# Studies on the Mechanism of Polymerization of Methyl Methacrylate in Tetrahydrofuran with Butyllithium at $-78^{\circ}$ C by Using Perdeuterated Monomer

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ABSTRACT: Perdeuterated methyl methacrylate (MMA-d<sub>8</sub>) was polymerized by C<sub>4</sub>H<sub>9</sub>Li in THF at  $-78^{\circ}$ C, and the resultant polymer and oligomer were analyzed for the initiator fragment by <sup>1</sup>H NMR spectroscopy. The structure of the oligomer was also studied by mass spectroscopy. The results indicated that the oligomer obtained had two butyl groups. One of them was attached to the initiating chain end and the other was incorporated as a butyl carbonyl group of the butyl isopropenyl ketone unit situated at the terminated chain end. The ketone was formed by an attack of  $C_4H_9Li$  on the carbonyl double bond of the monomer. The polymer contained 3–4 ketone units incorporated into the chain through copolymerization of the butyl isopropenyl ketone with MMA, while the polymer formed in toluene was found to have one ketone unit near the beginning of the chain. Analysis of the polymerization products of MMA- $d_8$  with  $C_4H_9Li$  in THF terminated with methanol- $d_4$  showed that a part of the polymer and oligomer anions abstracted the  $\alpha$ -methylene protons of butyl carbonyl group ( $-CO-CH_2-CH_2CH_3$ ) of the ketone unit during the polymerization. The mechanism of polymerization is discussed in detail on the basis of these results. **KEY WORDS** Anionic Polymerization / Perdeuterated Methyl

Methacrylate / Hydrogen Abstraction / Butyllithium / 1,1-Diphenylhexyllithium / Tetrahydrofuran / Butyl Isopropenyl Ketone / NMR Spectroscopy / Mass Spectroscopy /

Many papers have been published on the polymerization of methyl methacrylate (MMA) with alkyllithium in tetrahydrofuran. However, the mechanism of polymerization has not been completely understood. It has been pointed out that this polymerization is complicated possibly by side and termination reactions.<sup>1</sup>

In our previous paper perdeuterated MMA was polymerized in toluene with undeuterated butyllithium (BuLi), and the resultant polymer and oligomer were studied for initiator fragments by <sup>1</sup>H NMR spectroscopy.<sup>2</sup> The structure of the undeuterated MMA oligomer prepared with BuLi in toluene was also studied by liquid chromatography and <sup>1</sup>H NMR and mass spectroscopy.<sup>3</sup> From the results, it was concluded that the butyl isopropenyl ketone formed through the reaction of MMA and BuLi played an important role in the polymerization, and a new mechanism of polymerization was proposed.

In the present work this perdeuterated monomer technique was applied to the polymerization of MMA in tetrahydrofuran (THF) with BuLi at  $-78^{\circ}$ C and the mechanism of polymerization was discussed in detail. Hydrogen abstraction reaction by the polymer and oligomer anions was also investigated.

#### **EXPERIMENTAL**

Undeuterated MMA was obtained commercially. Perdeuterated MMA (MMA- $d_8$ ) was synthesized from acetone cyanohydrin- $d_7$  and methanol- $d_4$  according to the method of Crawford.<sup>4</sup> Both MMAs were purified by fractional distillation, stirred for one night over calcium dihydride, and then vacuum distilled. The MMAs thus purified were stirred again for 5 h over fresh calcium dihydride on the vacuum line and redistilled at room temperature before use.

BuLi was prepared from 1-chlorobutane and metallic lithium in heptane.

1,1-Diphenylhexyllithium was synthesized by the reaction of equimolar amounts of BuLi and 1,1diphenylethene in toluene at 40°C for 3 days.

Butyl isopropenyl ketone was prepared and purified as reported previously.<sup>2</sup>

THF was refluxed over calcium dihydride for 24 h under nitrogen pressure and fractionally distilled. The distillate was refluxed again over lithium aluminum hydride for 5 h, and distilled into a reservoir containing lithium aluminum hydride, from which the dried THF was distilled under vacuum just before use.

The polymerization reaction was carried out in a sealed glass ampoule and stopped by the addition of a small amount of methanol at the polymerization temperature. The reaction mixture was then poured into a large amount of methanol to precipitate the polymer formed. After standing it overnight, the precipitated polymer was collected by filtration, washed several times with methanol and dried in vacuo at 60°C. The filtrates and washings were combined and allowed to evaporate to dryness under reduced pressure. The residue was dissolved in benzene and a small amount of insoluble material was filtered off. The methanol-soluble oligomer was recovered from the benzene solution by a freezedrying technique. A portion of the oligomer obtained from the undeuterated MMA polymerization was fractionated by heptane and the soluble fraction (25%) was subjected to mass spectrum measurement.

Degradation of the polymer and oligomer was made by heating them to  $300-350^{\circ}$ C under vacuum.<sup>2</sup> The products were collected in a reservoir cooled in a liquid nitrogen bath.

In the polymerization designed to detect the formation of lithium methoxide, butane, and butyl isopropenyl ketone, the reaction was terminated by adding a small amount of acetic acid, and the reaction mixture was analyzed by gas-liquid chromatography. It was assumed that the lithium methoxide formed during the polymerization was converted quantitatively to methanol.<sup>5</sup>

The <sup>1</sup>H NMR spectra of the polymer and oli-

gomer in nitrobenzene- $d_5$  were taken on a JNM-FX100 pulse Fourier transform NMR spectrometer (JEOL) at 110°C and 100 MHz. The hydrogen content of the sample was determined from the intensity of the signal of interest relative to the signal due to the remaining protons in the nitrobenzene- $d_5$  used as the solvent. The hydrogen content for the latter signal was measured by a precision coaxial tubing method.<sup>6</sup> Spin-lattice relaxation time,  $T_1$ , was determined by the inversionrecovery Fourier transform method.

<sup>13</sup>C NMR spectrum of the oligomer was measured in chloroform- $d_1$  at 55°C and 25 MHz using the same spectrometer as in the <sup>1</sup>H NMR measurement.

The electron impact ionization and field desorption mass spectra were recorded by a JNS-01SG-2 mass spectrometer (JEOL).

Gas-liquid chromatographic experiments were carried out on a Shimadzu model GC-3 chromatograph with a column packed with PEG-6000/Celite 545 or TCP/Celite 545, using helium as the carrier gas.

The number average molecular weight was determined in toluene at 60.0°C by a Hitachi 117. vapor pressure osmometer.

### RESULTS

#### 1. Polymerization of MMA-d<sub>8</sub> with BuLi

Figure 1 shows the spectra of the polymer and oligomer of MMA- $d_8$  prepared with BuLi in THF at  $-78^{\circ}$ C, together with the spectrum of radically prepared poly(MMA-co-butyl isopropenyl ketone) containing 81 mol% of MMA units. The spectrum for the MMA oligomer prepared in THF at  $-78^{\circ}$ C (Figure 1A) very much resembles the spectrum<sup>2</sup> for the oligomer prepared with BuLi in toluene at  $-78^{\circ}$ C, thus indicating a similarity in structure of both oligomers.

In the spectrum of the oligomer prepared in THF (Figure 1A) the resonance at 0.79 ppm was assigned to the methyl protons in the butyl group coming originally from the initiator, and the singlet at 2.57 ppm to the terminal methine proton introduced from methanol through the termination reaction. The triplet at 2.40 ppm was due to the protons of the methylene group adjacent to the carbonyl group  $(-COCH_2CH_2CH_2CH_3)$  in the butyl isopropenyl ketone unit. The <sup>13</sup>C NMR spectrum of this oligo-

Mechanism of Polymn. of MMA with BuLi in THF



**Figure 1.** <sup>1</sup>H NMR spectra of (A) oligomer and (B) polymer of MMA- $d_8$  prepared with BuLi in THF at  $-78^{\circ}$ C, (C) copolymer of MMA and butyl isopropenyl ketone (MMA =  $81 \text{ mol}_{0}$ ) prepared with AIBN in toluene at 60°C. X, signals due to remaining protons in the monomer units.

	Yield			C <sub>4</sub> H <sub>9</sub> (total)		C₄ H <sub>9</sub> CO		Terminal CH	
	g	mmol <sup>b</sup>	$M_n \times 10^{-1}$	mmol	mol/mol <sup>c</sup>	mmol	mol/mol <sup>c</sup>	mmol	mol/mol <sup>c</sup>
Polymer	0.352	0.0099	35.5	0.043	4.4	0.033	3.4 <sup>d</sup>	0.010	1.0 <sup>d</sup>
Oligomer <sup>e</sup>	0.214	0.208	1.03	0.424	2.0	0.184	0.9	0.194	0.9

2.0

0.184

Table I. Polymerization of MMA- $d_8$  with BuLi in THF at  $-78^{\circ}$ C for 24 h<sup>a</sup>

<sup>a</sup> MMA-d<sub>8</sub> 5.05 mmol, BuLi 0.5 mmol, THF 5 ml.

0.187

<sup>b</sup> Calculated from the yield and  $M_n$ .

Oligomer

0.210

<sup>c</sup> Represents the number of butyl group or terminal methine proton per a polymer or oligomer molecule.

<sup>d</sup> The amount of  $C_4H_9CO$  group was calculated as follows:  $[C_4H_9 (total)] - [C_4H_9CO] = 1 \text{ mol/mol.}$ 

0.381

<sup>e</sup>. The values for the methanol-soluble fraction which includes dibutyl isopropenyl carbinol.

<sup>f</sup> The corrected values for the coexistence of the dibutyl isopropenyl carbinol.

1.14

mer showed peaks at 212.88 ppm which should be assigned to the ketone carbonyl carbon. This is also a strong evidence for the existence of butyl isopropenyl ketone units in the oligomer chain. Intensity measurements in the <sup>1</sup>H NMR spectrum indicated that the oligomer had 2.0 butyl groups in a molecule and about half of them was incorporated as the butyl carbonyl group of butyl isopropenyl ketone units. (Table I). A field desorption mass spectrum of the heptane-soluble fraction of undeuterated oligomer  $(M_n = 443)$  showed peaks of 385 and 285 which should be assigned to the (M+1) ions of the trimer and dimer containing one butyl isopropenyl ketone unit. There were no peaks associated with the

1.0

0.194

1.0



Figure 2. Electron impact ionization mass spectrum of the heptane-soluble oligomer of MMA prepared with BuLi in THF at  $-78^{\circ}$ C.

oligomer containing no ketone units in the chain. This suggests that each of the oligomer molecules contains one ketone unit. In Figure 2 is shown the electron impact ionization mass spectrum of the oligomer. There appear peaks of mass numbers of 127 and  $158 + 100n (n=0 \sim 5)$  corresponding to the following fragments:

$$\begin{bmatrix} CH_{2} - CH_{3} \\ CH_{2} - C-H \\ C=0 \\ C_{4}H_{9} \end{bmatrix}^{+}$$
  
Fragment A  
 $M/e = 127$ 
$$\begin{bmatrix} C_{4}H_{9} + CH_{2} - CH_{3} \\ C_{2}H_{9} + CH_{2} - CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{bmatrix}$$

Fragment B  $M/e = 158 + 100n \ (n = 0 \sim 5)$ 

The fragment B series should be generated through the elimination of butyl isopropenyl ketone units from the parent ion species of the oligomer molecules and also through subsequent elimination of MMA units. These results indicate that the ketone unit in the oligomer molecule is located at the chain end.

<sup>1</sup>H NMR spectrum of the oligomer fraction obtained from the polymerization of undeuterated MMA under the same conditions showed signals of appreciable intensity due to the methylene protons of the vinyl double bond of dibutyl isopropenyl carbinol. Formation of a very small amount of this alcohol through the reaction of BuLi and butyl isopropenyl ketone was found previously in the polymerization of MMA with BuLi in toluene at  $-78^{\circ}C.^{2}$ 



The content of the alcohol in the oligomer fraction prepared in THF at  $-78^{\circ}$ C was estimated from the NMR spectrum to be 1.24 mol% of MMA units in the chain. Assuming that the deuterated and undeuterated oligomers contained the same amounts of the alcohol, we corrected the yield, the molecular weight and the content of the butyl group for the MMA- $d_8$  oligomer, as shown in Table I. The total amount of butyl and butyl carbonyl goups, and terminal methine proton were calculated to be 2.0, 1.0, and 1.0, respectively, per oligomer molecule. The difference of 1.0 in the total number of butyl and butyl carbonyl groups should correspond to the number of butyl groups introduced at the beginning of the chain.

These facts clearly show that the oligomer formed in THF at  $-78^{\circ}$ C has the same structure, as that of most of the oligomers prepared in toluene with BuLi at  $-78^{\circ}$ C, *i.e.*,

$$\begin{array}{ccc} C_{4}H_{9} \leftarrow CD_{2} - \stackrel{CD_{3}}{\stackrel{}{\leftarrow}} \stackrel{CD_{3}}{\stackrel{}{\rightarrow}} \stackrel{CD_{3}}{\stackrel{}{\leftarrow}} \stackrel{CD_{3}}{\stackrel{}{\leftarrow} \stackrel{CD_{3}}{\stackrel{}{\leftarrow}} \stackrel{CD_{3}}{\stackrel{}{\leftarrow} \stackrel{CD_{3}}{\stackrel{}} \stackrel{CD_{3$$

The spectrum of the polymer prepared in THF at  $-78^{\circ}$ C (Figure 1B) is rather different from that of the oligomer, especially in the carbonyl methylene and terminal methine proton regions. From the intensity measurement of the methyl resonance at 0.85 ppm, this polymer was found to contain

4.4 of total butyl groups per molecule. The resonance in the carbonyl methylene region  $(-COCH_2CH_2CH_2CH_3)$  is composed of a broad signal centered at 2.55 ppm and a sharp triplet at 2.40 ppm; the latter has already been assigned to the methylene protons adjacent to the carbonyl group in the butyl isopropenyl ketone unit located near the beginning of the polymer chain.<sup>2</sup> The amount of butyl isopropenyl ketone unit of this type was roughly estimated to be 0.9 per polymer molecule from the intensity of the triplet signal. The chemical shift of the former broad signal was close to that of the signal assigned to the terminal methine proton of the oligomer. However, its intensity was too strong to be assignable to only the terminal methine proton of the polymer chain. The amount of the ketone formed in the depolymerization of the polymer was 0.99 mol% of MMA and corresponded to 3.2 of ketone units per polymer molecule. Thus, the broad resonance at 2.55 ppm should include the signals assignable to the terminal methine proton and also to the carbonyl methylene protons of the butyl isopropenyl ketone unit in a chemical environment different from that of the ketone unit located near the beginning of the chain.

A partially relaxed Fourier transform NMR spectrum (Figure 3) showed that the broad resonance involves a sharp singlet at 2.57 ppm. This is clearly due to the terminal methine proton and the



Figure 3. Partially relaxed Fourier transform NMR spectrum in nitrobenzene- $d_5$  at 110°C of the polymer prepared with BuLi in THF at  $-78^{\circ}$ C. Pulse sequence:  $(180^{\circ}-0.10 \text{ s}-90^{\circ}-10 \text{ s})$ , 4000 accumulations.

residual faster recovering broad component should be assigned to the carbonyl methylene protons in ketone units other than those located near the beginning of the chain. The spin-lattice relaxation time,  $T_1$ , for the broad component was 0.21 s and shorter than that for the carbonyl methylene protons of the ketone unit located near the beginning of the polymer chain, which was determined to be 1.0 s from the triplet at 2.40 ppm. This fact indicates that the ketone units giving the broad signal at 2.55 ppm are located within the interior sequence of the polymer chain. Poly(MMA-co-butyl isopropenyl ketone) containing 19 mol% of the ketone unit shows a broad peak at 2.55 ppm, which is additional evidence warranting this assignment.

Since it was reasonable to assume that the polymer contained one butyl group at the initiating end, the number of the ketone units located near the beginning and within the interior sequence were calculated to be 1.0 and 2.4 per a polymer molecule, respectively, and the terminal methine proton to be 1.0. Thus the polymer prepared with BuLi in THF at  $-78^{\circ}$ C should have the following structure.

### 2. Polymeization of undeuterated MMA with BuLi and 1,1-diphenylhexyllithium at -78°C

The polymerizations of undeuterated MMA was carried out in THF at  $-78^{\circ}$ C with BuLi for various periods of times. The results are shown in Figure 4. In the polymerization with BuLi, the oligomer was formed rapidly at the initial stage of the reaction



Figure 4. Polymerization, of MMA with BuLi in THF at  $-78^{\circ}$ C: MMA, 10 mmol; BuLi, 1.0 mmol; THF, 10 ml.



and its amount did not increase afterwards. However, the amount of polymer first increased very slowly and quickly about 3 h after the initiation. The butyl isopropenyl ketone in the polymerization mixture amounted to 11% of the BuLi used 2 min after the initiation and then gradually decreased close to zero (Figure 5), while the polymer started to form rapidly.

When 1,1-diphenylhexyllithium was used as the initiator at  $-78^{\circ}$ C, the polymerization proceeded very rapidly and the reaction was completed in the first few minutes (Figure 6).\*

## 3. Hydrogen abstraction by polymer and oligomer anions during the polymerization at $-78^{\circ}C$ There exists some possibility that during the

polymerization the polymer or oligomer anion abstracts hydrogen from the methylene group in the  $\alpha$ -position to the carbonyl group of the butyl isopropenyl ketone units in the chain, since these



Figure 5. Amount of butyl isopropenyl ketone existing in the polymerization system of MMA with BuLi in THF at  $-78^{\circ}$ C: MMA, 10 mmol; BuLi, 1.0 mmol; THF, 10 ml.

<sup>\*</sup> In this case most of the polymerization products was soluble in methanol. This is due to the relatively higher molar ratio of the initiator to the monomer and high initiator efficiency. Study on the structure of the products is now under way and the results will be published elsewhere.



Figure 6. Polymerization of MMA with 1,1-diphenylhexyllithium in THF at  $-78^{\circ}$ C: MMA, 10 mmol; 1,1-diphenylhexyllithium, 1.0 mmol; THF, 10 ml.

methylene protons are fairly acidic. In order to verify this, the polymerization with BuLi at  $-78^{\circ}C$  was terminated at  $-78^{\circ}C$  by perdeuterated methanol and the resultant polymer and oligomer were analyzed. The results for this are shown in Table II. As mentioned in Table I, the CH<sub>3</sub>OH terminated oligomer contained 1.0 terminal methine proton and 2.0 carbonyl methylene protons per molecule. On the other hand, the oligomer terminated by CD<sub>3</sub>OD had 0.61 terminal methine proton and 1.52 carbonyl methylene protons, as found from the singlet at 2.57 ppm and the triplet at 2.40 ppm, respectively. The existence of an appreciable amount of the terminal methine proton and the decrease in carbonyl methylene protons in the CD<sub>3</sub>OD terminated oligomer clearly indicate that a portion of the oligomeric anions are terminated through the hydrogen abstraction from the carbonyl methylene protons before being

killed with methanol. The hydrogen abstraction from the solvent tetrahydrofuran was eliminated since BuLi abstracted no hydrogen in THF at  $-78^{\circ}$ C.<sup>7</sup>

Hydrogen abstraction from the carbonyl methylene protons may occur similarly in the case of the polymer anion. However, it is very difficult to determine the extent of hydrogen abstraction by the polymer anion, since the resonances of the terminal methine proton and the carbonyl methylene protons overlap with each other in the spectrum of the polymer (cf. Figure 1B). A partially relaxed Fourier transform NMR spectrum of the polymer terminated with perdeuterated methanol showed that a slower recovering component was also included at 2.57 ppm in the carbonyl methylene proton region. As mentioned before this slower recovering component should correspond to the terminal methine proton introduced through the hydrogen abstraction reaction.

### DISCUSSION

In the previous paper<sup>2</sup> we proposed a new mechanism for the polymerization of MMA with BuLi in toluene at  $-78^{\circ}$ C, in which butyl isopropenyl ketone formed through the reaction of BuLi and MMA played an important role. In the polymerization in THF at  $-78^{\circ}$ C, the oligomer formed had a structure similar to that obtained in toluene and contained one butyl isopropenyl ketone unit at the chain end. The polymer formed in THF contained  $3 \sim 4$  ketone units in the chain, while the polymer prepared in toluene had one ketone unit. These facts lead us to the following mechanism for the polymerization of MMA

Table II. Polymerization terminated with CD<sub>3</sub>OD of MMA- $d_8$  with BuLi in THF at  $-78^{\circ}$ C for 24 h<sup>a</sup>

	Yield			C <sub>4</sub> H <sub>9</sub> (total)		Carbonyl meth- ylene protons		Terminal CH	
	g	mmol <sup>b</sup>	$M_n \times 10^{-1}$	mmol	mol/mol <sup>c</sup>	mmol	mol/mol <sup>c</sup>	mmol	mol/mol <sup>c</sup>
Polymer Oligomer <sup>d</sup>	0.308 0.149	0.0086 0.160	35.7 0.93	0.037 0.353	4.3 2.2	0.058 0.244	6.8 1.52	0.098	0.61

<sup>a</sup> Monomer 4.2 mmol, BuLi 0.42 mmol, THF 10 ml.

<sup>b</sup> Calculated from the yield and  $M_n$ .

<sup>e</sup> Represents the number of butyl groups or terminal methine proton per polymer or oligomer molecule.

<sup>d</sup> The corrected values for the coexistence of dibutyl isopropenyl carbinol.

with BuLi in THF.

When BuLi is added to the monomer solution, it reacts with both the olefinic and carbonyl double bonds of the monomer. Reaction with the olefinic double bond produces MMA anions which add the monomer to form the growing chains (A).



The attack of BuLi on the carbonyl double bond gives butyl isopropenyl ketone with the release of lithium methoxide, and the ketone formed soon attacks most of the growing chains owing to its higher reactivity than that of MMA. The higher reactivity of the ketone is evident from the Q(=1.02) and e (=0.86) values<sup>8</sup> which are larger than those for MMA (Q=0.74, e=0.40).<sup>9</sup>

$$C_{4H_{9}Li} + C_{H_{2}=c} \xrightarrow{CH_{3}}_{c=0} \longrightarrow C_{H_{2}=c} \xrightarrow{CH_{3}}_{c=0} + LiOCH_{3}$$

$$(A) + C_{H_{2}=c} \xrightarrow{CH_{3}}_{c=0} \xrightarrow{C_{4H_{9}}}_{c=0} \xrightarrow{C_{4H_{9}}}_{c=0} \xrightarrow{CH_{3}=c}_{c=0} \xrightarrow{CH_{3}=c}$$

The anions ended with the ketone units (B) are less reactive than the MMA anions, and most of them remain unreacted during the polymerization and are recovered as a methanol-soluble oligomer when the polymerization is terminated. Thus, the amount of the oligomer increases rapidly at the initial stage of the polymerization and remains constant afterwards.

The oligomeric anion (B) adds the monomer very rapidly once it is attacked by MMA, and also if no butyl isopropenyl ketone exists. Consequently, a small fraction of the oligomeric anions is transformed to a high molecular weight polymer chain containing one ketone unit near its beginning. This is the case with the polymerization in toluene at  $-78^{\circ}C.^{2}$ 



From the analyses of the ketone units in the polymer and oligomer, the amount of the ketone formed in THF and in toluene at  $-78^{\circ}$ C was found to correspond 43% (Table III) and  $38\%^{2}$  of the BuLi used, respectively, while the amount in mole of polymer and oligomer was 39% of the BuLi in THF (Table I) and 52% of the BuLi in toluene.<sup>2</sup> These results imply that in the initiation step the carbonyl attack by BuLi occurs more frequently in THF and less frequently in toluene than the attack on the vinyl double bond. Hence, in the polymerization in

Table III. Fate of the initiator in the polymerization of MMA in THF with BuLi at  $-78^{\circ}$ C

		Amount
_		0/a /0
Butane		4.8
ÇH3	Polymer	2.0
Bu–CH <sub>2</sub> –C~~~ COOCH <sub>3</sub>	Oligomer	39.3
<b>D</b>	∫ Polymer	6.6
BuCO-	Oligomer	36.8
СН <sub>2</sub> = С Ви-С-ОН Ви		8.6
	Total	98.1

<sup>a</sup> Percentage based on the BuLi used.

toluene, no ketone exists at all following the formation of the anion (B).

In contrast to this, in the polymerization in THF at  $-78^{\circ}$ C, a small amount of butyl isopropenyl ketone still remains in the reaction mixture after all of the oligomeric anion have been attacked by the ketone, as indicated in Figure 5. Thus, once attacked by MMA the oligomeric anion should again be attacked by the ketone after a short while, and a less reactive polymeric anion of low molecular weight should consequently be formed.

The incorporation of butyl isopropenyl ketone into the polymer of MMA prepared by BuLi at  $-78^{\circ}$ C in THF was first suggested by Cameron and his coworkers in an ESR study of spin-labelled polymer.<sup>10,11</sup> The results of the present work give clear evidence for the incorporation of the ketone unit in the oligomer and polymer chains and also provide information on the number and location of ketone units in the oligomer and polymer chains. The latter could not be determined by the ESR study.



Hence, no polymeric anion of high molecular weight can be formed until most of the ketone molecules are consumed. This is the reason why the plot of polymer yield against the polymerization time shows a sigmoidal curve (Figure 4) and why a high molecular weight polymer containing more than one ketone unit in the chain is formed as mentioned above. It is known that the extent of initiator attack on the carbonyl double bond decreases when the polymerization is initiated with 1,1-diphenylhexyllithium.<sup>7,12</sup> This should explain why the reaction was completed in the first few minutes in the polymerization with 1,1-diphenylhexyllithium in THF (Figure 6).

The polymerization of MMA with alkyllithium

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indicates that all the initiator molecules can not be accounted for if each polymer and oligomer molecule is assumed to have one initiator fragment.<sup>1</sup> As mentioned already, the polymer and oligomer prepared with BuLi in THF at -78°C had more than one butyl groups in each molecule. The total amount of butyl groups in the oligomer and polymer chains and dibutyl isopropenyl carbinol formed was 0.47 mmol and corresponded to 93.4% of the BuLi used (Table III). On the other hand, the formation of a small amount of butane was reported in the polymerization of MMA with BuLi,<sup>13-15</sup> and it was about 5% of the BuLi used in the polymerization in THF at  $-78^{\circ}C$ <sup>15</sup> Thus, all the BuLi used was completely accounted for in this polymerization.

The polymer and oligomer molecules formed in the polymerization at  $-78^{\circ}$ C each contained about one methine proton at their chain ends when the polymerization was terminated with undeuterated methanol (Table I). This, however, does not prove that all the polymer and oligomer anions remained living up to the end of the reaction since the polymer and oligomer molecules contained terminal methine protons to some extent even when the polymerization was terminated with perdeuterated methanol. The terminal methine proton of the CD<sub>3</sub>OD-terminated polymer or oligomer should come from the fairly acidic protons of methylene group in the  $\alpha$ -position to the carbonyl group of butyl isopropenyl ketone unit in the chain.

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The amount of terminal methine proton in the  $CD_3OD$ -terminated oligomer corresponds for the most part to the decrease in the amount of carbonyl methylene protons produced on termination with deuterated methanol. This may indicate the following rearrangement at the chain end, as postulated by Cameron.<sup>16</sup>



Hydrogen abstraction reaction by polymer or oligomer anions was also found to occur in the polymerization with toluene at  $-78^{\circ}$ C. But the extent of the reaction was much smaller than in the polymerization with THF.<sup>7</sup>

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