

Thermal Behavior of Methacrylic Acid–Ethyl Acrylate Copolymers

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SYNOPSIS

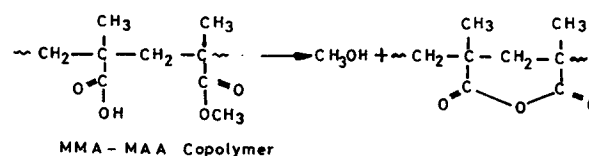
The thermal degradation behavior of copolymers of methacrylic acid (81.5–61.9 mol %) and ethyl acrylate (EA) (38.1–17.4 mol %) was studied using thermogravimetry (TGA) and differential scanning calorimetry (DSC) and the degradation products were analyzed using mass spectroscopy and DSC-FTIR. From mass spectroscopy, it was observed that in the copolymers the main degradation products obtained below 280°C included water, ethanol, and methanol, whereas at higher temperature (up to 400°C), CO₂, CO, and small olefins were liberated. Elimination of water and ethanol is attributed to anhydride formation, which is believed to result from two routes: (a) anhydride formation involving adjacent acid groups and (b) anhydride formation involving adjacent acid and ester groups. An endothermic transition in the DSC and percent weight loss in the TGA in the same temperature range (140–280°C) support the above proposal. An increase in weight loss with increase in EA content of the copolymer confirms the participation of EA in the anhydride formation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Acrylic acid (AA) and methacrylic acid (MAA) polymers undergo anhydride formation in the temperature range of 170–200°C and 180–260°C, respectively, by a reaction involving adjacent carboxylic acid groups, leading to the elimination of water.^{1,2} Kinetics of the dehydration reaction has also been studied for poly(MAA) (PMAA) and poly(AA) (PAA), and both of them were found to follow second-order kinetics with an activation energy of 37 ± 3 and 38 kcal/mol, respectively.^{1,3} Tacticity plays an important role in deciding the thermal stability and the *T_g* of PAA and PMAA.^{2,4} These acid units [MAA, AA, and itaconic acid (IA)], when present in the copolymers, were found to induce very profound changes in the thermal behavior of the copolymers.^{5–8}

The degradation of MAA–methyl methacrylate (MMA) copolymers provides a system in which the reaction between neighboring units in the polymer

chain plays an important role in the degradation process. Based on the thermal volatilization analysis (TVA), TG, GLC, and IR studies, it is shown that besides the two adjacent MAA units the neighboring MAA and MMA units can also react to form anhydride, thus leading to methanol liberation as shown below:



From the quantitative comparison of the yields of methanol liberated with the predicted yields based upon sequence distribution, it is believed that the methanol liberation may be via two routes: (i) intramolecular cyclization of adjacent acid and ester units at low temperature as mentioned above and (ii) fragmentation of ester units at high temperature.⁹ From the literature cited above, it is evident that, in addition to the nature of comonomer, thermal behavior is affected by tacticity and sequence distribution of the comonomer in the polymer chain.

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In the present investigation, the MAA-ethyl acrylate (EA) system was chosen with an objective to study the influence of EA on the anhydride formation of MAA. Various techniques (DSC, TGA, DSC-FTIR, and mass spectroscopy) were used to study whether EA units behave similarly to MMA as in the case of MAA-MMA copolymers.⁹ These copolymers with a higher amount of MAA (more than 50%) were synthesized using an emulsion polymerization technique with the aim of using the emulsion directly as a printing thickener for textiles. Though this system with a higher amount of water-miscible monomer (MAA) does not follow the conventional emulsion polymerization mechanism proposed by Smith-Ewart¹⁰ and Harkins,¹¹ it polymerizes according to a two-loci polymerization scheme.¹²

EXPERIMENTAL

Materials

Methacrylic acid (MAA), a Fluka product, was distilled at 75°C/12 mmHg and ethyl acrylate (EA) (BDH Chemicals, India) was distilled at 50°C/80 mmHg before use. Sodium lauryl sulfate (Glaxo Laboratories, India), potassium persulfate (KPS), and sodium metabisulfite (BDH Chemicals, India) were used as received.

Synthesis

Polymerization was carried out in demineralized water (water-to-monomer ratio = 3) using sodium lauryl sulfate and hyoxide AAO (5 wt % of monomer) as the mixed emulsifier and KPS (0.1 wt % of monomer) and sodium metabisulfite (0.2 wt % of monomer) as the redox initiators at 60°C in a nitrogen atmosphere. Polymerization was carried out for 4 h so as to obtain higher conversions (90–95%) and then terminated by pouring the emulsion into cold aqueous NaCl solution. Emulsion was then rapidly broken with small amounts of acetone, filtered, and washed with water (slightly acidic) and *n*-hexane, respectively, to remove the emulsifier and residual monomers. The polymer was dried in a vacuum oven at 70°C for 24 h.

Characterization

The structure of the copolymers was determined by IR spectroscopy. A strong intensity band at 1700 cm⁻¹ characteristic of carbonyl stretching of MAA and the bands at 1734 and 1020 cm⁻¹ due to carbonyl

stretching and the C—O—C stretching of esters establish the structure of the copolymer. The composition of the copolymer was determined by ¹H-NMR studies, using the ratio of the area of the signal at δ 0.9–1.2 (methyl protons of MAA and EA both) to that of the CH₂O resonance (EA) centered at 3.9 δ . The results are given in Table I. The intrinsic viscosity of the copolymers was determined in methanol at 30°C using an Ubbelohde viscometer (Table I).

Thermal Analysis

TGA and DSC studies were carried out on DSC7 and TGA7 modules of a Perkin-Elmer Delta Series thermal analyzer. The measurements were carried out at a heating rate of 5°C/min up to a temperature of 650°C for TGA and 300°C for DSC. The sample size was 10 mg in all the experiments and samples were purged with oxygen-free nitrogen. Before recording the DSC scans, the samples were held at 100°C for 3 min in the DSC cell itself to remove the absorbed water. The following equation was used to calculate the kinetic parameters from the dynamic DSC data¹³:

$$\frac{d\alpha}{dt} = K(1 - \alpha)^n = A \cdot \exp(-E_a/RT) (1 - \alpha)^n$$

where *n* is the order of the reaction; *K*, the overall rate constant; α , the extent of the reaction; and *E_a*, the activation energy for thermal-induced reactions. After the first heating cycle up to 300°C, the samples were cooled rapidly and reheated at a rate of 5°C/min up to 250°C.

On-line DSC-IR analysis was carried out on a Janssen (×16) + DSC system analyzer under similar conditions as mentioned above for DSC studies. IR spectra were recorded simultaneously to observe the structural changes occurring in the polymer during the heating cycle.

Mass Spectroscopy

A JEOL JMS-DX 300 mass spectrophotometer attached with JMA-2000 mass data analyzer system was used for recording the mass spectra. The polymer samples were pyrolyzed on the injection probe and pyrolyzed products were then fed to the ionization chamber. Spectra were recorded in two temperature ranges, i.e., 50–280°C and 280–400°C, and the voltage of the ionization chamber was maintained at 16 eV.

Table I DSC Data of Homo- and Copolymers

| Polymer Code | Feed Concn (mol %) | | Copolymer Composition (mol %) | | [η] (dL g ⁻¹) | Endotherm Range (°C) | | Onset Temp T_o (°C) | Peak Temp T_p (°C) | $T_p - T_o$ | Time of Reaction (min) | ΔH , Heat of Reaction per COOH unit | | Activation Energy kcal/mol (kJ/mol) |
|--------------|--------------------|------|-------------------------------|------|----------------------------------|----------------------|-------|-----------------------|----------------------|-------------|------------------------|---|--------|-------------------------------------|
| | MAA | EA | MAA | EA | | T_i | T_f | | | | | J/g | kJ/mol | |
| PMAA | 100 | 0 | 100 | 0 | 1.60 | 165.2 | 267.1 | 203.0 | 222.0 | 19.0 | 20.3 | 241.7 | 20.7 | 40.0 (166.8) |
| PME1 | 82.3 | 17.6 | 81.5 | 17.4 | 1.72 | 165.2 | 269.9 | 194.9 | 215.6 | 20.7 | 20.9 | 451.9 | 48.4 | 33.3 (138.8) |
| PME2 | 77.6 | 22.3 | 76.3 | 23.7 | 1.92 | 148.8 | 267.5 | 186.3 | 211.3 | 25.0 | 23.6 | 476.4 | 53.9 | 29.4 (122.6) |
| PME3 | 72.9 | 27.0 | 71.8 | 28.2 | 2.10 | 148.5 | 265.8 | 181.3 | 208.3 | 27.0 | 23.4 | 494.6 | 61.9 | 27.9 (116.3) |
| PME4 | 68.1 | 31.8 | 64.0 | 36.0 | 2.20 | 148.8 | 262.8 | 177.8 | 212.3 | 34.5 | 23.8 | 506.9 | 72.0 | 26.6 (110.9) |
| PME5 | 63.4 | 36.6 | 61.9 | 38.1 | 2.27 | 144.1 | 261.7 | 171.5 | 207.3 | 36.0 | 23.5 | 525.7 | 72.5 | 24.6 (102.5) |

RESULTS AND DISCUSSION

DSC Studies

DSC scans of the copolymers of MAA with a varying content of EA and that of PMAA are presented in Figure 1. All the samples showed a well-pronounced endothermic transition in the temperature range of 145–270°C. The homopolymer of EA did not show any transition in this temperature range. The endothermic transition in PMAA as well as in copolymers can be attributed to the anhydride formation reaction as reported by various authors^{2,3} for PAA and its copolymers. The analysis of the DSC curves showed that the initial temperature (T_i), onset temperature (T_o), and peak temperature (T_p) of the endotherm (Table I) are lower in copolymers as compared to the homopolymer of MAA and it decreases further with increase in the EA content, but the final temperature (T_f) remains the same. The initial temperature is the temperature at which the curve first deviates from the base line. It is a measure of the initiation of the reaction. The onset temperature is obtained at the intercepts of the tangents to the base line and the lower temperature side of the endothermic peak. Peak temperature is the temperature at which the bulk of the polymer has undergone a dehydration reaction and the difference between the peak temperature and onset temperature ($T_p - T_o$) is a measure of overall rate of reaction; the smaller the difference, the greater the rate of reaction. An increase in the $T_p - T_o$ values with increase in the EA content of the copolymer suggests a decrease in the overall rate of the reaction. Another important observation made from DSC scans is that the heat of reaction (ΔH) increased with increase in the EA content (Table I) from 241.7 J/g in PMAA to 525.7 J/g in the copolymer containing 38.1 mol % EA. From these data, it may be inferred that EA units participate in the dehydration reaction when present in the copolymer, whereas the homopolymer of EA does not undergo any reaction, as evident from the absence of any transition in the DSC curves. A decrease in the initial temperature and the onset temperature on introduction of EA units indicates that EA units participate in the dehydration reaction, which is initiated at a lower temperature as compared to the homopolymer of MAA. However, increase in the total time of the reaction as well as in $T_p - T_o$ indicates that in the copolymer it takes longer for the reaction to complete. For comparing the effect of comonomer on the heat of the dehydration reaction, ΔH values were also calculated by applying the correction for the

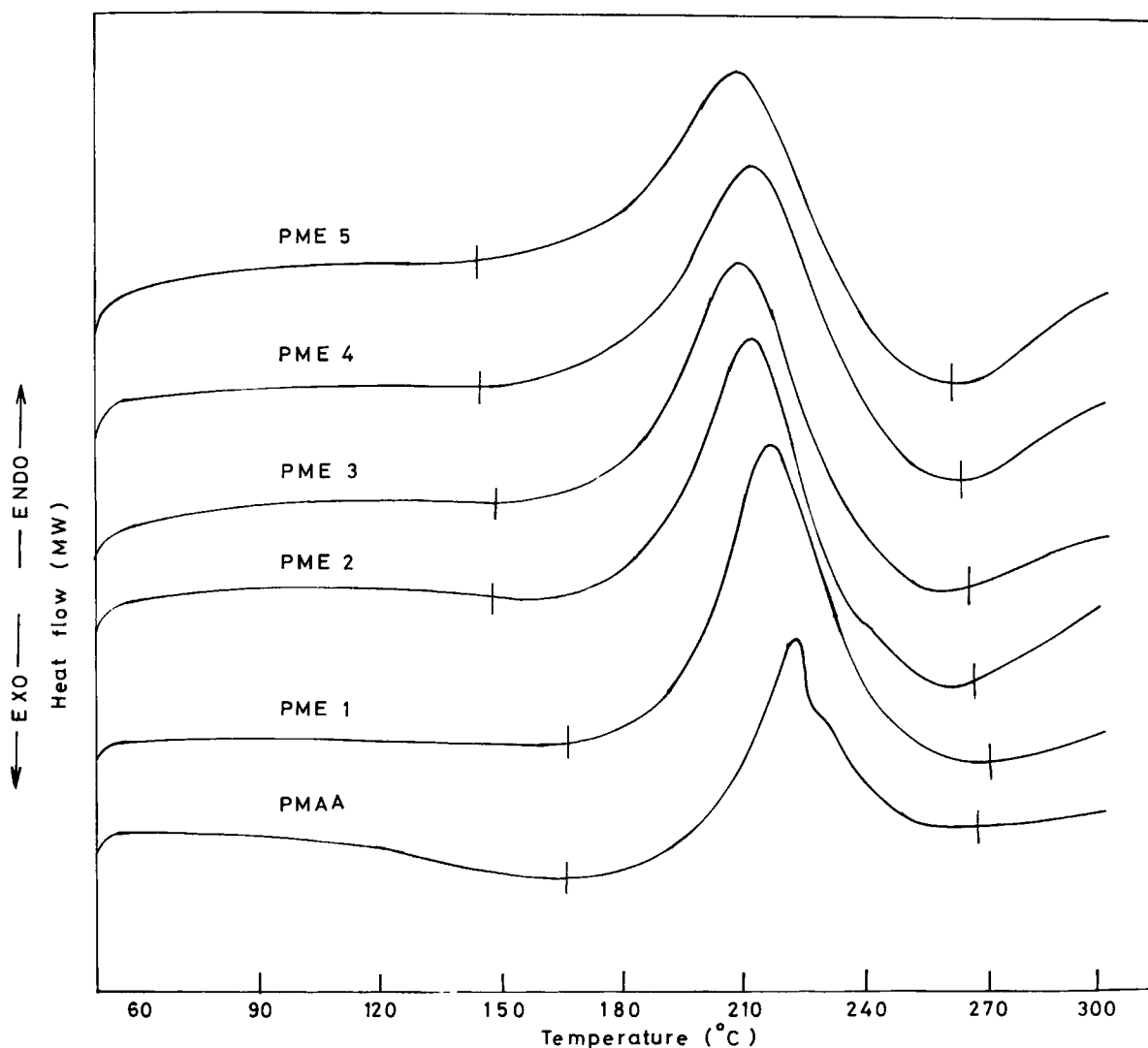


Figure 1 DSC thermograms of homo- and copolymers (first heating cycle).

comonomer content. The values thus calculated (Table I) show a significant increase with enhancement in the EA comonomer content, thereby confirming the effective participation of EA in the anhydride formation. A similar observation has been made for acrylonitrile (AN)-acrylate/methacrylate copolymers, where the comonomers were suggested to accelerate the oligomerization reaction.¹⁴

Kinetic parameters such as order of reaction and activation energy were also calculated to further establish the effect of EA on the anhydride formation of MAA. In the MAA homopolymer, the reaction was found to follow second-order kinetics, and the activation energy is 40 kcal/mol, which is in conformity with the results obtained by Grant and Grassie.¹ However, in copolymers, the activation

energy shows a significant drop to 25 kcal/mol in the PME5 (MAA:EA/61.9 : 38.1) copolymer. These data suggest that the comonomer not only participates but also promotes the anhydride reaction to be initiated at a lower temperature. A similar accelerating effect of neighboring acid groups is reported by Bajaj et al.⁸ in saponified AN terpolymers through the exotherms appearing at lower temperatures than for the polyacrylonitrile homopolymer.

It is reported that the PMAA does not possess a glass transition temperature (T_g) below its degradation temperature: 180°C.¹⁵ Between 180 and 260°C, dehydration occurs¹⁶ and the anhydride of PMAA has a T_g in the range of 140–180°C depending on the tacticity.⁴ In the present investigation, the polymers heated in the first heating cycle of DSC

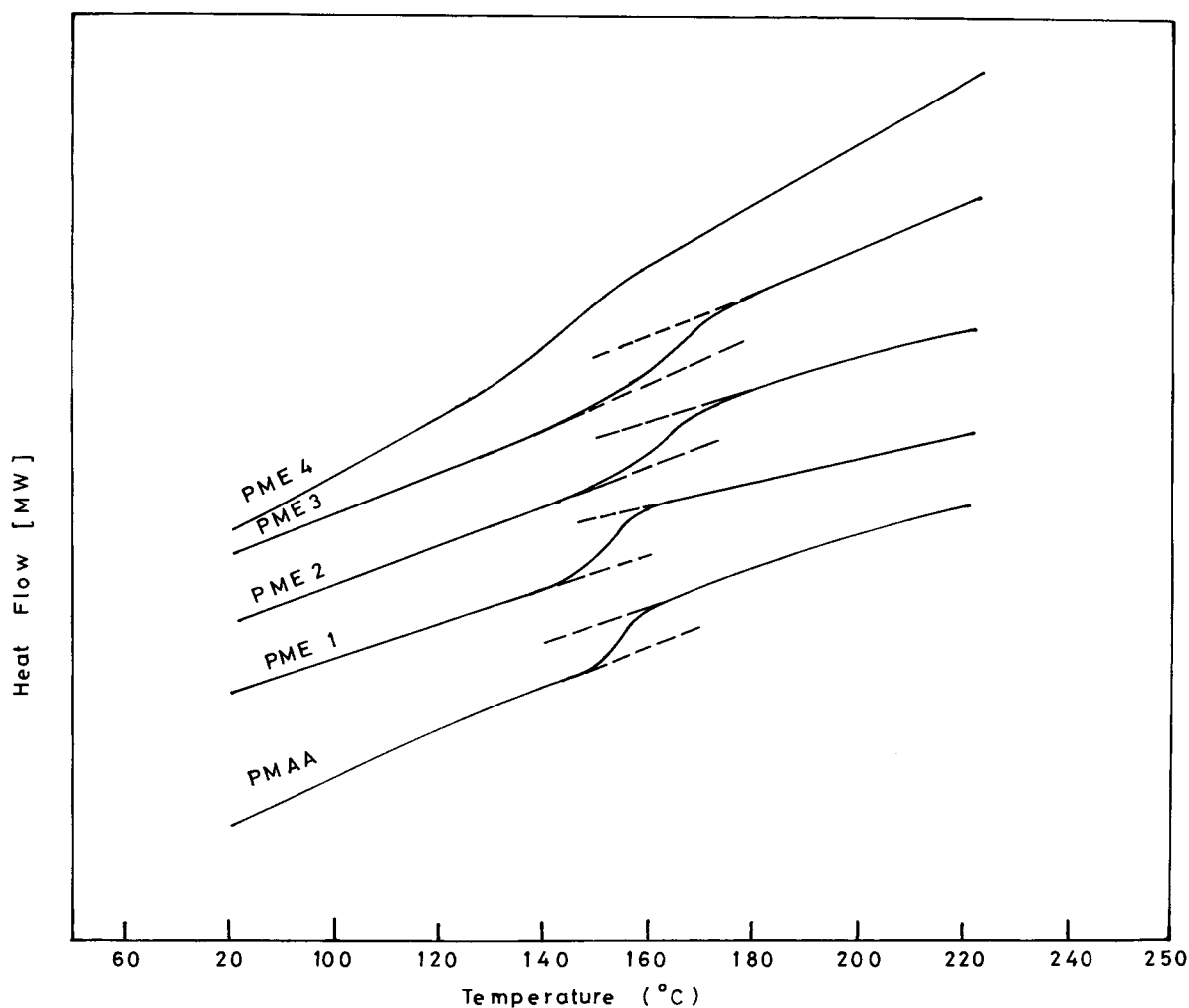


Figure 2 DSC thermograms of homo- and copolymers (second heating cycle).

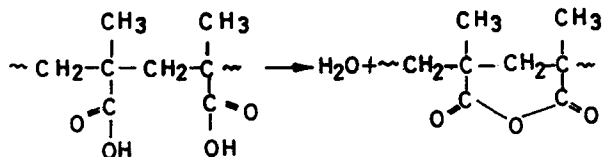
were reheated in the same DSC cell up to 250°C in order to observe any transition in the second heating cycle. In copolymers, a transition obtained in the temperature range of 155–169°C (Fig. 2) may be attributed to the glass transition temperature of their anhydrides. However, no significant effect of the copolymer composition on the T_g was observed. An important observation made was that the sharpness of the T_g transition decreases with increase in the EA content in the copolymer, and it disappeared completely in copolymers containing 36 mol % or more EA. A plausible explanation of this may be given on the basis of the polymerization behavior of the MAA-EA system. That the EA radical is less reactive than the MAA radical¹⁷ will add preferentially to the MAA radical than with its own radical in earlier stages of the reaction; however, in later stages, when highly reactive MAA is consumed, the remaining EA will form blocks containing EA units

only. These blocks behave in similarly to poly(EA) (PEA) and cannot undergo anhydride formation. The presence of such unreacted (PEA) blocks may decrease the sharpness of the T_g transition. More quantitative studies on the participation of EA in the dehydration reaction of MAA has been carried out using TGA and is discussed below.

TGA Studies

Analysis of TG curves of PMAA and its copolymers reveals that there are three distinct steps of weight loss (Fig. 3). The first step of weight loss in the range of 170–285°C may be attributed to the elimination of side products in the process of anhydride formation as indicated by an endothermic transition in the same temperature range from DSC scans. Grant and Grassie¹ studied the anhydride formation

in the case of PMAA where water is eliminated as shown below:

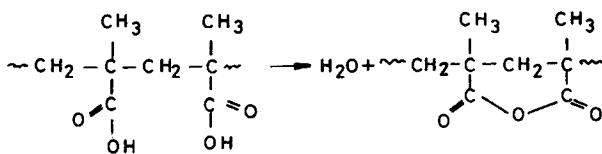


The 3–4% weight loss below 170°C is attributed to the loss of absorbed water.^{2,3} The second and third steps observed in the temperature ranges of 285–470°C and 470–650°C, respectively, are the regions of major weight loss and appear to be due to the extensive degradation of the polymer backbone chain leaving a residue of 4–6% of the original sample weight.

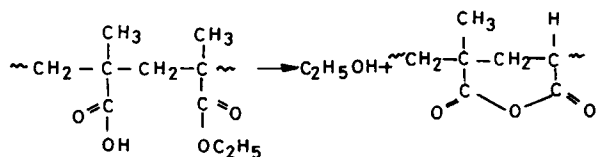
Interestingly, the PEA homopolymer does not show any weight loss up to 280°C, and above that, 81.6% weight loss takes place rapidly up to 425°C (Fig. 3). The absence of any weight loss up to 280°C is in accordance with the observation made from DSC studies that the homopolymer of EA does not undergo dehydration or any other reaction in this temperature range. In the TG curves of PMAA and the copolymers, it is interesting to compare the weight loss for each sample at 285–290°C, where the first step of degradation is completing and the second step is just beginning to occur under programmed heating conditions. In PMAA, a weight loss of 10.8% was observed on account of a loss of water due to anhydride formation, which is comparable to the theoretical maximum yield of water expected in the PMAA dehydration reaction, i.e., 10.47%.

In the case of the copolymers, the observed weight loss was found to be higher than that of PMAA and an increase in the weight loss was observed with increase in the EA content (Table II). This further confirms the participation of the EA comonomer also in the anhydride formation as the comonomer participation is expected to yield ethanol along with water, and since ethanol is a higher molecular weight product than water, it would lead to more weight loss in the copolymers. So, two types of reactions can take place in MAA–EA copolymers:

(i) An anhydride formation involving adjacent methacrylic acid units:



(ii) An anhydride formation involving neighboring MAA and EA units:

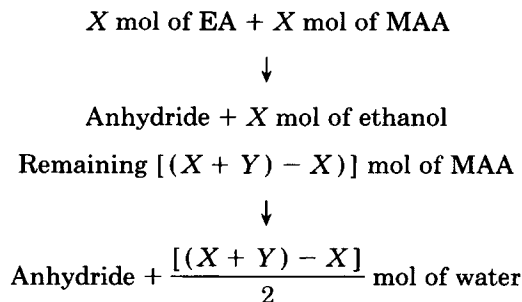


On the basis of DSC and TGA studies, considering the comonomer participation in the dehydration reaction, the theoretical maximum weight loss was calculated by assuming that all the MAA and EA units of the copolymer participate in the dehydration reaction, irrespective of their sequence distribution and tacticity. Thus, weight loss would be equal to the total weight of the water and the ethanol liberated in this process:

Total weight of the polymer

$$= [X \times 100] + [(X + Y) \times 86] = Z \text{ g}$$

where X is the mol of EA; $X + Y$, the mol of MAA; 100, is the mol. wt. of EA; and 86, the mol. wt. of MAA:



Therefore,

Total weight loss

$$= [X \times 46] + [\{(X + Y) - X/2\} \times 18] = W \text{ g}$$

where 46 is the mol. wt. of ethanol, and 18, the mol. wt. of water:

$$\% \text{ wt loss} = W/Z \times 100 = S\%$$

As the calculations were based on this assumption, a difference of 2–4% in the experimental and calculated weight loss % was observed. From this difference, a rough estimate of the EA units present in the form of blocks containing EA units only, which are unable to undergo anhydride formation, was calculated:

Difference in the experimental

$$\text{and calculated weight loss \%} = A$$

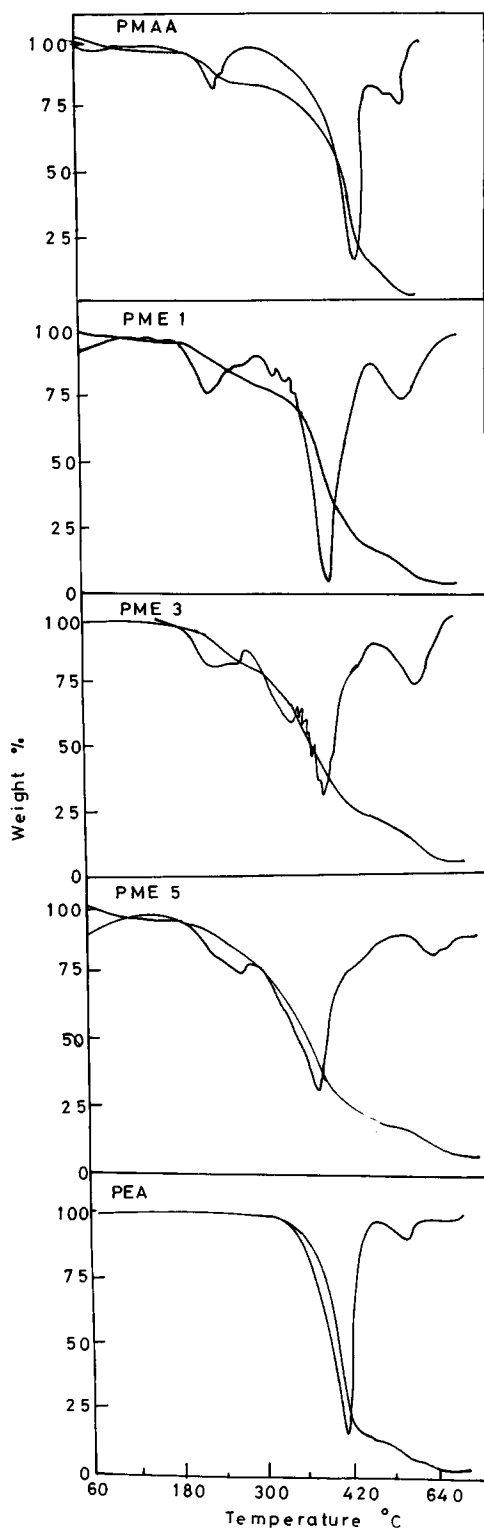


Figure 3 TGA traces of homo- and copolymers.

Assuming this difference, ($A\%$) is equal to the amount of ethanol, which is not being produced, as all the EA units are not present in the neighborhood

of MAA units and such units will not participate in the anhydride formation.

Therefore, $A/100 \times Z = B \text{ gm} = B/46 = C \text{ mol}$ of ethanol = $C \text{ mol}$ of EA. Out of total of $X \text{ mol}$ of EA, $C \text{ mol}$ are not able to participate in the anhydride formation. Results of these calculations are given in Table III, which demonstrates that as the content of EA in the feed increases as more of EA in the copolymer is present as blocks. In PME1 (MAA:EA/81.5 : 17.4), only 3.16 mol % of EA is present in the form of blocks, whereas in PME5 (MAA:EA/61.9 : 38.1), this amount increased to 8.73 mol %.

The second and third stages of the weight loss in the copolymers are due to the fragmentation of anhydride chains into several products like CO_2 , CO , CH_4 , C_2H_4 , etc. The degradation has been studied in detail with the help of mass spectroscopy and the results are discussed in a later section of this paper.

DSC-FTIR

To establish the structural changes occurring with temperature, on-line DSC-FTIR analysis was carried out, and the spectra recorded at various temperatures for PMAA and the copolymer PME1 are shown in Figures 4 and 5. Disappearance of the characteristic bands of acid at 1700 cm^{-1} ($>\text{C}=\text{O}$ stretching vibration) and $2500\text{--}3500 \text{ cm}^{-1}$ ($-\text{OH}$ stretching vibration), which starts at 172.1°C and becomes completed at 260°C , and appearance of the twin peaks at 1758 and 1800 cm^{-1} , characteristic of a glutaric-type anhydride ring,¹⁸ and a peak at 1020 cm^{-1} ($\text{C}-\text{O}-\text{C}$ stretching) prove the formation of anhydride. These results are in conformity with the observations made by Grant and Grassie¹ in the formation of anhydropoly(methacrylic acid). The copolymers had carbonyl stretching bands at 1734 and 1700 cm^{-1} for EA and MAA, respectively, though the two were not resolvable due to very close proximity. Disappearance of both the carbonyl bands on heating the copolymer up to 260°C and appearance of twin peaks at 1758 and 1800 cm^{-1} confirm the participation of EA in conjunction with MAA in the anhydride formation as proposed earlier by DSC and TGA studies. The intensity of the band at 1020 cm^{-1} ($\text{C}-\text{O}-\text{C}$ stretching), which was already present due to EA, increased as a result of anhydride formation.

Mass Spectroscopy

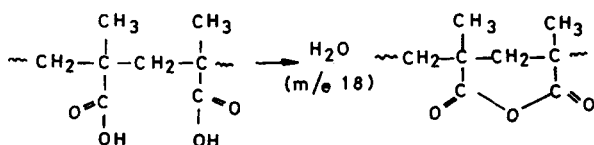
Mass spectra of both the homopolymers (PMAA and PEA) and one of the copolymers PME4 were

Table II Thermal Degradation Data of Homo- and Copolymers

| Polymer Code | Copolymer Composition (mol %) | | Wt Loss (%) | | |
|--------------|-------------------------------|------|------------------------|-------------------------|------------------------|
| | MAA | EA | First Step (170–285°C) | Second Step (285–470°C) | Third Step (470–650°C) |
| PMMA | 100 | 0 | 10.8 | 69.5 | 15.0 |
| PME1 | 81.5 | 17.4 | 13.8 | 62.1 | 15.2 |
| PME2 | 76.3 | 23.7 | 14.8 | 59.5 | 16.7 |
| PME3 | 71.8 | 28.2 | 15.5 | 59.0 | 17.6 |
| PME4 | 64.0 | 36.0 | 16.7 | 65.4 | 13.9 |
| PME5 | 61.9 | 38.1 | 17.1 | 59.2 | 12.5 |
| PEA | 0 | 100 | — | 81.7 | 15.6 |

recorded at two temperature ranges, from 50 to 280°C and from 280 to 400°C.

In PMAA, a peak at m/e 18 due to water was observed as the base peak in the low-temperature range. Water is a product of intra- or intermolecular dehydration as depicted below:



Though intramolecular dehydration is predominant, occasionally, intermolecular dehydration also takes place, resulting into loosely cross-linked anhydride, insoluble in common organic solvents as observed by Grassie et al.¹ These data corroborate the anhydride formation in PMAA as observed by

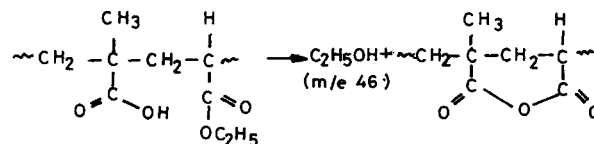
Table III Analysis of First Step of Thermal Degradation in Homo- and Copolymers

| Polymer Code | Copolymer Composition (mol %) | | Weight Loss % | | EA (mol %) in Form of Blocks |
|--------------|-------------------------------|------|---------------|-------|------------------------------|
| | MAA | EA | Exptl | Calcd | |
| PMAA | 100 | 0 | 10.8 | 10.4 | — |
| PME1 | 81.5 | 17.4 | 13.8 | 15.7 | 3.6 |
| PME2 | 76.3 | 23.7 | 14.8 | 17.1 | 4.5 |
| PME3 | 71.8 | 28.2 | 15.5 | 18.8 | 6.4 |
| PME4 | 64.0 | 36.0 | 16.7 | 20.9 | 8.3 |
| PME5 | 61.9 | 38.1 | 17.1 | 21.5 | 8.7 |

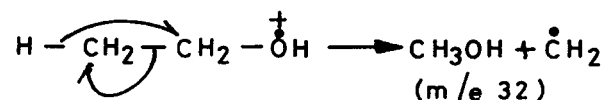
DSC and TGA studies. PEA does not show any degradation in the low-temperature range up to 280°C as observed earlier in TGA studies (Fig. 1).

In the copolymer PME4 also, m/e 18 (water) was observed as the base peak in the temperature range of 50–280°C, indicating that the anhydride formation involving adjacent MAA units is the major event taking place in this temperature range.

The appearance of two peaks at m/e 46 and 32 due to ethanol and methanol only in the case of the copolymer proved the participation of EA in the anhydride formation as predicted earlier from DSC and TGA studies, and the reaction involved is shown below:



The peak due to methanol, which is of higher intensity than the ethanol peak, may be explained on the basis of the general behavior of primary alcohols, where the cleavage of the C—C bond next to the oxygen atom is of a general occurrence.¹⁹ Thus, the ethanol loses a methylene unit and rearranges itself spontaneously to methanol as shown below:



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