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Studies on the Anionic Polymerization of Methyl Methacrylate with Butyllithium by Using Perdeuterated Monomer

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Introduction

A number of investigations have been published on the mechanism of the stereoregular polymerization of methyl methacrylate by alkyllithium in nonpolar solvent such as toluene. In the initiation step a rapid attack of alkyllithium on monomer was reported to occur in the first few seconds (COTTAM 1963, GLUSKER 1961a, WILES 1965) and take place on both olefinic and carbonyl double bond (GOODE 1960, KAWABATA 1965, WILES 1965). KAWABATA and TSURUTA (1965) tried to elucidate the mechanism of polymerization by investigating the reaction mode of butyllithium with methyl methacrylate and methyl acrylate in a polar and a nonpolar solvent, but they did not study how the butyl group of the initiator being incorporated into the polymer. In this work perdeuterated methyl methacrylate was polymerized by butyllithium in toluene at -78°C and the resultant polymer and oligomer were studied for the butyl group by using ^{1}H NMR spectroscopy.

Experimental

Perdeuterated methyl methacrylate was prepared from acetone cyanohydrin-d_7 and methanol-d_4 according to the method of CRAWFORD (1934).

The polymerization was carried out in toluene at -78°C with butyllithium as an initiator for 5 hr and was terminated by the addition of a small amount of methanol. The reaction mixture was poured into a large amount of methanol to precipitate the polymer of high molecular weight, which was separated by filtration. The methanol-soluble fraction was recovered by the evaporation of the filtrate. The oligomer thus obtained was redissolved in benzene to remove a small amount of insoluble material and was freeze-dried.

The ^{1}H NMR spectra of the polymer and oligomer were measured in nitrobenzene-d_5 at 110°C on JNM-FX100 Fourier transform NMR spectrometer (JEOL) being operated at 100MHz. The free-induction decays were accumulated 100 times. Hydrogen content of the sample was determined from the relative intensity of the signal of interest to the signal due to the partially undeuterated nitrobenzene contained in small quantities in the

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solvent. The absolute intensity of the latter signal was measured by using precision coaxial tubing according to the procedure of HATADA et al. (1977a). Spin-lattice relaxation time, T_1, was measured by the inversion-recovery Fourier transform method.

Number average molecular weight was determined in benzene by Hitachi 117 vapor pressure osmometer at 42°C.

Results and Discussion

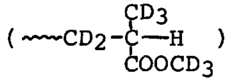
Polymerization of perdeuterated methyl methacrylate was carried out in toluene with 0.50mmol of undeuterated butyllithium at -78°C. The results are shown in Table 1 and ^{1}H NMR spectra of the resultant polymer and oligomer are given in Fig. 1. The triplets at 0.79ppm should be due to the methyl protons in the butyl group, which originally came from butyllithium used as an initiator. The singlet at 2.57ppm can be assigned to the terminal methine proton ( $\sim\!\sim CD_2-\overset{CD_3}{\underset{COOCD_3}{C}}-H$), which was introduced from the methanol in the termination reaction. The contents of the latter proton in the polymer and oligomer obtained were measured to be 0.011 and 0.167mmol, respectively, from which the molecular weights were calculated to be 26,800 for the polymer and 1,630 for the oligomer by assuming that each molecule has one terminal methine proton. The molecular weight of the polymer thus obtained is consistent with that measured by vapor pressure osmometer, but the molecular weight of the oligomer determined by NMR method is greater than that measured by vapor pressure osmometer (Table 1). These facts indicate that most of the polymer chain is still living at the end of the polymerization and the spontaneous termination through the formation of cyclic ketone structure does not occur at the growing end of the polymer chain during the polymerization. The chains of the oligomer is reported to be essentially inactive at the later stage of the polymerization, owing to the pseudo-cyclization (GLUSKER 1961b). The difference between the molecular weights determined for the oligomer by NMR and vapor pressure osmometer showed that about 30% of the oligomer

TABLE 1
Polymerization of perdeuterated methyl methacrylate with butyllithium in toluene at -78°C for 5hr[a]

	Yield (g)	$\bar{M}_n \times 10^{-3}$	
		VPO	NMR
Polymer	0.295	26.9	26.8
Oligomer	0.271	1.09	1.63

[a] Monomer 5.2mmol, Butyllithium 0.50mmol.

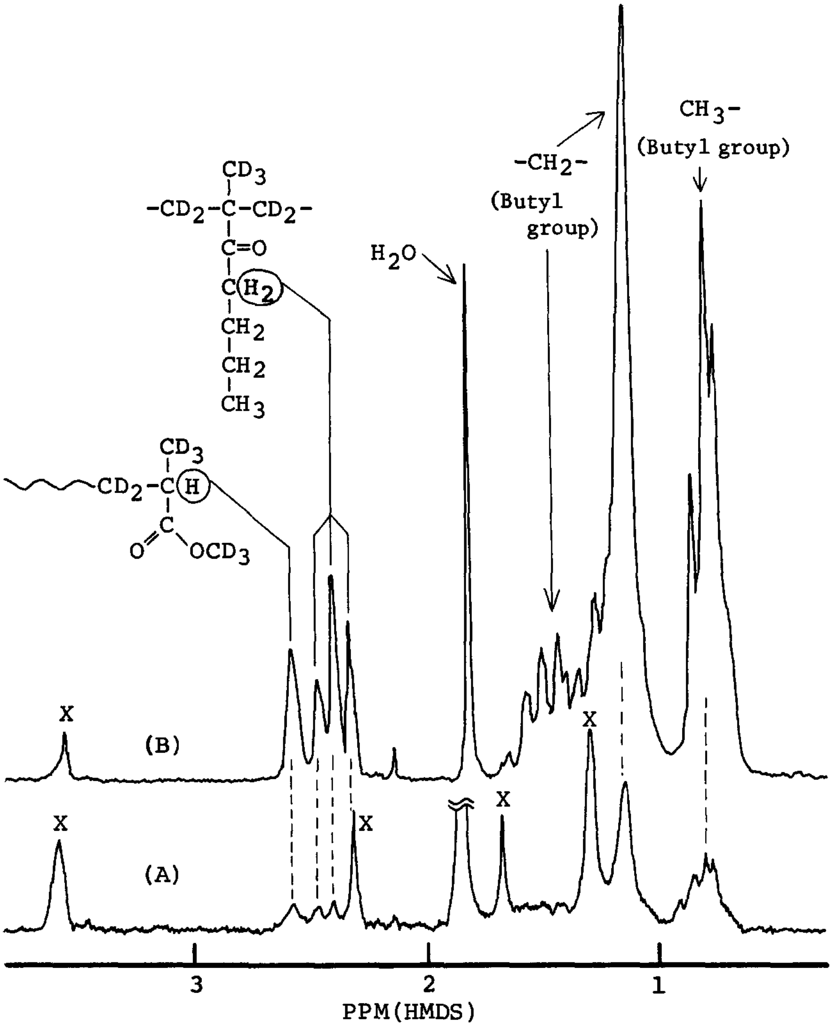


Figure 1. ^1H NMR spectra of the polymer(A) and oligomer(B) of perdeuterated methyl methacrylate prepared in toluene with butyllithium at -78°C. The signals labelled X are due to the residual protons in the monomer unit of the chain.

molecules have not a terminal methine proton (Table 2), indicating the possibility of the termination by a true cyclization with a release of the methoxide but to a small extent.

TABLE 2
Analysis of butyl group and terminal methine proton in the polymer and oligomer

	Amount[a]	C_4H_9-(total)		C_4H_9CO-		Terminal methine	
	(mmol)	mmol	mol/mol[b]	mmol	mol/mol[b]	mmol	mol/mol[b]
Polymer	0.0110	0.0203	1.8	0.0107	1.0	0.0110	1.0
Oligomer	0.249	0.424	1.7	0.182	0.7	0.167	0.7

[a] Calculated from the yield and the $\overline{M}_n$ measured by vapor pressure osmometer shown in Table 1.

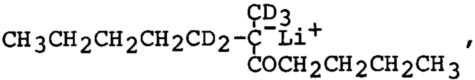
[b] Represents the number of butyl group or terminal methine proton in a molecule of polymer or oligomer.

Measurement of the intensity of methyl proton signal indicated that a polymer and an oligomer molecule has 1.8 and 1.7 butyl groups, respectively, as shown in Table 2. These should be introduced at the initiation step and also through the attack of butyllithium on the carbonyl group. The triplet at 2.40ppm should be due to the protons of the methylene group adjacent to the carbonyl group ($-CO\underline{H}_2CH_2CH_2CH_3$). This peak assignment was confirmed by the inspection of the spectra of some model compounds and also by spin-spin decoupling technique. The contents of the C_4H_9CO- group in a polymer and an oligomer molecule were thus determined to be 1.0 and 0.7 moles, respectively. It follows then that a polymer and an oligomer chain has each about one terminal butyl group which was introduced at the initiation step. The spin-lattice relaxation time, T_1, of the methylene protons adjacent to the carbonyl group was nearly the same level as the T_1 of the methyl protons or the terminal methine proton (Table 3) but much longer than the T_1 of the protons

TABLE 3
^1H spin-lattice relaxation times T_1's in second of the protons in butyl group and the terminal methine proton in nitrobenzene-d_5 at 110°C

	$C\underline{H}_3CH_2CH_2CH_2$-	$CH_3CH_2CH_2C\underline{H}_2CO$-	Terminal methine
Polymer	3.9	1.8	5.1
Oligomer	5.4	2.1	6.1

in the interior sequences of the poly(methyl methacrylate) (HATADA 1977b), indicating that the C_4H_9CO- group in the polymer or oligomer locates very near to the chain end. Butyllithium disappears almost instantaneously on mixing the reactants in the polymerization of methyl methacrylate (COTTAM 1963, GLUSKER 1961a) and reacts first with many more carbonyl groups than with the monomer vinyl double bond at lower temperature (WILES 1965). So the results mentioned here might suggest that the initiating species for the polymer and oligomer are the ion-pair of



$CH_3CH_2CH_2CH_2CD_2-\overset{CD_3}{\underset{COCH_2CH_2CH_2CH_3}{C^-}}Li^+$

, which is the reaction product of butyllithium and butyl isopropenyl ketone. The latter is produced by the carbonyl attack of butyllithium on the monomer and much more reactive at the vinyl double bond than the unreacted monomer.

In the polymerization of methyl methacrylate with butyllithium in toluene the high molecular weight polymer accounted for less than 10% of the initiator molecules and a large fraction existed as petroleum ether-soluble polymer, but all the butyllithium added could not be accounted for if each polymer molecule was assumed to contain one butyl group (COTTAM 1963). In this work it was revealed that a polymer and an oligomer molecule each has some two butyl group and about half of them was introduced through the attack of the initiator on the carbonyl group. The total amount of the butyllithium residue incorporated in both the polymer and oligomer was measured to be 0.45mmol and almost corresponded to the amount of the butyllithium used (0.50mmol).

A method for investigating the reaction mechanism mentioned here can be applied to a wide variety of the polymerization. An extensive study is now under way and the results will be published in the future.

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Summary

Methyl methacrylate-d_8 was polymerized by C_4H_9Li in toluene at -78°C and the resultant polymer and oligomer were studied for butyl group by ^1H NMR spectroscopy according to the precision coaxial tubing method (HATADA 1977a). A polymer and an oligomer molecule was found to have about one butyl group incorporated through the attack of C_4H_9Li on the carbonyl group as well as one terminal butyl group. The total amount of the C_4H_9Li residue introduced in both the polymer and oligomer molecules was measured to be 0.45mmol and almost corresponded to the amount of the C_4H_9Li used (0.50mmol).

References

B.J.COTTAM, D.M.WILES and S.BYWATER,: Can. J. Chem., 41, 1905 (1963)

J.W.C.CRAWFORD,: B.P. 405,699 (1934)

D.L.GLUSKER, E.STILES and B.YONCOSKIE,: J. Polym. Sci., 49, 297 (1961a)

D.L.GLUSKER, I.LYSLOFF and E.STILES,: J. Polym. Sci., 49, 315 (1961b)

W.E.GOODE, F.H.OWENS and W.L.MYERS,: J. Polym. Sci., 47, 75 (1960)

K.HATADA, Y.TERAWAKI and H.OKUDA,: Org. Magn. Res., 9, 518 (1977a)

K.HATADA, H.ISHIKAWA, T.KITAYAMA and H.YUKI,: Makromol. Chem., 178, 2753 (1977b)

N.KAWABATA and T.TSURUTA,: Makromol. Chem., 86, 231 (1965)

D.M.WILES and S.BYWATER,: Trans. Faraday Soc., 61, 150 (1965)

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