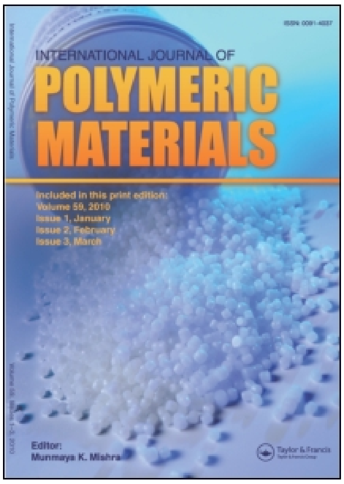

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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Sergei M. Lomakin[a]; Guennady E. Zaikov[a]
[a] Institute of Chemical Physics, Moscow, Russia

To cite this Article Lomakin, Sergei M. and Zaikov, Guennady E.(1995) 'Pyrolysis and Carbonization of Cross-Linked Poly(methyl methacrylate)', International Journal of Polymeric Materials, 27: 3, 223 — 230
To link to this Article: DOI: 10.1080/00914039508009671
URL: http://dx.doi.org/10.1080/00914039508009671

Intern. J. Polymeric Mater., 1995, Vol. 27, pp. 223–230
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Pyrolysis and Carbonization of Cross-Linked Poly(methyl methacrylate)

SERGEI M. LOMAKIN and GUENNADY E. ZAIKOV
Institute of Chemical Physics, Moscow 117977, Russia

(Received July 21, 1994)

The thermal degradation of 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 trimethyllolpropane triacrylate and trimethylolpropane trimethacrylate networks were found to char when burned. The differences in the thermal degradation of these polymers are interpreted in terms of a simple model for kinetics of polymerization.

KEY WORDS Cross-linked poly(methyl methacrylate), pyrolysis, carbonization.

INTRODUCTION

Our research 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.[1] 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 unburned material. The tendency of a polymer to char can be increased with chemical additives and by altering its molecular structure. We have identified some factors which promote the formation of char. Here, we extend this research to consider the thermal degradation behavior and flammability of chemically cross-linked poly(methyl methacrylate) (PMMA).

EXPERIMENTAL

PMMA samples were synthesized by thermal radical polymerization of MMA in the presence of BPO (1.5% wt.). MMA was dissolved in toluene to produce a 50% by weight solution. This solution was heated at 60°C for 3 hours. When this solution started to become viscous it was poured into hexane. Then, after origin a solid phase of PMMA it was dried and solid polymer was put into Petri dishes and cured for 72 hours at 80°C and after that for 6 hours at 120° to remove additional solvent.[2] The number average molecular weight (M_n) and polydispersity obtained from size exclusion chromatography (in THF) were 2.9–3.9 × 10^4, respectively. The two cross-linked PMMA networks were prepared in toluene solution by free radical copolymerization of MMA with trimethylolpropane triacrylate (TTA) and trimethylolpropane trimethacrylate (TTM). The actual cross-link densities of the copolymers were determined by solvent swelling in toluene and acetone using the technique described in references,[3,4]

$$-\ln(1 - \nu_r) - \nu_r - \chi_1\nu_r^2 = \rho V_0 \left(\frac{1}{M_c} - \frac{2}{M}\right)(\nu_r^{1/3} - \nu_r/2)$$

where ν_r = volume fraction of polymer in the swollen system, χ_1 = polymer/solvent interaction parameter, ρ = density of unswollen polymer, V_0 = molar volume of solvent, M_c = average mol.wt. of polymer between cross-links, M = average mol.wt. before cross-linking.

The solvents in which the network was swollen to equilibrium were toluene with V_0 = 106.3 cm^3/mol and χ_1 = 0.45 (25°, 27°C) and acetone with V_0 = 77.3 cm^3/mol and χ_1 = 0.48 (17°C).[3]

The cross-link density (α) was defined as $1/2M_c$. For an approximate result, if M is much greater than M_c and if swelling is considerable, the negative terms on the right-hand side of the equation can be neglected, since then $2/M$ is small compared with $1/M_c$, and $\nu_r/2$ is small compared with $\nu_r^{1/3}$.[4]

The Final Swollen Equilibrium Polymer Volume Fraction, ν_r, was determined as

$$\nu_r = \frac{W_0\rho_s}{(W_1 - W_0)\rho_p} \times 100\%$$

where W_0 = weight of polymer before swelling, W_1 = weight of polymer after swelling, ρ_p = density of polymer, ρ_s = density of solvent.

Thermogravimetric analyses (TGA) were performed in a nitrogen atmosphere using a Mettler TA 2000 thermoanalyzer at a slow heating rate (2°C/min). Char yield measurements were made under controlled conditions using the NIST Cone Calorimeter.[5] The samples (10–20 g) were placed in dishes which were exposed to a radiant heat flux of 20 kW/m^2.

RESULTS AND DISCUSSION

It is well known that depolymerization to the monomer is a major reaction path in the low temperature thermal degradation of PMMA.[6] The derivative thermogram of linear PMMA (Figure 1) 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), and chain (E) and random (S) scission initiation respectively.[6]

It is well known a simple kinetic model for global depolymerization can be based on the assumption that the total number of radical polymer fragments (R) attains a steady state. The rate of weight loss from the condensed phase polymer (W_0 −

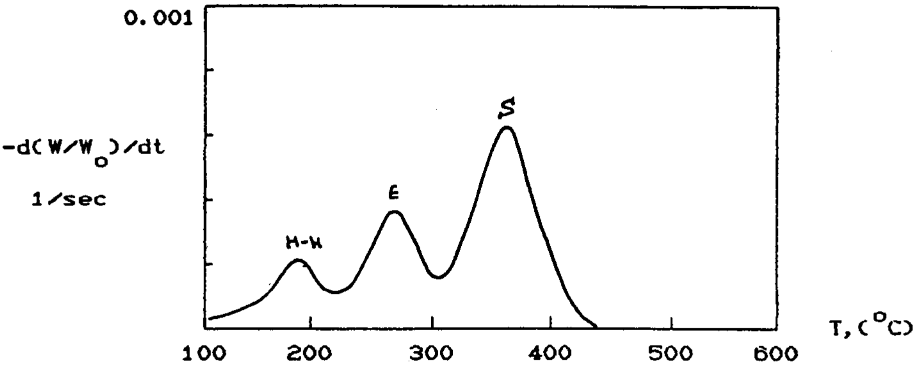

FIGURE 1 The DTG of linear PMMA.

W) should be proportional to the rate at which monomer molecules (P_1) are formed.[7]

$$dM_1/dt = dP_1/dt = -(k_i d_0/m_0 + k_t \beta)R_1 - k_p(R - R_1) \tag{1}$$

P_n and R_n = the number of polymer molecules and free radical polymer fragments having degree of polymerization n, m_0 = molecular weight of the monomer, V is the volume occupied by the condensed phase polymer, $M_1 = \Sigma\, nP_n = W/m_0 = d_0V/m_0$, 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 $R_r + R_{n-r} \rightarrow P_n$ ($\beta = R/V$); and depropagation: $R_n \rightarrow R_{n-1} + P_1$ are k_1, βk_t and k_p, respectively.

The first term on the right hand side of Equation (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 the 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 changes in the number of radicals having degree of polymerization $n = 1$ and $n \geq 2$ are

$$dR_1/dt = (2k_s + k_iRd_0/M_1m_0 + k_e) \sum_{j=2} P_j + k_eP_2 - (k_id_0/m_0 + k_t\beta)R_1 + k_pR_2 \tag{2}$$

$$dR_n/dt = (2k_s + k_iRd_0/M_1m_0) \sum_{j=n+1} P_j + k_eP_{n+1} - (k_id_0/m_0 + k_p + k_t\beta)R_1 + k_pR_{n+1} \tag{3}$$

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 endgroup. Setting the sum over n equal to zero gives the following equation for the number of radicals at the steady state:

$$0 = (2k_s + k_i Rd_0/M_1 m_0) \sum (n - 1)P_n + 2k_e \sum P_n - (k_i Rd_0/m_0 + k_t\beta)R \quad (4)$$

The solution for $x >> 1$ is

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

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

After substituting into Equation (1) for R from Equation (5), we obtain

$$dM/dt = -2(k + k/x)\gamma^{-1}M \quad (6)$$

where the average number of monomer molecules which unzip before termination (γ^{-1}) is less than the number average degree of polymerization (x).

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

$$\Delta E_s = \begin{array}{l} E_s + E_p - E_t \text{ (first order termination)} \\ (E_s - E_t)/2 + E_p \text{ (second order termination)} \end{array} \quad (7)$$

and

$$\Delta E_e = \begin{array}{l} E_s + E_p - E_t \text{ (first order termination)} \\ (E_s - E_t)/2 + E_p \text{ (second order termination)} \end{array} \quad (8)$$

where E_s, E_p, E_t and E_e are the activation energies for the elementary reactions.

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 polymer molecules. Each of these fragmented polymer molecules will unzip an average of x molecules during the time it takes to terminate depropagation, $(\beta k_t)^{-1}$. After substituting for R from Equation (5) we obtain,

$$dM_1/dt = Rx\beta k_t/2 = -(k_s + k_e/x)xM_1 \quad (9)$$

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

$$\Delta E_s = E_s$$

At lower temperatures, only End-chain initiation can occur.

$$\Delta E_e = E_e$$

The generalization of Equations (6) and (9) to account for other forms of initiation, such as the scission of Head-to-Head (h—h) bonds in PMMA, is straightforward. Thus, when $\gamma^{-1} > x$, there will be additional peak in the derivative thermogram corresponding to the term ${}_2(k_{\text{h—h}}/x)\gamma^{-1}M_1$ with

$$\Delta E_{\text{h—h}} = \begin{array}{l} E_{\text{h—h}} + E_p - E_t \text{ (first order termination)} \\ (E_{\text{h—h}} - E_t)/2 + E_p \text{ (second order termination)} \end{array}$$

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

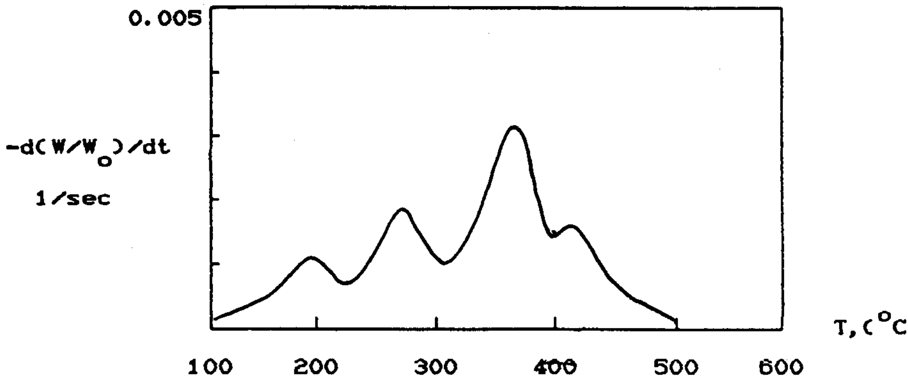

FIGURE 2 The DTG of PMMA-co-TTM 56:1.

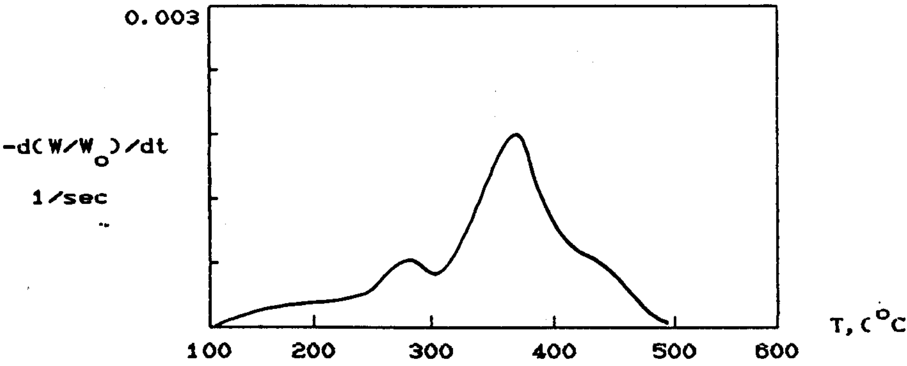

FIGURE 3 The DTG of PMMA-co-TTA 45:1.

TABLE I

Effective kinetic parameters of the thermal degradation of cross-linked PMMA-co-TTM

PMMA-co-TTM 56:1	A, s^{-1}	E, kJ/mole
1 peak	0.77×10^{11}	152
2 peak	1.73×10^{15}	218
3 peak	1.30×10^{16}	263
4 peak	0.75×10^{15}	276

TABLE II

Effective kinetic parameters of the thermal degradation of cross-linked PMMA-co-TTA

PMMA-co-TTA 45:1	A, s^{-1}	E, kJ/mole
1st peak	—	—
2nd peak	0.50×10^{14}	203
3rd peak	3.50×10^{16}	270

Cross-linked PMMA may be viewed as an inter-connected network of linear chains. We assume that the average kinetic chain length (x_1) of cross-linked polymer molecules is comparable to the average degree of polymerization in the linear polymer. If the cross-linking agent does not interfere with depropagation, then the rate of depolymerization should be given by

$$dM_1/dt = Rx\beta k_t/2 = -(k_s + k_e/x)xM_1 \text{ with } x = x_1$$

On the other hand, if the cross-linking agent obstructs further depropagation, then x should be replaced by N_c, the average number of monomer molecules per cross-link.

This analysis suggests that it may be possible to stabilize PMMA and other polymers which degrade by depolymerization as well, by co-copolymerization.

The features present in the derivative thermograms of TTM-co-PMMA network copolymers (Figure 2) are qualitatively similar to those observed for linear PMMA.

In contrast to this behavior, there are differences between the derivative thermograms of TTA-co-PMMA network copolymers (Figure 3) and PMMA. The peaks corresponding to H—H and end-chain initiated depolymerization are less pronounced in the derivative thermograms of the TTA-co-PMMA network copolymers.

Our explanation for this behavior is based on the recognition that acrylate polymers, unlike the corresponding methacrylates, do not depolymerize.[8] The assumption is that the presence of a TTA in the network suppresses further depropagation so that the average zip length of TTA/MMA copolymer is equal to the average number of monomer units between 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 (Tables

I and II). The Arrhenius constants for copolymer thermal degradation were calculated using the Kissinger method.[9]

$$\ln(b/T_m^2) = \ln(AR/E) - E/RT_m$$

where b = the heating rate, T_m = temperature of the maximum of the DTG peak, E = effective activation energy, A = pre-exponential factor.

Measured values of the global activation energies are surprisingly low for scission of the corresponding C—C bonds (≈335 kJ/mole). 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. This effect would be expected to play an increasingly important role in determining the kinetics of weight loss from more cross-linked polymers. 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. The radical sites formed by scission of σ bonds between monomer units are made by concurrent formation of π bonds as they propagate down the chain. The derivative thermograms of some of the more highly cross-linked polymers exhibit a peak, centered at about 420–450°C. This peak was present in the derivative thermograms of all 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 between the intensity of this peak and the amount of char produced when the polymer was burned (Tables III and IV).

The copolymerization of MMA with TTM does not appear to offer a significant improvement in thermal stability. The more highly cross-linked PMMA-co-TTM,

TABLE III

Char yield after TGA analysis (600°C)

Polymer	% wt. char residue
PMMA	—
PMMA-co-TTM 26:1	—
PMMA-co-TTM 56:1	—
PMMA-co-TTM 82:1	—
PMMA-co-TTM 125:1	—
PMMA-co-TTA 20:1	1.4
PMMA-co-TTA 45:1	0.8
PMMA-co-TTA 78:1	—

TABLE IV

Char yield after Cone Calorimeter tests

Polymer	% wt. char residue
PMMA	—
PMMA-co-TTA 50:1	0.32
PMMA-co-TTA 26:1	1.42
PMMA-co-TTA 32:1	0.32
PMMA-co-TTA 62:1	—

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 PMMA-co-TTA 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 PMMA-co-TTM 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 PMMA, are almost completely shut down in the more highly cross-linked PMMA-co-TTA. We 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 copolymers. 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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