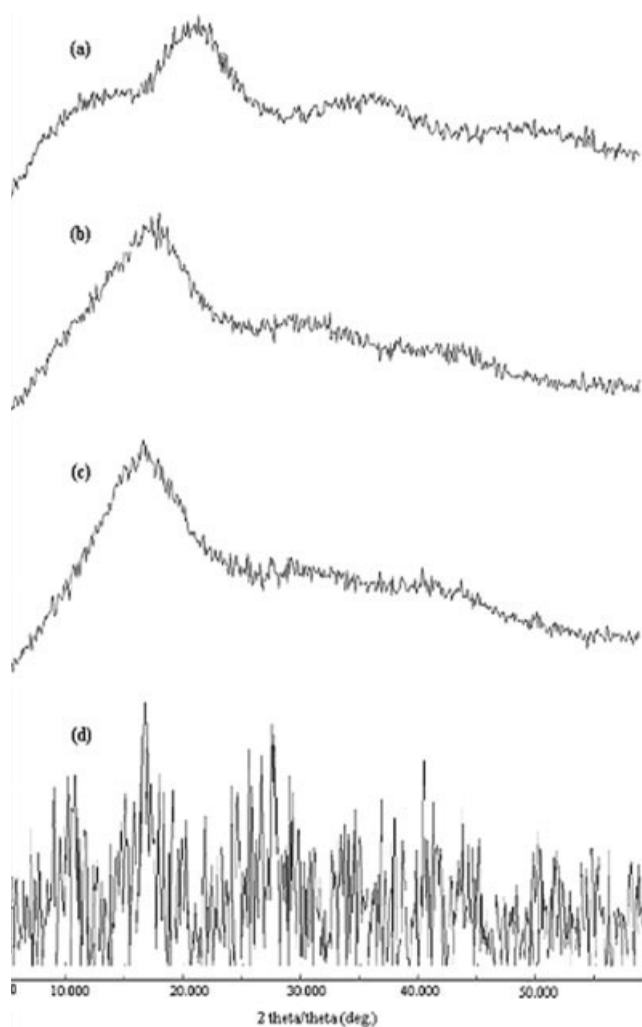
were also degraded. In the FTIR spectrum [Fig. 10(a)], the peaks corresponding to H—C= (3050 cm^{-1}), H—C (2800–2900 cm^{-1}), CO, CO$_2$ (2300–2400 cm^{-1}), C=O (1700 cm^{-1}), CH$_2$—CH=CH$_2$ (1600 cm^{-1}), and other peaks corresponding to CH$_2$, CH$_3$, C—O—C were observed at respected wavenumbers. This type of fragmentation continued up to about 313°C [Fig. 10(b)], at which the evolution of —OH was also started and the allyl fragmentation at this stage became less. This trend continues further up to 399°C [Fig. 10(c)]. When the degradation is almost completed, the only degradation fragments observed were that of CO and CO$_2$ [500°C, Fig. 10(d)]. At this stage, about 10% of the sample was remained undegraded. To understand the nature of this product, a PAMA sample was thermal treated further up to 800°C. After thermal treatment at 800°C, about 5% undegraded polymer remained and the FTIR spectrum of this sample is given in Figure 11. The peaks are corresponding to aromatization as a carbon fiber.[20]

X-ray investigation

The structural information was investigated by XRD. The XRD diffraction patterns of PAMA (a) with 62% conversion, (b) cured at 125°C, and (c) 175°C is shown in Figure 12. The powder pattern showed that PAMA is generally amorphous, but there are certain regular orientations and also some crystallinity appearing as small peaks on the amorphous polymer curve. These are scale extended in Figure 12(d). When the sample is cured, some of the crystallinity peaks disappeared and the main peak showing orientations overlapped with a broad peak, which is typical for a network polymer.

Figure 12 The XRD patterns of (a) PAMA with 62% conversion, (b) same PAMA cured at 125°C, (c) cured at 175°C, and (d) extended form of (c).

Figure 11 FTIR spectrum of PAMA cured at 800°C.

CONCLUSIONS

AMA was polymerized by radiation under different conditions. The molecular weight of the polymer increased sharply in the early stage of polymerization, resulting with insoluble gel type polymer. In most of the literature, the formation of gel is attributed to the crosslinking or/and lactones formation by allyl groups. However, in this study it was shown that the gel formation was mostly due to the high molecular weights rather than the crosslinking by allyl groups. The FTIR and NMR result showed clearly that even in very high conversions most of the allyl groups were retained as pendant groups and about 1–2% went to crosslinking or cyclization. The chemical nature of polymers obtained by radiation under different polymerization conditions were the same and did not change with conversion. However, the soluble fraction of polymer is relatively more for ATRP and least for bulk polymerization. This is related to the molecular

weights rather than chemical differences. The nature of PAMA by TGA indicates the differences in thermal degradation of PAMA with those of the other acrylates. PAMA, contrary to PMMA, did not show depolymerization in the degradation process. The investigation by TGA combines with FTIR gave detailed information about the structure of polymer and thermal degradation. Since most of the allyl groups are not used in polymerization, they can be used as crosslinking agents in many industrial applications and also makes PAMA very useful as a biomaterial to be used in dentistry and bone cement type of applications.

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