

# Thermal Degradation of Poly(2,2-dialkyl-3-hydroxypropionic acid). 2. Thermal Degradation Initiated by Random Scission

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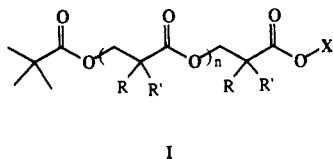
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**ABSTRACT:** The thermal degradation of poly(2,2-dialkyl-3-propiolactones) (I) has been studied. By comparing the thermal degradation of capped (methyl esterified) and uncapped (carboxylic acid terminated) polymer, it is demonstrated that above  $\sim 350^\circ\text{C}$ , I degrades by unzipping from carboxylic acid termini. Random scissions can generate chains with carboxylic acid termini. Capped I requires random scission generation of carboxylic acid termini before polymer unzipping can ensue. One random scission process elucidated requires the presence of a C-H group at the 2 position of one of the alkyl side groups in I and generates two distinguishable chains. One of the chains has a carboxylic acid terminus that can unzip. The second chain is still capped and must undergo further random scissions before mass loss can occur.

## Introduction

We previously established<sup>1</sup> that thermal degradation of poly(2,2-dialkyl-3-hydroxypropionic acid)s (I, usually prepared by living anionic polymerization of the corresponding 2,2-dialkyl-3-propiolactone) occurs by reverse polymerization when the terminal carboxylate is deprotonated ( $X = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cs}^+, \text{R}_4\text{N}^+, \text{R}_4\text{P}^+$ ). We define reverse polymerization as a monomer-producing reaction starting at the synthetic chain terminus and moving sequentially toward the synthetic chain initiator end. We define unzipping as a reaction starting at a chain end and moving sequentially toward the other end.



Here we report results from the thermal degradation of a number of examples of I (Table I) which demonstrate that at higher temperatures ( $\geq 300^\circ\text{C}$ ), carboxylic acid terminated chains efficiently unzip. Furthermore, carboxylic acid terminated chains can be formed via an initial random heterolytic scission that ultimately produces two chains. One chain is carboxylic acid terminated. The other chain has an acrylate group on one end. For the case where X (in I) is an alkyl group (capped polymer), the second chain must undergo another random heterolytic scission before it can degrade further. The observed random scission requires the presence of a C-H group at the 2 position of the R or R' group in I. This random scission competes efficiently with unzipping when the terminal carboxylate group is protonated ( $X = \text{H}$ ) and is prerequisite when the carboxylate is esterified ( $X = \text{CH}_3$ ), for which case microscopic-reverse polymerization cannot occur.

Our proposed mechanism for thermal degradation of I is shown in Scheme I. For carboxylic acid terminated chains the mechanism is similar to what we observed previously with carboxylate terminated chains.<sup>1</sup> However, the higher temperature necessary to degrade carboxylic acid terminated chains leads to simultaneous transesterification (Scheme I, reaction 9).

An added complication observed at these higher temperatures is random scission generation of carboxylic acid terminated chains. Many polymers thermally degrade by

**Table I**  
Effect of Alkyl Side Chain on Temperature of Polymer Degradation

polymer	DP <sub>0</sub>	R	R'	peak degrad, <sup>a</sup> °C
I(MM)-COOH	1070	CH <sub>3</sub>	CH <sub>3</sub>	445
I(MN)-COOCH <sub>3</sub>	1080	CH <sub>3</sub>	CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	445
I(ME)-COOCH <sub>3</sub>	1000	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	415
I(MP)-COOCH <sub>3</sub>	1000	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	405
I(MsB)-COOCH <sub>3</sub>	900	CH <sub>3</sub>	CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	390

<sup>a</sup> Peak degradation temperature when sample is heated at  $10^\circ\text{C}/\text{min}$ .

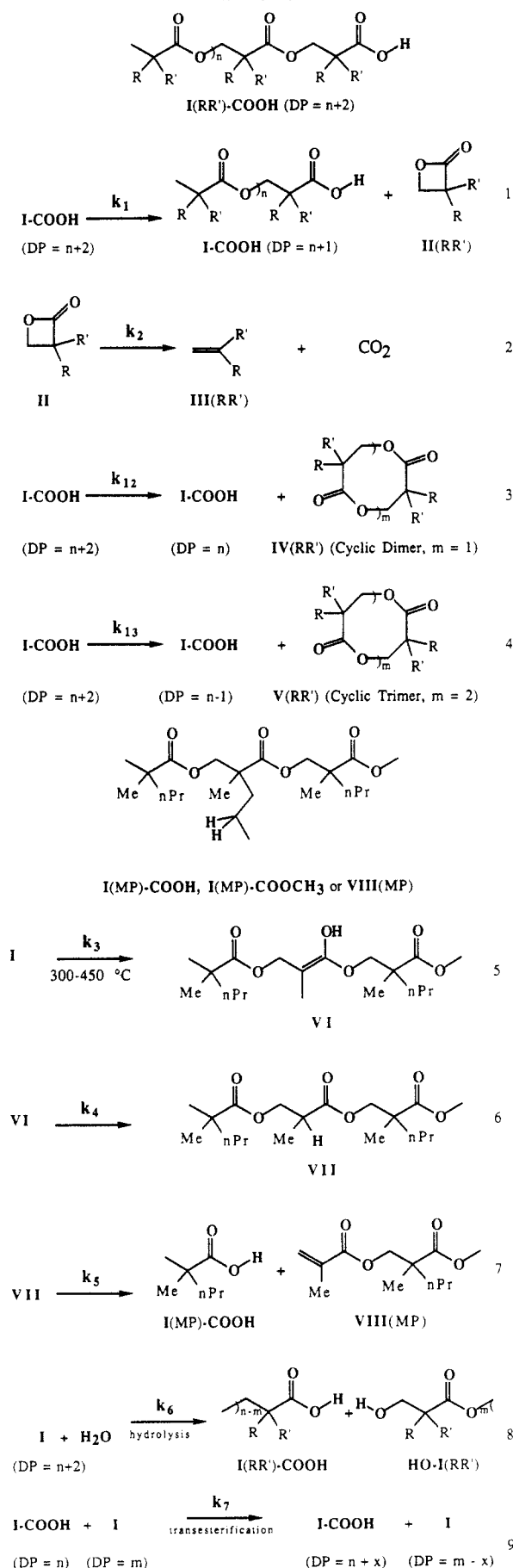
random scission initiated processes. Examples include PMMA<sup>3</sup> (random homolytic scission), and poly(3-hydroxypropionic acid)<sup>4</sup> (random heterolytic scission). In the case of PMMA, the entire molecule "unzips" following the initial scission as long as the chains have an initial degree of polymerization (DP<sub>0</sub>) less than  $\sim 200$ .<sup>5</sup> In contrast, poly(3-propiolactone) shows no tendency to unzip, and significant mass loss occurs only after a large number of scissions have taken place. When the degree of polymerization of the polymer (DP) is monitored as a function of polymer mass loss (Grassie plot), the above two mechanisms appear very different. Whereas the molecular weight of PMMA (DP<sub>0</sub>  $\sim 54$ ) changes slowly with mass loss, the molecular weight of poly(3-propiolactone) (DP<sub>0</sub>  $\sim 1200$ ) decreases to less than 5% of the initial value after only 5% mass loss. Scheme I combines features from the above two examples (poly(3-hydroxypropionic acid) and PMMA) and yet is unique. For example, subsequent to random scission, unzipping occurs only in one direction. Furthermore, once generated by the random scission, the carboxylic acid terminated chain can completely unzip (i.e., competitive termination is not certain).

In Scheme I and throughout the text, I(RR')-COOH designates a carboxylic acid terminated poly(2,2-dialkyl-3-hydroxypropionic acid) chain where the alkyl groups (R and R') are designated as M = methyl, E = ethyl, P = propyl, sB = *sec*-butyl, and N = neopentyl (Table I). The vast majority of our studies were done on poly(2-methyl-2-propyl-3-hydroxypropionic acid), I(MP)-COOH. I(MP)-COOCH<sub>3</sub> is the corresponding methyl-esterified polymer.

## Experimental Section

**Polymer Synthesis.** The 2,2-dialkyl-3-propiolactones (II) were prepared by literature procedures.<sup>6</sup> Polymerizations were

Scheme I



initiated by tetrabutylammonium pivalate (TBAP). Initiator solutions were prepared by adding equimolar amounts of tetrabutylammonium hydroxide and pivalic acid to toluene followed by azeotropic removal of the methanol and water. The final

volume was adjusted to give a 0.2 M solution of TBAP initiator in toluene. A typical polymerization was carried out as follows: To a 500-mL round-bottom flask was added 200 mL of hexane, 38.4 g (0.3 mol) of II(MP), and 1.6 mL of 0.2 M TBAP initiator. The solution was heated at reflux ( $\sim 2$  h) until no lactone was detected by IR ( $1834\text{ cm}^{-1}$ ). The solution was cooled and the polymer filtered from the hexane. The product had an  $M_n$  of 117 000 and  $M_w/M_n$  of 1.05. Polymers of varying DP were prepared by adjusting the monomer/initiator ratio. The chain termini were converted from tetrabutylammonium carboxylate to carboxylic acid by taking the polymer up in THF, adding dilute HCl, and precipitating the polymer with excess water.

Poly(2-methyl-2-propylpropiolactone) with acid end groups was methyl esterified by reaction with diazomethane<sup>7</sup> or dimethylformamide dimethyl acetal.<sup>8</sup> NMR analysis on low-MW material (DP  $\sim 50$ ) indicated that either procedure esterified  $>90\%$  of the carboxylic acid termini.

**Other Syntheses.** 3,3-Dideuterio-2-methyl-2-propyl-3-propiolactone,  $D_2$ II(MP), was prepared from the corresponding hydroxy acid. 3,3-Dideuterio-2-methyl-2-propyl-3-acetoxypropionaldehyde (prepared with  $CD_3O$ )<sup>9</sup> was oxidized by sodium chlorite<sup>10</sup> followed by hydrolysis of the acetoxy group, yielding 3,3-dideuterio-2-methyl-2-propyl-3-hydroxypropionic acid.

Methylpropylketene (MPK) was prepared by the addition of triethylamine to 2-methylpentanoic acid chloride. Cyclic trimer (V) was isolated from a large-scale condensation polymerization of 2-methyl-2-propyl-3-hydroxypropionic acid. 2-Methyl-2-pentene, III(MP), was purchased from Aldrich Chemical Co.

**Polymer Degradations.** Polymer degradations were done in a Mettler TG 50 thermobalance purged with a steady flow of nitrogen or helium. The oxygen concentration in the heated zone was measured with a Teledyne Analytical Instruments Model 310 trace oxygen analyzer. The oxygen concentration during TGA experiments was  $<150$  ppm.

Thermal/mass spectral analysis on the evolved gases was done with the Mettler TG 50 interfaced to a HP 5970A mass-selective detector. The purge gas was helium, and a small positive pressure was maintained in the heated zone by sealing the balance pan access to the Mettler TG 50 thermobalance. A small portion of the gas evolved during degradation was drawn into the mass spectrometer inlet via a  $1/16$ -in. stainless steel conduit heated to  $200^\circ\text{C}$ . The oxygen concentration in the heated zone during thermal/mass spectral analysis was  $<15$  ppm. Polymer samples were either placed in quartz boats (samples  $> 1$  mg) or coated on 7-mm-diameter quartz plates from a dilute  $CH_2Cl_2$ /*tert*-butyl alcohol solution. Uniform films of  $0.1\text{--}4\text{ }\mu\text{m}$  were prepared by adjusting the polymer solution concentration or the volume of solution placed on the quartz plate. Profilometry of coated quartz plates was done with a Sloan Dektak IIA. After removal of the outer edge, the remaining film had a uniform thickness  $\pm 20\%$ .

GC/MS analyses of isolated products (both EI and CI) were done on a VG Instruments 70E spectrometer coupled to a Hewlett Packard 3790 GC. Part of the sample was split off and detected by FID.

DP-MS with  $NH_4^+$  CI was done on a Finnigan 4615B GC/MS system. Approximately 1 mg of polymer was loaded into the solids probe. The sample was inserted into chemical ionization source and heated from  $50$  to  $490^\circ\text{C}$  at  $15^\circ\text{C}/\text{min}$ . Ammonia (Union Carbide Corp.) was used as the chemical ionization reagent gas. The ion source pressure was set at 0.85 Torr and the source temperature was  $200^\circ\text{C}$ . An electron energy of  $70\text{ eV}$  was used. The mass spectrometer was scanned at  $75\text{--}700\text{ D/s}$ . Response factors for II(MP), III(MP), and V(MP) were determined by injecting standard mixtures of the compounds onto a 25-m DB-5 fused-silica capillary column (J&W Scientific) initially at  $50^\circ\text{C}$  and heated to  $360^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ . The MS conditions for the standards were the same as used for the polymer samples.

IR spectra (Nicolet Model 5DXC FTIR) of the evolved gases as a function of temperature were obtained with a setup similar to that used for MS analysis. The IR extinction coefficients for II(MP), III(MP),  $CO_2$ , and MPK are  $\epsilon = 714, 85, 300\text{--}450$ , and  $650\text{ M}^{-1}\text{ cm}^{-1}$  at  $1840, 893, 2350$ , and  $2120\text{ cm}^{-1}$ , respectively. Values of  $\epsilon$  for II(MP), III(MP), and MPK at  $1840, 893$ , and  $2120\text{ cm}^{-1}$  were calculated from the peak absorbances of  $0.1\text{ g}/10\text{ mL}$  methylene chloride solutions in a  $0.1\text{-mm}$  path length cell. For  $CO_2$ ,  $\epsilon$  was determined from standard gas samples.<sup>11</sup>

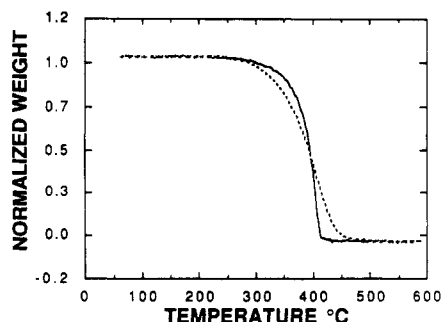


Figure 1. TGAs from I(MP)-COOH (—) and I(MP)-COOCH<sub>3</sub> (---) heated at 20 °C/min, DP<sub>0</sub> = 200.

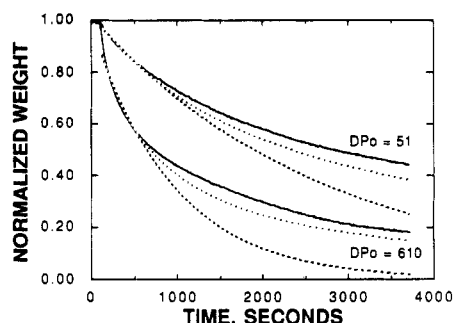


Figure 2. Isothermal degradation of I(MP)-COOCH<sub>3</sub> with DP<sub>0</sub> of 50 and 610 at 330 °C (—) along with first-order (---) and second-order (···) fits to the data.

**Other Analyses.** NMR spectra of the initial and partially degraded polymer were run in CDCl<sub>3</sub> on a Nicolet/GE NT 360-MHz spectrometer. The samples contained 50 mg of polymer in 1.5 mL of CDCl<sub>3</sub>. The spectra shown in Figures 9 and 10 are the average of ~1000 scans.

Molecular weights were determined by GPC using PMMA standards.

## Results

**Thermogravimetric Analysis (TGA).** Figure 1 compares TGAs of I(MP)-COOH (DP ~ 200) with the same polymer esterified at the terminal carboxylic acid site, I(MP)-COOCH<sub>3</sub>. The initial samples were ~5 mg and the heating rate was 20 °C/min. Degradation of both polymers starts about 300 °C, peaks around 400–410 °C, and is complete by 450 °C. By 500 °C the samples have lost >99% of their initial mass.

For I(MP)-COOH the rate of polymer degradation at a given temperature is not very dependent on the initial molecular weight. However, for I(MP)-COOCH<sub>3</sub>, the rate of polymer degradation is dependent on the molecular weight of the sample. Figure 2 compares the rate of mass loss from two samples of I(MP)-COOCH<sub>3</sub> with DP<sub>0</sub>'s of 50 and 610. The samples were temperature-jumped from 60 to 330 °C at 100 °C/min. The initial degradation of the polymer with DP<sub>0</sub> = 610 is considerably faster than the DP<sub>0</sub> = 50 sample. Also shown in Figure 2 are first-order ( $k = \text{time} \times \ln(\text{mass})$ ) and second-order ( $k = \text{time} \times 1/\text{mass}$ ) fits to the data at the initial stages of degradation. Mass loss appears close to second order. The second-order fits to the data give apparent rates of  $1.68 \times 10^{-3}$  and  $4.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  for the DP<sub>0</sub> = 610 and 50 polymers, respectively.

The thermal degradation temperature of I is also sensitive to the alkyl groups (R and R') present in the polymer. Table I lists the peak degradation temperatures for I (similar DP<sub>0</sub>) with varying alkyl group substitution. I(MsB)-COOCH<sub>3</sub> degrades 55 °C lower than I(MN)-COOCH<sub>3</sub> and I(MM)-COOCH<sub>3</sub>.

**FTIR Analysis of the Evolved Gases.** TGA/FTIR analysis of the gas evolved at 300, 350, and 400 °C from

degradation of I(MP)-COOH (DP ~ 1000) indicates carbon dioxide (2350 and 700 cm<sup>-1</sup>) and III(MP) (3000, 1650, 1450, and 893 cm<sup>-1</sup>) are the major products. Above 400 °C, a distinctive peak appears in the TGA/FTIR at 2120 cm<sup>-1</sup>. We assign the 2120 cm<sup>-1</sup> peak to methylpropylketene (MPK), which is a minor product. Relative amounts of CO<sub>2</sub>, III(MP), and MPK are 1:1:0.005 based on the IR extinction coefficients.

**Mass Spectral Analysis of the Evolved Gases.** A variety of mass spectral (MS) analysis were done on the volatile polymer degradation products.

(1) *GC/MS of Volatiles Trapped in Liquid N<sub>2</sub>*: Both electron impact (EI/MS) and chemical ionization (CI/MS) employing isobutane were used. The CI/MS active chemical reagent ((CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup>) usually transferred a proton to the parent compound generating [M + H]<sup>+</sup>.

(2) *Analysis of the Volatiles Generated by Direct Pyrolysis-Mass Spectrometry (DP-MS) Using NH<sub>4</sub><sup>+</sup> Chemical Ionization Which Generated [M + NH<sub>4</sub>]<sup>+</sup>*: These experiments were similar to those reported previously by Garozzo et al.<sup>19</sup>

(3) *Analysis of Volatiles Generated during TGA by a HP 5970A Mass-Selective Detector*: The sensitivity of the MS detector allows the use of thin polymer films (0.1–20 μm), which reduces complications due to volatile diffusion out of the samples.

Product for GC/MS analysis was isolated from large-scale degradations (~250 mg) carried out as described previously.<sup>20</sup> Briefly, the polymer is placed in a glass tube and heated to the desired degradation temperature with a high flow of He passing over the sample. All volatiles leaving the sample are carried away by the He and trapped in liquid N<sub>2</sub>. When I(MP)-COOCH<sub>3</sub> (DP = 50) is degraded to ~50% mass loss, GC/MS analysis (CI/MS with (CH<sub>3</sub>)<sub>3</sub>C<sup>+</sup> as the active chemical reagent) indicates major products are III(MP), II(MP), and cyclic oligomers. Flame ionization detection of the GC effluent (no standardization) indicates 95% III(MP), 0.35% II(MP), and 1.4% cyclic trimer (V).

Direct pyrolysis-mass spectrometry ((DP-MS) using NH<sub>4</sub><sup>+</sup> chemical ionization) confirmed the products observed by GC/MS; however, considerably more cyclic oligomer is estimated than in the GC/MS experiments. The intensities of CI/MS signals ([M + NH<sub>4</sub>]<sup>+</sup> adduct, ratio of V/(II + III + V)) suggest 5–10% of I(MP) (DP = 50) is converted to cyclic oligomer (Table III). However, analysis of standard mixtures of III(MP), II(MP), and V(MP) indicates that III(MP) is chemically ionized by NH<sub>4</sub><sup>+</sup> much less efficiently than either II(MP) or V(MP). Interestingly, whereas II and III give [M + NH<sub>4</sub>]<sup>+</sup> and [M + NH<sub>4</sub>NH<sub>3</sub>]<sup>+</sup> signals in CI/MS (the signal ratios are 146<sup>+</sup>/163<sup>+</sup> = 2.3 for II and 102<sup>+</sup>/119<sup>+</sup> = 3.3 for III), V shows only the [M + NH<sub>4</sub>]<sup>+</sup> signal at 402<sup>+</sup>. It is likely that NH<sub>4</sub><sup>+</sup> sits nicely in the middle of the trimer ring of V(MP) whereas NH<sub>4</sub>NH<sub>3</sub><sup>+</sup> does not. The response factors were normalized based on the [M + NH<sub>4</sub>]<sup>+</sup> signals. Estimated normalization factors are 50.3:1 (weight normalized) for III(MP), II(MP), and V(MP), respectively. With these normalization factors considered, ~1% cyclic oligomer forms from carboxylic acid terminated or esterified I(MP) regardless of the polymers initial molecular weight.

The major products of I(MP) degradation (CO<sub>2</sub>, III(MP), MPK, and II(MP)) are easily distinguished by TGA/MS. MS analysis of CO<sub>2</sub> shows an intense peak at mass 44, a smaller peak at mass 28, and the <sup>13</sup>C isotope peak at mass 45. MS analysis of III(MP) shows a typical unsaturated hydrocarbon ion series with the molecular ion at mass 84 and a base peak at mass 56 (loss of ethylene). MPK shows a parent ion at mass 98 along with a strong peaks with masses 69, 41 (base), and 39. II(MP) shows no

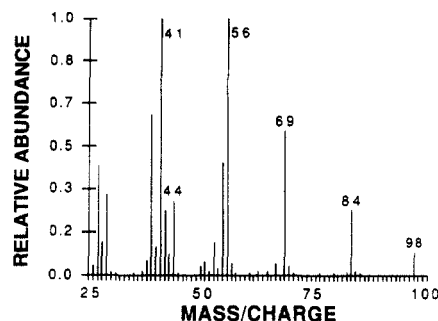


Figure 3. Mass spectrum of the gases evolved during thermal degradation of I(MP)-COOCH<sub>3</sub>, DP<sub>0</sub> = 5880.

Table II  
Amounts of III and II Observed during I(MP) Degradation

polymer	evolved gas heated to 400 °C	44 <sup>+</sup> :84 <sup>+</sup> :98 <sup>+</sup>	% III	% II
I(MP)-COOH (DP = 50)	no	0.94:1:0.42	52	39
I(MP)-COOCH <sub>3</sub> (DP = 50)	yes	1.75:1:0.05	97	5
I(MP)-COOCH <sub>3</sub> (DP = 50)	no	1.20:1:0.30	67	27
I(MP)-COOCH <sub>3</sub> (DP = 50)	yes	1.34:1:0.06	74	<5
I(MP)-COOCH <sub>3</sub> (DP = 5880)	no	1.34:1:0.24	74	21
I(MP)-COOCH <sub>3</sub> (DP = 5880)	yes	1.75:1:0.002	97	<0.5

evidence of the parent ion at mass 128. Apparently, the 2-methyl-2-propyl-3-propiolactone radical ion fragments to III(MP)<sup>+</sup>, (84<sup>+</sup>) and CO<sub>2</sub> or MPK<sup>+</sup> (98<sup>+</sup>) and formaldehyde. The ratios of the 44<sup>+</sup>, 84<sup>+</sup>, and 98<sup>+</sup> signals from II(MP) are ~0.06/1/0.09. The cyclic oligomers are not volatile enough to see with our TGA/MS apparatus.

The mass spectrum of II(MP) changes considerably when it is thermally degraded prior to entering the mass spectrometer. Only CO<sub>2</sub> and III(MP) are observed as products; little (if any) MPK forms. The ratios of the 44<sup>+</sup>, 84<sup>+</sup>, and 98<sup>+</sup> signals are ~2/1/0. This is consistent with the observation that thermal degradation of β-propiolactone yields CO<sub>2</sub> and ethylene exclusively; ketene is not formed.<sup>12-14</sup> We can distinguish the source of MPK during polymer degradation (lactone or a direct product of degradation) by passing the evolved gasses through a heated quartz tube prior to entering the mass spectrometer. Under these conditions, MPK<sup>+</sup> from lactone degradation is eliminated, and any MPK seen must form during polymer degradation.

The MS data indicate the peaks at 44<sup>+</sup>, 84<sup>+</sup>, and 98<sup>+</sup> can be assigned to CO<sub>2</sub>, III(MP), and MPK, respectively. Furthermore, if III(MP), CO<sub>2</sub>, and II(MP) are the major products (assuming polymer degradation forms little MPK directly), the fraction of volatiles entering the mass spectrometer as III(MP)(CO<sub>2</sub>) or II(MP) can be estimated based on the ratios of the 44<sup>+</sup>, 84<sup>+</sup>, and 98<sup>+</sup> signals. III(MP)(CO<sub>2</sub>) ~ (44<sup>+</sup>/1.8 × 84<sup>+</sup>) ~ 1 - (98<sup>+</sup>/1.1 × 84<sup>+</sup>); II(MP) ~ (98<sup>+</sup>/1.1 × 84<sup>+</sup>) ~ 1 - (44<sup>+</sup>/1.8 × 84<sup>+</sup>).

Figure 3 is a mass spectrum of the gases evolved during thermal degradation of I(MP)-COOCH<sub>3</sub> (4-μm film, heated at 20 °C/min, DP<sub>0</sub> = 5880). The observed spectrum is consistent with the major products being CO<sub>2</sub>, III(MP), and II(MP), giving rise to peaks at 44<sup>+</sup>, 84<sup>+</sup>, and 98<sup>+</sup>. Because II(MP) thermally degrades to III(MP) and CO<sub>2</sub>, the ratios at the 44<sup>+</sup>, 84<sup>+</sup>, and 98<sup>+</sup> signals will be sensitive to the temperature/time profile to which the evolved gases are exposed. The temperature/time profile is dependent on sample geometry and can be adjusted experimentally. Table II lists the ratios of the 44<sup>+</sup>, 84<sup>+</sup>, and 98<sup>+</sup> signals (at peak degradation) when I(MP)-COOCH<sub>3</sub> and I(MP)-COOH are degraded under various conditions. In all cases the 98<sup>+</sup> signal decreases when the evolved gases are passed through a quartz tube heated to 400 °C. Comparison of TGA data with MS data for various II(MP) polymers

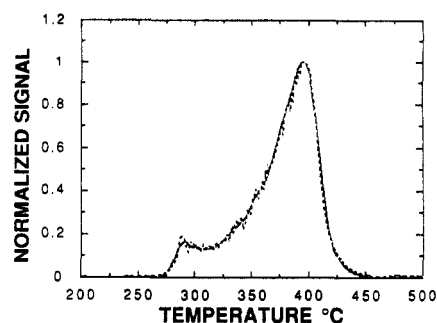


Figure 4. Appearance of 84<sup>+</sup> (---, III) during thermal degradation of I(MP)-COCH<sub>3</sub> (DP<sub>0</sub> = 5880) overlaid with the rate of mass loss (—).

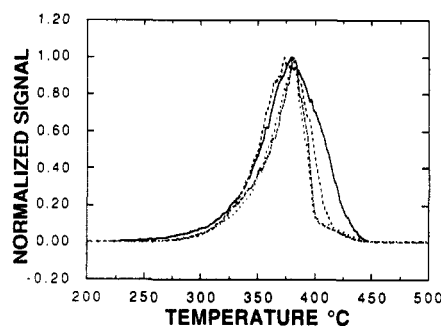


Figure 5. Appearance of ion 84<sup>+</sup> (III) when ~5-μm-thick samples of I(MP)-COOH with DP<sub>0</sub> = 5880 (—), 610 (---), 200 (- - -), and 50 (···) are heated at 20 °C/min.

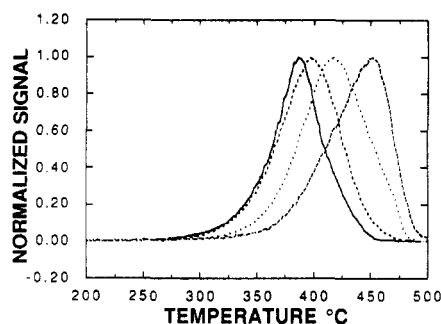


Figure 6. Appearance of ion 84<sup>+</sup> (III) when ~5-μm-thick samples of I(MP)-COOCH<sub>3</sub> with DP<sub>0</sub> = 5880 (—), 610 (---), 200 (- - -), and 50 (···) are heated at 20 °C/min.

indicates the first derivative of mass loss is by the appearance of the 44<sup>+</sup> and 84<sup>+</sup> MS signals (Figure 4). Therefore, monitoring the 84<sup>+</sup> (or 44<sup>+</sup>) MS peak accurately represents the relative amount of weight loss from the sample. However, the methylpropylketene peak (98<sup>+</sup>) does not accurately reflect weight loss in the samples.

Figure 5 shows the appearance of the 84<sup>+</sup> MS signal when ~5-μm-thick samples of I(MP)-COOH (DP<sub>0</sub> = 5880, 610, 200, and 50) are heated at 20 °C/min. The temperature of peak degradation occurs at ~380 °C, almost independent of the initial molecular weight.

Figure 6 shows the appearance of the 84<sup>+</sup> MS signal when ~5-μm-thick samples of I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 5880, 610, 200, and 50) are heated at 20 °C/min. In contrast to the data for I(MP)-COOH (Figure 5), the temperature of peak degradation decreases as the molecular weight of the polymer increases, consistent with the isothermal mass loss data (Figure 2).

Figure 7 shows the appearance of the 84<sup>+</sup> (III(MP)) and 86<sup>+</sup> (D<sub>2</sub>III(MP)) MS signals when a ~5-μm-thick sample of the block copolymer D<sub>2</sub>I(MP)||I(MP)-COOH (DP<sub>0</sub> = 120) is heated at 20 °C/min. It is apparent that the termination end of the molecule degrades before the initiation end. This is the same result observed when carboxylate-terminated polymers degrade by reverse polym-

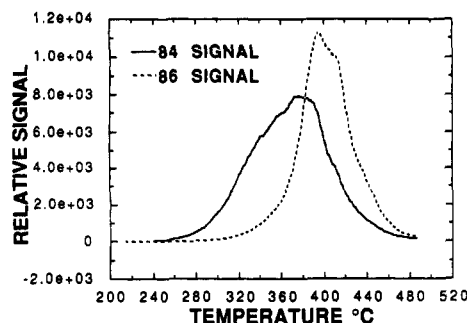


Figure 7. Appearance of ion 84<sup>+</sup> (—, III) and ion 86<sup>+</sup> (---, D<sub>2</sub>-III) when D<sub>2</sub>I(MP)I(MP)-COOH (DP<sub>0</sub> = 120) is heated at 20 °C/min.

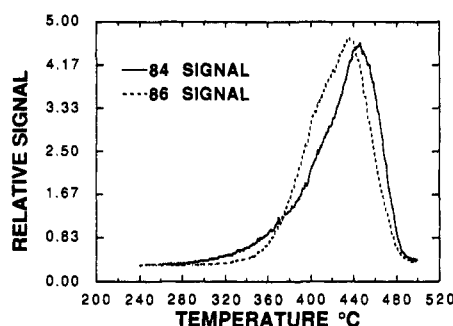


Figure 8. Appearance of ion 84<sup>+</sup> (—, III) and ion 86<sup>+</sup> (---, D<sub>2</sub>-III) when D<sub>2</sub>I(MP)I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 120) is heated at 20 °C/min.

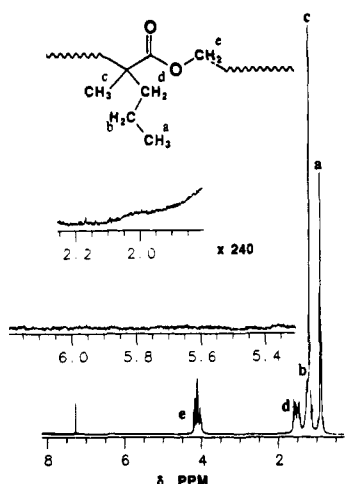


Figure 9. <sup>1</sup>H NMR spectrum of I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 5880) before thermal degradation.

erization, suggesting that reverse polymerization (or at least unzipping from the synthetic chain terminus) contributes to degradation in this case.<sup>1</sup>

In contrast, when D<sub>2</sub>I(MP)I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 120) is degraded under identical conditions (Figure 8), the initiation end of the molecule degrades before the termination end.

**NMR Analysis of Partially Degraded Polymer.** Figures 9 and 10 compare <sup>1</sup>H NMR spectra of I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 5880) before and after 73% thermal degradation. Before degradation (Figure 9), expansions of the regions from 1.8–2.25 and 5.3–7.0 ppm (×240 insets) show no peaks. Figure 10 shows the same polymer after 73% thermal degradation. The general spectrum is essentially identical to that of the initial polymer. However after partial degradation, expansion from 5.3–7.0 ppm (×240 inset) reveals vinyl protons at 5.54 and 6.05 ppm. We assign these peaks to the “stable” end group of VIII formed in reaction 7 of Scheme I. The structure of this end group is similar to methyl methacrylate which has

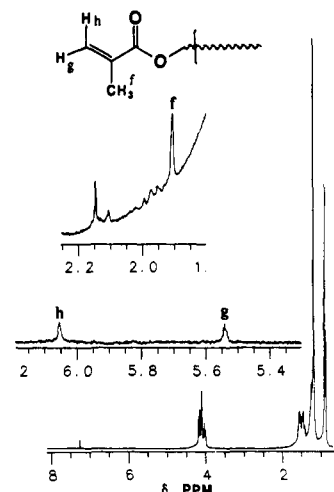


Figure 10. <sup>1</sup>H NMR spectrum of I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 5880) after 73% thermal degradation.

vinyl peaks at 5.51 and 6.06 ppm and a methyl group at 1.90 ppm. The second inset in Figure 10 shows a relatively strong peak at 1.90 ppm. The relative integrations (RI) for protons e, f, g, and h in the degraded polymer (see Figure 10) are 1000:2.3:1:1. The integration suggests that one acrylate end group exists for every 500 monomers; however, GPC analysis on the degraded polymer shows DP ~ 150. Being mindful of the inherent errors associated with NMR integrations and GPC data, the results indicate ~30% of the polymer chains have acrylate end groups. The degraded polymer shows other absorptions in the NMR at 1.70 (singlet, RI ~ 1.1), 1.97 (triplet with 7-Hz coupling constant, RI = 0.7), 2.43 (multiplet, RI < 0.5), 2.15 (singlet, RI < 0.5), 4.65 (doublet, RI = 1.0), and 4.95 ppm (doublet, RI = 1.0), which are possibly other end groups but cannot be attributed to the β-scission in reaction 7 of Scheme I. The multiplet at 2.43 ppm could be due to the proton α to the carbonyl group in VII. If this is correct it would indicate that formation and scission of VII occur on a similar time scale.

Methacrylate end groups are formed regardless of the initial molecular weight of the polymer. With I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 100), relative integrations (RI) for protons e, f, g, and h from polymer degraded 65% are 1000:6.1:2.4:2.3. Other absorptions are still observed at 1.70 (singlet, RI ~ 5), 1.97 (apparent triplet with 7-Hz coupling constant, RI = 3.2), and 4.65 ppm (doublet, RI ~ 5) but signals at 2.15, 2.43, and 4.95 ppm are not present. In this sample a singlet is seen at 3.72 ppm due to the methyl ester end group. Relative integration of the methyl end group increases from 14 to 27 during the degradation process. The integration suggests that the polymer initially has one methyl ester end group for every 107 monomers (consistent with DP<sub>0</sub> = 100) but the degraded polymer has one methyl ester end group for every 55 monomers. GPC analysis on the degraded polymer indicates DP ~ 50. This result further confirms that the esterified synthetic chain terminus is not degrading as fast as the initiator end of the chain.

D<sub>2</sub>I-COOCH<sub>3</sub> has no main-chain methylene protons. When 60% degraded D<sub>2</sub>I-COOCH<sub>3</sub> (DP<sub>0</sub> = 40) is analyzed by <sup>1</sup>H NMR, a significant peak is observed at 1.90 ppm along with a smaller signal is at 1.70 ppm (in this experiment, the 1.70 ppm signal appears as a doublet). The triplet at 1.97 ppm is smaller than in previous experiments using I(MP)-COOCH<sub>3</sub>, and there are virtually no signals from 4.3 to 6.1 ppm. This observation confirms that main-chain CH<sub>2</sub> groups are converted to acrylic groups during polymer degradation.

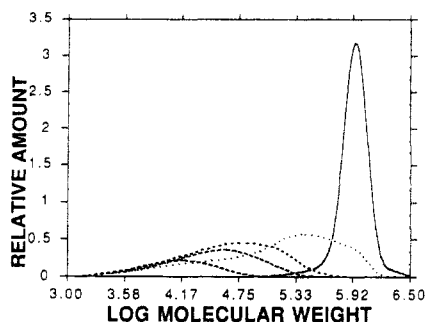


Figure 11. Molecular weight distributions for I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 5880) after 0, 20, 40, 60, and 80% degradation.

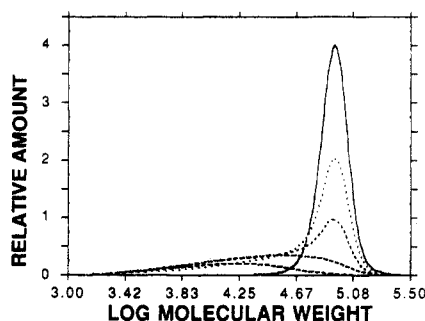


Figure 12. Molecular weight distributions for I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 610) after 0, 20, 40, 60, and 80% degradation.

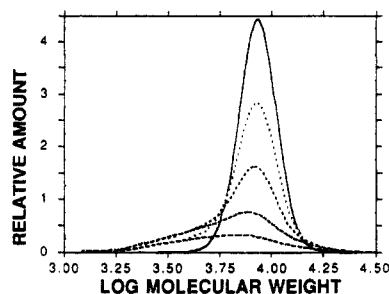


Figure 13. Molecular weight distributions for I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 50) after 0, 20, 40, 60, and 80% degradation.

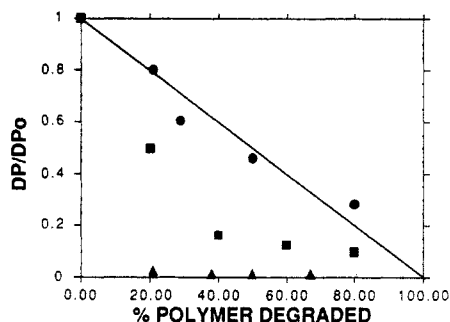


Figure 14. Effect of degradation on DP/DP<sub>0</sub> for I(MP)-COOCH<sub>3</sub> with DP<sub>0</sub>s of 50 (●), 610 (■), and 5880 (▲).

Methacrylate end groups are also observed when I(ME)-COOCH<sub>3</sub> and I(MsB)-COOCH<sub>3</sub> are ~50% thermally degraded. However, no methacrylate end groups are observed when I(MN)-COOCH<sub>3</sub> is partially degraded.

**Molecular Weight Analysis of Degraded Polymers.** Figures 11–13 show GPC data for I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 5880, 610, and 50) during various stages of degradation. It is apparent that MW decreases much faster for the higher MW polymer (Figure 11) than for the low-MW material (Figure 13). A plot of DP/DP<sub>0</sub> versus percent polymer degradation (Figure 14) for the three polymers indicates that for the DP<sub>0</sub> = 50 polymer DP is apparently a linear function of the percent degradation. The point for DP<sub>0</sub> = 50 polymer at 80% degradation is skewed toward a higher molecular weight due to interference from the solvent peak,

which obscures the GPC traces below DP = 10. The appearance of low molecular polymer even after short periods of thermal degradation confirms that random scission degradation occurs under these conditions. This is in sharp contrast to the results reported earlier for living depolymerization of I.

## Discussion

**Description of Scheme I.** The remaining discussion will compare our observations with what is anticipated based on the proposed mechanism, Scheme I. A detailed description of Scheme I follows.

Scheme I assumes that low molecular weight volatiles are generated by unzipping (sometimes referred to as back-biting) from carboxylic acid terminated chains. This unzipping process competitively produces monomer (II, rate =  $k_1$ ), cyclic dimer (IV, rate =  $k_{12}$ ), cyclic trimer (V, rate =  $k_{13}$ ), and larger cyclic oligomers. The relative amounts, II/(II + IV + V + ...), are simply the ratio of the rates  $k_1/(k_1 + k_{12} + k_{13} + k_{14} + \dots)$ . This is in accord with what has been previously proposed.<sup>15,16,19</sup> When each chain initially has a carboxylic acid terminus, degradation will start at this synthetic chain end, assuming little transesterification (reaction 9, rate =  $k_7$ ) occurs prior to degradation. However, any reaction that increases the number of carboxylic acid terminated chains (two examples are shown in Scheme I, reactions 5–7 and 8) will further contribute to mass loss.

For polymer samples that do not initially have carboxylic acid terminated chains (esterified polymer), reactions 5–7 can produce carboxylic acid termini. This sequence is initiated by hydrogen abstraction  $\gamma$  to the carbonyl, reaction 5 with rate  $k_3$ . This random heterolytic cleavage produces a carbonyl with an  $\alpha$  hydrogen. Analogous to poly(3-hydroxypropionic acid),<sup>4</sup> the presence of the hydrogen  $\alpha$  to the carbonyl allows the polymer to undergo random heterolytic scission, forming one carboxylic acid terminated chain and one methacrylate terminated chain. The section of polymer with the stable methacrylate end group will not degrade further until another side chain heterolytic cleavage occurs.

**Support for Scheme I.** After demonstrating the reverse polymerization mechanism for deprotonated I<sup>1</sup> (e.g., I(MP)-COO-X<sup>+</sup>), we anticipated that I(MP)-COOH would also degrade by reverse polymerization. cursory comparison of the thermal degradation of I(MP)-COO-X<sup>+</sup> with I(MP)-COOH and I(MP)-COOCH<sub>3</sub> (which cannot undergo reverse polymerization) suggests they are similar. Thermal degradation of polymers with the various end groups (N<sub>2</sub> or He atmosphere) are clean and mass loss is >99.9%; the major isolated products are CO<sub>2</sub> and 2-methyl-2-pentene (III(MP)).

Under some conditions, Grassie plots for I(MP)-COOH and I(MP)-COOCH<sub>3</sub> degradation are consistent with a reverse polymerization mechanism. For example, we have demonstrated that DP/DP<sub>0</sub> is proportional to the fraction of polymer degraded when I-COO<sup>+</sup>PBu<sub>4</sub> degrades by reverse polymerization.<sup>1</sup> Figure 14 is a plot of DP/DP<sub>0</sub> vs fraction of polymer degraded for I(MP)-COOCH<sub>3</sub>. For the DP<sub>0</sub> = 50 polymer, DP/DP<sub>0</sub> is an approximately linear function of the fraction of polymer degraded. In contrast, higher MW I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 610 and 5880) undergoes extensive chain scission during thermal degradation. Furthermore, the changes in molecular weight distribution during degradation (Figures 11–13) clearly demonstrate that this is not a simple reverse polymerization process.<sup>1</sup> Computer models of the proposed mechanism indicate that the resemblance of the Grassie plot from I(MP)-COOCH<sub>3</sub> (DP<sub>0</sub> = 50) with that for "living

depolymerization" is a fortuitous consequence of the mechanism outlined in Scheme I.<sup>2</sup>

Other observations imply that a second process contributes to the degradation of I above 300 °C. For example, end-capping of polyesters formed by ring-opening polymerization is known to inhibit reverse polymerization.<sup>17</sup> Figure 1 compares TGAs for I(MP)-COOH and I(MP)-COOCH<sub>3</sub> (DP ~ 200). There is little indication that esterification of the active carboxylate end inhibits degradation. Indeed I(MP)-COOCH<sub>3</sub> starts to degrade at a slightly lower temperature than I(MP)-COOH but I(MP)-COOH degrades over a narrower temperature range. Comparing the degradation of these two polymers is complicated by the difference in [COOH] (a large fraction of the COOH chain ends in I(MP)-COOH will exist in the form of dimers<sup>24</sup>) and disparate changes in molecular weight distributions during degradation; however, the comparison demonstrates that reverse polymerization is not the only degradation mechanism available since end-capped polymer cannot undergo reverse polymerization. In further contrast to degradation by reverse polymerization, the degradation rate for I(MP)-COOCH<sub>3</sub> increases with DP. This latter observation suggests I(MP)-COOCH<sub>3</sub> and PMMA degradations are similar, i.e., random scission initiation followed by unzipping.

**Degradation Products.** Scheme I indicates the major product of polymer degradation is lactone (II). Although II(MP) is not seen by FTIR, its presence is confirmed by the MS data. We believe that lactone is not observed by FTIR from I(MP)-COOH degradation because the lactone is too unstable above 350 °C, degrading by reaction 2 in less than 1 s.<sup>1</sup> The lower sensitivity of FTIR requires larger samples (~50 µm thick) compared to MS (~0.1–1 µm thick), and the instrument geometry exposes the evolved gases to the degradation temperature for longer periods. We can estimate the time required for II(MP) to diffuse out of 50- and 4-µm films to be >2 and ~2 × 10<sup>-2</sup> s, respectively (assuming a diffusion constant of ~1 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup> for II(MP) in a polymer melt). These observations show the importance of sample geometry on product distributions obtained from degradation of these polymers, especially above 300 °C.

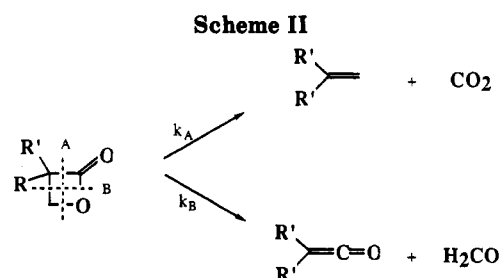
Thermal degradation of poly(2,2-dimethyl-3-propiolactone) (polypivalolactone, I(MM)) has been previously studied by pyrolysis-mass spectrometry, which indicated that cyclic oligomers are primary volatile products.<sup>15,16,19</sup> For the related I(MP), our GC/MS results indicate that cyclic oligomers are minor products (<2%) of polymer degradation. In contrast, simple analysis (Table III) of our DP-MS data suggests greater amounts of cyclic oligomer (5–10%). However, this simple analysis underestimates the amount of olefin (III, a direct product of II formed by reaction 2 in Scheme I) because of the difference in the energy of association between olefin and NH<sub>4</sub><sup>+</sup> versus ester and NH<sub>4</sub><sup>+</sup>. When the difference in CI/MS sensitivity for II, III, and V is considered (Table III), it is apparent that cyclic oligomers account for less than 2% of the volatiles. Regardless, Scheme I suggests monomer (II) is formed in competition with cyclic oligomer (IV, V, etc.). We do not know how the rates *k*<sub>1</sub>, *k*<sub>12</sub>, and *k*<sub>13</sub> vary with temperature (i.e., if the relative amount of cyclic oligomers increases or decreases with temperature). In this context it is interesting to note that thermal degradation of I-COO<sup>-</sup>PBu<sub>4</sub> under living depolymerization conditions (which occurs at considerably lower temperatures)<sup>1</sup> produces no cyclic oligomers (<0.1%).

A recent note by Garozzo and Montaudo<sup>21</sup> uses the theory of Jacobson and Stockmayer (J-S)<sup>22</sup> to predict the amounts of cyclic oligomers (II, IV, V, etc.) formed during thermal degradation of I(MM). Here we address why we

**Table III**  
Distribution of Cyclic Oligomers from I(MM) and I(MP) Degradation

<i>n</i>	I(MM) obsd <sup>a</sup>	MS abundance			~ring strain <sup>e</sup>
		I(MP) obsd <sup>b</sup>	I(MP) corr <sup>c</sup>	calcd <sup>d</sup>	
1	100	100	100	100	26
2	0.3	0.4 ± 0.3		17.7	9.6
3	10.0	6 ± 5	0.6 ± 0.3	6.4	3.6
4	1.5	0.4 ± 0.3		3.1	<3.6

<sup>a</sup> From ref 21. <sup>b</sup> Average of MS peak intensities from eight I(MP) runs with different MWs and end groups. Not adjusted for thermal conversion of II to III + CO<sub>2</sub>. <sup>c</sup> Average of MS peak intensities from eight I(MP) runs with different MWs and end groups. Adjusted for thermal conversion of II to III + CO<sub>2</sub> and the difference in degree of chemical ionization of III, II, and V by NH<sub>4</sub><sup>+</sup>. <sup>d</sup> From ref 21, calculated according to J-S (ref 22). <sup>e</sup> From combustion of hydrocarbon rings; see ref 23.



believe such an analysis is inappropriate. Table III shows the distribution of cyclic oligomers reported by Garozzo and Montaudo from I(MM) degradation, along with data from this study for I(MP) degradation and what is predicted by the J-S theory. Also shown in Table III are approximate ring strain energies for 4-, 8-, 12-, and 16-membered rings. We believe the application of J-S theory to this system is incorrect for two reasons.

First, Jacobson and Stockmayer correctly assume that their theory will apply to large rings (~>15-membered rings) where short-range steric effects are not dominant. Accordingly, Garozzo and Montaudo attribute the discrepancy between the predicted and observed amount of cyclic dimer to known steric strain in 8-membered rings (relative to 12-membered rings; see Table III). However, they chose to ignore the much greater ring strain in the 4-membered-ring monomer, which accounts for ~90–99% of the observed product.

Secondly, J-S theory assumes ring-chain equilibration has been achieved. There is no reason to believe the system is at equilibrium under the typical polymer degradation conditions employed. Indeed it is more realistic to assume the product distributions are kinetically controlled. As noted earlier, the product ratios simply reflect the relative rates *k*<sub>1</sub>, *k*<sub>12</sub>, *k*<sub>13</sub>, *k*<sub>14</sub>, etc. and, as such, are only indirectly influenced by the stabilities of the various rings.

Above 400 °C, methylpropylketene (MPK) appears in the TGA/FTIR at 2120 cm<sup>-1</sup>. MPK either is a direct product of polymer degradation or is formed from the thermal degradation of lactone (Scheme II).

All literature data indicate that thermal degradation of 3-propiolactones yields CO<sub>2</sub> and olefin exclusively; little ketene is formed.<sup>12–14</sup> We also observe no ketene (monitored by mass spectral analysis) when 2-methyl-2-propyl-3-propiolactone is thermally degraded at 400 °C. Some MPK appears to be a primary product formed in the later stages of I(MP) degradation; we do not know the details of how it forms.

**Random Heterolytic Side-Group Cleavage (Scheme I, Reactions 5–7).** A number of observations support initial heterolytic side chain cleavage. Polymer stability correlates with the relative ease for heterolytic cleavage



of the side chain group (Table I), i.e.,  $I(\text{MM})\text{-COOH}$  and  $I(\text{MN})\text{-COOCH}_3 > I(\text{ME})\text{-COOCH}_3 \sim I(\text{MP})\text{-COOCH}_3 > I(\text{MsB})\text{-COOCH}_3$ .<sup>25</sup> With  $I(\text{MM})\text{-COOH}$  and  $I(\text{MN})\text{-COOCH}_3$ , the active chain end ( $\text{COOH}$ ) must be formed by a mechanism other than that shown in Scheme I, reactions 5–7, because they do not possess the requisite C–H at the 2 position of the R or R' group in I. Regardless, thermal degradation of  $I(\text{MM})\text{-COOH}$  and  $I(\text{MN})\text{-COOCH}_3$  gives products similar to the other polymers, suggesting that  $\text{COOH}$  termini are involved.

Scheme I, reaction 7, indicates the most likely reaction following random heterolytic side group cleavage will produce a methacrylate end group on one-half of the polymer chain. The NMR spectra in Figures 9 and 10 establish that when  $I(\text{MP})\text{-COOCH}_3$  is degraded, a large fraction of the remaining polymer chains have methacrylate end groups ( $\sim 30\%$  in this case). We observe similar amounts of methacrylate end groups from  $I(\text{MP})\text{-COOCH}_3$ ,  $I(\text{ME})\text{-COOCH}_3$ , and  $I(\text{MsB})\text{-COOCH}_3$ . Methacrylate end groups are not observed after partial degradation of  $I(\text{MN})\text{-COOCH}_3$ . We believe that such a large fraction of the chains having this specific end groups is only consistent with reactions 5–7 occurring.

#### Kinetics for Capped versus Uncapped Polymer.

Formation of carboxylic acid termini by reactions 5–7 of Scheme I simultaneous with unzipping from the synthetic chain terminus has a leveling effect upon the degradation temperature for  $I(\text{MP})\text{-COOH}$  of different  $\text{DP}_0$ . Therefore, these polymers all show peak degradation at  $\sim 380^\circ\text{C}$  (Figure 5). Degradation of block copolymers by reverse polymerization demonstrates that, on average, the termination end degrades before the initiation end of the chain.<sup>1</sup> This reverse polymerization is a zero-order process, and its rate is inversely proportional to  $\text{DP}_0$ .<sup>1</sup> However, the rate of the random scission initiated degradation is proportional to  $\text{DP}_0$ . Consequently, high-MW  $I(\text{MP})\text{-COOH}$  will degrade efficiently by random heterolytic scission initiation (Scheme I) whereas low-MW  $I(\text{MP})\text{-COOH}$  will degrade by unzipping from the synthetic chain terminus.

In contrast,  $I(\text{MP})\text{-COOCH}_3$  must generate  $\text{COOH}$ -terminated chains by the random scission process (Scheme I, reactions 5–7) before mass loss can ensue. As such, higher molecular weight polymer degrades at a lower temperature. Peak degradation occurs at  $\sim 385, 395, 415$ , and  $450^\circ\text{C}$  for polymers with  $\text{DP}_0 = 5880, 610, 200$ , and  $50$ , respectively (Figure 6).

**Direction of Polymer Unzipping.** We have previously used block copolymer degradation to determine which end of a polymer chain degrades first.<sup>1</sup> A unique property of polylactones (and many other polymers formed by ring-opening polymerization) is the anisotropy along the polymer chain. For example, in I, the dialkyl carbon is encountered immediately prior to the carbonyl when moving along a chain from the initiator end toward the termination end. For labeling purposes we will place the above orientation on the polymer chain and designate the two ends of the chain as the "initiation end" and the "termination end". Degradation of A–B block copolymers by reverse polymerization or unzipping from the synthetic chain terminus will produce products from the B block prior to those from the A block. It is interesting to note that Scheme I predicts qualitatively the opposite result

for random scission initiated degradation; i.e., products from the A block will appear prior to those from the B block!

As noted (*vide supra*),  $I(\text{MP})\text{-COOH}$  can degrade by a combination of random scission and unzipping from the synthetic chain terminus whereas  $I(\text{MP})\text{-COOCH}_3$  must degrade by the random heterolytic scission initiated process. Accordingly, the block copolymers  $\text{D}_2\text{I}(\text{MP})\text{I}(\text{MP})\text{-COOH}$  and  $\text{I}(\text{MP})\text{D}_2\text{I}(\text{MP})\text{-COOH}$  ( $\text{DP}_0 = 120$ ) degrade from the termination end of the molecule toward the initiator end (Figure 7). However, after esterification ( $\text{D}_2\text{I}(\text{MP})\text{I}(\text{MP})\text{-COOCH}_3$  or  $\text{I}(\text{MP})\text{D}_2\text{I}(\text{MP})\text{-COOCH}_3$ ) the initiation end of the molecule degrades first (Figure 8). Other than Scheme I, the only process that can produce this effect would be polymer unzipping from the initiator end toward the termination end of the chain. However, this is not a random scission initiated process.

#### Conclusions

We have determined that poly(2,2-dialkyl-3-propiolactones) (I) efficiently degrade by unzipping of carboxylic acid terminated chains. The unzipping forms lactone ( $\sim 99\%$ ) and cyclic oligomers ( $\sim 1\%$ ). For polymers that initially contain no carboxylic acid termini, random scission processes generate them above  $\sim 300^\circ\text{C}$ .

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