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Thermal Stabilities of Poly(N-acryloyl-N'-methylpiperazine), its Blends With Poly(methyl methacrylate), and Poly(N-acryloyl-N'-methylpiperazine-co-methyl methacrylate)

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Thermal Stabilities of Poly(N-acryloyl-N'-methylpiperazine), its Blends With Poly(methyl methacrylate), and Poly(N-acryloyl-N'-methylpiperazine-co-methyl methacrylate)

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Poly(N-acryloyl-N'-methylpiperazine-co-methyl methacrylate)s, poly(methyl methacrylate), poly(N-acryloyl-N'-methylpiperazine), have been prepared by free radical polymerization using AIBN as initiator. Blends of the homopolymers in similar composition with those of the copolymers have been prepared by casting films from CHCl₃ solution, followed by drying for a few days. The homopolymer, the copolymers and the blends have been characterized by differential scanning calorimetry (DSC), FTIR spectroscopy and ¹H NMR spectroscopy. The single glass transitions observed from DSC curves of the blends indicated that the blend components were miscible. Thermal stabilities of the blends and the copolymers have been investigated by thermogravimetric analysis (TGA) and FTIR as comparing with each other and those of the homopolymers. In thermal degradation of poly(N-acryloyl-N'-methylpiperazine), during product identification by gas chromatography-mass spectrometry (GC-MS), N-methyl piperazine has been detected as a main product in the ratio of 70.8% as GC peak area. Some differences in thermal behavior of the copolymer and the blend in similar composition have been observed.

Keywords thermal stability, poly(N-acryloyl-N'-methylpiperazine), blend, poly(methyl methacrylate)

Introduction

Polymers are frequently blended in order to improve physico-mechanical properties. It has been reported that blending has a great influence on the thermal stability of polymers, and thermal stability of blends depend on the interaction between blend components (1–4).

The thermal degradation of poly(methyl methacrylate), poly(MMA) (5–9) and its blends with some other polymers such as poly(acrylonitrile) (10), polycarbonate (11), poly-4-bromstyrene (12), polystyrene (13), cellulose acetate hydrogen phthalate (14) has been the subject of numerous publications. Poly(MMA) is regarded as a polymer

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that depropagates to monomer in thermal degradation up to about 500°C (5, 7, 8). On the other hand, amino polymers containing piperazine moieties have been reported especially as unique chelating agents (15–19). Although thermal stabilities of some polymers containing amido-amine moieties have been reported (20–22), no report on thermal stability of amino polymers containing piperazine moieties has been given. Thermal degradation studies on poly[(meth)acrylamide]s indicated that cyclic imidation between two neighboring (meth)acrylamide units along the polymer chain is an important reaction in the decomposition (21–24).

In the present study, we report on the thermal degradation behavior of poly(N-acryloyl-N'-methylpiperazine), poly(AcMP), its blends with poly(methyl methacrylate), poly(MMA), and poly(N-acryloyl-N'-methylpiperazine-co-methyl methacrylate), poly(AcMP-co-MMA), using thermogravimetric analysis, FTIR and GC-MS in identification of main products of the degradation.

Experimental

Materials

Ethanol, 1,4-dioxane and diethyl ether (Aldrich) were used as received.

N-acryloyl-N'-methylpiperazine, AcMP, was prepared from acryloyl chloride and N-methylpiperazine according to the literature (17).

Preparation of the Polymers and Blends

The homopolymerization and copolymerization of AcMP and MMA were carried out in dioxane in a sealed tube purged with Ar gas at 70°C in the presence of AIBN as a radical initiator.

Poly(MMA) was precipitated in ethanol, but poly(AcMP) and poly(AcMP-co-MMA) were precipitated in dried diethyl ether. All the polymers were purified by reprecipitation in corresponding precipitor from the dioxane solutions at least twice. The polymers were dried under vacuum. The desired amount of poly(AcMP) and poly(MMA) samples were dissolved in 1,4-dioxane, and then the blend was prepared by a solvent casting technique slightly above room temperature. The blend films were dried in a vacuum oven at 70°C.

Characterization and Thermal Degradation Studies

Thermogravimetric measurements were carried out in a Shimadzu TGA-50 thermobalance at a heating rate of 10°C/min. The polymer films prepared on salt plates were heated to 150, 250, 300, 360, 380, 420, 440, 460 and 480°C under N₂ flow in order to investigate the changes in IR spectra during thermal degradation. A Mattson 1000 FTIR spectrometer was used for all IR spectra. NMR spectra were recorded on a Jeol FX-90Q spectrometer. The glass transition temperatures of the polymers and blends were determined using a Shimadzu DSC-50 (differential scanning calorimeter) by a heating rate of 20°C/min in a sample size of 5–8 mg. The products collected in liquid nitrogen trap from degradation of the polymer heated under vacuum were examined by gas chromatography-mass spectrometry (GC-MS), FTIR and ¹H NMR.

Results and Discussion

Characterization Studies

The IR spectra of poly(AcMP), for one poly(AcMP-*co*-MMA) and one poly(AcMP)-poly(MMA) blend are shown in Figure 1. The carbonyl absorptions of the MMA and AcMP units in the copolymer and blend raised separately at 1731 and 1640 cm^{-1} . Copolymer compositions were determined from the absorbance of these carbonyl bands using also their molar extinction coefficients (17). The copolymers, prepared from three different AcMP:MMA (0.35:0.65, 0.50:0.50 and 0.75:0.25) feed ratios, became relatively rich in the AcMP unit and the compositions of corresponding copolymers became 0.48:0.52, 0.55:0.45 and 0.77:0.23, respectively. These results are in disagreement with that of Reference 17. The ^1H NMR spectrum of the copolymer shows the signals at 4.0–3.5 ppm ($-\text{OCH}_3$ in the MMA unit, and $\text{N}-\text{CH}_3$ in the AcMP unit), 2.4–2.0 ppm (piperazine ring protons in the AcMP unit), 1.9–1.2 ppm ($-\text{CH}_2-\text{CH}-$ and $\text{CH}_2-\text{C}-$ protons in the backbone), 1.1–0.8 ppm ($-\text{CH}_3$ protons on the polymer backbone) and 7.25 ppm (solvent signal, CDCl_3) (Figure 2). T_g values for poly(AcMP0.48-*co*-MMA), poly(AcMP0.55-*co*-MMA) and poly(AcMP0.77-*co*-MMA) were obtained as 97, 87, and 79°C, respectively. Three different blends of poly(AcMP) and poly(MMA) [poly(AcMP): poly(MMA) = 0.48:0.52(B1); 0.55:0.45(B2) and 0.77:0.23(B3) as mole number of units in the homopolymers] were prepared in composition corresponding to those of the copolymers, and T_g values are 82°C, 71°C, and 60°C, respectively, which

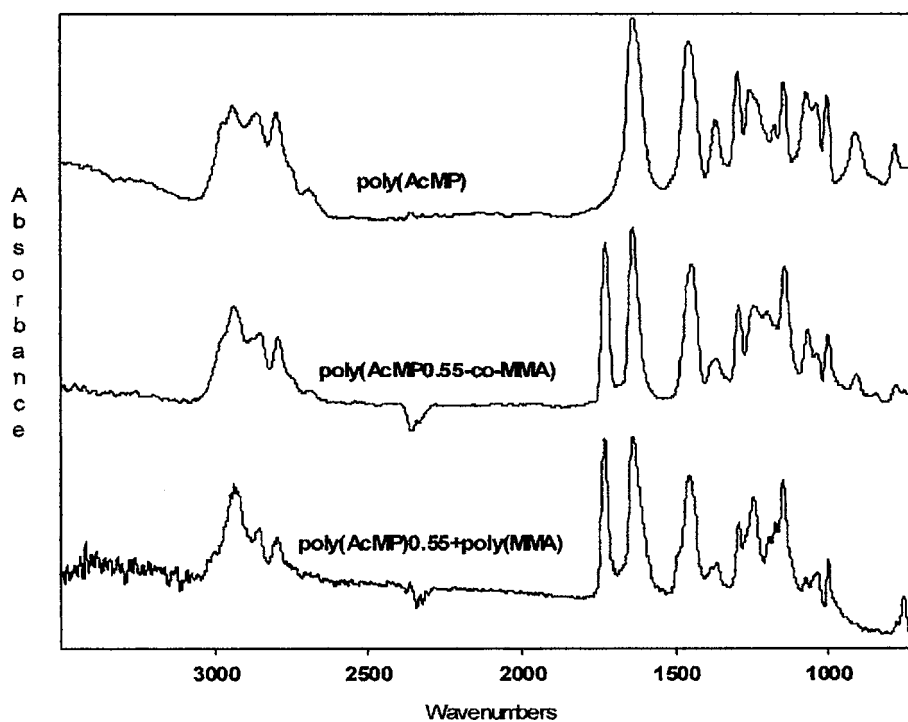


Figure 1. IR Spectra of poly(AcMP), Poly(AcMP0.55-*co*-MMA) and poly(AcMP)0.55-poly(MMA) blend.

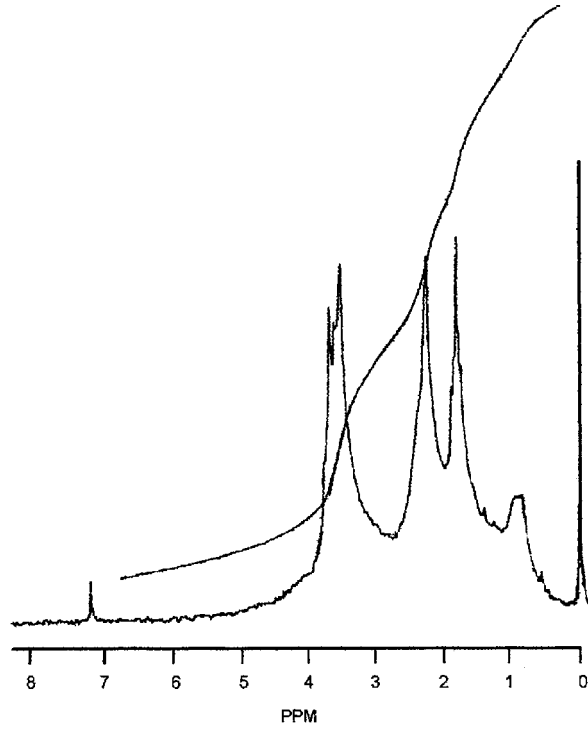


Figure 2. ^1H NMR Spectrum of poly(AcMP0.55-co-MMA).

are obtained from DSC curves. The plots of (Figure 3) T_g values vs. the copolymer or blend composition as mole fraction shows that those of the copolymers give a positive deviation from the linearity, but in the case of the blends, give a negative deviation. This means that free volume in the blend is more than that of the copolymer with similar composition.

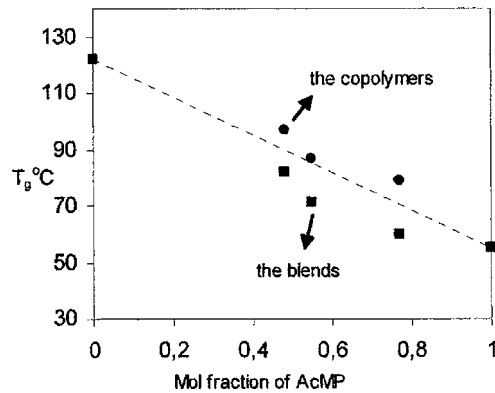


Figure 3. Plots of T_g values vs the copolymer or the blend composition.

Thermogravimetric Studies of the Polymers

Figure 4 shows the thermogravimetric (TG) curves of some of the copolymers and some blends, in comparison with those of the homopolymers. While poly(MMA) shows an initiation temperature of about 250°C and two maximum rates of decomposition at 298 and 378°C, poly(AcMP) shows a rapid decomposition at about 350°C after a weight loss of about 3% up to 250°C and 5% between 250–350°C and clearly two maximum rates of decomposition at 430 and 480°C. Some thermal characteristics of the homopolymers, the copolymers and blends are shown in Table 1. If the temperatures corresponding to 50 wt% loss of the polymers were taken as a measure for comparing their thermal stability, these temperatures are 355, 370 and 405°C for poly(AcMP0.48-*co*-MMA), poly(AcMP0.55-*co*-MMA) and poly(AcMP0.77-*co*-MMA), respectively, and are 390, 395 and 407°C for the blends B1, B2 and B3, respectively. These values are between those of the homopolymers which are 430 and 360°C for poly(AcMP) and poly(MMA), respectively. The copolymers have more residue than that of the blends at 500°C and it has increased with increasing the AcMP unit in the copolymers and blends. The residue of the copolymer which becomes highly rich in AcMP unit is more than that of poly(AcMP).

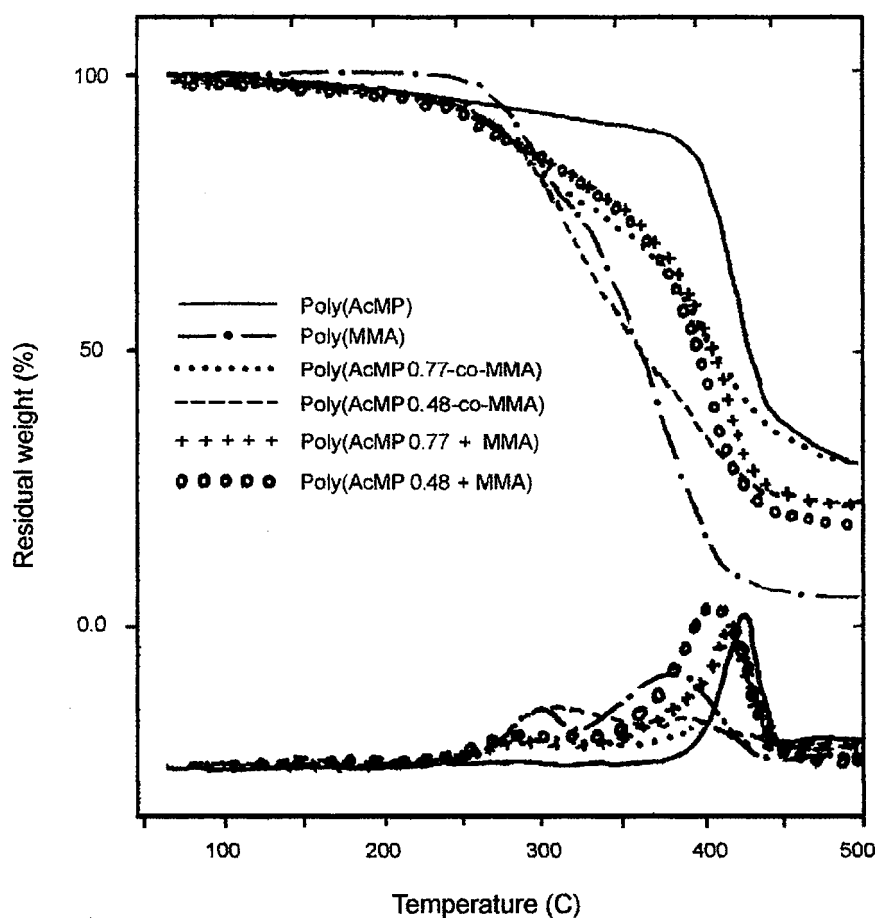


Figure 4. TGA curves of the polymers.

Table 1
Thermal characteristics of the homopolymers, the copolymers and the blends

Polymer	T _{in} (°C) ^a	T _{max} (°C) ^b	50 wt% loss at (°C)	Residue (%) at 500°C
Poly(MMA)	250	298;378	360	1.5
Poly(AcMP)	240;350	430;480	430	25.0
Poly(AcMP0.48-co-MMA)	240	310;385	355	20.0
Poly(AcMP0.55-co-MMA)	240	305;380	370	22.0
Poly(AcMP0.77-co-MMA)	240	305;405	405	32.0
B1	230	280;402	390	15.0
B2	230	280;405	395	16.0
B3	230	280;415	407	21.0

^aInitial decomposition temperature.

^bTemperatures corresponding to maximum decomposition rates.

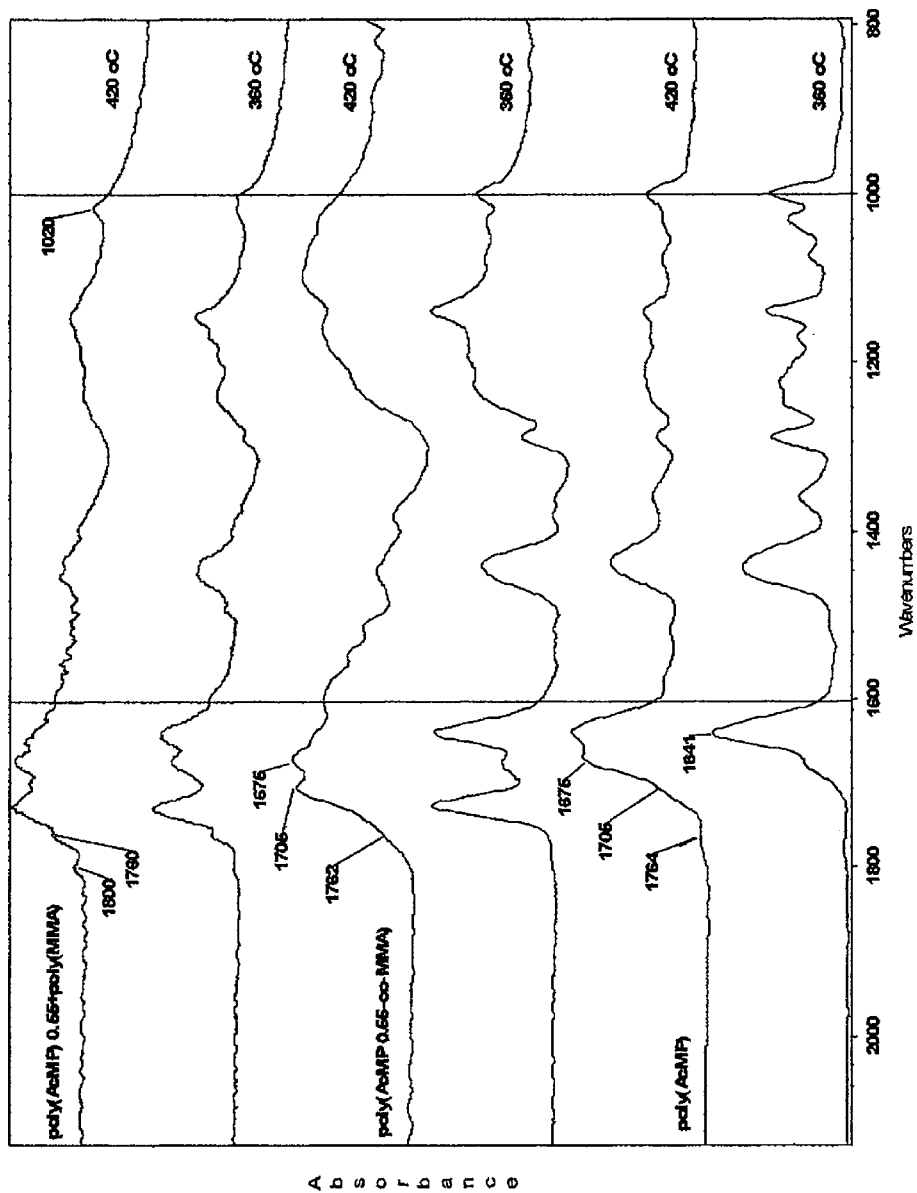
Changes in IR Spectra During Degradation of the Polymers

The polymer films on salt plates were heated to 150, 300, 360, 380, 420 and 480°C under N₂ flow in order to investigate the changes in IR spectra during thermal degradation. The IR spectra were recorded in each heating stage for each polymer, and Figure 5 shows the IR spectra of poly(AcMP), poly(AcMP)0.55 + poly(MMA) blend and poly(AcMP0.55-co-MMA) heated to 360 and 420°C. There were some small changes in the poly(AcMP) spectrum at 300°C, such as small bands appearing at 1675 (as shoulder) and 1512 cm⁻¹, and shifting of the band at 1454 to 1445 cm⁻¹ (not seen in Figure 5). In the IR spectrum at 360°C, it showed a weight loss of about 15%, and the shoulder at 1675 cm⁻¹ was clearly seen. The IR spectrum of poly(AcMP), heated to 420°C, (a 40 wt% loss) showed that the intensity of the band at 1641 cm⁻¹ (C=O stretching in amide) decreased, and new bands at 1764, 1705 and 1575 cm⁻¹ appeared. The intensities of the band at 1675 and 1512 cm⁻¹ increased relatively. All these spectroscopic changes suggested disappearance of the amide structures in the polymer and appearance of cyclic ring imides. The band at 1764 cm⁻¹ may be also related to a four-membered ketone ring.

In the spectra of the copolymer and blend having similar comonomer composition, there are some differences such as the appearance of bands at 1800, 1760 and 1020 cm⁻¹ at 360°C and those of the poly(AcMP)0.55 + poly(MMA) blend becoming stronger at 420°C. However, that was not observed at 360°C and was not clear at 420°C in the case of poly(AcMP0.55-co-MMA). A new band rising at 1675 cm⁻¹ for both spectra at 360°C is due to symmetric stretching of the carbonyl in cyclic imide, asymmetric vibration of the same group is seen at 1705 cm⁻¹ for both the blend and the copolymer, respectively. These bands are more clear at 440 and 420°C, another new band appearing at these temperatures is at about 1600 cm⁻¹, which may be attributed to some aromatic structures.

Degradation of the Polymers

To identify degradation products, poly(AcMP) was heated to 500°C under vacuum, and the products volatile at degradation temperature but not at ambient temperature were collected on the cooled upper part of the degradation tube. The degradation products



A b s o r b a n c e

Figure 5. IR Spectra of poly(AcMP), poly(AcMP0.55-co-MMA) and poly(AcMP0.66-co-MMA) blend heated to 360°C and 420°C.

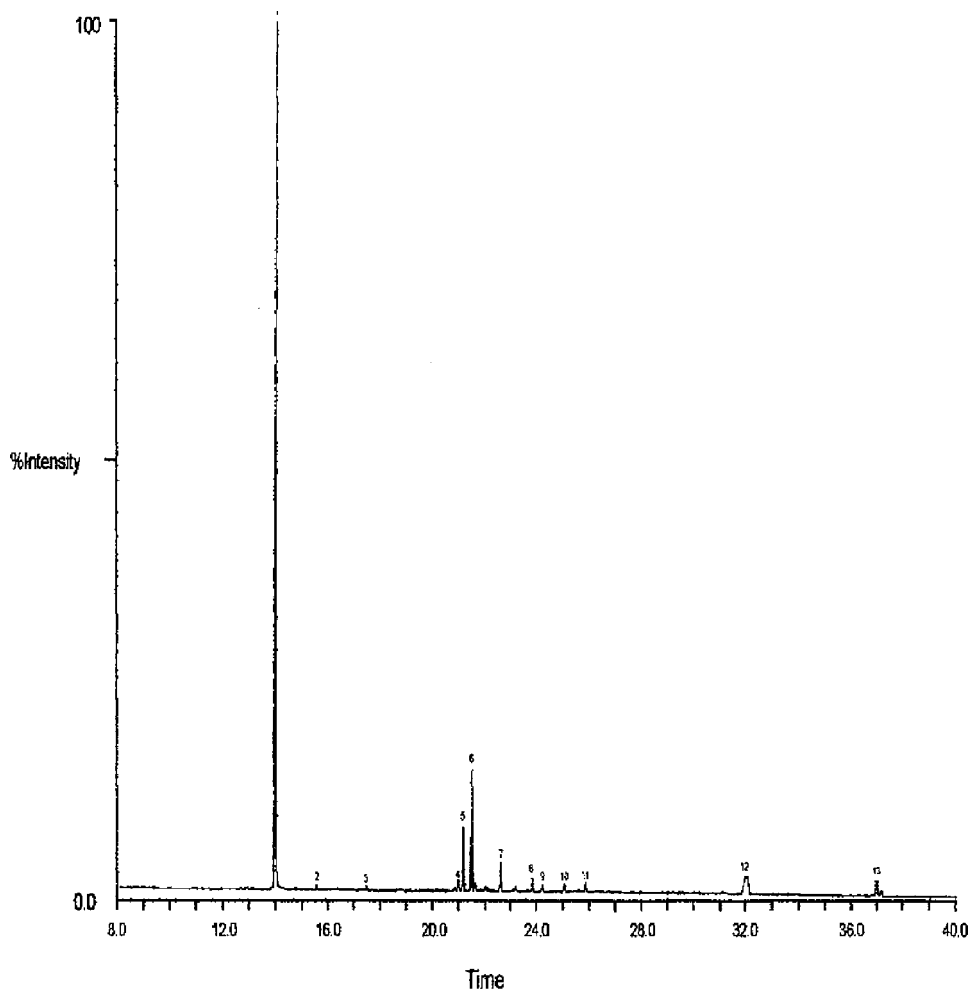
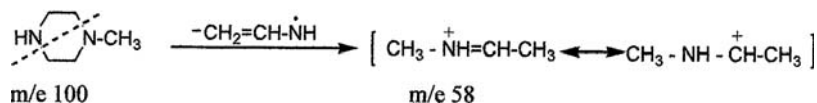


Figure 6. Gas chromatogram of thermal degradation products of poly(AcMP) heated to 500°C.

were examined by FTIR, gas chromatography-mass spectrometry (GC-MS) and ^1H NMR. The FTIR spectra of the degradation products show some characteristic bands at 3316 cm^{-1} (N–H stretching), $3000\text{--}3100\text{ cm}^{-1}$ ($=\text{C}\text{--}\text{H}$ stretching), 2190 cm^{-1} ($\text{--N}=\text{C}=\text{O}$ stretching), 1761 cm^{-1} ($\text{--C}=\text{O}$, small), 1665 cm^{-1} [$\text{--N}\text{--}\text{C}(=\text{O})\text{--}$], 1563 cm^{-1} (N–H bending). Characteristic signals in the ^1H –NMR of the product mixture are at 0.8–1.3 ppm (protons far from heteroatoms), 2.2–2.4 ppm ($\text{CH}_3\text{--N}$, etc.), 2.5–3.6 ppm (piperazine ring protons and others), 4.9–5.2 ppm ($\text{HN}\text{--}$, $\text{--CH}=\text{C}$, etc), 6.5–7.4 ppm (protons in some aromatic and olefinic structures) and 8.0 ppm (amidic protons).

When the GC-MS data (the chromatogram is illustrated in Figure 6) have been interpreted together with the above mentioned spectroscopic data, it is seen that the main product of poly(AcMP) degradation is N-methylpiperazine (peak area in GC: 70.8%) which m/e values of fragments in MS are 100 (M^+ , 22%), 83, 70, 58 (base peak), 56.

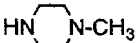
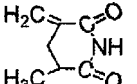

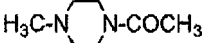
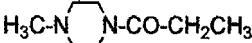
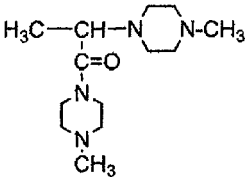
Some another assignments, which have a GC peak area in the ratio of at least 1%, are given in Table 2.



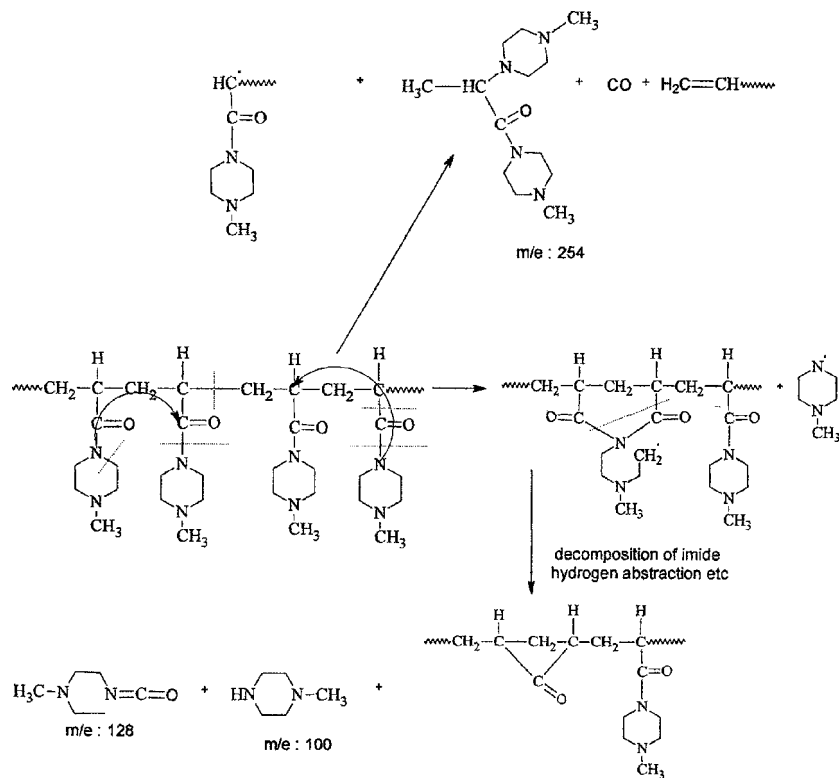
The monomer is not obtained among the degradation products. Major degradation products that side chain decomposition occurs during the heating of poly(AcMP), and depolymerization does not take place as seen in Scheme 1.

All spectroscopic data and GC-MS investigation of the degradation products indicate that thermal decomposition of poly(AcMP) starts by intramolecular cyclization between two adjacent units to give a cyclic imide and *N*-methylpiperazine. The band at 1764 cm^{-1} in the spectra of poly(AcMP), heated to 420°C , was attributed to a four-ring cyclic ketone forming during decomposition of the cyclic imide. In thermal degradation of the blends and copolymers, the product identification studies were not done, but there are some differences in the changes in IR spectra of the blend and copolymer in close composition during heating. For example, at 360°C , although corresponding bands cyclic imide and cyclic anhydride structures, 1705 cm^{-1} , 1675 cm^{-1} , and

Table 2
Degradation products of poly(AcMP)

Peak no (GC peak area) ^a	m/e values of major peaks in MS	Assignments
1 (70.8%)	100(M ⁺ ,22%),83,70,58(b.p.),56	
5 (4.3%)	139(M ⁺ ,30%),99,70,56,42(b.p.),40	
6 (8.7%)	128(M ⁺ ,32%),99,70,56,42(b.p.),39	
7 (2.1%)	142(M ⁺ ,8%),99,83,70,56, 43(b.p.),42(93%)	
8 (1.1%)	156(M ⁺ ,8%),127,99,70,57(93%), 42(b.p.)	
12 (6.0%)	208 (M ⁺ ,3%),207,194,193,115, 103,91(b.p.),77,65	Probably, an aromatic compound
13 (2.8%)	242(M ⁺ ,7%),208,207,143,99,70, 56(76%),42(b.p.)	Unknown
14 (1.0%)	254(M ⁺ ,7%),198,184,141,99, 70(86%),56(57%),42(b.p.)	

^aNo attribution was done on peaks 2,3,4,9,10,11, which had a peak area lower than 1%.



Scheme 1.

1800 cm^{-1} , 1762 cm^{-1} , 1020 cm^{-1} , respectively, are clearly observed in the IR spectra of the blend. These bands, especially belonging to the cyclic anhydrides, are lower in intensity than that of the copolymer because of less cyclic anhydride formation, since MMA units were disconnected by AcMP units in the copolymer. The cyclic imidization and cyclic anhydride formation have also been observed in the copolymers of *tert*-butyl methacrylate with some *N*-alkyl methacrylamides (24).

Acknowledgements

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