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THERMAL DEGRADATION CHARACTERISTICS OF POLY(ACRYLAMIDE-CO-ACRYLIC ACID) AND POLY(ACRYLAMIDE-CO-SODIUM ACRYLATE) COPOLYMERS*,**

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ABSTRACT

The oxidative and thermal degradation characteristics of poly(acrylamide-co-acrylic acid) (AM-co-AA) and poly(acrylamide-co-sodium acrylate) (HPAM) have been explored via DSC, TG and TG–MS techniques. Several complications are described which limit the utility of a literature TG method for determining HPAM composition via analysis of its oxidative degradation. An improved TG method is described which is based on HPAM degradation in a nitrogen atmosphere. The utility of DSC and TG–MS experiments for elucidating the complex degradation characteristics of these polymer systems is illustrated for an AM-co-AA system. Multiple water and ammonia evolution stages were noted in TG–MS experiments and possible mechanisms are suggested.

INTRODUCTION

The thermal degradation of poly(acrylic acid) (PAA), and of poly(acrylamide) (PAM), in inert atmosphere, has been shown to be a complex process [1–4]. For example, among other features, PAA may exhibit loss of extraneous water, loss of water due to anhydride formation, and subsequent decomposition of the anhydride. Similarly, PAM degradation characteristics may include loss of extraneous water, ammonia loss due to imide formation and subsequent decomposition of the imide. This paper will examine two aspects of the equally complex degradation characteristics of two acrylamide-containing copolymers: poly(acryl-co-acrylic acid) (AM-co-AA) and poly(acrylamide-co-sodium acrylate) (HPAM). One of the topics considered is the feasibility of determining the composition of these copolymers via an oxidative degradation technique recently reported for the

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** Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

analysis of commercial HPAM copolymers [5]. The second topic is a combined DSC, TG and thermogravimetry–mass spectrometry (TG–MS) study of selected HPAM and AM-co-AA compositions. The general objectives are to examine the nature and compositional dependence of the degradation characteristics of these polymers in both oxidizing and inert atmospheres and to establish whether improved methods for determining HPAM and AM-co-AA compositions can be developed based on thermal analysis procedures.

EXPERIMENTAL

Polymers

Conventional methods were used to prepare PAM (free radical polymerization) and HPAM (base-catalyzed hydrolysis). AM-co-AA was prepared from HPAM via ion-exchange resins [6]. Poly(sodium acrylate) (PNaA) was prepared via neutralization of PAA.

TG

DuPont 950 TG and 990 TA system, air or nitrogen atmosphere (see text); 10 °C min^{-1}; sample size (mg): solution-blended PAM and PNaA (5–10), other samples (1–2).

DSC

DuPont DSC and 990 TA system. Air or nitrogen atmosphere (see text). For experiments shown in Fig. 4, sample size was 3–6 mg and heating rate was 5 °C min^{-1}. For all other experiments, the values were ~ 2 mg and 10 °C min^{-1}, respectively. All samples pre-dried for 2 h at 115 °C in a vacuum oven.

TG–MS

Mettler 2000C TG system and U.T.I. Model mass spectrometer. Helium atmosphere; 10 °C min^{-1}, α-Al_2O_3 crucibles and references. Further details given elsewhere [7].

Sample type and preparation

Except as otherwise indicated, samples consisted of 1–2 mg of granulated cast films. Drying conditions were 2 h at 115 °C in vacuum (for TG or DSC), or in helium (for TG–MS).

RESULTS AND DISCUSSION

HPAM analysis via TG: literature method

Dassanayake and Phillips have described a method for determining the composition of HPAM via evaluating the cumulative weight loss which occurs up to a temperature of 492°C when the sample (8–9 mg in powder form) is heated in air in a TG unit [5]. Their method was developed using polymers precipitated from emulsions. The present study examines the applicability of this method for determining the composition of HPAMs synthesized by non-emulsion methods, via analysis of small samples of cast polymer films.

This literature method [5] was used to analyze larger samples (10–15 mg) of HPAM powder obtained by precipitation following standard free radical polymerization. It was possible to discriminate among a set of laboratory-prepared HPAM samples in the 19–48 mol% sodium acrylate range (Table 1). The code for polymer composition shown in Table 1, i.e., HPAM (19), indicates the mole percent hydrolysis based on an ion-exchange/titration method described elsewhere [6]. Examination of other polymers, however, raised several questions concerning the general utility of the method (Table 1). For example, errors can arise due to the presence of extraneous salt, as in the polymer HPAM (30), and the method does not distinguish between the homopolymers and the copolymers on the basis of the cumulative weight loss to 492°C.

Examination of the oxidative degradation characteristics of PAM and PNaA (Fig. 1) indicates significant differences in weight loss characteristics, and suggests the use of ~ 450°C as a reference temperature for quantitative analysis of HPAM composition via TG analysis. A calibration curve was

TABLE 1

Evaluation of polymer composition via a thermal degradation method

Polymer	Known composition (mol%) (titration method)		TG composition (mol%) (weight loss method) [a]	
	AM	NA acrylate	AM	Na acrylate
HPAM (19)	81	19	87	13
HPAM (26)	74	26	80	20
HPAM (40)	60	40	60	40
HPAM (48)	52	48	52	48
HPAM (30)	70	30	50	50
PAM	99	1	76 [b]	24 [b]
PNaA	0	100	58 [b]	42 [b]

[a] Similar to method of Assanayake and Phillips [5].

[b] Apparent composition based on TG method.

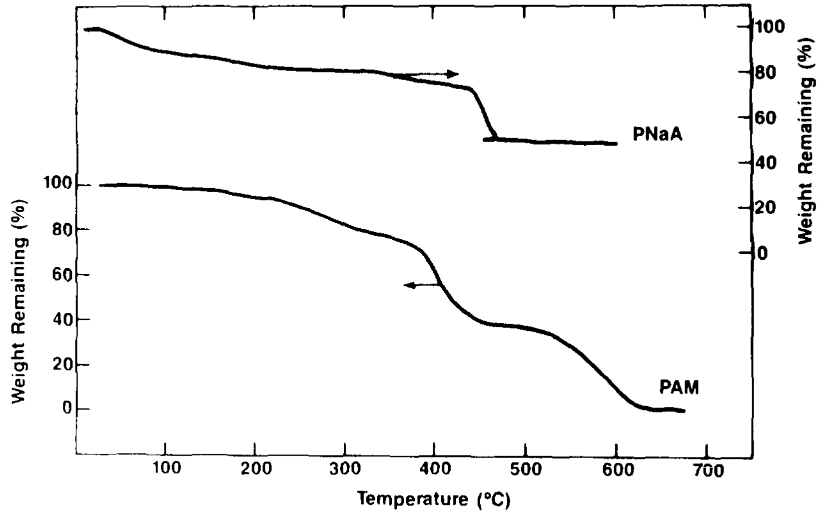

Fig. 1. Degradation characteristics of PAM and PNaA (air atmosphere).

therefore developed for a series of PAM and PNaA blends prepared in solution and then cast as films. As shown in Fig. 2, the 450°C reference temperature should enable better discrimination of HPAM composition compared to a 500°C reference temperature. However, as evident in Fig. 2, the method was not successful when applied to a series of HPAMs of known composition.

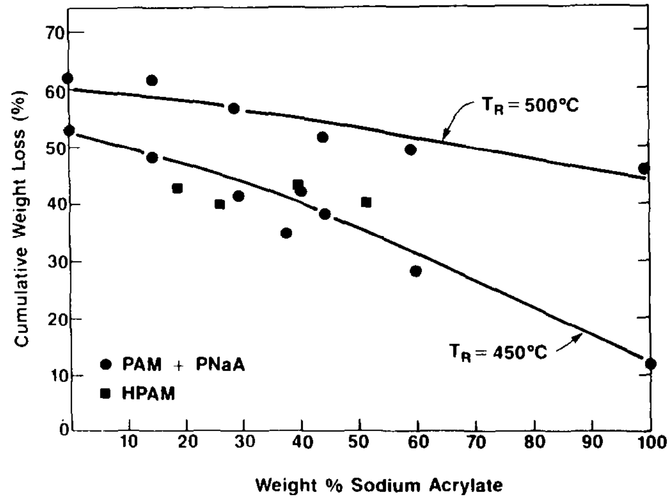

Fig. 2. Degradation characteristics of PAM+PNaA blends versus HPAM. T_R = reference temperature at which weight loss was measured.

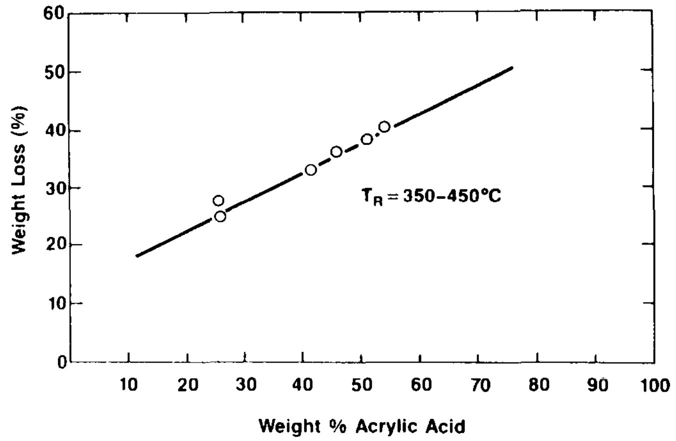

Fig. 3. Degradation characteristics of AM-co-AA. T_R = reference temperature at which weight loss was evaluated.

A number of variables which influence the TG degradation characteristics of HPAM were explored in a limited study. One which showed some potential for improving this analysis is the use of polymers in the acid versus the salt form. There appears to be a reasonable correlation between weight loss in the 350–450°C region and AM-co-AA composition (Fig. 3), but the sensitivity of the method seems limited.

Oxidative degradation of HPAM

Detailed analysis of the complex degradation characteristics of HPAM was undertaken to determine whether an improved TG method could be developed for determining the composition of this polymer. Comparison of the thermal stability of a series of HPAMs of varying composition (Fig. 4) indicates two problems regarding the method proposed by Dassanayake and Phillips, i.e., the weight loss at 492°C does not always correlate with polymer composition and there appears to be a strongly exothermic event, evident near about 425°C, which disrupted the heating rate during the analysis of HPAM (53). Further information regarding the latter point was obtained by examining the degradation characteristics of HPAM (42) versus HPAM (16) as shown in Fig. 5. Evidence of a strongly exothermic event is observed in the TG experiment for HPAM (42) but not for HPAM (16). However, the DTG trace for HPAM (16) does suggest a small weight loss in the 425°C region. The overall complexity of the thermal degradation of HPAM (16) is indicated by the multiple DTG maxima. Analysis of the region between about 100 and 350°C will be considered elsewhere in this paper. DSC analysis (Fig. 6) confirms the existence of a strongly exothermic process near 400°C in HPAM (42). It also reveals additional exothermic

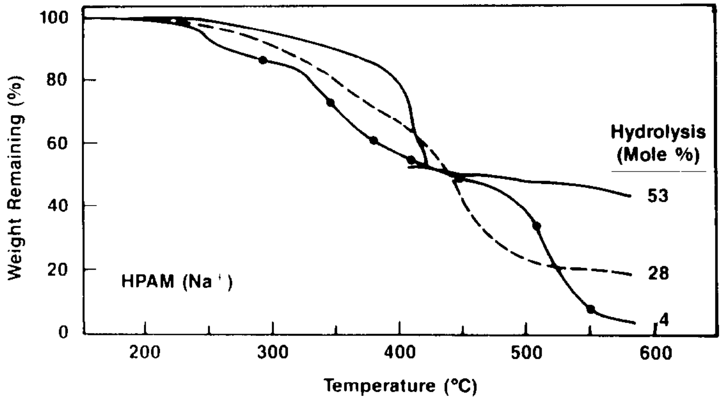

Fig. 4. Oxidative degradation characteristics of selected HPAM compositions.

processes above this temperature, as well as one or more endothermic processes in the ~ 150–350°C region. DSC analysis of HPAM (16) (Fig. 7) indicates a weak exothermic process near ~ 400°C, additional exotherms near ~ 450 and ~ 525°C, and endotherms in the ~ 150–350°C region. The complex degradation characteristics of HPAM revealed by this study indicate some of the complications regarding TG analysis of HPAM composition by the method of Dassanayake and Phillips.

Thermal degradation of HPAM

The degradation characteristics of pre-dried PAM and PNaA differ significantly in nitrogen versus air (Fig. 8). For example, in nitrogen atmo-

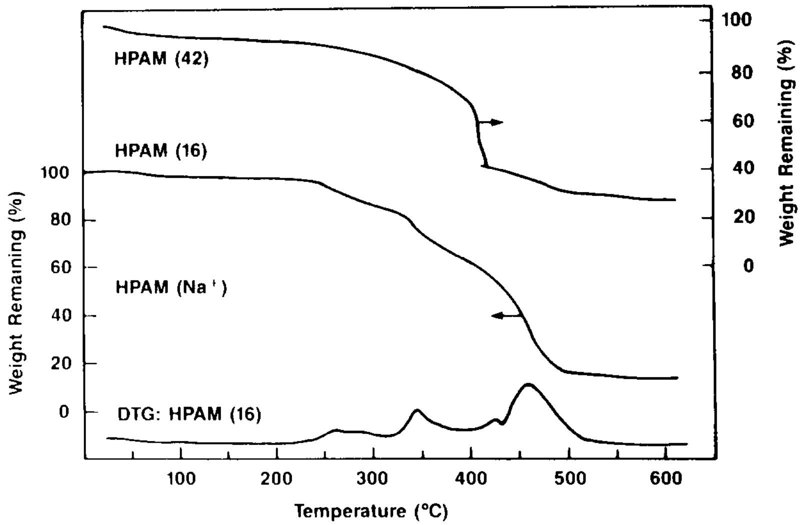

Fig. 5. Influence of HPAM composition on degradation characteristics (air atmosphere). Numbers in parentheses indicate mol% hydrolysis.

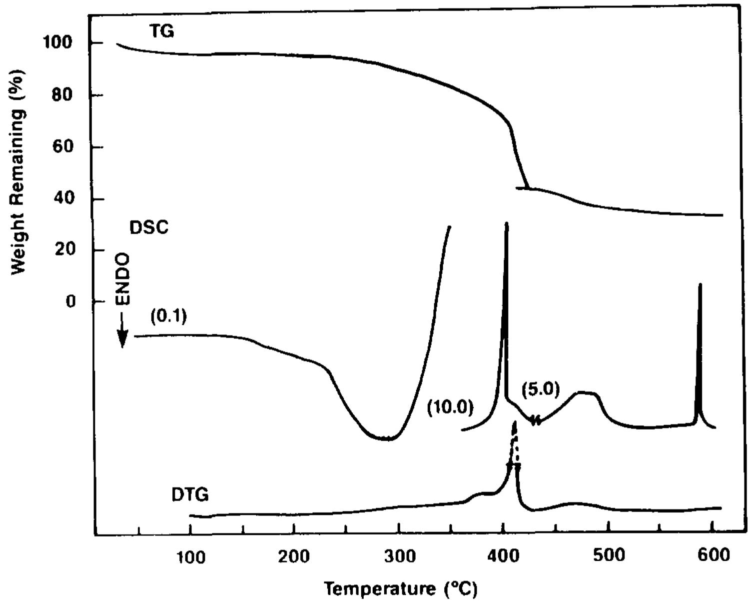

Fig. 6. TG, DSC and DTG analysis of HPAM (42 mol% hydrolysis) degradation in air atmosphere. Numbers in parentheses indicate DSC sensitivity (mcal s^{-1} in.).

sphere PNaA does not exhibit an exothermic region, and there is a much larger weight loss difference between PAM and PNaA in the ~ 450–500°C region versus that observed in air. The latter feature suggested that TG

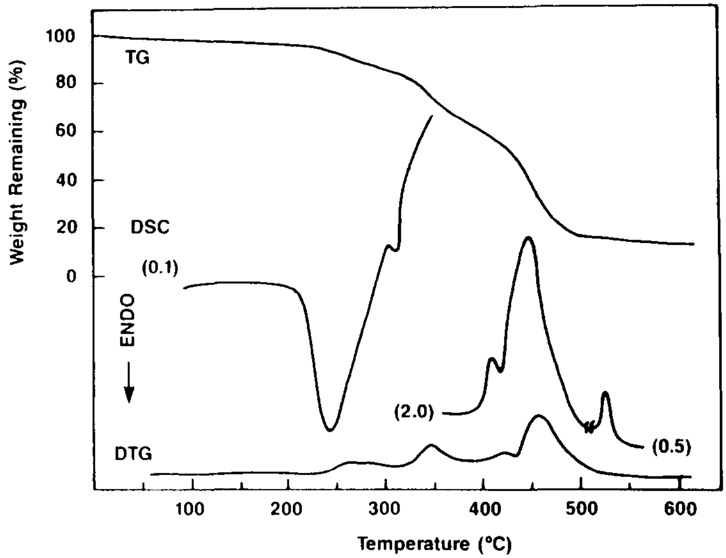

Fig. 7. TG, DSC and DTG analysis of HPAM (16 mol% hydrolysis) degradation in air atmosphere. Numbers in parentheses indicate DSC sensitivity (mcal s^{-1} in.).

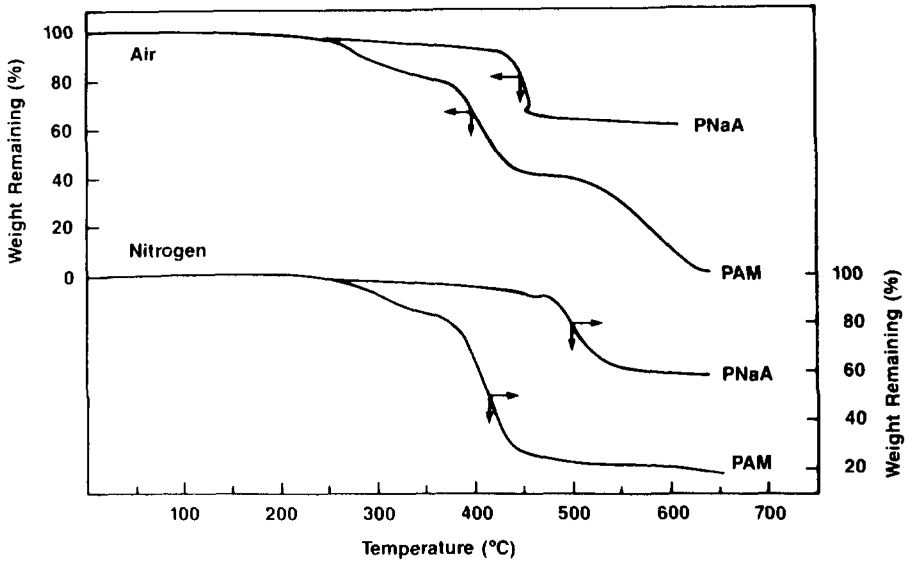

Fig. 8. Influence of atmosphere on degradation characteristics of PAM vs PNaA.

analysis of HPAM composition could be improved if conducted in nitrogen. This has been verified as shown in Fig. 9. One of the interesting features of these data is that the weight loss in the 200–325°C region varies with HPAM composition. Weight loss in this region has been attributed to ammonia evolution accompanying imide formation [8]. Compositional analysis based on this feature of the thermogram does not appear attractive,

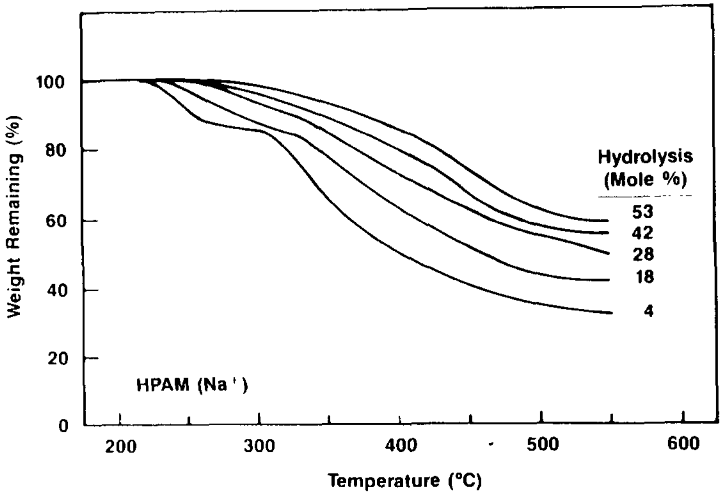

Fig. 9. Influence of HPAM composition on degradation characteristics in nitrogen atmosphere.

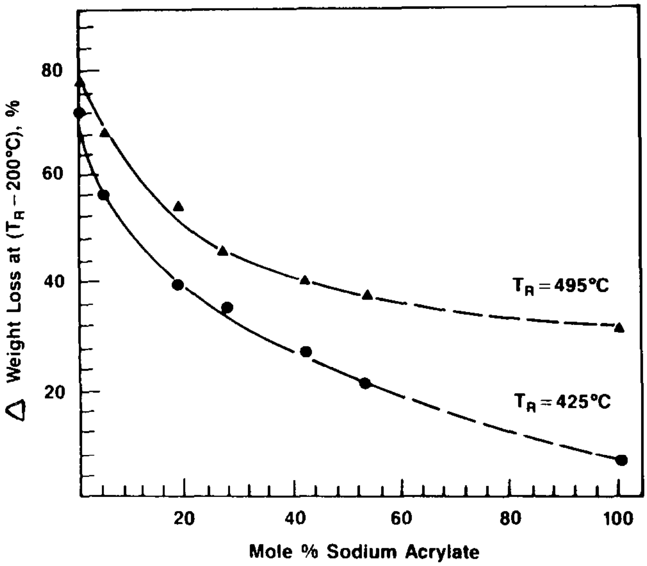

Fig. 10. Correlation of HPAM composition versus weight loss characteristics during degradation in nitrogen atmosphere. T_R = reference temperature at which total weight loss was evaluated. Weight loss at 200° C was subtracted from that at T_R to correct for volatiles in the orignal HPAM.

however, due to the limited resolution observed for samples of higher degrees of hydrolysis. However, these data suggest that improved TG analysis of HPAM composition can be achieved based on the total weight loss at 495 or 425°C, minus that at 200°C (Fig. 10). This subtraction procedure is intended to correct for the water content of non-dried samples. Thus TG analysis of HPAM composition via degradation in nitrogen appears to overcome several of the problems noted earlier regarding the oxidative degradation method of Dassanayake and Phillips. It should be noted, however, that errors could still be introduced if extraneous salts are present in the polymer.

Comprehensive thermal analysis of HPAM degradation

Elucidation of the complex degradation characteristics of these polymers is beyond the scope of this investigation. However, the utility of DSC and TG–MS techniques for conducting such studies will be illustrated for HPAM (4). The influence of polymer composition (acid versus salt form) and of atmosphere on the degradation of this polymer is shown by the DSC thermograms between about 200 and 375°C in Fig. 11. The nature and intensity of these degradation endotherms is clearly influenced by both these variables. For the present purpose, however, we shall focus on the acid form of the polymer, and the degradation region up to about 325°C. In particular

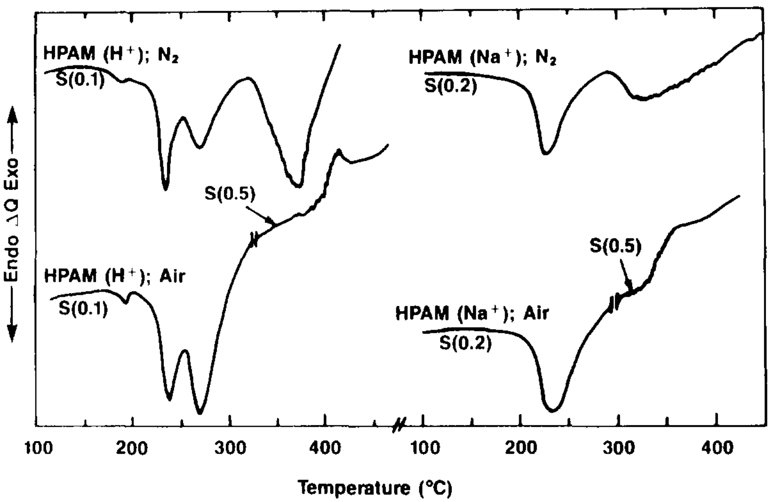

Fig. 11. DSC degradation characteristics of HPAM (4 mol% hydrolysis) in acid versus sodium salt form. Air versus nitrogen atmosphere. Numbers in parentheses indicate sensitivity (mcal s^{-1} in.)

the discussion will be concerned with the multiple endotherms which are evident in both nitrogen and air and hence do not appear to involve oxidative processes.

Based on the reported degradation characteristics of PAM and PAA (1–4), it was considered that the endotherms in Fig. 11 might involve water, ammonia and/or CO_2 evolution. In order to examine this possibility, an experiment was conducted in which the sample was heated in a Mettler 2000C TG system and the volatiles were carried by a stream of helium to a U.T.I. Model 100 mass spectrometer. The results from this TG–MS analysis are shown in Fig. 12. The dashed lines shown in Fig. 12 are the results from similar experiments in which no polymer was present.

Both the DSC and TG–MS results indicate that multiple processes occur in the region from about 200 to 400 °C during the thermal degradation of the acid form of HPAM (4). It is not possible from these DSC and TG–MS data alone to deduce the nature of the multiple events taking place during the indicated thermal treatment of this polymer. However, some reasonable, although speculative, possibilities will be suggested to illustrate the utility of DSC and TG–MS studies in guiding research to establish the processes operable. The most prominent feature of Fig. 12 is the set of three water peaks. One occurs near 350 °C in the same region as the CO_2 maximum, and may be associated with degradation of acrylamide units in the HPAM main chain. Possible sources of the other two water peaks include (a) strongly bound water, for the peak at ~ 240 °C and possibly also the one at ~ 280 °C; and/or (b) degradation of the acid, for the intermediate peak at ~ 280 °C.

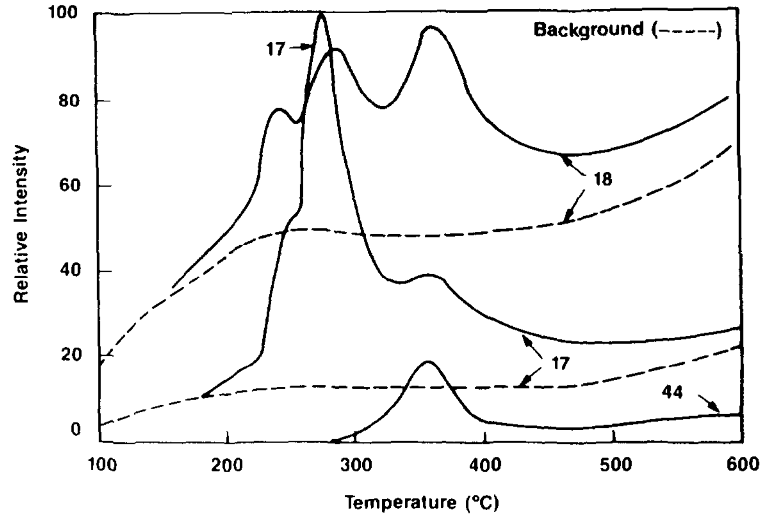

Fig. 12. Evolved gases (mass 18, 17 and 44) from TG–MS analysis of AM-co-AA (4 mol% acrylic acid). Dashed line represents background data from blank runs in which no polymer was present.

Another interesting feature of Fig. 12, is the nature of the curve for mass 17. This curve could contain contributions from both ammonia and water. The shoulder on the mass 17 curve near ~ 240°C is interesting since it is considered too intense to result solely from water fragmentation [9]. This suggests that there are two degradation processes resulting in NH_3 formation. The stronger one, near ~ 275°C, is considered to arise from imide formation; the weaker one, near ~ 240°C, may indicate hydrolysis of acrylamide units and thus involve the water present in the polymer and acid catalysis by the carboxyl groups.

SUMMARY AND CONCLUSIONS

It has been shown that both the thermal and oxidative degradation of HPAM are complex processes. This complexity appears to limit determination of HPAM composition via TG analysis of the oxidative degradation of these polymers. DSC and TG studies, however, indicated that degradation in an inert atmosphere should provide an improved basis for such an analysis. This was successfully demonstrated for a series of HPAMs of known composition.

The nature of the complex HPAM degradation characteristics was probed via combined DSC, TG and TG–MS analyses of selected polymer compositions. Evidence of multiple water and ammonia evolution processes was detected and possible mechanisms were suggested. This limited study illustrates a comprehensive thermal analysis approach for elucidating the degradation characteristics of AM-co-AA and HPAM.

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