



# An investigation of the thermal stability and char-forming tendency of cross-linked poly(methyl methacrylate)

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The thermal degradation of two network copolymers of methyl methacrylate was studied as a function of the chemical nature of the cross-linking agent and the frequency of cross-links. Unlike the linear homopolymer, both the trimethylolpropane triacrylate and trimethylolpropane trimethacrylate networks were found to char when burned. The corresponding derivative thermograms indicate that there are dramatic differences in the thermal degradation of these polymers even in the absence of oxygen. These differences are interpreted in terms of a simple model for the kinetics of depolymerization.

## INTRODUCTION

Flammability is a major concern when polymeric materials are used in buildings, aircraft and ships.<sup>1</sup> This realization has provided the impetus for research into the synthesis of new and more fire-resistant polymers. An alternate, and perhaps a more practical, approach is to develop new treatments for reducing the flammability of existing polymers. This presents a formidable challenge since the increase in fire resistance must be achieved without sacrificing cost, intended use or environmental safety.

Research conducted in this laboratory has focused on finding ways to increase the tendency of plastics to char when they are burned. There is a strong correlation between char yield and fire resistance.<sup>2</sup> This follows because char is formed at the expense of combustible gases and because the presence of a char inhibits further flame spread by acting as a thermal barrier around the

unburnt material. The tendency of a polymer to char can be increased with chemical additives and/or by altering its molecular structure. The authors have identified factors which promote the formation of char in molecular dynamic simulations of degrading polymers. In particular, it was observed that cross-linked model polymers charred more readily than their linear counterparts.<sup>3</sup> This prediction was confirmed in experiments with both  $\gamma$  and high energy electron-beam-irradiated polyethylene (PE). Here, the authors extend this research to consider the thermal degradation behavior and flammability of chemically cross-linked poly(methyl methacrylate) (PMMA).

Under normal circumstances, linear PMMA depolymerizes to its constituent monomers and leaves little carbonaceous residue when it is burned. Wilke *et al.*, however, have demonstrated that certain transition metal compounds can induce char formation in PMMA.<sup>4</sup> The authors' computer calculations on model polymers indicated that the cross-linked polymer should also char. Unfortunately, this possibility was not examined in a previous investigation of

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the thermal degradation of cross-linked PMMA.<sup>5</sup> In the present paper, observations concerning the thermal degradation of two network copolymers of methyl methacrylate (MMA) are reported. Char residues and rates of weight loss were measured by thermogravimetry as functions of the chemical nature of the cross-linking agent and the frequency of cross-links. The thermograms and corresponding rate constants are interpreted on the basis of a simple model for the kinetics of depolymerization.

## EXPERIMENTAL

Linear PMMA was synthesized by free radical polymerization of MMA in the presence of 1.5% (relative to the weight of monomer) benzoyl peroxide (BPO) at 60°C. The number average molecular weight ( $M_n$ ) and polydispersity obtained from size exclusion chromatography (in THF) were  $2.9 \times 10^4$  and 3.9, respectively. The two cross-linked PMMA networks considered in this investigation were prepared in toluene (Mallincrodt Chemical Co.†) solution by free radical copolymerization of MMA with trimethylolpropane triacrylate (TTA) and trimethylolpropane trimethacrylate (TTM). The MMA (Aldrich Chemical CO.), TTA (Scientific Polymer Products) and TTM (Scientific Polymer Products) were passed through a column (DHR-4, Scientific Polymer Products) to remove the hydroquinone (used in Both TTA and TTM) and hydroquinone monomethyl ether (used in MMA) inhibitors. The corresponding homopolymers of TTA (PTTA) and TTM (PTTM) were synthesized by thermal initiation without BPO. Further details relating to the synthetic method are reported in Ref. 6.

The chemical structures of TTA and TTM are represented in Figs 1 and 2. Three cross-link densities of the TTA/MMA network copolymers were obtained by varying the relative amounts of the comonomers in the reaction mixture. Only two stoichiometries of the TTM/MMA network were examined. In all cases the actual cross-link densities were determined by solvent swelling in toluene and acetone using the technique

† Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure. Such identification does not imply that the material or equipment identified is necessarily the best available for the purpose.

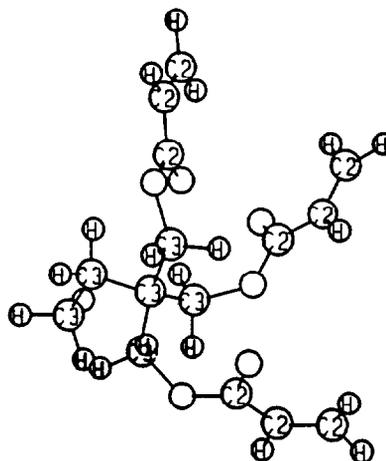


Fig. 1. The molecular structure of TTA. The labels H, C3 and C2 are used to indicate hydrogen, and  $sp^3$  and  $sp^2$  hybridized carbon atoms, respectively. The unlabeled circles represent oxygen atoms.

described in Refs 7 and 8. These data are presented in Table 1. Both cross-linking agents are trivalent so that the stoichiometric ratio of the number of MMA to TTA or TTM monomers is three times the average number of MMA monomers per cross-link ( $N_c$ ).

Thermogravimetric analyses (TGA) were performed in a nitrogen atmosphere using a Mettler TA 2000 thermoanalyzer. The cross-linked PMMA was prepared by grinding the glass into a powder with an average particle size of about 20  $\mu\text{m}$ . In the case of linear PMMA, the samples were a film with a maximum thickness of

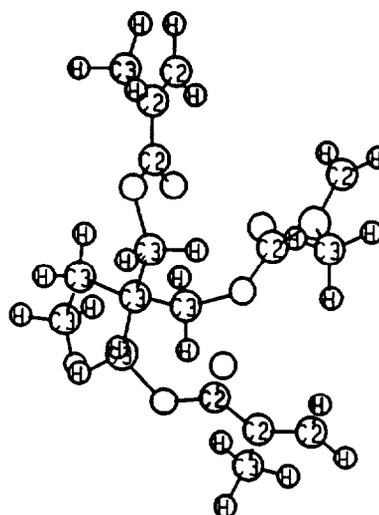


Fig. 2. The molecular structure of TTM. The labels H, C3 and C2 are used to indicate hydrogen, and  $sp^3$  and  $sp^2$  hybridized carbon atoms, respectively. The unlabeled circles represent oxygen atoms.

**Table 1. Characterization of cross-linked PMMA by solvent swelling**

Theoretical stoichiometry (TTA or TTM:MMA)	Solvent	Average molecular weight between cross-links (g)	Actual stoichiometry (TTA or TTM:MMA)	$N_c$
<i>TTA copolymers</i>				
1:120	Acetone	3 266	1:98	33
1:120	Acetone	3 131	1:94	31
1:120	Toluene	3 228	1:97	32
AVG		3 208	1:96	32
1:300	Acetone	5 630	1:169	56
1:300	Toluene	6 595	1:198	66
1:300	Toluene	6 246	1:187	62
AVG		6 157	1:185	62
1:60	Acetone	2 497	1:75	25
1:60	Toluene	2 643	1:79	26
1:60	Toluene	2 614	1:78	26
AVG		2 585	1:77	26
<i>TTM copolymers</i>				
1:120	Acetone	5 037	1:151	50
1:60	Acetone	811	1:24	8

approximately 20  $\mu\text{m}$ . Samples ranged from 3 to 5 mg in weight. The dynamic TGAs were performed at a slow heating rate (2°C/min) to minimize the effects of thermal conduction and mass transport of the degradation products on the measured weight losses. Global rate constants were obtained from isothermal measurements and are listed in Table 2. In this application, the samples were heated rapidly at a rate of  $\approx 50^\circ\text{C}/\text{min}$  until they reached a specified temperature. This temperature was maintained to within  $\pm 0.5^\circ\text{C}$  while the weight loss data were collected. The corresponding pre-exponential factors and activation energies (Table 3) were evaluated from the intercepts and slopes of Arrhenius plots of the tabulated rate constants.

Infrared analyses of the gases evolved during the thermal degradation of the linear and cross-linked PMMA were performed using a cell and programmable pyrolyzer manufactured by Chemical Data Systems Instruments. Samples

**Table 3. Arrhenius constants**

Polymer	$E_a$	$A$
PMMA	168 kJ/mol	$3.7 \times 10^{11} \text{ s}^{-1}$
(1:24) TTM/MMA	146 kJ/mol	$4.7 \times 10^9 \text{ s}^{-1}$
(1:185) TTA/MMA	208 kJ/mol	$4.8 \times 10^{14} \text{ s}^{-1}$
(1:77) TTA/MMA	61 kJ/mol	$3.6 \times 10^1 \text{ s}^{-1}$

were placed in a quartz tube which was surrounded by a resistance heating element. This assembly was inserted into an IR cell which was heated to approximately 50°C to prevent tars, that formed in the thermal degradation of the cross-linked polymers, from condensing on the KBr windows. The level of atmospheric oxygen was minimized by purging the cell with  $\text{N}_2$ . The pyrolyzer was set at the maximum attainable rate (advertised as 20 000°C/s), thereby heating the samples to the final temperature of 500°C almost instantaneously. The spectra were measured after 15 min at this temperature on a Mattson Sirius

**Table 2. Rate constants**

Polymer	Temperature		
	350°C	370°C	390°C
PMMA	$2.91 \times 10^{-3} \text{ s}^{-1}$	$7.43 \times 10^{-3} \text{ s}^{-1}$	$2.08 \times 10^{-2} \text{ s}^{-1}$
(1:24) TTM/MMA	$2.40 \times 10^{-3} \text{ s}^{-1}$	$5.84 \times 10^{-3} \text{ s}^{-1}$	$1.33 \times 10^{-2} \text{ s}^{-1}$
(1:185) TTA/MMA	$1.90 \times 10^{-3} \text{ s}^{-1}$	$6.11 \times 10^{-3} \text{ s}^{-1}$	$2.02 \times 10^{-2} \text{ s}^{-2}$
(1:77) TTA/MMA	$3.19 \times 10^{-4} \text{ s}^{-1}$	$3.87 \times 10^{-4} \text{ s}^{-1}$	$6.48 \times 10^{-4} \text{ s}^{-1}$

**Table 4. Char yields from cross-linked PMMA**

	$N_c$	% Char yield
TTA	62	0.00
	32	0.32
	26	1.42
TTM	50	0.30
	8	0.32

100 FTIR at  $4\text{ cm}^{-1}$  resolution. Each spectrum was signal averaged over 16 scans.

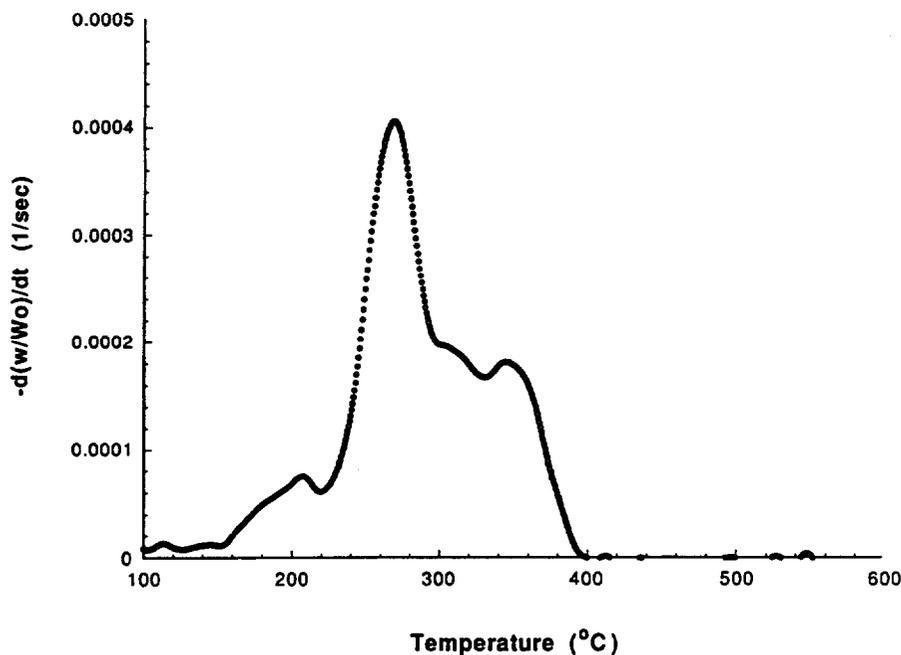
Char yield measurements were made under controlled conditions using the NIST Cone Calorimeter.<sup>9</sup> The samples, which ranged in weight from about 10 to 20 g, were placed in a dish which was open to the atmosphere and exposed to a radiant heat flux of  $22\text{ kW/m}^2$ . A high voltage arc, situated above the sample, was used to ignite the off-gases. Continuous measurements of sample weight loss were made until the flame self-extinguished. Char yields (Table 4) were computed by dividing the weight of residue by the weight of the original sample.

## THEORY

It is generally conceded that depolymerization to the monomer is the major reaction path in the

low temperature thermal degradation of PMMA.<sup>10-16</sup> This process, which is well described by first-order (in the weight of the residual polymer) kinetics,<sup>16</sup> is thought to involve three distinct steps. The reaction is initiated when free radical fragments are formed by dissociation of C—C bonds. The constituent monomers are released into the gas phase as these fragments depropagate by  $\beta$ -scission. Termination occurs when the radicals are deactivated by recombination or disproportionation reactions. The derivative thermogram of linear PMMA displayed in Fig. 3 indicates at least three reaction channels. The peaks centered at 200, 270 and 350°C have been previously assigned to head-to-head (H—H), end-chain (E) and random (S) scission initiation, respectively.<sup>13</sup> The mechanistic details of the chemical processes represented by these features continues to be the focus of debate.<sup>14,15</sup> Serious questions have been raised concerning the assignment of the first peak in particular. The data presented in this paper on the thermal degradation of cross-linked PMMA, however, can be interpreted without a full resolution of this issue.

A simple kinetic model for global depolymerization based on the assumption that the total number of radical polymer fragments ( $R$ ) attains a steady state has been advanced by Boyd<sup>17</sup> and others.<sup>16,18</sup> The rate of weight loss



**Fig. 3.** The derivative thermogram of linear PMMA.

from the condensed phase polymer ( $W_0 - W$ ) should be proportional to the rate at which monomers ( $P_i$ ) are formed. This relationship is expressed in eqn (1):

$$\frac{dM_1}{dt} = \frac{dP_1}{dt} = -\left(\frac{k_1 d_0}{m_0} + k_T \beta\right) R_1 - k_P (R - R_1) \quad (1)$$

Adopting the nomenclature used by Boyd,  $P_n$  and  $R_n$  denote the number of polymers and free radical polymer fragments having degree of polymerization  $n$ ,  $m_0$  is the molecular weight of the monomer,  $V$  is the volume occupied by the condensed phase polymer and  $M_1 = \sum n P_n = W/m_0 = d_0 V/m_0$ . The rate constants for intermolecular radical transfer:  $P_n + R_s \rightarrow P_r + R_{n-r} + P_s$ ; termination:  $R_n \rightarrow P_n$  ( $\beta = 1$ ) or  $R_r + R_{n-r} \rightarrow R_n$  ( $\beta = R/V$ ); and depropagation:  $R_n \rightarrow R_{n-1} + P_1$  are  $k_1$ ,  $\beta k_T$  and  $k_P$ , respectively. The first term on the right-hand side of eqn (1) corresponds to the rate of formation of monomer from radical transfer and termination. The second term represents the rate of formation of monomer from depropagation. Radical transfer and termination account for a relatively small fraction,  $\approx x^{-1}$  (where  $x$  is the average degree of polymerization), of the total weight loss. Consequently, the contribution from the first term to the integrated area of a peak in the derivative thermogram of a depolymerizing sample will be negligible compared to the contribution from the second term and can, therefore, be ignored.

The net rates of change in the number of radicals having degree of polymerization  $n = 1$  and  $n \geq 2$  are:

$$\frac{dR_1}{dt} = \left(2k_s + \frac{k_1 R d_0}{M_1 m_0} + k_E\right) \sum_{j=2} P_j + k_E P_2 - \left(\frac{k_1 d_0}{m_0} + k_T \beta\right) R_1 + k_P R_2 \quad (2)$$

$$\frac{dR_n}{dt} = \left(2k_s - \frac{k_1 R d_0}{M_1 m_0}\right) \sum_{j=n+1} P_j + k_E P_{n+1} - \left(\frac{k_1 d_0}{m_0} + k_P + k_T \beta\right) R_n + k_P R_{n+1} \quad (3)$$

where  $k_s$  denotes the rate constant for scission of C—C bonds at random positions along the polymer chain and  $k_E$  is the rate constant for the scission of a vinyl end-group. Setting the sum over  $n$  equal to zero gives the following equation

for the number of radicals at steady state:

$$0 = \left(2k_s + \frac{k_1 R d_0}{M_1 m_0}\right) \sum_{n=1} (n-1) P_n + 2k_E \sum_{n=2} P_n - \left(\frac{k_1 R d_0}{m_0} + k_T \beta\right) R \quad (4)$$

The solution for  $x \gg 1$  is:

$$R = \frac{2(k_s + k_E/x)}{\beta k_T} M_1 = [2(k_s + k_E/x)/k_T(m_0/d_0)^{N-1}]^{1/N} M_1 \quad (5)$$

where  $N = 1$  for the first-order termination and  $N = 2$  for second-order termination.

On the basis of eqn (5), it is clear that the total concentration of radicals at steady state does not depend on the rates of depropagation and radical transfer. The distribution of  $R_n$ , however, does depend on the relative rates of these reactions with respect to the rate of termination. This fact has no bearing on the overall kinetics of depolymerization as long as the kinetic zip-length,  $\gamma^{-1} = k_P/(\beta k_T)$ , is less than the number average degree of polymerization ( $x$ ). In this case, the average number of monomers which unzip before termination ( $\gamma^{-1}$ ) is less than  $x$ , which implies that  $R_1$  should be approximately zero. After substituting into eqn (1) for  $R$  from eqn (5), we obtain:

$$\frac{dM_1}{dt} = -2\left(k_s - \frac{k_E}{x}\right) \gamma^{-1} M_1 \quad (6)$$

The rate of weight loss given in eqn (6) is constant with respect to time as long as there is a steady-state concentration of radicals. The peaks corresponding to the individual reactions which contribute to the total rate of depolymerization can be resolved by dynamic heating to the extent that  $\int k_E(T) k_S(T) dT$  approaches zero. Assuming this to be the case, the global activation energies for random and end-chain initiation corresponding to this model are:

$$\Delta E_S = \begin{cases} E_S + E_P - E_T & \text{(first-order termination)} \\ (E_S - E_T)/2 + E_P & \text{(second-order termination)} \end{cases} \quad (7)$$

and:

$$\Delta E_E = \begin{cases} E_E + E_P - E_T & \text{(first-order termination)} \\ (E_E - E_T)/2 + E_P & \text{(second-order termination)} \end{cases} \quad (8)$$

where  $E_S$ ,  $E_P$ ,  $E_T$  and  $E_E$  are the activation energies for the elementary reactions.

The kinetic zip-length for PMMA is thought to be on the order of  $10^3$ .<sup>11,16</sup> This is significantly larger than the average degree of polymerization of the PMMA considered in this investigation which was determined to be  $\approx 290$  by size exclusion chromatography. On the basis, we anticipated that a kinetic expression based on analysis of the opposite asymptote, that is when  $\gamma^{-1} > x$ , would be more relevant. The analysis of this limit is more involved than it was for the case when  $\gamma^{-1} < x$ , since it depends on assumptions concerning the relative amounts of  $R_n$  ( $n > 1$ ) and  $R_1$ . An instant after scission,  $R_1 \approx 0$ ; and the rate of weight loss is given by eqn (6). However, since  $k_p > \beta k_t$ , the  $R_n$  will, on average, completely unzip to  $R_1$  before they can terminate. At some point  $R_1$  will become equal to  $R$  and the rate of depropagation should fall to zero until new free radical fragments with  $n > 1$  are formed from random scission of the remaining polymers.

An expression for the average rate of weight loss can be derived from the following argument. At any given moment there is a total of  $R/2$  activated polymers. Each of these fragmented polymers will unzip an average of  $x$  monomers during the time it takes to terminate depropagation,  $(\beta k_T)^{-1}$ . After substituting for  $R$  from eqn (5) we obtain:

$$\frac{dM_1}{dt} = \frac{Rx\beta k_T}{2} = -(k_s + k_E/x)xM_1 \quad (9)$$

This expression for the rate of weight loss indicates that the derivative thermogram of PMMA should have two peaks. The high temperature reaction is random scission initiated depolymerization which should have an activation energy of:

$$\Delta E_s = E_s \quad (10)$$

At lower temperatures, only end-chain initiation can occur. According to eqn (8), the global activation energy of this reaction is:

$$\Delta E_E = E_E \quad (11)$$

The generalization of eqns (6) and (9) to account for other forms of initiation, such as the scission of a head-to-head (H—H) bond in PMMA, is straightforward. Thus, when  $\gamma^{-1} > x$ , there will be an additional peak in the derivative thermogram corresponding to the term  $-2(k_{H-H}/x)\gamma^{-1}M_1$  with  $\Delta E_{H-H} = E_{H-H} + E_P - E_T$  or  $\Delta E_{H-H} = (E_{H-H} - E_T)/2 + E_P$  (depending on whether the termination reaction is first- or

second-order) and when  $\gamma^{-1} < x$ , there should be a peak corresponding to the term  $-k_{H-H}M_1$  with  $\Delta E_{H-H} = E_{H-H}$ .

Measured values of the global activation energy for random scission initiated depolymerization of PMMA ( $\Delta E_s$ ) are on the order of 270 kJ/mol (obtained for the anionically polymerized polymer) or less.<sup>16,19-21</sup> This is significantly smaller than the dissociation energy of a C—C bond ( $\approx 335$  kJ/mol). The global activation energies for end-chain ( $E_E$ ) and H—H ( $E_{H-H}$ ) initiation are also surprisingly low for scission of the corresponding C—C bonds,<sup>20,21</sup> although somewhat smaller values (by  $\approx 40$ – $80$  kJ/mol) would be expected in these cases. The source of this discrepancy may be that mass transport of the degradation products plays an important role in determining the rate of weight loss. Indeed, this effect would be expected to play an increasingly important role in determining the kinetics of weight loss from the more highly cross-linked polymers, since monomers evolved from the thermal degradation of a network must diffuse through a viscous gel as opposed to a fluid melt. On the other hand, it is also possible that the activation energies are low because the radical character of the degrading polymers is never fully developed in the transition state. A structure which conforms to this hypothesis is depicted in Fig. 4. Here radical

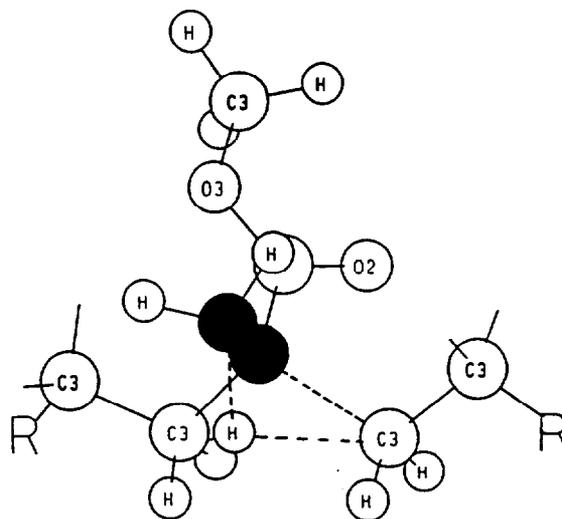


Fig. 4. A hypothetical transition state for the random scission initiated depolymerization of PMMA. The dotted lines denote bonds in the process of forming or breaking. A  $\pi$  bond forms between two of the carbon atoms (shaded) while a hydrogen on one of these carbon transfers and the  $\sigma$  bond to an adjacent carbon breaks.

sites formed by scission of the  $\sigma$  bonds between monomers are stabilized by the concurrent formation of  $\pi$  bonds (indicated by shaded spheres) as they propagate down the chain. A similar transition state has been proposed by Bailey for the depolymerization of poly(isobutylene).<sup>22</sup>

Cross-linked PMMA may be viewed as an interconnected network of linear chains. The authors assume that the average kinetic chain length ( $x_1$ ) of the cross-linked polymers considered in this investigation is comparable to the average degree of polymerization in the linear polymer since both were prepared by identical procedures using the same concentration of initiator (relative to the total amount of monomer). If the cross-linking agent does not interfere with depropagation, then the rate of depolymerization should be given by eqn (9) with  $x = x_1$ . On the other hand, if the cross-linking agent obstructs further depropagation, then  $x$  should be replaced by  $N_c$ , the average number of monomers per cross-link. This analysis suggests that it may be possible to stabilize PMMA, and other polymers which degrade by depolymerization as well, by copolymerization. Unfortunately, the magnitude of  $k_s$  will almost certainly be affected by the presence of cross-links in the polymer which introduces an additional complication into the process of choosing an appropriate cross-linking agent.

## RESULTS AND DISCUSSION

The first-order kinetics of the thermal degradation of TTM/MMA, TTA/MMA and PMMA are confirmed in Fig. 5. The rate constants for depolymerization at 350, 370 and 390°C are listed in Table 2. The correlation coefficients for the linear regressions of  $\ln(W(t))$  were 0.99 or better in each case. A comparison of the IR spectrum of the gases evolved (FTIR-EGA) during the thermal degradation of both linear (Fig. 6) and cross-linked PMMA (Figs 7 and 8) to the spectrum of MMA (Fig. 9) reveals that the monomer is indeed the major gas evolved in the thermal degradation of these polymers at 500°C. The presence of  $\text{CO}_2$ , above ambient levels, is also indicated by the characteristic peaks centered at  $\approx 650$  and  $2350 \text{ cm}^{-1}$  in the FTIR-EGA spectra of the cross-linked polymers.

The features present in the derivative thermo-

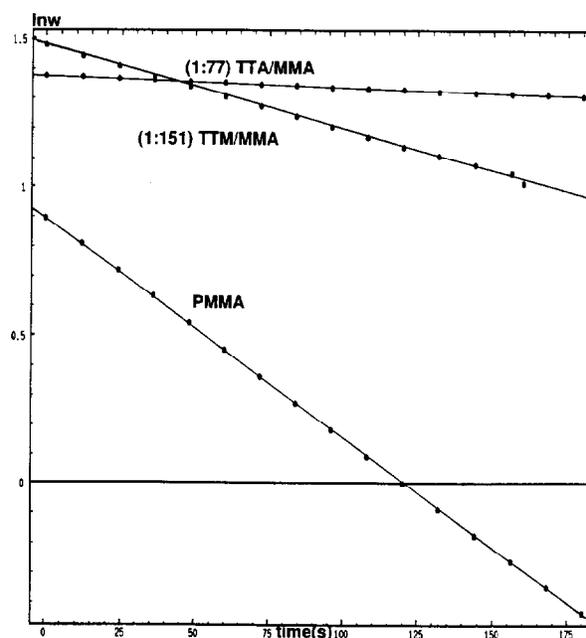
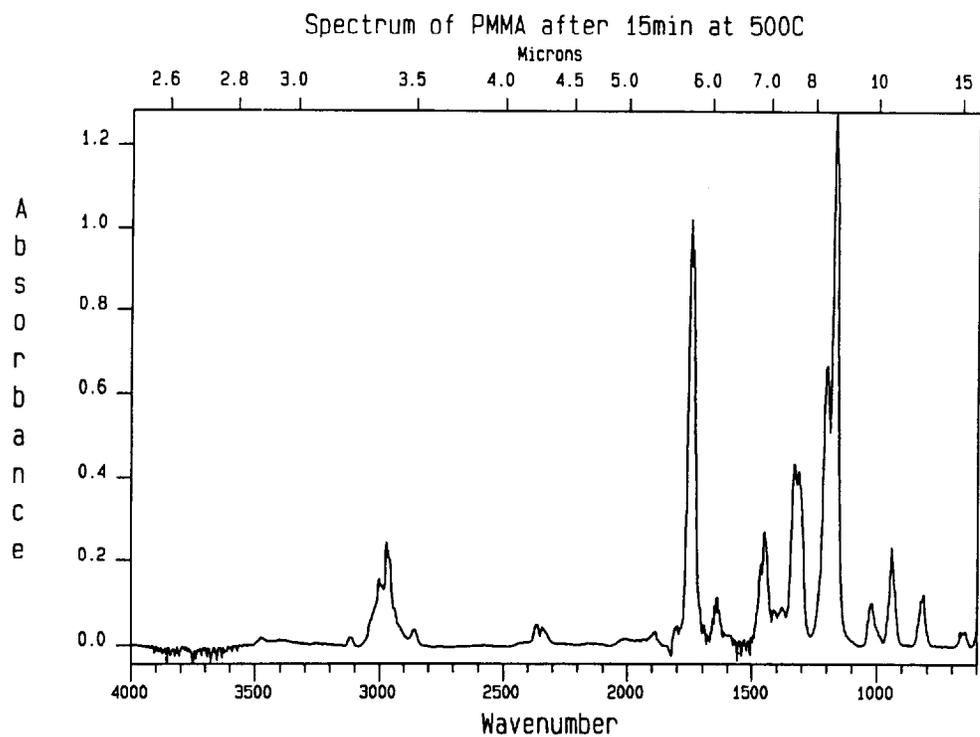


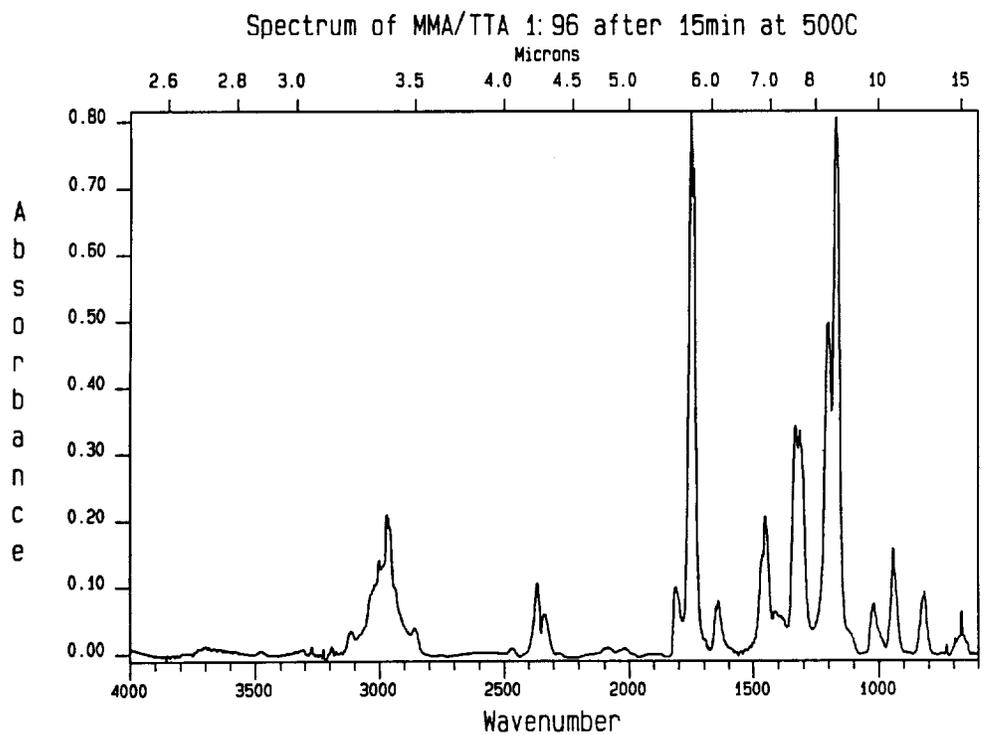
Fig. 5. The measured values of the  $\ln(W(t))$  at 370°C for linear and cross-linked PMMA fall on a straight line confirming that the degradation is first-order in the weight of the residual polymer.

grams of the TTM/MMA network copolymers (Figs 10 and 11) are qualitatively similar to those observed for linear PMMA. The rate constants corresponding to random scission initiated depolymerization, which are listed in Table 2, are also very comparable. The corresponding peaks in the derivative thermogram of the PTTM homopolymer (Fig. 12), however, appear at much higher temperatures. Furthermore, there is a new feature in the region between 420 and 440°C which also appears in the derivative thermogram of the (1:24) TTM/MMA copolymer. The presence of this peak in the derivative thermograms of those copolymers which contain significant amounts of the comonomer suggests that it may be related to the decomposition of TTM itself.

In contrast to the behavior noted above for the TTM/MMA copolymers, there are dramatic differences between the derivative thermograms of the TTA/MMA network copolymers (Fig. 13) and PMMA. The peaks corresponding to H—H and end-chain initiated depolymerization are less pronounced in the derivative thermograms of the TTA/MMA network copolymers, eventually disappearing by the time a frequency of 1 TTA for every 77 MMA monomers (1:77) is attained. The authors' explanation for this behavior is



**Fig. 6.** The FTIR-EGA spectrum of linear PMMA taken after 15 min at 500°C.



**Fig. 7.** The FTIR-EGA spectrum of the 1:96 TTA/MMA copolymer taken after 15 min at 500°C.

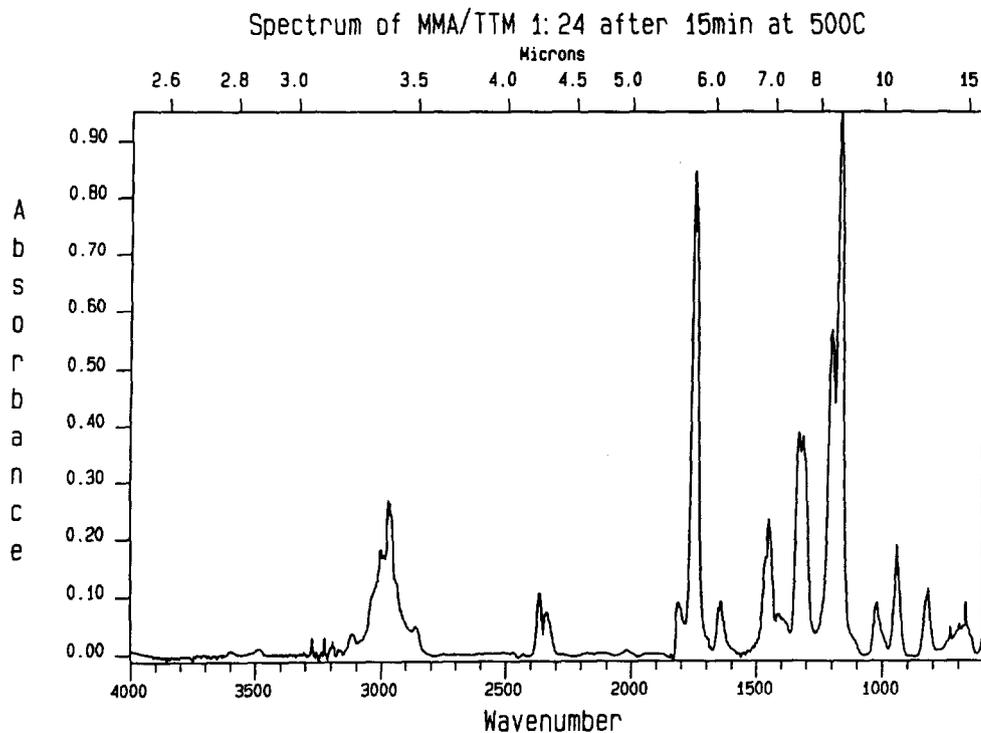


Fig. 8. The FTIR-EGA spectrum of the 1:24 TTM/MMA copolymer taken after 15 min at 500°C.

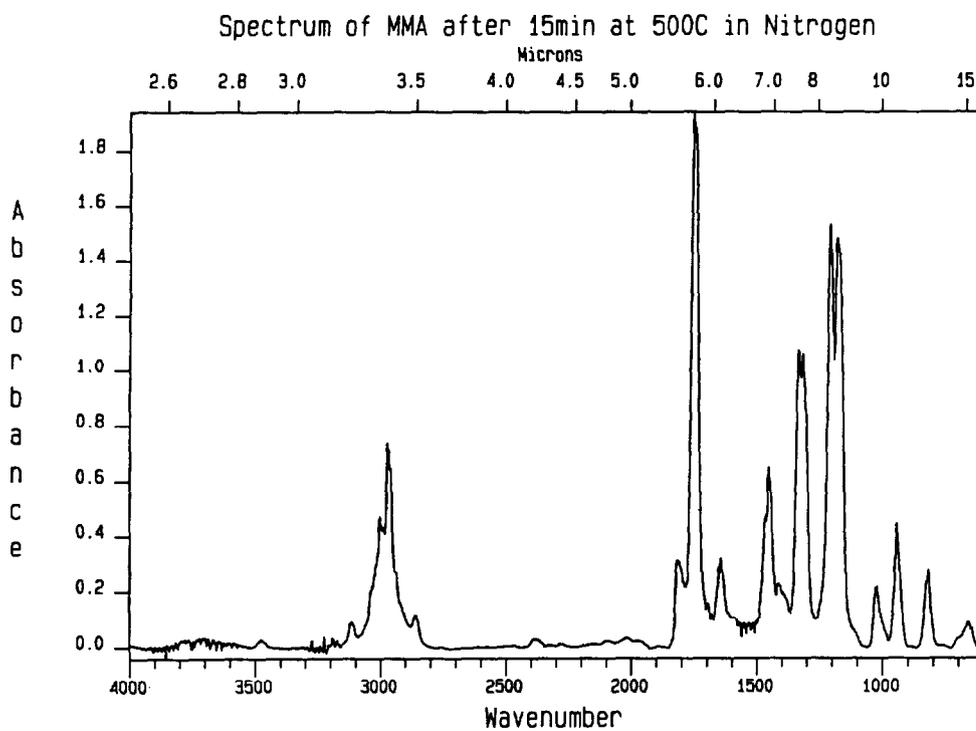


Fig. 9. The FTIR-EGA spectrum of the MMA monomer taken after 15 min at 500°C.

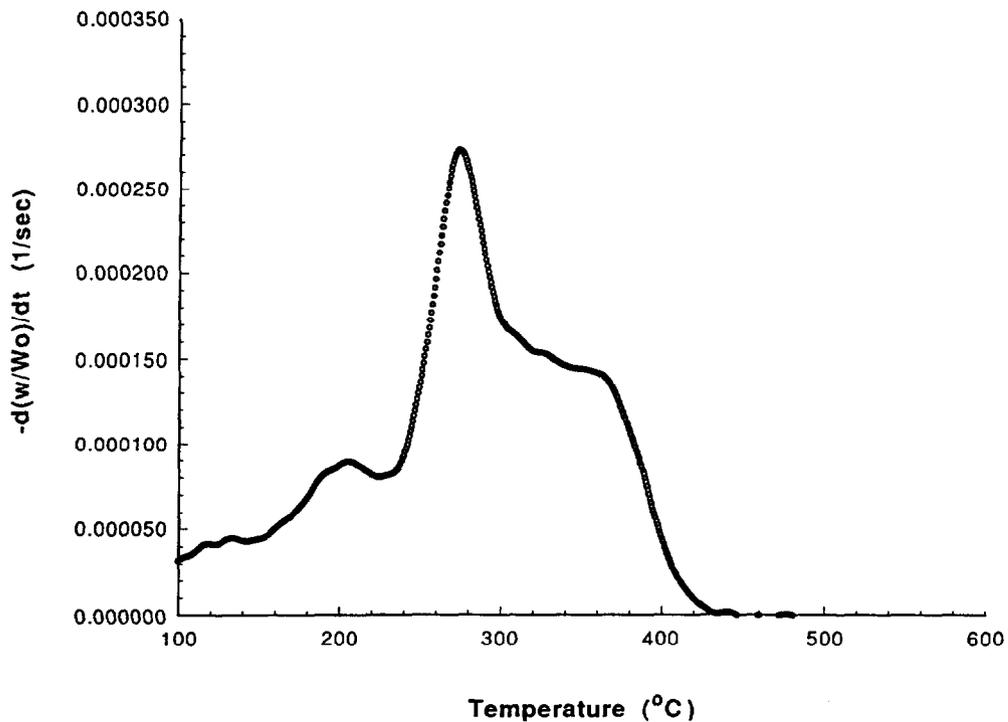


Fig. 10. The derivative thermogram of the 1:151 TTM/MMA copolymer.

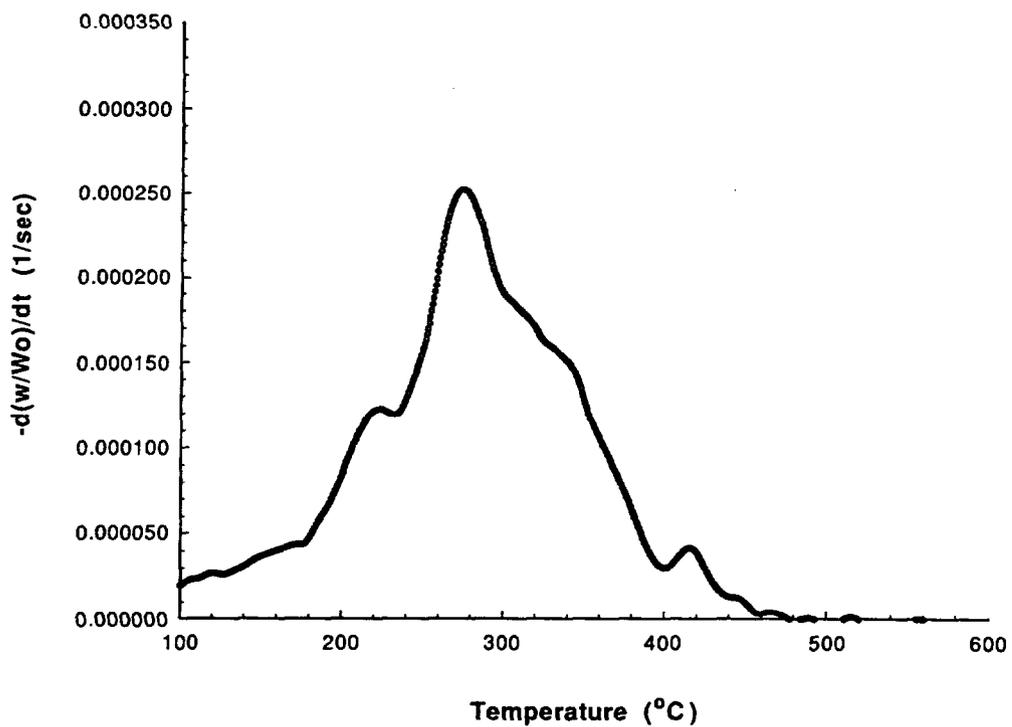


Fig. 11. The derivative thermogram of the 1:24 TTM/MMA copolymer.

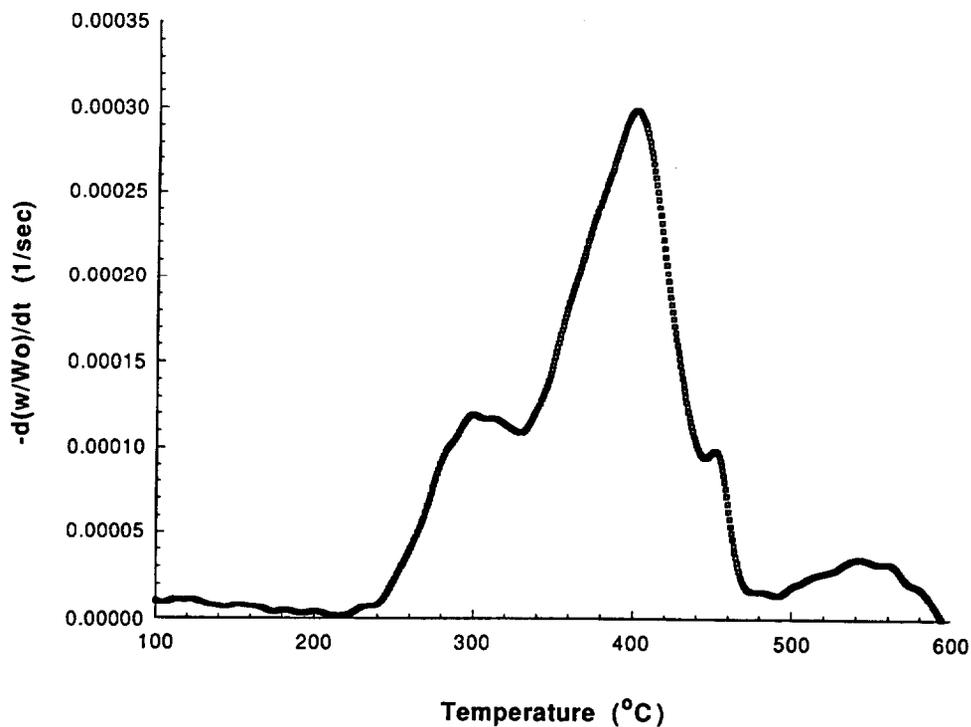


Fig. 12. The derivative thermogram of PTTM.

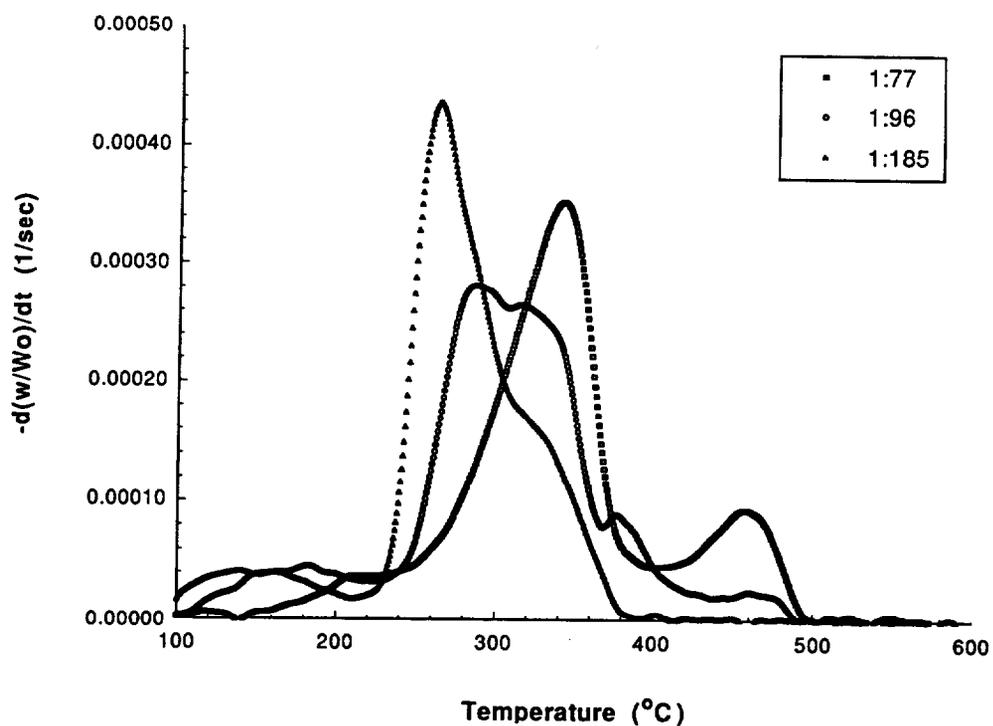


Fig. 13. The peaks corresponding to low temperature depolymerization are less pronounced in the derivative thermograms of the 1:185 and 1:96 TTA/MMA network copolymers, eventually disappearing by the time a frequency of 1 TTA for every 77 MMA monomers (1:77) is attained.

based on the recognition that acrylate polymers, unlike the corresponding methacrylates, do not depolymerize.<sup>10,12</sup> The assumption is that the presence of a TTA node in the network suppresses further depropagation so that the average zip length of a TTA/MMA copolymer is equal to the average number of monomers between successive cross-links ( $N_c$ ). As a result, each initiation is less productive in TTA/MMA than it was in either TTM/MMA or PMMA, and the H—H and end-chain sites are depleted without significant weight loss. The loss in intensity of the peaks corresponding to the low temperature depolymerization of the TTA/MMA network copolymers is accompanied by an increase in the peak attributed to random scission initiated depolymerization. This is a necessary consequence of the fact that the polymer chains which survive H—H and end-chain initiated depolymerization are susceptible to depolymerization initiated by random scission.

The activation energy for random scission initiated depolymerization should increase when cross-links are present because breaking a bond in the interior necessarily places an additional strain on the other bonds in the network. Furthermore there should be a large entropy of activation as torsional modes, which are restricted by cross links in the condensed phase polymer, are excited in the depolymerization of the network. A large entropy of activation usually means that the pre-exponential factor in the rate constant will also be large.<sup>23</sup> The Arrhenius constants for the degradation of the (1:185) TTA/MMA copolymer, which are larger than those obtained for PMMA, are consistent with this hypothesis. The corresponding values obtained for the (1:24) TTM/MMA copolymer, however, do not follow this trend. A possible explanation for this discrepancy is that molecular diffusion has become an important factor in determining the rate of weight loss in the more highly cross-linked polymers. On this basis, the small degree of stabilization exhibited by the TTM/MMA copolymer over the temperature range extending from 350 to 390°C may be attributed to the simple fact that it takes more time for the evolved monomers to diffuse through a viscous gel than through a fluid melt. A much more dramatic effect was observed in the degradation of the (1:77) TTA/MMA copolymer. In this case, the rate constants are an order of magnitude smaller than the values observed in

the degradation of the other polymers. The values of the corresponding Arrhenius constants give a clear indication that, in this instance, the rate of weight loss is diffusion-controlled. Presumably, the diminished importance of the low temperature degradation reactions makes this effect more pronounced in highly cross-linked TTA than in comparably cross-linked TTM copolymers.

As expected, there are no indications of significant weight loss at the temperatures corresponding to depolymerization in the derivative thermogram of the PTTA homopolymer displayed in Fig. 14. The peak centered at  $\approx 420^\circ\text{C}$ , although much more prominent in this instance, is reminiscent of the feature noted in the thermograms of PTTM and the (1:24) TTM/MMA copolymer. The corresponding Arrhenius constants,  $\Delta E = 369 \text{ kJ/mol}$  and  $A = 1.9 \times 10^{25} \text{ s}^{-1}$ , are within the expected range for bond scission in a network and are distinctly different from the values we obtained for the thermal degradation of the other polymers considered in this study. A comparison of FTIR-EGA spectra indicates that the volatile fraction (at  $50^\circ\text{C}$ ) of the thermal degradation products of PTTA (Fig. 15) contains less ester and significantly more  $\text{CO}_2$  and  $\text{CO}$  (indicated by the peak centered at  $2150 \text{ cm}^{-1}$ ) than the corresponding fractions evolved from either PMMA or the TTA and TTM/MMA copolymers (Figs 6–8). The peaks centered at  $\approx 1750$  and  $1150 \text{ cm}^{-1}$ , which are characteristic of esters, are probably not due to TTA since the vapor pressure of this compound is negligible at the temperature of the cell ( $50^\circ\text{C}$ ). The sharp feature at  $\approx 3020 \text{ cm}^{-1}$ , which is present in the FTIR-EGA spectra of the TTA/MMA copolymers but absent from the spectra of PMMA and the TTM/MMA copolymers, coincides with a prominent peak in the spectrum of formaldehyde which, along with  $\text{CO}$  and  $\text{CO}_2$ , is a likely degradation product of acrylate monomers.

The derivative thermograms of some of the more highly cross-linked polymers exhibit another peak, which is centered at about  $460^\circ\text{C}$  in the TTA copolymers, but it is shifted to much higher temperatures in both PTTM and PTTA. This peak is present in the derivative thermograms of all of the polymers which produced char when they were burned, while it is absent from the thermograms of those polymers which did not char. Furthermore, there is a positive correlation

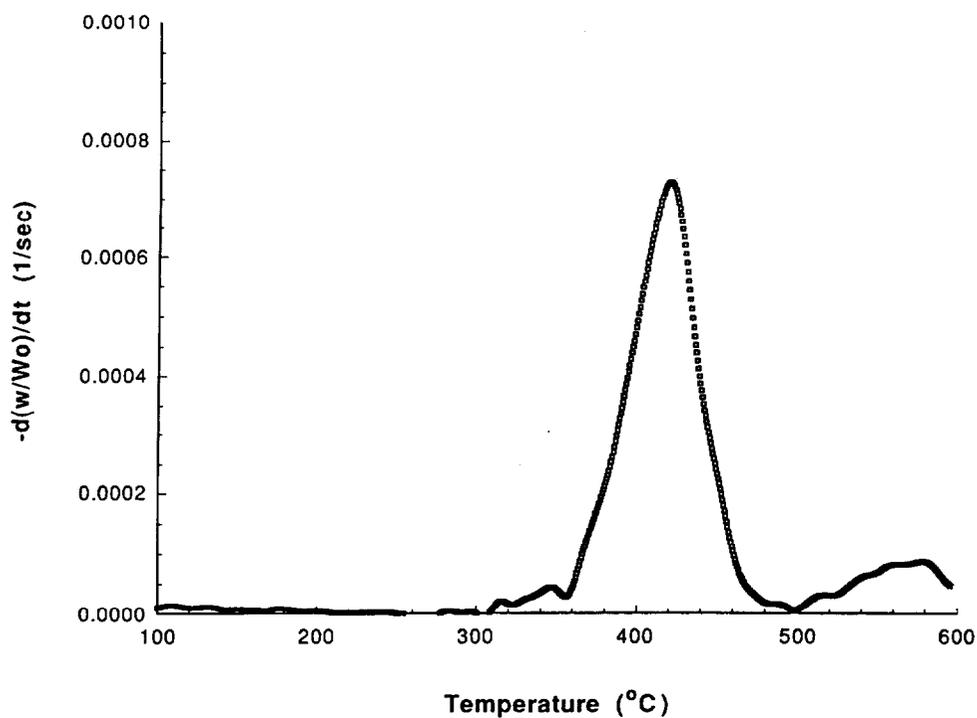


Fig. 14. The derivative thermogram of PTTA.

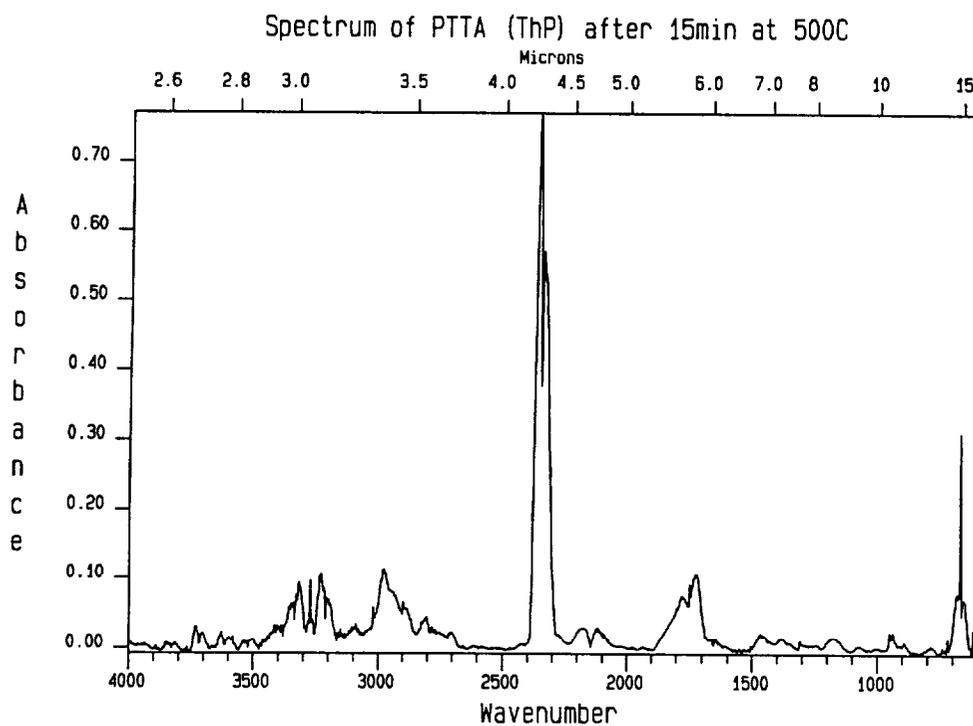


Fig. 15. The FTIR-EGA spectrum of PTTA taken after 15 min at 500  $^{\circ}\text{C}$ . The sharp feature at  $\approx 3020 \text{ cm}^{-1}$  coincides with a prominent peak in the spectrum of  $\text{CH}_2\text{O}$ .

between the intensity of this peak and both the frequency of cross-links and the amount of char that was produced when the polymer was burned (Table 4).

## SUMMARY AND CONCLUSIONS

The thermal degradation kinetics of linear and cross-linked PMMA were studied as functions of the chemical nature of the cross-linking agent and frequency of cross-links. Although all of the cross-linked polymers exhibited some degree of stabilization over linear PMMA, the most dramatic effect was observed in the case of the (1:77) TTA/MMA copolymer. The Arrhenius constants for random scission initiated depolymerization indicate that, in the thermal degradation of this material, the rate of weight loss is controlled by the diffusion of the evolved monomers through the gel, as opposed to the chemistry of their formation.

Consideration of the derivative thermograms of the TTM/MMA network copolymers suggests that their thermal degradation is qualitatively similar to linear PMMA. The authors did observe a slight decrease in the activation energy for random scission initiated depolymerization, but this was offset by a corresponding decrease in the pre-exponential factor. This was attributed to the effects of molecular diffusion which should take on increasing importance in polymers with high cross-link densities. In any case, the copolymerization of MMA with TTM does not appear to offer a significant improvement in thermal stability. The more highly cross-linked TTM/MMA copolymers, however, do produce some char when they are burned.

The fact that TTA itself does not depolymerize has a dramatic effect on the thermal degradation behavior of the TTA/MMA network copolymers. The presence of a TTA node in the network suppresses further depolymerization so that each initiation is less productive than it was in either TTM/MMA or PMMA. Indeed, the low temperature reaction channels (H—H and end-chain initiated depolymerization), which play a prominent role in the thermal degradation of linear (free-radical polymerized) PMMA, are almost completely shut down in the more highly cross-linked TTA/MMA copolymers. The authors have already alluded to the fact that the rate of weight loss due to random scission

initiated depolymerization is dramatically reduced in the most highly cross-linked TTA copolymer. These observations indicate that it may be possible to improve thermal stability by substituting MMA/acrylate copolymers for PMMA in some applications. The char-forming tendency of the cross-linked copolymers should contribute to a further reduction in the flammability of these materials.

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