Polymer Bulletin 2, 125-129 (1980)

Polymer Bulletin

Structure of Methyl Methacrylate Oligomers Formed in the Polymerization with Butyllithium in Toluene

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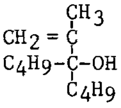
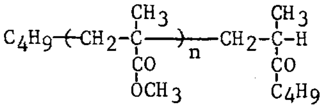
Summary

Methyl methacrylate was polymerized with butyllithium in toluene at -78°C. The heptane-soluble oligomers were fractionated by using a high-speed liquid chromatograph and five fractions were collected. These were found by ^{1}H-NMR and mass spectroscopy to contain the tertiary alcohol, dimer, trimer, tetramer, and pentamer of the following structures:



$CH_2=C(CH_3)\text{-}C(OH)(C_4H_9)\text{-}C_4H_9$



$C_4H_9\text{-}(CH_2\text{-}C(CH_3)(COOCH_3))_n\text{-}CH_2\text{-}CH(CH_3)\text{-}CO\text{-}C_4H_9$

n = 1, 2, 3, 4.

From the results, the mechanism of polymerization was proposed.

Introduction

Many papers have been published on the polymerization of methyl methacrylate initiated with butyllithium. It was reported that in the initiation step an attack of alkyllithium on monomer occurred in the first few seconds and took place on both the olefinic and carbonyl double bond, and a considerable amount of low molecular oligomer was formed in the early stage of the polymerization (COTTAM et al. 1963; GLUSKER et al. 1961a; WILES and BYWATER 1965; GOODE et al. 1960; KAWABATA and TSURUTA 1965). Glusker and his coworkers postulated a pseudo-cyclization of the chain end as a cause of the formation of oligomers (GLUSKER et al. 1961b). In a previous communication we polymerized perdeuterated methyl methacrylate with undeuterated butyllithium in toluene and the resultant polymer and oligomers were analyzed for the initiator fragment by ^{1}H-NMR spectroscopy (HATADA et al. 1978a).

In this work, the oligomers of methyl methacrylate formed in the polymerization initiated with butyllithium in toluene were fractionated by high-speed liquid chromatography and the structures of the five fractions

0170-0839/80/0002/0125/$01.00

collected were studied by ^{1}H-NMR and mass spectroscopy. From the results, the mechanism of formation of oligomers was discussed in some detail.

Experimental

Methyl methacrylate(98mmol) was polymerized in 100ml of toluene with 9.8 mmol of butyllithium(heptane solution) at -78°C for 24hr. The reaction product was poured into a large amount of methanol to precipitate the high molecular weight polymer. The precipitant was removed by filtration and the filtrate was concentrated under vacuum to dryness. The residue was redissolved in benzene and a small amount of insoluble material was filtered off. The methanol-soluble oligomers were recovered from the benzene solution by freeze-drying. The oligomers thus isolated were separated into soluble and insoluble portions in heptane. The yields of polymer, heptane-insoluble and -soluble oligomers were 64.5, 27.3 and 8.2%, respectively.

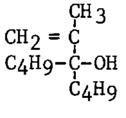
Preparative high-speed liquid chromatography was performed by a JASCO model FLC-A10 with a polystyrene gel column using chloroform as an eluant. The gel was prepared and kindly given by Professor Y. Tanaka of Tokyo University of Agriculture and Technology.

^{1}H-NMR spectra were recorded by a JEOL Fourier transform NMR spectrometer(JNM-FX100) at 100MHz in chloroform-d_1 at 60°C or in benzene-d_6 at 80°C using tetramethylsilane as an internal standard. The field desorption and electron impact ionization mass spectra were recorded by using a Matsuda-type double focussing spectrometer(MATSUDA 1976) equipped with a silicon emitter(MATSUO et al. 1979) and JNS-01SG-2 mass spectrometer(JEOL), respectively.

Results and Discussion

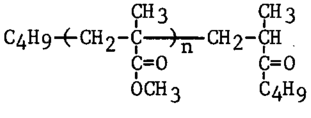
The heptane-soluble fraction of the polymerization product prepared in toluene by butyllithium at -78°C was subjected to chromatographic separation by using a high-speed liquid chromatograph, and five fractions were collected. By the inspection of the ^{1}H-NMR and mass spectra these fractions were found to contain the tertiary alcohol, dimer, trimer, tetramer and pentamer of the following structures:

(A)



$CH_2{=}C(CH_3)\text{-}C(OH)(C_4H_9)\text{-}C_4H_9$

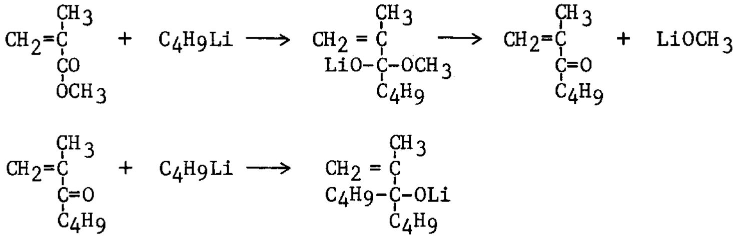
(B)



$C_4H_9\text{-}\left(CH_2\text{-}C(CH_3)(C{=}O)(OCH_3)\right)_n\text{-}CH_2\text{-}CH(CH_3)\text{-}C({=}O)\text{-}C_4H_9$

n = 1, 2, 3, 4.

The existence of the alcohol(A) shows that the carbonyl double bond of the monomer reacted with butyllithium and the resultant butyl isopropenyl ketone was again attacked by the initiator.

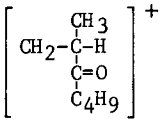


$$\begin{array}{r@{}l} & CH_3\\ & |\\ CH_2{=}&C\\ &|\\ &CO\\ &|\\ &OCH_3\end{array} + C_4H_9Li \longrightarrow \begin{array}{r@{}c@{}l} & CH_3 & \\ & | & \\ CH_2 = & C & \\ & | & \\ LiO{-} & C & {-}OCH_3\\ & | & \\ & C_4H_9 & \end{array} \longrightarrow \begin{array}{r@{}l} & CH_3\\ & |\\ CH_2{=}&C\\ &|\\ &C{=}O\\ &|\\ &C_4H_9\end{array} + LiOCH_3$$

$$\begin{array}{r@{}l} & CH_3\\ & |\\ CH_2{=}&C\\ &|\\ &C{=}O\\ &|\\ &C_4H_9\end{array} + C_4H_9Li \longrightarrow \begin{array}{r@{}c@{}l} & CH_3 & \\ & | & \\ CH_2 = & C & \\ & | & \\ C_4H_9{-} & C & {-}OLi\\ & | & \\ & C_4H_9 & \end{array}$$

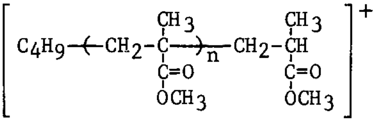
In the field desorption mass spectra of the trimer, tetramer and pentamer, there appeared the M^+ peaks, the mass number of which were 384, 484, and 584, respectively, and no peaks corresponding to any fragments produced from the molecular ions. On the other hand, in the electron impact ionization mass spectra of the tetramer, there appeared peaks of the mass numbers of 127, 158, 258, and 358, which corresponded to the following ions: (C), (D, n=0), (D, n=1), and (D, n=2), respectively (Figure 1).

(C)



$$\left[\begin{array}{r@{}c@{}l} & CH_3 & \\ & | & \\ CH_2{-} & C & {-}H\\ & | & \\ & C{=}O & \\ & | & \\ & C_4H_9 & \end{array}\right]^+$$

(D)



$$\left[C_4H_9{-}\left(CH_2{-}\begin{array}{c} CH_3\\ |\\ C\\ |\\ C{=}O\\ |\\ OCH_3\end{array}\right)_n{-}CH_2{-}\begin{array}{c} CH_3\\ |\\ CH\\ |\\ C{=}O\\ |\\ OCH_3\end{array}\right]^+$$

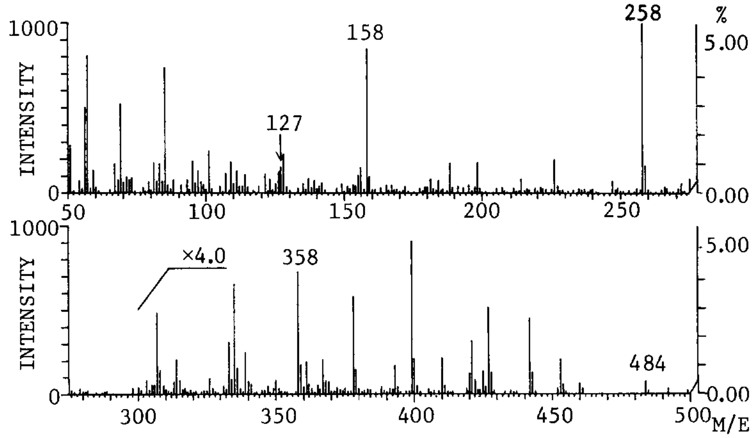
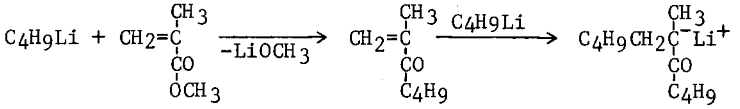


Figure 1. Electron impact ionization mass spectrum of the tetramer

The trimer showed mass peaks of 127, 158 and 258, and the dimer showed the peaks of 127 and 158. The results strongly indicate that the ketone unit is located at the chain end, which cannot be determined by ^1H-NMR spectroscopy.

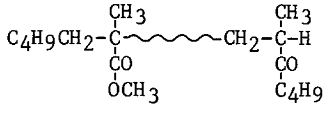
In a previous communication (HATADA et al. 1978a) we analyzed the polymer and oligomer of perdeuterated methyl methacrylate, prepared with undeuterated butyllithium in toluene, by ^1H-NMR spectroscopy and found that the polymer and oligomer molecule contain 1.0 and 0.7 of butyl isopropenyl ketone units in the chain. The measurement of the spin-lattice relaxation time indicates that the ketone unit is located at or near both chain ends, and the following initiation step is postulated:



$$C_4H_9Li + CH_2{=}\underset{\substack{|\\ CO\\ |\\ OCH_3}}{\overset{\substack{CH_3\\ |}}{C}} \xrightarrow[-LiOCH_3]{} CH_2{=}\underset{\substack{|\\ CO\\ |\\ C_4H_9}}{\overset{\substack{CH_3\\ |}}{C}} \xrightarrow{C_4H_9Li} C_4H_9CH_2\underset{\substack{|\\ CO\\ |\\ C_4H_9}}{\overset{\substack{CH_3\\ |}}{C^-}}Li^+$$

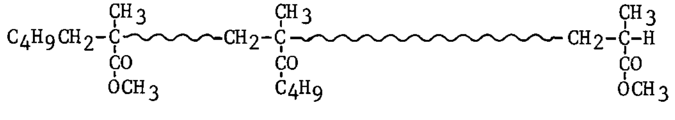
However, the results obtained in this work strongly suggest that the ketone unit is located at the terminal of the oligomer chain and not at the forefront, and a somewhat different mechanism will be proposed for the polymerization of methyl methacrylate with butyllithium in toluene. On mixing the reactants, butyllithium reacts with both the olefinic and carbonyl double bonds of the monomer. The attack on the olefinic double bond produces the methyl methacrylate anions which add to the monomer to form the growing chains. The attack of the initiator on the carbonyl group gives butyl isopropenyl ketone with release of lithium methoxide, and all the ketone molecules formed soon attack most of the growing chain ends owing to their higher reactivity compared to that of methyl methacrylate. The resulting anions are less reactive than methyl methacrylate anions and add to the monomer very slowly, but once attacked by methyl methacrylate they then add the monomer rapidly to form high molecular weight polymers. Most of the chains with ketonic end groups remain unaffected during the polymerization and are recovered as methanol-soluble oligomers after the polymerization is terminated. Only a small fraction can be transformed to a high molecular chain which contains one ketone unit near to its forefront.

Oligomer



$$C_4H_9CH_2-\underset{\substack{|\\ CO\\ |\\ OCH_3}}{\overset{\substack{CH_3\\ |}}{C}}\sim\!\sim\!\sim\!\sim CH_2-\underset{\substack{|\\ CO\\ |\\ C_4H_9}}{\overset{\substack{CH_3\\ |}}{C}}-H$$

Polymer



$$C_4H_9CH_2-\underset{\substack{|\\ CO\\ |\\ OCH_3}}{\overset{\substack{CH_3\\ |}}{C}}\sim\!\sim\!\sim\!\sim CH_2-\underset{\substack{|\\ CO\\ |\\ C_4H_9}}{\overset{\substack{CH_3\\ |}}{C}}\sim\!\sim\!\sim\!\sim\!\sim\!\sim\!\sim\!\sim\!\sim\!\sim CH_2-\underset{\substack{|\\ CO\\ |\\ OCH_3}}{\overset{\substack{CH_3\\ |}}{C}}-H$$

Transformation of the oligomer to a high polymer chain was also suggested in the polymerization of ethyl methacrylate in toluene with butyllithium(HATADA et al. 1978b).

When the polymerization of perdeuterated methyl methacrylate was carried out in toluene with undeuterated butyllithium at -78°C and terminated by the addition of a small amount of undeuterated methanol, 30% of the oligomer molecules formed lacked a terminal methine proton and 70% of them contained a butyl isopropenyl ketone unit(HATADA et al. 1978a). This may indicate that the spontaneous termination by true cyclization at the chain ends occurs with a part of the growing chains before the latter are attacked by the ketone. The reason why this type of termination occurs only with the growing chains of short length is not clear at present.

The authors express their sincere thanks to Professor H. Matsuda and Dr. T. Matsuo, College of General Education, Osaka University, and to Dr. I. Katakuse and Dr. S. Kusumoto, Faculty of Science, Osaka University for the measurements of mass spectra. They are also indebted to Mrs. F. Yano for her clerical assistance in preparing the manuscript.

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Received November 9/3o, 1979