

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

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**ABSTRACT:** Perdeuterated methyl methacrylate (MMA- $d_8$ ) was polymerized by  $\text{C}_4\text{H}_9\text{Li}$  in THF at  $-78^{\circ}\text{C}$ , and the resultant polymer and oligomer were analyzed for the initiator fragment by  $^1\text{H}$  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  $\text{C}_4\text{H}_9\text{Li}$  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  $\text{C}_4\text{H}_9\text{Li}$  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 ( $-\text{CO}-\text{CH}_2-\text{CH}_2\text{CH}_2\text{CH}_3$ ) 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 alkylolithium 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  $^1\text{H}$  NMR spectroscopy.<sup>2</sup> The structure of the undeuterated MMA oligomer prepared with BuLi in toluene was also studied by liquid chromatography and  $^1\text{H}$  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 polymer-

ization, 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  $-78^{\circ}\text{C}$  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 1,1-diphenylethene 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 freeze-drying 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°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*<sub>5</sub> 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*<sub>5</sub> 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*<sub>1</sub>, was determined by the inversion-recovery Fourier transform method.

<sup>13</sup>C NMR spectrum of the oligomer was measured in chloroform-*d*<sub>1</sub> 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.

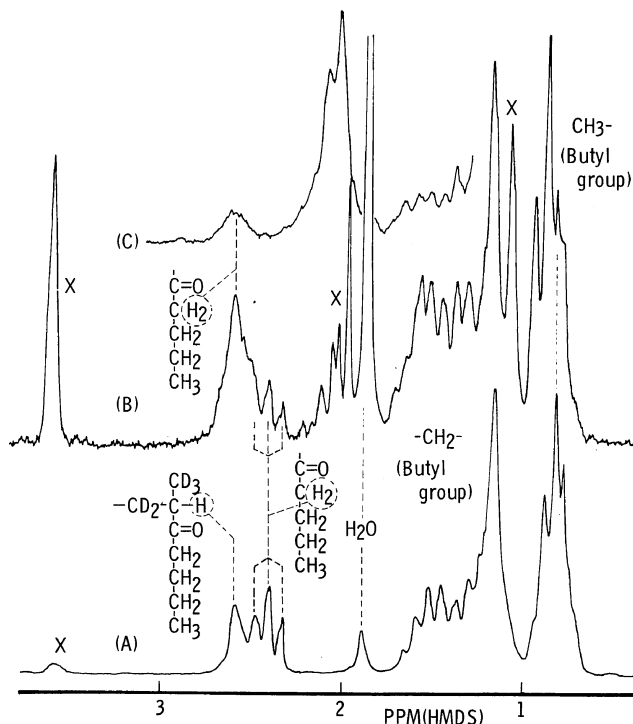
The number average molecular weight was determined in toluene at 60.0°C by a Hitachi 117 vapor pressure osmometer.

## RESULTS

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

Figure 1 shows the spectra of the polymer and oligomer of MMA-*d*<sub>8</sub> prepared with BuLi in THF at –78°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°C (Figure 1A) very much resembles the spectrum<sup>2</sup> for the oligomer prepared with BuLi in toluene at –78°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<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) in the butyl isopropenyl ketone unit. The <sup>13</sup>C NMR spectrum of this oligo-



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

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

|                       | Yield |                   | $M_n \times 10^{-3}$ | $\text{C}_4\text{H}_9$ (total) |                      | $\text{C}_4\text{H}_9\text{CO}$ |                      | Terminal CH |                      |
|-----------------------|-------|-------------------|----------------------|--------------------------------|----------------------|---------------------------------|----------------------|-------------|----------------------|
|                       | g     | mmol <sup>b</sup> |                      | 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                  |
| Oligomer <sup>f</sup> | 0.210 | 0.187             | 1.14                 | 0.381                          | 2.0                  | 0.184                           | 1.0                  | 0.194       | 1.0                  |

<sup>a</sup>  $\text{MMA-}d_8$  5.05 mmol, BuLi 0.5 mmol, THF 5 ml.

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

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

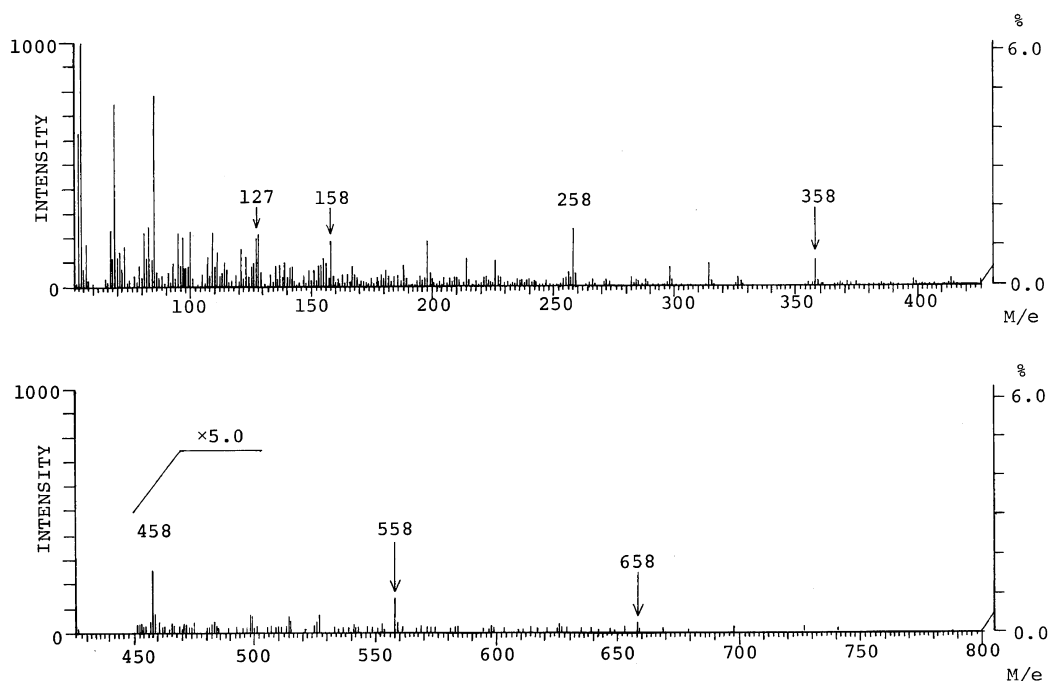
<sup>d</sup> The amount of  $\text{C}_4\text{H}_9\text{CO}$  group was calculated as follows:  $[\text{C}_4\text{H}_9 \text{ (total)}] - [\text{C}_4\text{H}_9\text{CO}] = 1 \text{ mol/mol}$ .

<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.

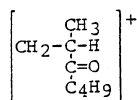
mer showed peaks at 212.88 ppm which should be assigned to the ketone carbonyl carbon. This is also a strong evidence for the existence of butyl isopropenyl ketone units in the oligomer chain. Intensity measurements in the  $^1\text{H}$  NMR spectrum indicated that the oligomer had 2.0 butyl groups in 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

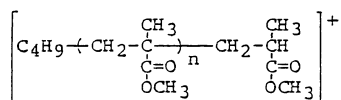


**Figure 2.** Electron impact ionization mass spectrum of the heptane-soluble oligomer of MMA prepared with BuLi in THF at  $-78^{\circ}\text{C}$ .

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  $127 + 100n$  ( $n=0 \sim 5$ ) corresponding to the following fragments:



Fragment A  
 $M/e = 127$

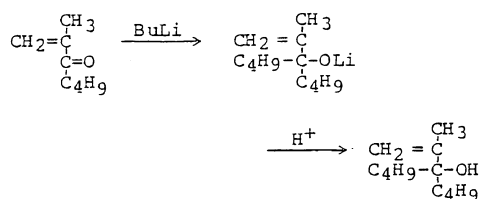


Fragment B  
 $M/e = 158 + 100n$  ( $n=0 \sim 5$ )

The fragment B series should be generated through the elimination of butyl isopropenyl ketone units from the parent ion species of the oligomer mol-

ecules 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.

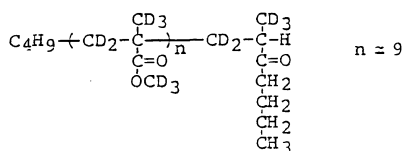
$^1\text{H}$  NMR spectrum of the oligomer fraction obtained from the polymerization of undeuterated MMA under the same conditions showed signals of appreciable intensity due to the methylene protons of the vinyl double bond of dibutyl isopropenyl carbinol. Formation of a very small amount of this alcohol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



The content of the alcohol in the oligomer fraction prepared in THF at  $-78^{\circ}\text{C}$  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 groups, 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.

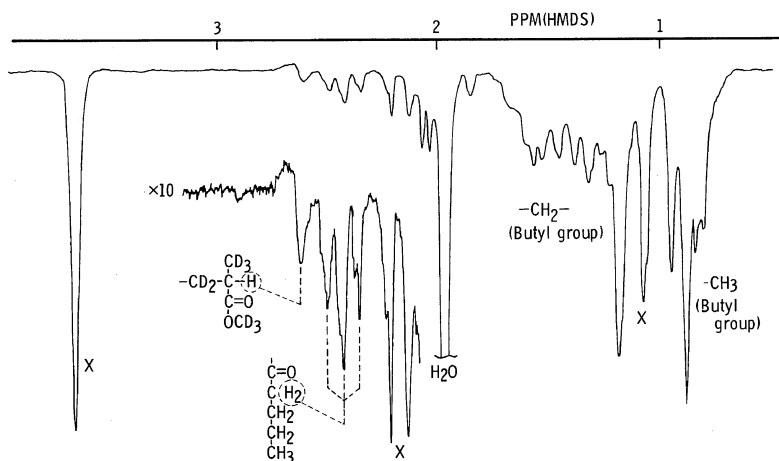
These facts clearly show that the oligomer formed in THF at  $-78^\circ\text{C}$  has the same structure, as that of most of the oligomers prepared in toluene with BuLi at  $-78^\circ\text{C}$ , *i.e.*,



The spectrum of the polymer prepared in THF at  $-78^\circ\text{C}$  (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

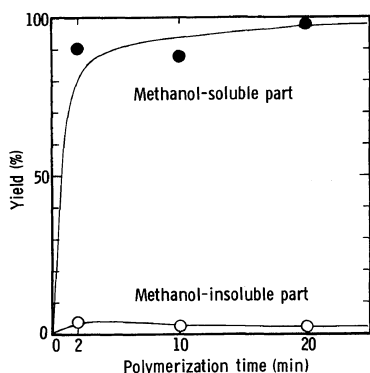
4.4 of total butyl groups per molecule. The resonance in the carbonyl methylene region ( $-\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) is composed of a broad signal centered at 2.55 ppm and a sharp triplet at 2.40 ppm; the latter has already been assigned to the methylene protons adjacent to the 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  $110^\circ\text{C}$  of the polymer prepared with BuLi in THF at  $-78^\circ\text{C}$ . Pulse sequence:  $(180^\circ-0.10\text{s}-90^\circ-10\text{s})$ , 4000 accumulations.





**Figure 6.** Polymerization of MMA with 1,1-diphenylhexyllithium in THF at  $-78^{\circ}\text{C}$ : 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  $-78^{\circ}\text{C}$  was terminated at  $-78^{\circ}\text{C}$  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  $\text{CH}_3\text{OH}$  terminated oligomer contained 1.0 terminal methine proton and 2.0 carbonyl methylene protons per molecule. On the other hand, the oligomer terminated by  $\text{CD}_3\text{OD}$  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  $\text{CD}_3\text{OD}$  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  $-78^{\circ}\text{C}$ .<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  $-78^{\circ}\text{C}$ , in which butyl isopropenyl ketone formed through the reaction of BuLi and MMA played an important role. In the polymerization in THF at  $-78^{\circ}\text{C}$ , 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 3~4 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  $\text{CD}_3\text{OD}$  of  $\text{MMA-}d_8$  with BuLi in THF at  $-78^{\circ}\text{C}$  for 24 h<sup>a</sup>

|                       | Yield |                   | $\text{C}_4\text{H}_9$ (total) |       |     | Carbonyl methylene protons |                      | Terminal CH |                      |
|-----------------------|-------|-------------------|--------------------------------|-------|-----|----------------------------|----------------------|-------------|----------------------|
|                       | g     | mmol <sup>b</sup> | $M_n \times 10^{-3}$           |       |     | mmol                       | mol/mol <sup>c</sup> | mmol        | mol/mol <sup>c</sup> |
| Polymer               | 0.308 | 0.0086            | 35.7                           | 0.037 | 4.3 | 0.058                      | 6.8                  | —           | —                    |
| Oligomer <sup>d</sup> | 0.149 | 0.160             | 0.93                           | 0.353 | 2.2 | 0.244                      | 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  $M_n$ .

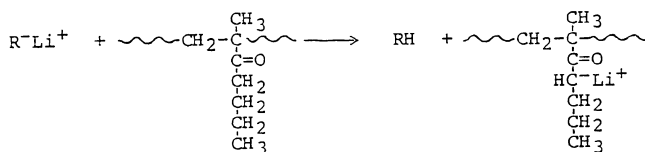
<sup>c</sup> Represents the number of butyl groups or terminal methine proton per polymer or oligomer molecule.

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

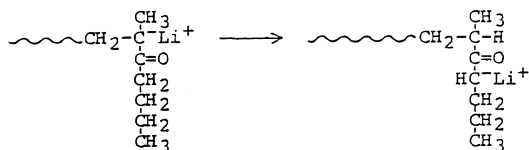








The amount of terminal methine proton in the CD<sub>3</sub>OD-terminated oligomer corresponds for the most part to the decrease in the amount of carbonyl methylene protons produced on termination with deuterated methanol. This may indicate the following rearrangement at the chain end, as postulated by Cameron.<sup>16</sup>



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

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