

Pyrolysis-Evolved Gas-Infrared Spectroscopic Characterization of Poly(methyl methacrylate) Copolymer Glazing Materials

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Synopsis

The linear temperature programmed pyrolysis of some commercial crosslinked poly(methyl methacrylate) copolymers has been examined by the technique of pyrolysis-evolved gas-infrared analysis. Methyl methacrylate monomer, methanol, and carbon dioxide were detected in the pyrolysis gases. The profiles of rate of evolution against temperature were used to identify the presence of occluded monomer and thermally unstable end groups such as unsaturation. The evolution profiles for methyl methacrylate and methanol were found to be characteristic for each type of crosslink. Evolution of methanol between 250°C and 300°C, and between 300°C and 350°C has been attributed to condensation reactions of carboxylic acid and primary amide groups, respectively, with adjacent ester groups. The evolution profiles were used to distinguish between samples from different manufacturers, and to identify material in aircraft canopies.

INTRODUCTION

Pyrolysis-evolved gas-infrared analysis (py-EGA-IR) has applications in qualitative and quantitative analysis and thermal degradation studies.¹⁻³ We have recently demonstrated its possibilities for polymer characterization using a dispersive spectrometer.⁴ The technique is similar to the thermal volatilization analysis (TVA) of McNeill,⁵ in that the gases evolved from a heated sample are monitored continuously, and an evolution profile of a suitable parameter is constructed in terms of time or temperature. In py-EGA-IR, the sample is heated in a stream of gas (inert or reactive) and eluant is monitored by infrared spectroscopy as the gas passes through a suitable cell. Spectra of the evolved gases are recorded continuously, so that components may be identified and their concentration determined as they are evolved. The evolution profile is of absorbance against time or temperature, and the areas under the profiles are a quantitative measure of each component. Under controlled conditions, the profiles are reproducible, and can be used for sample identification and comparison purposes.

Copolymers of poly(methyl methacrylate) (PMMA) are widely used as glazing materials. The commercial "homopolymer" usually contains a small amount of comonomer such as methyl acrylate which is included to reduce the number of thermally unstable end groups and to act as a block to thermally or photochemically induced depropagation. Comonomers which can form crosslinks confer increased toughness and solvent resistance on the copolymer.

These materials may craze and crack in service, and it useful to be able to identify the general type of comonomer to assist in studies of crazing susceptibility, and to distinguish between different samples of the same material type. Our earlier work on py-EGA-IR⁴ suggested that it could be a useful method for characterization of PMMA copolymers, particularly as only small amounts may be available from field samples.

A range of commercial PMMA copolymers has been analysed by linear temperature programmed py-EGA-IR to determine whether the evolution profiles of various pyrolysis gases against temperature were sufficiently distinctive to allow reliable identification of different types, and to distinguish between different batches of the same type. The results show that, with one exception, the different types and batches can be reliably identified, and reactions to account for some of the compounds evolved have been presented. The potential value of py-EGA-IR analysis of PMMA polymers for both production control and research is demonstrated.

EXPERIMENTAL

Furnace

A 20 cm × 1.25 cm quartz tube (1 mm wall) was wound with nichrome tape (0.25 × 1.5 mm) with a total resistance of 7 ohms. The windings were encapsulated in a silicate cement and insulated with several layers of asbestos tape. This unit was then inserted into 3.75 cm diameter stainless steel tube and retained by heat-resistant discs at both ends. At 400°C in the central 5 cm zone, temperature variation was 2°C and the maximum temperature gradient was 1°C/cm.

Pyrolysis System

A pyrex tube, 5 mm id, 30 cm long, was used for pyrolysis. Samples (4-5 mg) were placed in aluminum pans as used for differential scanning calorimetry,

TABLE I

Sample	Comonomer ^a
Linear "homopolymers" A1, A2, A3 (Plex 201, Roehm GmbH)	—
Copolymer B1, B2 (P-76 Polycast)	—COOH, methacrylamide
Copolymer C1, C2 (S-350 Swedlow Inc.)	<i>N</i> -hydroxymethyl methacrylamide methacrylamide
Copolymer D1, D2, D3 (Plex 55, Rohm & Haas)	<i>N</i> -methoxymethyl methacrylamide
Copolymer E1, E2 (S-708 Swedlow Inc.)	2,2 dimethyl 1,3 propanediol dimethacrylate
Copolymer F1, F2 (Plex 249, Roehm GmbH)	2,4,6- <i>tris</i> (allyloxy) triazine

^aIdentified by solvent extraction, chemical and spectroscopic analysis.⁷

folded to fit inside the tube, and located centrally by 3 mm diameter pyrex glass rods of appropriate length either side of the sample pan. Teflon plugs with 1.5 mm diameter stainless steel inlet and outlet tubes conducted the dry nitrogen carrier gas (50 mL/min) through the system to the gas cell. A temperature ramp of 5° min from ambient to 500°C was used for all analyses. A chromel-alumel control thermocouple was placed between the pyrolysis tube and the wall of the furnace, adjacent to the sample.

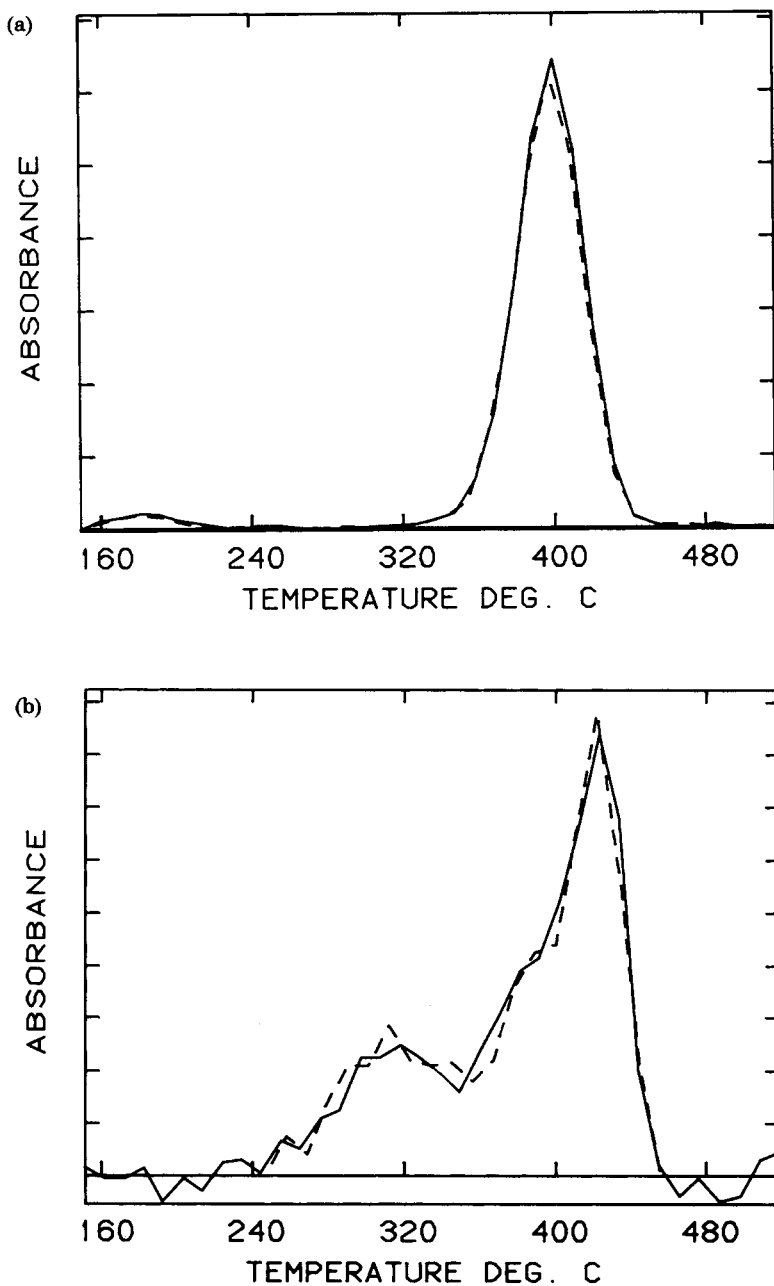


Fig. 1. (a) Methyl methacrylate evolution from type C copolymer, duplicate analyses, 1310 cm^{-1} . (b) Methanol evolution from type C copolymer, duplicate analysis, 1050 cm^{-1} .

Spectroscopy

A Specac multipass gas cell (5974) was used in a Perkin Elmer 580B infrared spectrometer which was purged with dry, CO₂ free air. Spectra were recorded continuously in SURVEY mode, corrected for empty cell background and stored on disk.

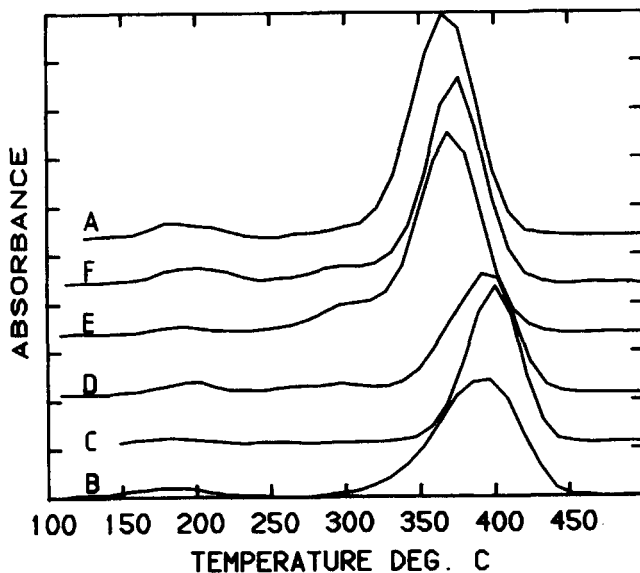


Fig. 2. Methyl methacrylate evolution from PMMA copolymers; letters refer to Table I. 1310 cm⁻¹. Displaced vertically for clarity.

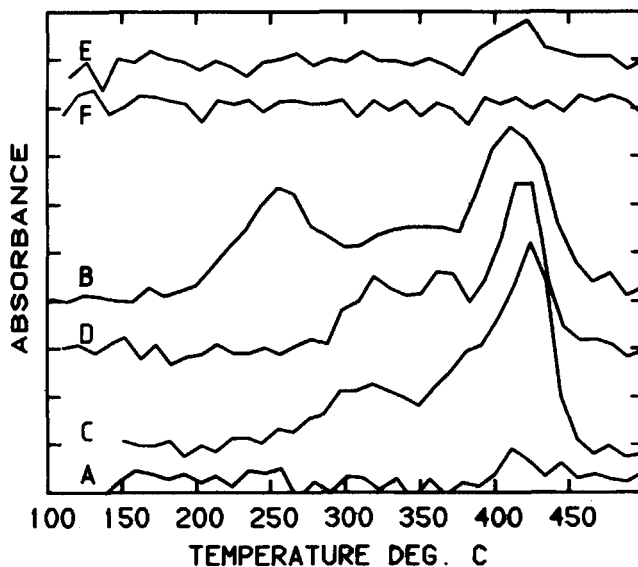


Fig. 3. Methanol evolution from PMMA copolymers; letters refer to Table I. Displaced vertically for clarity. 1050 cm⁻¹.

Evolution profiles were constructed as plots of net absorbance against temperature for selected absorption bands which were known to be free from interferences. Procedures used for data reduction and calculation of temperatures appropriate to absorption bands of interest were as described previously,⁴ except that absorbances were normalized to 10 mg sample mass to allow direct comparison of profiles.

Materials

The PMMA copolymers were commercial materials, used as received, and are listed in Table I. Homopolymers of PMMA with a high proportion of either saturated or unsaturated end groups⁶ were examined under the same conditions as the copolymers.

RESULTS

Evolution profiles for methyl methacrylate monomer (MMA) were of similar form for all samples, consisting of a major evolution event and several minor events. The peak rate temperatures represented by the temperature at maximum absorbance and major event profiles were characteristic for each material, though some batch variation was observed. All samples except F1 and F2 yielded carbon dioxide, usually as a single event near 400°C, and methanol in one or more events between 250 and 450°C. Duplicate determinations showed that the profiles were superimposable within 1°C as shown in Figures 1(a) and 1(b) for MMA and methanol for one sample. MMA profiles are shown in Figure 2, methanol in Figure 3, and carbon dioxide in Figure 4. Samples B, C, and D yielded small amounts of complex carbonyl compounds at high temperatures, usually starting at about the peak rate temperature.

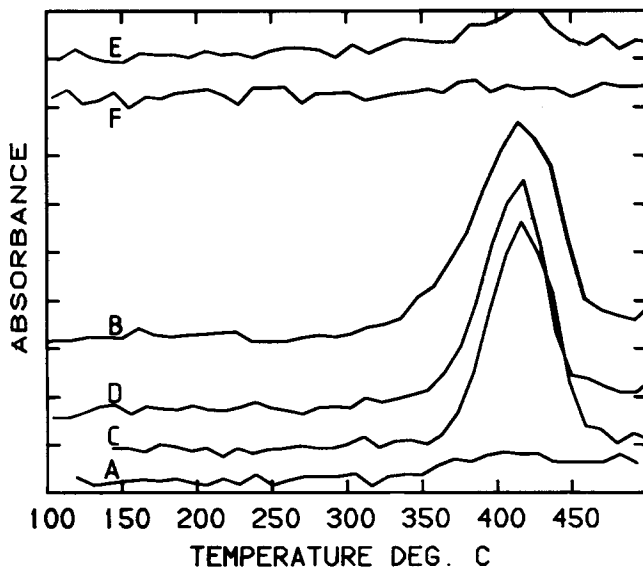


Fig. 4. Carbon dioxide evolution from PMMA copolymers; letters refer to Table I. Displaced vertically for clarity.

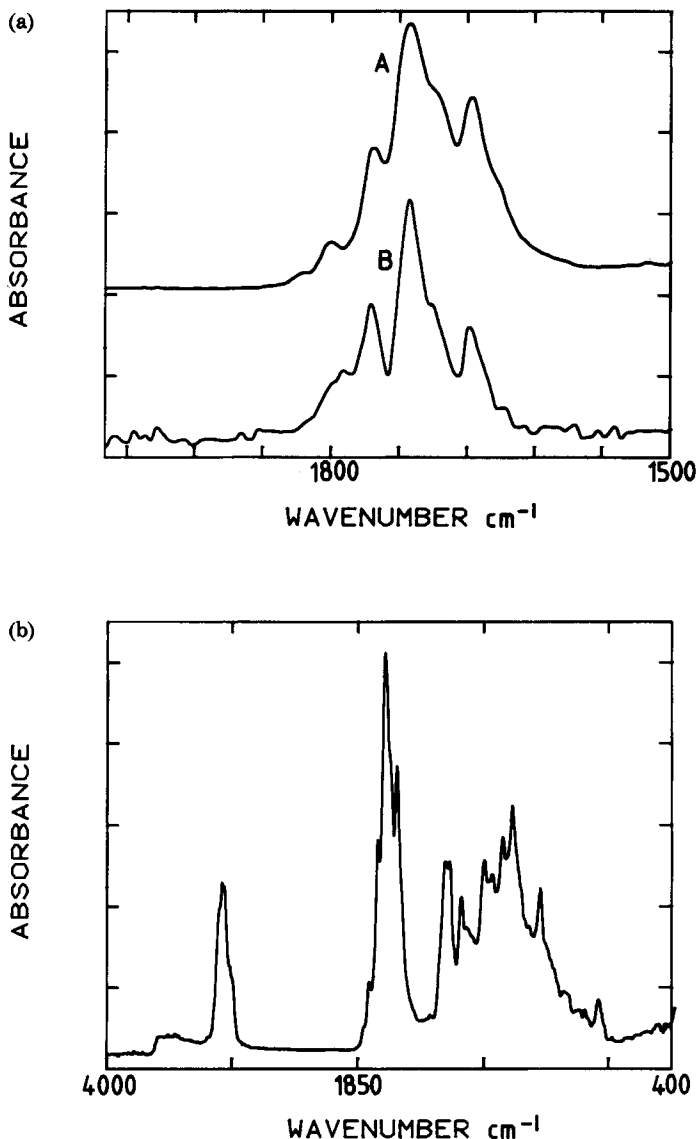


Fig. 5. (a) Type D copolymer A. liquid pyrolyzate; B. aerosol at 430°C, corrected for MMA carbonyl. (b) Type D copolymer, liquid pyrolyzate.

The carbonyl region spectra of these compounds were enhanced by subtracting out that of MMA. Liquid condensates also collected in the cooler parts of the pyrolysis tube. Representative spectra are shown in Figure 5(a) and 5(b). Further examination of the spectra suggested that a second component was present with MMA evolved below 200°C in samples C1 and C2. Subtraction of MMA carbonyl bands in the 1600–1800 cm^{-1} range revealed the characteristic spectrum of formaldehyde. The evolution profile was similar to that previously observed for occluded methanol.⁴

DISCUSSION

Discrimination Between Samples

Peak rate temperatures and evolution profile shapes were characteristic for each copolymer type, and the best means of discrimination between samples is superimposition of evolution profiles, most conveniently done in real time on a video monitor. The irregular spacing and small number of points in each profile makes mathematical comparison unreliable. For complete assurance profiles for MMA, methanol, and carbon dioxide should be compared. Discrimination between the different copolymer types was generally achieved, but between different samples of the same type sometimes required care, especially the commercial linear A1–A3 polymers from one manufacturer. Although the peak rate temperatures for different samples of the same copolymer types agreed within 1–2°C, the MMA peak rate temperatures of samples E1 and E2 differed by about 10°C and it was not possible to distinguish between E2 and the linear (type A) polymers since the CO₂ and methanol profiles were also similar. This result is not unexpected, since the comonomers are so similar. These two types are readily distinguished by their solubility in dichloromethane; the linear polymer dissolves, the crosslinked material does not. Discrimination of the carbon dioxide and methanol profiles of A, E, and F is somewhat limited by signal/noise ratio (S/N).

The samples may be divided into two groups, those for which the MMA event peaked near 400°C, and which had significant methanol and carbon dioxide profiles (B, C, D) and those for which the MMA event peaked near 370°C, and which yielded only traces of methanol and carbon dioxide (A, E, F). The former group contains those materials in which the crosslink is formed in a secondary condensation reaction, usually between two copolymer chains. In the latter group, crosslinks are formed in the addition polymerization process by incorporation of polyfunctional vinyl compounds.

The technique has been tested on a series of unmarked samples, some common to those in Table I, and some not. Positive identification was made in all cases. Material used in several aircraft canopies has also been satisfactorily identified.

Interpretation of the Evolution Profiles

Methyl Methacrylate

The peak rate temperatures for unsaturated end group materials of number average molecular weight (*M_n*) of 1500, 5000, and 10,000 were 276°C, 286°C, and 291°C, respectively. For saturated material with *M_n* of 5000 and 10,000 peak temperatures were 399°C and 397°C. These profiles were quite reproducible, and the differences must therefore be regarded as significant. Some consideration of the reason for these results is relevant because the average molecular weight (*M_w*) between crosslinks has been determined for some commercial copolymers⁷ as being in the range 1000–20,000. If the peak rate temperature is sensitive to *M_w*, then that relationship could be useful for material characterization, since crosslink density may affect resistance to crazing and cracking.

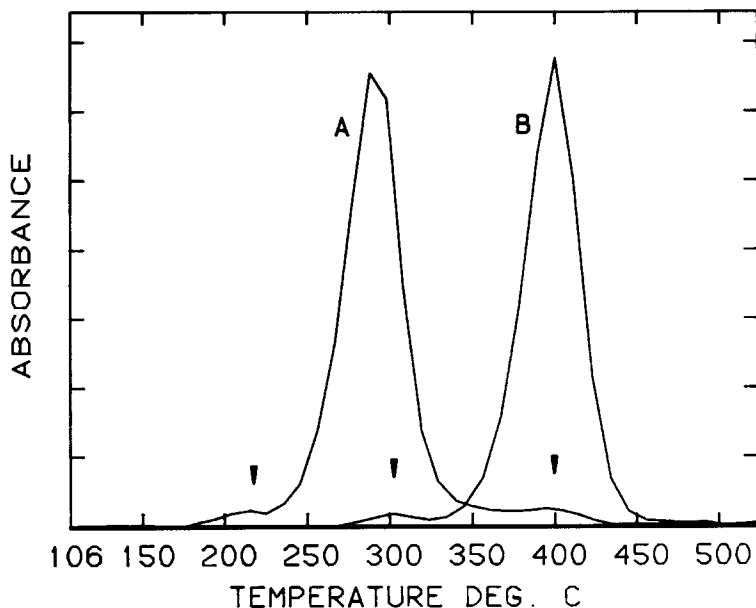


Fig. 6. Methyl methacrylate evolution from model compounds, PMMA, $M_n = 10,000$. A. Unsaturated end groups; B. saturated end groups. Presence of minor components indicated by arrows.

The lower decomposition temperature for the unsaturated polymer is consistent with end group initiation of depropagation,⁶ rather than chain scission. The relationship between M_n and peak rate temperature for the unsaturated polymer suggests that the initiation rate is the dominant factor in MMA evolution at relatively low MWs. At higher MWs the effect is likely to diminish and the peak rate temperature may plateau. For the saturated end group polymer, the results are consistent with chain scission as the initiation of depropagation, since the rate of monomer evolution would then depend only on chain length. Any contribution made by end group initiation is likely to be small because of the low concentration of end groups compared with in chain bonds, despite the probability of similar thermal stability (Fig. 6).

These results and interpretations are consistent with those of McNeill,⁸ who found from TVA of PMMA polymers that the peak temperature of the event near 300°C, associated with unsaturated end groups increased with initial MW; that of the higher temperature event decreased with initial MW, consistent with chain scission initiation of depropagation. McNeill's results indicated a tendency to levelling off in both events at high initial MW ($> 10^6$). Thus, for degradations in which only one initiation process occurred, the peak rate temperature was related to MW.

In order to interpret the MMA evolution profiles of the copolymers, it is first necessary to establish the range of effective MW of the PMMA chains. This will depend on the MW of the copolymer, the comonomer content, and whether the comonomer molecule blocks, passes, or initiates depropagation. McNeill⁸ showed that incorporation of initiation sites in the polymer chain shifts the peak rate temperature well below that of the pure polymer. He used a phenyl acetylene/MMA copolymer, but any group thermally less stable

than the chain C—C bonds would have a similar effect. The reverse effect, of a shift to higher temperatures caused by shorter zip lengths at higher comonomer levels, may also be significant, since copolymer E was found to have an average MW between crosslinks of 3000.⁷ The actual peak rate temperature may then be the balance between higher zip length and comonomer initiation tending to lower temperatures, and shorter zip lengths tending to higher temperatures. Any correlation between peak rate temperature and comonomer content will thus be specific to each type of copolymer, and not of general use.

Evolution profiles for the three amide type copolymers B, C, D peak at 392, 399, and 395°, respectively. These high temperatures are consistent with zip lengths below 200 which is of the same order as the average MW between crosslinks.⁷ The relatively large amounts of liquid pyrolysate and low monomer yield indicate that the comonomer effectively blocks depropagation and does not itself initiate depropagation.

The remaining copolymers, A, E, and F have peak rate temperatures of 374, 374, and 370°C, respectively. Such low temperatures require explanation in terms of high MW or in-chain initiation by comonomer molecules. Assuming that A is an acrylate/methacrylate copolymer, then according to Grassie and Torrance,⁹ as many as 1 in 4 of the acrylate molecules may pass the depropagation along the chain. This alone does not seem enough to account for the low peak rate temperature. The mechanism proposed by Grassie and Torrance¹⁰ to account for the production of carbon dioxide (see later) from acrylate/methacrylate copolymers yields a radical and unsaturated chain end, both of which can initiate depropagation. The net result is two zip lengths depropagating compared with effectively only one from random chain scission. Even this may not be enough to account for the low temperature, and the overriding factor may still be MW. McNeill⁸ found that the peak rate temperature of an 8/1 methacrylate/acrylate copolymer was only 8°C above that of the pure polymer of comparable MW (~ 500,000) and the profiles were very similar above 300°C. At 8/1 copolymer ratio, the effective zip length should be about 10, if most of the acrylate molecules act as blocks to depropagation, but by comparison with peak rate temperatures of pure PMMA,⁸ the equivalent zip length of the 8/1 copolymer should be closer to 1000. However, Grassie and Torrance¹⁰ found a zip length of 74 for a 7.7/1 copolymer, and concluded that both random chain scission and scission at acrylate groups occur during degradation. For acrylate/methacrylate copolymers then, peak rate temperature alone is not a reliable guide to MW or zip length.

Similar arguments may apply to the copolymer F with *tris*(allyloxy)triazine, since this material would have a tertiary hydrogen atom available for abstraction. That no carbon dioxide was detected in the pyrolysis of this material may be attributed to its very low comonomer content of less than 0.1%,⁷ so that any carbon dioxide (or methanol) evolved would be below our detection limit. In this case, the peak rate temperature may be an indication of high MW. McNeill⁸ found that ethyl methacrylate comonomer had no significant effect on the depropagation of the copolymer, and behaved as an MMA group. The dimethacrylate comonomer in copolymer E can also be expected to behave like an MMA group, and should not hinder depropagation. The peak rate temperature of this material should be related to total MW

rather than MW between comonomer groups. Thus, the 10°C difference in peak rate temperature between E1 and E2 may be directly attributed to MW, and by comparison with McNeill's⁸ results, MWs of about 350,000 and 1,000,000 are indicated.

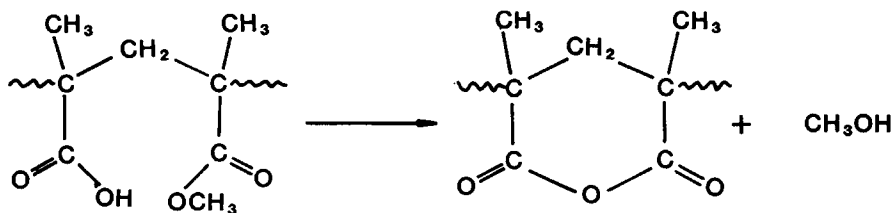
In many samples, MMA is evolved below 200°C, and this may be attributed to occluded material. Head-head links are probably responsible for MMA evolved between 200°C and 250°C.⁶

Methanol and Carbon Dioxide

All samples except F evolved methanol and carbon dioxide during pyrolysis. For types A and E, the levels were so low as to approach the S/N limit for the data and confirmation by examination of the spectra was necessary. A very small amount of carbon dioxide was evolved roughly concurrently with the MMA evolution profile, and a better defined event occurred at about 420°C. The former is possibly the result of scission at the comonomer molecule, as suggested by Grassie and Torrance¹⁰ for methyl acrylate, in which hydrogen abstraction from a methyl acrylate unit is followed by dissociation into carbon dioxide, an unsaturated group and a radical which then liberates MMA and chain fragments. For the 2,2-dimethyl 1,3 propanediol dimethacrylate comonomer, hydrogen transfer from the methylene groups in the chain or crosslinks may cause scission into carbon dioxide, an unsaturated group and an active radical,¹⁰ though this reaction does not appear to occur to any extent in the PMMA model polymer with saturated end groups. It is quite possible that the type F copolymer contains a small amount of acrylate or similar material which would account for the carbon dioxide and methanol.

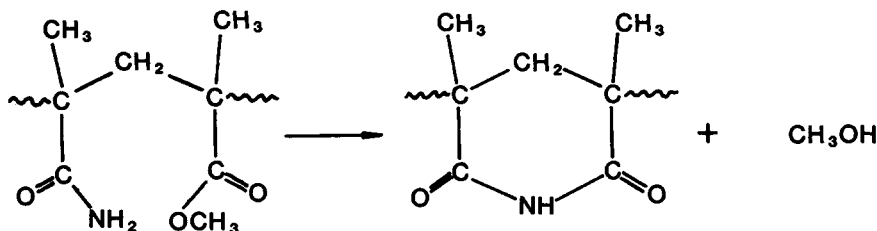
In both cases the effect is very small since the amount of carbon dioxide evolved is < 0.05% of the polymer, and this itself may be indicative of the level of acrylate, assuming methyl acrylate comonomer, based on the work of Grassie and Torrance.⁹ The higher temperature event peaks well above the MMA peak rate and is considered to arise from ultimate decomposition of fragments of residual copolymer. The very small amount of methanol peaks at about 415°C, and may come from MMA adjacent to the comonomer molecules. This pattern of methanol and carbon dioxide evolution may be characteristic of ester comonomers. Neither methanol nor carbon dioxide were detected in the pyrolysis gases from the model compound with saturated end groups, even above 400°C. Thus there would be negligible contributions to the methanol and carbon dioxide profiles of the samples from decomposition of MMA as suggested by Grassie and Torrance.¹⁰

The larger amounts of methanol and carbon dioxide from samples B, C and D are more readily explained. Only B yields methanol below 300°C, with a

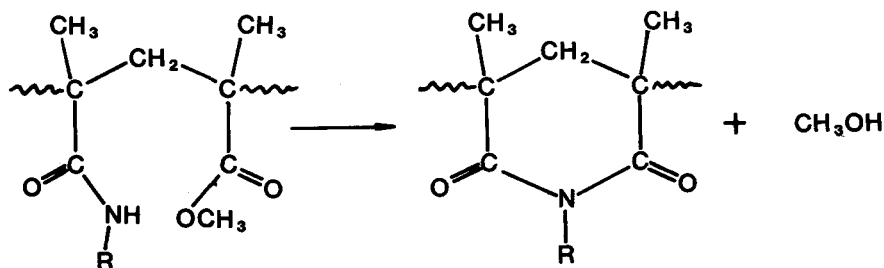


peak rate near 260°C. Since this copolymer is known to contain carboxylic acid groups, a likely source of methanol is condensation with an adjacent ester group, as suggested by Jamieson and McNeill.¹¹

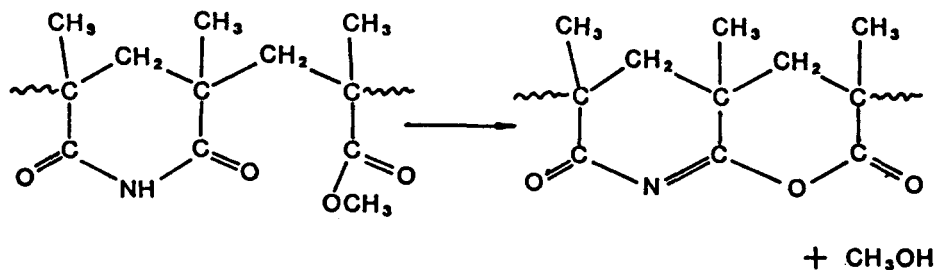
Methanol evolution between 300° and 350°C may be ascribed to a condensation reaction between primary amide and adjacent ester, to yield an imide and methanol.¹²



Samples C and D both have a well defined event in this temperature range, suggesting that D contains primary amide as well as C. Sample B yields methanol between 300° and 350°C, but the event is minor and poorly defined. Above 350°C, all three samples yield methanol, with a peak rate near 415°C. Samples C and D have smaller evolution events peaking at 385°C and 365°C respectively. Further condensation reactions may be responsible for this methanol. The major event may be a combination of a secondary amide/ester reaction, especially in crosslinks:



and further reaction of imides, through a keto-enol type rearrangement.¹¹



The two minor events appear to be specific to the crosslink systems in these two copolymers. It does not seem likely that either of them is associated with

a secondary amide/ester reaction involving the residual secondary amide not involved in crosslinks, since their reactivity should be similar to that of secondary amides in crosslinks. One possible reaction is between hydroxyl and ester;



No evidence of dimethyl ether from the analogous methoxymethyl/ester reaction was observed. Above 400°C, small amounts of carbon monoxide were detected. The single, broad carbon dioxide event in each sample peaked near 420°C. The source of these components is likely to be ultimate decomposition of comonomer fragments, particularly the imides and anhydrides formed in condensation reactions. The presence of such compounds is supported by the spectra of aerosol material swept into the cell above 400°C, [Fig 5(a)] and the liquid condensates [Fig. 5(b)]. Both spectra contain carbonyl bands associated with imides and anhydrides (1,800–1,700 cm^{-1}) and amides (1,675 cm^{-1}).

Formaldehyde

Formaldehyde was detected only in the pyrolysis gases from sample C. As the evolution profile was consistent with that of an occluded material, rather than the result of a reaction, it may be present in the polymer as paraformaldehyde, and its reaction with methacrylamide is responsible for the presence of *N*-hydroxymethyl methacrylamide.

Quantitative Aspects

On the basis that the area under the evolution profile is proportional to the total concentration of component in the gas stream, the reproducibility of the technique as described here and elsewhere^{2,3} is good enough to consider its use for quantitative analysis. The potential of the present equipment is limited by the uncertain evolution profile shape and the low degree of separation of events, caused partly by the cell residence time, so that curve resolving techniques cannot be generally applied to determine the true profile of each event. A second limitation is that of S/N ratio and mainly affects the methanol and carbon dioxide profiles.

Minor components such as occluded material and thermally unstable end groups can be readily estimated by using a more sensitive absorption band, such as that near 1700 cm^{-1} . The area under the curve yields the total polymer associated with such groups, and the peak rate temperature may be related to zip length as indicated earlier so that the number of thermally unstable groups can be estimated.

It could be argued that the comonomer content of the copolymer will be reflected in the yield of MMA from the decomposition event. Thus, two samples of type B copolymer yielded 439 and 732 area units of monomer, respectively. Although the lower yield sample may be more highly crosslinked than the other, the lower yield of MMA is only an indication of more

comonomer, not crosslinks, since not all comonomer sites are necessarily crosslinked. The production of high MW liquid pyrolyzates which clearly contain PMMA residues suggests that the pyrolysis conditions are not optimum for the production of MMA, so that comparison by this means, though reproducible, can only be qualitative. Methanol and carbon dioxide profiles are only useful for the amide type copolymers, since the S/N is too low for reliable results from the vinyl type comonomers. The similarity in shape for the carbon dioxide profiles and the obvious association with the ultimate decomposition of the sample suggests a possible connection with total copolymer content. For the type B samples referred to above, there was only 3% difference in the total area of the carbon dioxide profiles. Comparison of MMA and carbon dioxide yields for the three types of amide copolymer system indicates that the correlation, if any, is negative. Carbon dioxide yields are very similar for range of samples and it may be that the yield is limited by the experimental conditions, i.e. residence time in the hot zone.

The methanol profiles are more promising. Events peaking near 260°C and 320°C give a reasonable estimation of free carboxylic acid¹¹ and primary amide,¹² even at the low S/N of the present system. The remaining events below 400°C are not well enough separated for quantitative work, and the final event does not appear to be correlated with monomer. Better resolution of the profiles with a small volume cell or light pipe, and more frequent sampling, as with FT-IR, might yield more useful results.

Detection of MMA originating from occluded material and from thermal weak links could find application in characterization of both homopolymers and copolymers. Py-EGA-IR could be used to distinguish between polymers of different MW, and made by different processes, in the same way that McNeill⁸ used TVA. The advantage of simultaneous identification and estimation of volatile components by IR may be balanced by the lower sensitivity and inability to detect infrared inactive species such as hydrogen compared with TVA. Changes in composition with degree of polymerization could thus be monitored; the efficiency of polymerization processes designed to yield specialty polymers such as the model polymers used in this study could be assessed; the progress and effectiveness of crosslinking processes using amide type systems could also be checked as, for example, in the determination of residual free acid or amide groups.

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References

1. S. A. Liebman, D. H. Ahlstrom, and P. R. Griffiths, *Appl. Spectrosc.*, **30**, 355-357 (1976).
2. J. O. Lephardt, *Appl. Spectrosc. Rev.*, **18**, 265-303 (1982-83).
3. J. O. Lephardt, in *Analytical Pyrolysis; Techniques and Applications*, edited by Kent J. Voorhees, Butterworth, London, 1984, pp. 95-120.
4. R. G. Davidson and G. I. Mathys, *Anal. Chem.*, **58**, 837-841 (1986).
5. I. C. McNeill, *J. Polym. Sci.*, Part A1, 2479-2485 (1966).
6. P. Cacioli, G. Moad, E. Rizzardo, A. K. Serelis, and D. H. Solomon, *Polym. Bull.*, **11**, 325-328 (1984).

7. P. J. Burchill, R. H. Stacewicz, and G. I. Mathys, *Polymer* 85, Int. Symp. Charact. and Anal. of Polym. Melb. Aust. 116 (1985).
8. I. C. McNeill, *Eur. Polym. J.*, 4, 21-30 (1968).
9. N. Grassie and B. J. D. Torrance, *J. Polym. Sci., Part A1*, 6, 3303-3314 (1968).
10. N. Grassie and B. J. D. Torrance, *J. Polym. Sci., Part A1*, 6, 3315-3326 (1968).
11. A. Jamieson and I. C. McNeill, *Eur. Polym. J.*, 10, 217-225 (1974).
12. N. Grassie, I. C. McNeill, and J. N. R. Samson, *Eur. Polym. J.*, 14, 931-937 (1978).

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