Thermal Degradation of Poly(methyl methacrylate). 4. Random Side-Group Scission†

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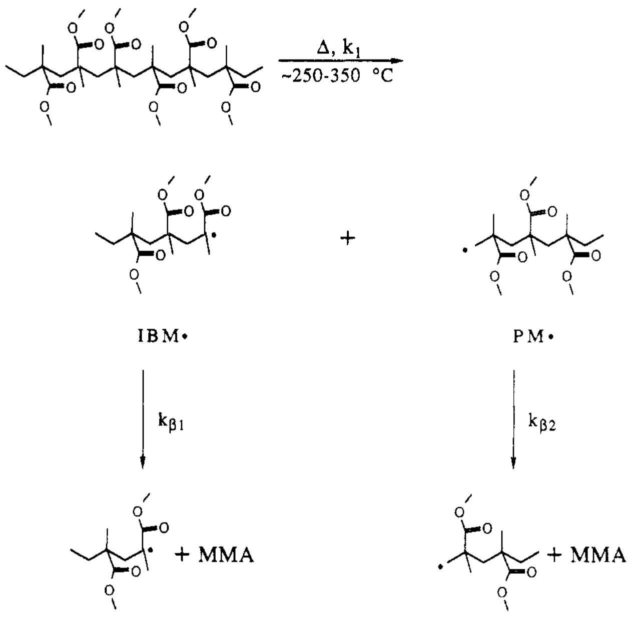
ABSTRACT: It has long been accepted that the thermal degradation of saturated PMMA (PMMA-H) is initiated by a main-chain scission. In this paper it is proposed that a side-group scission of a methoxycarbonyl group initiates PMMA-H degradation. Side-group scission is favored due to a large "cage" recombination effect which reduces the contribution of main-chain scission. It is anticipated that side-group scission will initiate polymer degradation whenever side-group bonds are of similar energy or weaker than main-chain bonds.

Introduction

The random main-chain scission mechanism (Scheme I) for the thermal degradation of poly(methyl methacrylate) (PMMA) is a cornerstone in our understanding of polymer thermal degradation. In considering this mechanism, it is easily accepted that the isobutyryl macroradical (IBM•) formed will depolymerize to give MMA. However, a problem with Scheme I, which has been pointed out by a number of researchers, is that the simultaneously formed primary macroradical (PM•) is very different from the IBM• and should not efficiently depolymerize.[1-3] This problem has been recently addressed by Kashiwagi et al., who proposed a modified random main-chain scission mechanism for the thermal degradation of PMMA (Scheme II).[1] In this proposal the primary radical undergoes facile β scission to form a methoxycarbonyl radical and a methallyl-terminated PMMA (PMMA-MA-=). It is anticipated that PMMA-MA-= is less stable than saturated PMMA (PMMA-H).

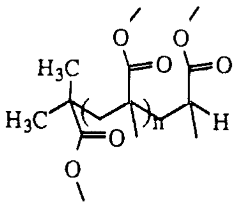
Schemes I and II assume initial main-chain scission leads to PMMA thermal degradation. Recent evidence suggests main-chain scissions are kinetically inhibited relative to side-group or chain-end scissions (possibly due to efficient recombination of caged radicals).[4] In the present paper it is proposed that random scission degradation of PMMA is initiated by homolytic scission of a methoxycarbonyl side group (Scheme III) rather than by main-chain scission. Results from previous studies are combined to predict specific trace PMMA degradation products that will form on the basis of Scheme III.[2,4,5] GC/MS analysis of the gases evolved during PMMA thermal degradation supports the proposed mechanism.

Scheme I



Experimental Procedures

Polymers. The preparation and purification of all polymer samples have been previously described.[2,5-9] GTP polymerizations were initiated with methyl trimethylsilyl 2,2-dimethylketene acetal. This initiator produces a methylisobutyryl group at the initiation end of the PMMA chain. Aqueous workup (after GTP) produces a methylisopropionyl group at the termination end of the PMMA chain. This polymer will be labeled IB-PMMA-IP and is a specific example of PMMA-H. The three IB-PMMA-IP samples studied in detail had DP_0 of 20, 79, and 170 with M_w/M_n of 1.19, 1.15, and 1.13, respectively. After purification, the powdered samples were dried by heating to ~80 °C at reduced pressure (~0.5 mmHg) for 1-2 days. This drying procedure is not sufficient to remove all traces of solvent (detectable by GC/MS); however, I believe small traces of residual solvent do not interfere with polymer degradation or product analysis.



IB-PMMA-IP

Polymer Degradation. Polymer degradations were carried out in the apparatus shown in Figure 1. A $^1/_4$-in. glass tube was bent, scored with a triangular file (along the horizontal connection between the two U-shaped sections), and weighed. In the larger U-shaped section was placed 250 mg of powdered polymer. With helium (~500 mL/min) passing through the tube, the sample was heated to 150 °C for ~15 min to further remove residual solvent. The large U tube was then placed into a silicon carbide fluidized bed preheated to the desired PMMA-H degradation temperature. The small U tube was immersed in liquid nitrogen. Samples were heated until 30-70% of the polymer in the large U tube was degraded. As the tube was removed from the hot and cold baths, the He flow was stopped. After the tube equilibrated

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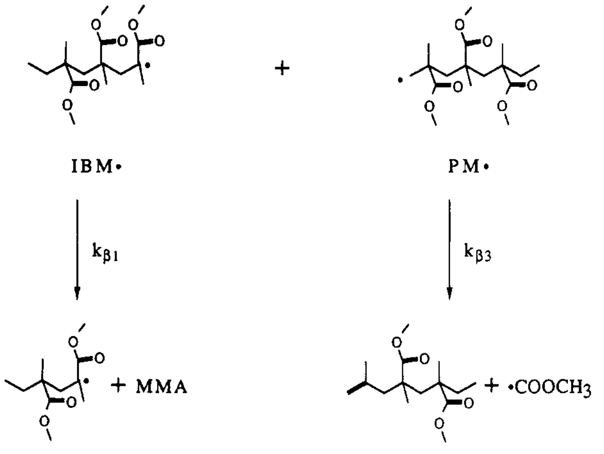
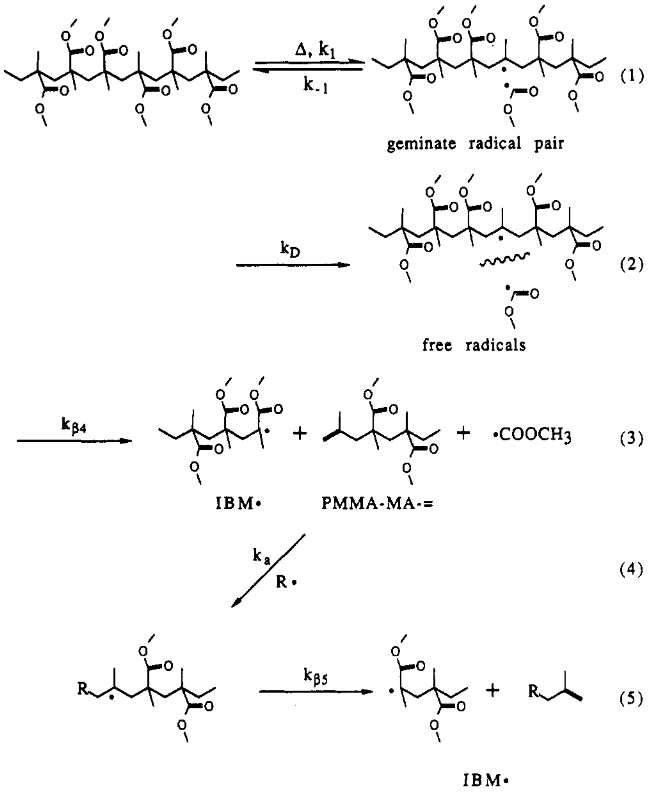
Scheme II



Scheme III



to room temperature, it was weighed and broken at the scored position; both halves were weighed to determine the percent of polymer degradation.

GC/MS Analysis. Analyses were done with a Varian Vista 6000 GC coupled to a VG Micromass 7070 HS mass spectrometer operated at 70 eV. The sample was split after separation and simultaneously analyzed by flame ionization detection (FID) and MS. As expected, the major product from all samples is MMA. When necessary, to keep the large amount of MMA from disrupting the MS detector, the inlet to the MS was closed as the MMA peak passed. Relative amounts of product were determined from the FID signal. Standard solutions of the products in MMA were not run; however, it is known that the FID signal is roughly proportional to the number of reduced carbon atoms in the flame.[10] Therefore, to get approximate molar ratios, the relative FID peak area is multiplied by (the number of reduced carbon atoms in MMA)/(the number of reduced carbon atoms in detected compound). For the data shown in Figures 2 and 3 the GC column was a 30-m DB-1 fused silica capillary column initially heated to 60 °C and ramped to 180 °C at 8 °C/min and then to 275 °C at 12 °C/min (J&W Scientific). The data shown in Figure 4 were obtained with an 8-ft, $^1/_8$-in.-diameter stainless steel column packed with 3% SP1500 on carbopack B initially heated to 70 °C and ramped to 125 °C at 4 °C/min and then to 200 °C at 8 °C/min (Supelco).

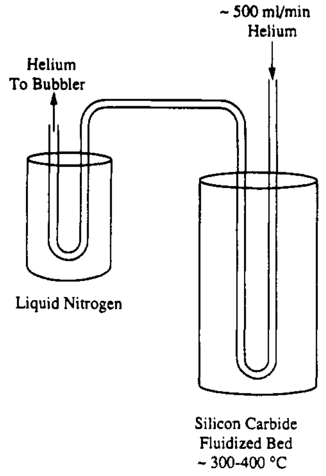


Figure 1. Schematic of apparatus used to degrade and collect volatiles from IB-PMMA-IP thermal degradation.

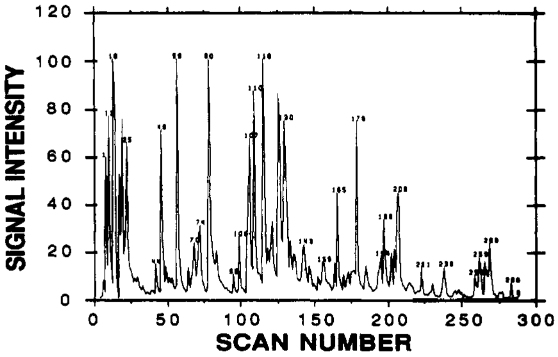


Figure 2. GC/MS trace from the products collected when a IB-PMMA-IP sample with DP_0 = 20 is heated to 370 °C for 15 min.

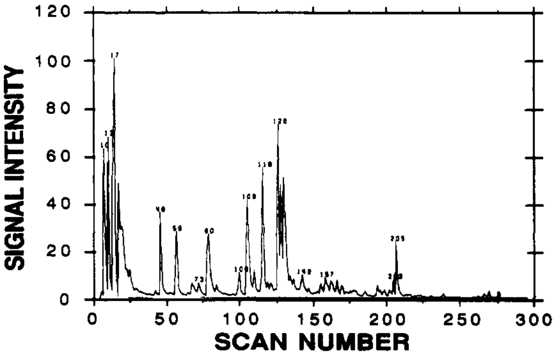


Figure 3. GC/MS trace from the products collected when a IB-PMMA-IP sample with DP_0 = 170 is heated to 350 °C for 15 min.

MS Standards. Methyl propionate (I), methyl isobutyrate (II), dimethyl itaconate (VIII), and methyl methacrylate (III) were commercial samples purified by distillation. Dimethyl 2,4-dimethylglutarate (IXa,b, two diasteriomers), methyl 2,4-dimethyl-4-pentenoate (V), methyl 2,2,4-trimethyl-4-pentenoate (VI), and dimethyl 2-methylsuccinate (VII) were prepared by methyl esterification of the corresponding acids. 2,4-Dimethyl-4-pentenoic acid and 2,2,4-trimethyl-4-pentenoic acid were prepared by addition of 3-chloro-2-methylpropene to the dilithium salt of propanoic and isobutyric acids, respectively.[11] Methyl 3-methyl-3-pentenoate (IV) was prepared by photochemical rearrangement of methyl 3-methyl-2-pentenoate.[12] PMMA dimer (XII) and trimer were separated by distillation after the polymerization of MMA with excess cobalt chain-transfer agent.[8,13]

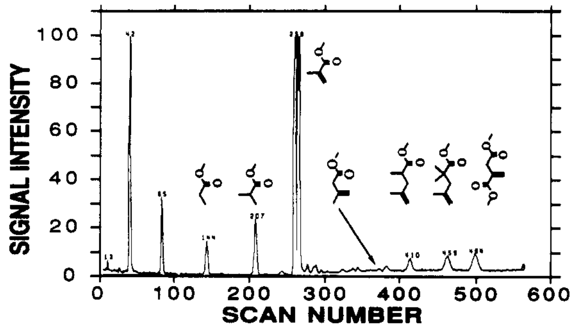


Figure 4. GC/MS trace from the lower molecular weight products collected when a IB-PMMA-IP sample with DP$_0$ = 170 is heated to 350 °C for 15 min.

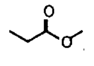
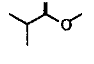
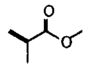
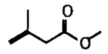
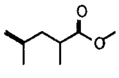
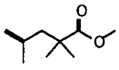
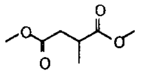
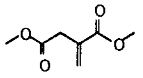
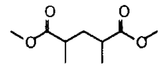
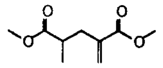
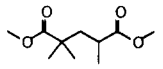
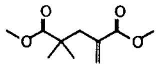
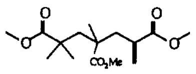
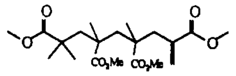
Results

Figure 2 shows a GC/MS trace from the products collected when a IB-PMMA-IP sample with DP$_0$ = 20 is heated to 370 °C for 15 min (50% degradation). The MS inlet was closed from scan 16 to scan 21 to keep the large amount of MMA out of the MS. It is obvious from Figure 2 that a very large number of products are produced under these conditions. Table I shows the compounds responsible for the major peaks in the chromatogram up to scan 116. All structure assignments (except compound XIV) have been checked against authentic samples. The evidence supporting the proposed mechanism is based on smaller fragments (<MMA dimer). The structures for most of the compounds above scan 116 (MMA dimer) were not determined.

Figure 3 shows a similar GC/MS trace for the products collected when an IB-PMMA-IP sample with DP$_0$ = 170 is heated to 350 °C for 15 min (40% degradation). Similar products are formed during degradation of this higher molecular weight IB-PMMA-IP. Because of overlap of the various peaks under these GC conditions, it is not possible to accurately integrate all the peaks present. However, it was observed that more small fragments are formed from the low molecular weight polymer.

The amounts of products I–VIII formed during degradation of the three IB-PMMA-IP samples are used to support the proposed mechanism. Figure 4 is a second GC/MS trace of the products formed when IB-PMMA-IP with DP$_0$ = 170 is heated to 350 °C for 15 min (40% degradation). The GC conditions have been designed to separate the seven products of particular interest. Table II lists the relative amount of each product from the three IB-PMMA-IP samples studied.

Table I
Peak Assignments from GC/MS Analysis of IB-PMMA-IP Degradation (See Figures 2 and 3)

scan no.	compd no.	structure
13	I	
16	II	
21	III	
25	IV	
48	V	
59	VI	
74	VII	
80	VIII	
96 & 100	IXa & IXb	
107	X	
110	XI	
116	XII	
201	XIII	
266	XIV	

Discussion

In Scheme III, the initiating event is a random homolytic scission of a methoxycarbonyl side group (rate = k_1). Table III lists calculated bond dissociation energies (BDE) for the relevant bonds in PMMA. The heats of formation (ΔH°_f, used to calculate the BDEs) for many of the anticipated radicals are not well-known. The methoxycarbonyl radical ($^\bullet$COOCH$_3$) is a particular problem. The generally accepted ΔH°_f for $^\bullet$COOCH$_3$ is −168.9 kJ/mol.[14] However, some reported data suggest ΔH°_f for $^\bullet$COOCH$_3$ is >210 kJ/mol.[15,16] By use of these extreme values it can be concluded that the $(CH_2)_2(CH_3)C{-}COOCH_3$ bond is either considerably weaker or slightly stronger than the main-chain linkages. However (vide infra), initial side-group scission is a kinetic and not, necessarily, a thermodynamic consequence.

Following the initiating scission, the small methoxycarbonyl radical (MC$^\bullet$) either recombines with (rate = k_{-1}, no net reaction) or diffuses away from (rate = k_D) the polymeric radical. A third possibility (β scission to form CH$_3^\bullet$ and CO$_2$, rate = $k_{\beta 6}$) will be addressed later. The kinetic factor favoring side-group over main-chain scission is the faster diffusion of a monomeric radical (relative to a polymeric radical) out of the initially formed cage.

The remaining polymeric radical will undergo β scission (rate = $k_{\beta 4}$) which cleaves the polymer chain (random scission), generating an IBM$^\bullet$ and a methallyl-terminated PMMA chain. The IBM$^\bullet$ will depolymerize (rate = $k_{\beta 3}$), forming MMA until the chain terminus is reached (it has been demonstrated that little second-order termination occurs under these conditions[2]). Each IB-PMMA-IP chain has one isobutyryl and one isopropionyl terminus; therefore, depolymerization will produce either isobutyryl (IB$^\bullet$) or isopropionyl (IP$^\bullet$) radicals.

The support for Scheme III is dependent on the details of formation and subsequent reactions of small radicals

Table II
Relative Amount of Product Formed when IB-PMMA-IP Is Thermally Degraded (See Figure 4)

	rel amt[a,c]		
compd no.	$DP_0 = 20$	$DP_0 = 79$	$DP_0 = 170$
I	0.017	0.007	0.005
II	0.041	0.011	0.007
III	≡1.0 (89.7)	≡1.0 (95.1)	≡1.0 (98.7)
IV	0.0034	0.0014	*b*
V	0.0024	0.0017	0.0010
VI	0.0041	0.0026	0.0010
VIII	0.008	0.006	0.002

[a] (Area of FID signal)(no. of reduced carbons in MMA (4))/(area of MMA FID signal)(no. of reduced carbons in compound). [b] Too little to be accurately integrated. [c] The estimated absolute errors in the amounts of trace products are large, ±80%. However, the relative errors are smaller, ±20%.

during IB-PMMA-IP thermal degradation. It is important to consider the sources and fate of small radicals in the melt. Three radicals (MC•, IB•, and IP•) are accounted for in Scheme III. Radical loss from the system occurs by a number of processes, some of which are addressed in the following paragraphs.

Evaporation from the Sample.

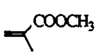
$$R^\bullet \xrightarrow{k_6} R_g^\bullet \tag{6}$$

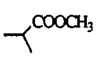
It has been previously established that radical loss by diffusion can decrease the efficiency of step 4 in Scheme III.[5] When a minimum diffusion path of 5 mm and a diffusion constant of $\log_{10} D = 5.9-5870/T$ are used, it is estimated that many seconds are required for a radical to diffuse out of the polymer melt under the present reaction conditions.[5,17] It will be assumed that radical diffusion out of the sample is not important.

Disproportionation or Recombination with a Second Radical.

$$2R^\bullet \xrightarrow{k_7} R\text{–}R \text{ or } R_H + R_= \tag{7}$$

If radical diffusion out of the system is not important, then second-order processes in the melt will ultimately consume all the radicals generated. Second-order reactions of the anticipated radicals will produce five products by disproportionation


III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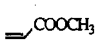
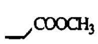
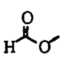
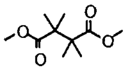
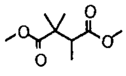

MA

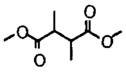

I

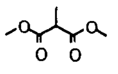

MF

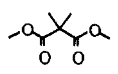
and six products by recombination

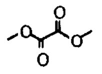






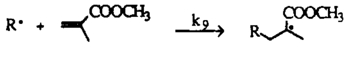




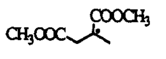


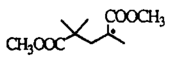
Of these 11 potential products, only I–III (all disproportionation products) are formed in significant amounts, suggesting that recombination does not occur to a large extent under the reaction conditions.

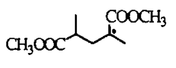
Reaction with MMA Forming R-MMA•.


(8)

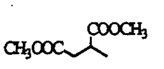
This is a particularly important reaction because R-MMA•, IB•, and IBM• (similar isobutyryl radicals) are probably the most stable radicals in the system. During degradation there is considerable MMA present so that radicals less stable than R-MMA• should react by step 8. Conversely, it is possible that IP-MMA• (and possibly even IB-MMA•) will lose MMA (depolymerize) more slowly than $k_{\beta 1}$. This analysis leads to the conclusion that if MC•, IB•, and IP• are present in significant amounts, then the corresponding MMA addition products should also be present.

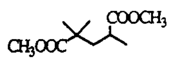

MC-MMA•

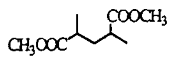

IB-MMA•

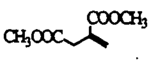

IP-MMA•

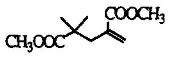
Reconsideration of step 7 (disproportionation) with these radicals leads to six more anticipated products:

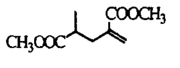

VII


XI


IXa & IXb


VIII


XII


X

Significant amounts of all six products are produced during thermal degradation of IB-PMMA-IP. The unsaturated products (VIII, X, and XII) were present in higher concentration than the saturated counterparts (VII, IX, and XI). I can think of no obvious mechanism for formation of compounds VII and VIII other than the proposed addition of MC• to MMA.

Hydrogen Abstraction from a Neutral Compound (MMA or a Polymer Chain).

$$R^\bullet + R_2\text{–}H \xrightarrow{k_8} R\text{–}H + R_2^\bullet \tag{9}$$

This is not a radical loss process, but rather a radical redistribution reaction. It is not possible from these data to determine if reaction 9 is occurring.

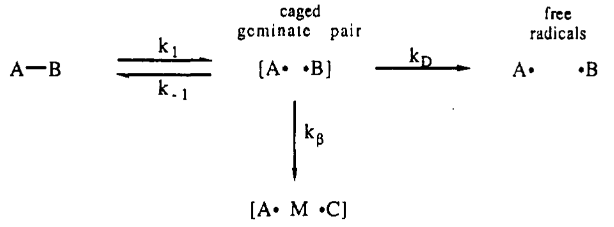
It has been noted that each IB-PMMA-IP initially has one isobutyryl and one isopropionyl terminus. Therefore, ideally, each chain degrading via Scheme III will produce three radicals: one MC•, one IB•, and one IP•. To a first approximation, polymer degradation should produce sim-

Table III
Estimated Bond Dissociation Energies (BDE) for Bonds in PMMA

bond	est BDE, kJ/mol
$(CH_2)_2(CH_3)C\text{–}COOCH_3$	302–342[a]
$(CH_2)(CH_3)(COOCH_3)C\text{–}CH_2$	<322.6[b,c] (316)[c,f]
$(CH_2)_2(COOCH_3)C\text{–}CH_3$	<340.7[d,c] (330.6)[c,f]
$(CH_2)_2(CH_3)CCO\text{–}OCH_3$	393.2[e]

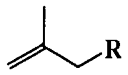
[a] From Benson additivity thermodynamic data using the relationship between $(CH_3)_3C\text{–}COOCH_3$, $(CH_3)_3C\cdot$, and $\cdot COOCH_3$ with $\Delta H^\circ_f = -474.4$, 36.4, and -209[15] kJ/mol or -474.4, 36.4, and -168.9[14] kJ/mol, respectively. [b] From the relationship between $(CH_3)_3C\text{–}CH_2CH_3$, $(CH_3)_3C\cdot$, and $\cdot CH_2CH_3$ using $\Delta H^\circ_f = -186.8$, 28.4, and 107.4 kJ/mol, respectively.[22] [c] This value does not take into account the anticipated stabilization effect of having a carboalkoxy group α to the radical site.[23] This effect might reduce the BDE by as much as a 20 kJ/mol. [d] From the relationship between $(CH_3)_3C\text{–}CH_3$, $(CH_3)_3C\cdot$, and $\cdot CH_3$ using $\Delta H^\circ_f = -166.1$, 28.4, and 146.7 kJ/mol, respectively.[22] [e] From the relationship between $CH_3CO\text{–}OCH_3$, $CH_3CO\cdot$, and $\cdot OCH_3$ using $\Delta H^\circ_f = -386.9$, -22.6, and 16.3 kJ/mol, respectively.[22] [f] The "best available" BDE from a recent review of the literature by McMillen and Golden.[24]

Scheme IV

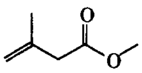


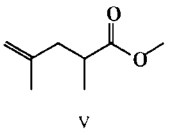
ilar amounts of methyl propionate and methyl isobutyrate (compounds I and II) via radical loss step 7. However, as indicated in Table II, more methyl isobutyrate than methyl propionate is observed from IB-PMMA-IP. Furthermore, degradation of R-PMMA-IP samples that contain no isobutyryl endgroups (GTP initiated with a silylketene acetal other than methyl trimethylsilyl 2,2-dimethylketene acetal) still produces some methyl isobutyrate. It is apparent that chain ends are not the only source of methyl isobutyrate (and possibly IB•) present. A complete understanding of all the paths leading to the observed products will require further study.

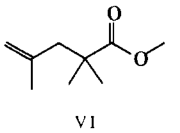
As demonstrated for similar double bond terminated PMMA chains (PMMA-A-=),[5] the PMMA-MA-= remaining after step 3 of Scheme III will react relatively quickly with small, mobile radicals (R•) to form a new macroradical which will depolymerize (steps 4 and 5, Scheme III). The first β scission during this depolymerization process will produce unique, stable products of the general structure



The small radicals anticipated (MC•, IB•, and IP•) should generate compounds IV–VI.


IV


V


VI

Therefore, Scheme III predicts that compounds IV–VI will be formed in significant amounts during the thermal degradation of PMMA-H. Furthermore, the amount of these products should be a function of the number of polymer chains present (i.e., inversely proportional to the initial molecular weight). GC/MS analysis confirms the presence of the anticipated products (Tables I and II) and indicates that the relative amounts vary with polymer molecular weight as expected (Table II).

The cage or geminate effect, first considered by Franck and Rabinowitch,[18] is well established in condensed-phase radical reactions. The kinetic consequences of the cage constraint on homolytic scission reactions are shown in Scheme IV.[19] It is often assumed that initial homolytic scission (rate = k_1) will have an Arrhenius activation energy close to the A–B BDE. The caged radical pair can either re-form the A–B bond (rate = k_{-1}), diffuse out of the cage (rate = k_D), or undergo a β scission forming a radical pair separated by a molecule (rate = k_β). It can be estimated that β scission of the macroradicals in Schemes I–III will occur more slowly than cage recombination (k_{-1}). On the basis of literature data for similar reactions, k_{-1} will be ~1×10^9–1×10^{10} s^{-1}.[19] β scissions that involve carbon-centered radicals forming an olefin and a new carbon-centered radical are usually much slower than ~1×10^9 s^{-1}. For example, an estimated rate of depolymerization ($k_{\beta 1}$) is ~1×10^5 s^{-1} at 350 °C.[20] On the basis of this analysis it is concluded that k_β is too slow to compete with k_{-1}, and therefore diffusion is the dominant mechanism for the radicals to escape the cage. It is possible (but not certain) that $•COOCH_3$ will undergo β scission fast enough for k_β to compete with k_{-1}. Some researchers have estimated that $•COOCH_3$ will decarboxylate in ~1×10^{-7} s at ~300 K.[14] However, recent experiments have demonstrated that $•COOCH_3$ has a longer lifetime than previously thought.[21] Furthermore, for decarboxylation of $•COOCH_3$ to play an important role in PMMA-H degradation, it must be assumed that Scheme III is correct. Therefore, the consequences of $•COOCH_3$ decarboxylation will be ignored.

Table IV
Comparison of Predicted and Observed Amounts of MMA Formed during IB-PMMA-IP Thermal Degradation

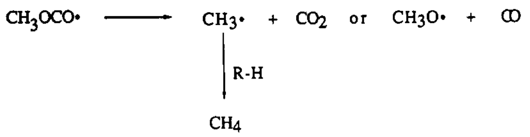
	% MMA		
	$DP_0 = 20$	$DP_0 = 79$	$DP_0 = 170$
predicted by Scheme I	92.5	98.1	99.1
predicted by Scheme II or III	87.5	96.5	98.5
obsd	89.7[a]	95.1[a]	98.7[a]

[a] The estimated error is ±2%.

With small organic molecules, k_D is dependent on viscosity, whereas k_{-1} is not.[19] In the melt, it is certain that the diffusion rate of large polymeric radicals will decrease as the molecular weight of the radical and polymer increases. However, the effect of macroscopic viscosity on the diffusion of small species ($•COOCH_3$) will be much less dramatic. Therefore, the observed rate of initiation should decrease as MW_0 increases for polymer degradations initiated by main-chain scission. In contrast, the rate of initial side-group scission will be relatively insensitive to MW_0. A previous publication demonstrated that PMMA containing weak head-to-head bonds (PMMA-HH) can degrade by main-chain scission.[4] However, for PMMA-HH, main-chain scission is efficient when DP_0 is <100 but inefficient when DP_0 is >200. On the basis of the accepted mechanism of initial random main-chain scission for PMMA-H, a similar decrease in the rate of degradation over this molecular weight range is expected. This effect is not observed. Degradation of PMMA-H with DP_0 = 50 and 180 has the same Arrhenius preexponent (2×10^{16} s^{-1}, after adjustment for the statistical effect of DP_0 on a random scission process), indicating the initial degradation step has the same probability over this molecular weight range.[2]

The results in Table II indicate the relative amount of MMA increases with IB-PMMA-IP molecular weight. Since the kinetic zip length is >DP_0 for these polymers, the fraction of polymer that should be converted to MMA can be estimated. Scheme I predicts that each chain degradation will produce ~1.5 fragments that are not converted to MMA. In contrast, Scheme III predicts that each chain degradation will produce ~2.5 fragments that are not converted to MMA (in both cases it is assumed that IB• will disproportionate to MMA ~50% of the time). The fraction of polymer converted to MMA should be % MMA = $(DP_0 - 1.5)/DP_0$ for Scheme I or % MMA = $(DP_0 - 2.5)/DP_0$ for Scheme III. Table IV compares the observed amounts of MMA with what is predicted on the basis of Scheme I and III. The observed amounts of MMA are closer to what is predicted by Scheme III.

The similarity of Schemes II and III should be addressed. The difference between the two mechanisms is, in many ways, a chicken vs the egg type argument. However, this difference critically affects the general understanding of polymer degradation and the ability to anticipate how other polymers will degrade. Any product analysis that supports Scheme III will also support Scheme II. The main evidence used by Kashiwagi et al. to support Scheme II is the observation of trace products attributed to the degradation of MC•.[1]



$$CH_3OCO\cdot \longrightarrow \underset{\substack{\downarrow\,\text{R-H}\\ CH_4}}{CH_3\cdot} + CO_2 \text{ or } CH_3O\cdot + CO$$

It is not certain that MC• will degrade to CO_2 and CO under the reaction conditions. Indeed, detection of compounds IV and VIII suggests at least some of the MC• is trapped prior to degradation. Kashiwagi et al. also observed much more CO and CO_2 than is predicted by Schemes II or III (~6-fold excess when PMMA-H with $DP_0 = 300$ is degraded). A better understanding of MC• chemistry is necessary before these concerns can be properly addressed.

Conclusions

Thermal degradation of PMMA-H is initiated by scission of a methoxycarbonyl side group rather than main-chain scission. Side-group scission is favored due to a large cage recombination effect which reduces the contribution of main-chain scission. It is proposed that side-group scission will initiate polymer degradation whenever side-group bonds are of similar energy to or weaker than main-chain bonds.

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