

SHORT COMMUNICATIONS

NMR Assignment of the Terminal Methine Proton in Poly(methyl methacrylate) and Location of the Butyl Isopropenyl Ketone Unit in the Polymer Molecule Produced by Butyllithium and Butylmagnesium Chloride

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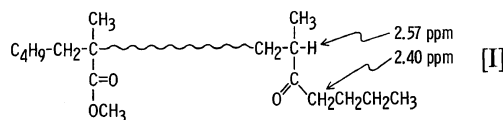
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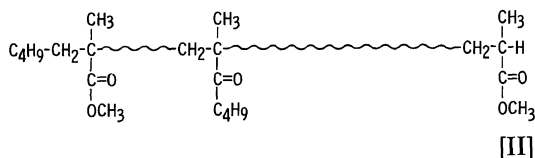
Analyses of polymers for initiator fragments provide important understanding of the mechanism of polymerization. The present authors have developed a new method for this purpose using totally deuterated monomers.¹⁻⁵ When a deuterated monomer is polymerized by an undeuterated initiator, the fragment of the initiator and/or that of terminating reagent incorporated in the polymer chain can be easily detected by ¹H NMR spectroscopy without disturbance from signals due to monomeric units. By this technique, we found that the polymer and oligomer of methyl methacrylate (MMA) produced in toluene using butyllithium (BuLi) as an initiator had about one butyl isopropenyl ketone (BIPK) unit.¹ The ketone is formed through the attack of BuLi onto the carbonyl double bond of MMA. The polymer and oligomer of MMA-*d*₈ obtained in this polymerization showed a singlet peak at 2.57 ppm and a triplet at 2.40 ppm. These peaks were assigned to the terminal methine proton and the methylene proton adjacent to the carbonyl group of BIPK unit, respectively.¹ The oligo-

mers (DP = 3—5) of undeuterated MMA separated by HPLC were found to each have a BIPK unit at the terminating chain end in consideration of the fragmentation pattern in their mass spectra.⁶ The structure was described as follows:



In the case of a polymer, it was difficult to obtain spectroscopic evidence specifying the location of a BIPK unit in the chain. We believed the BIPK unit to be located near the beginning of the chain in view of the followings; (1) a polymer of lower molecular weight formed in the early stage of polymerization contained one BIPK unit as well as the higher molecular weight polymer formed later, (2) hardly any BIPK monomer could be detected in the reaction mixture even in the early stage of polymerization and thus was considered to be already incorporated in the polymer chain, and (3) the methylene protons adjacent to carbonyl group of BIPK unit showed a

relatively long spin-lattice relaxation time.¹ Thus, the following structure of the polymer in the previous paper¹ was postulated as follows:



Recently, we extended our study to the polymerization of MMA by the Grignard reagent and found a polymer and an oligomer molecule of MMA-*d*₈ prepared with butylmagnesium chloride (BuMgCl) in toluene at -78°C to have only 0.3 and 0.4 terminal methine proton which showed a signal at 2.57 ppm, respectively. We tried to find a cyclic ketone structure at the chain end, as proposed by Glusker *et al.*,⁷ using ¹³C NMR and a cyclic model compound but could detect it at most 0.05 per chain. This prompted us to look for another type of terminal methine proton signal.

MMA-*d*₈ was polymerized by 10 mol% of sodium methoxide at 55°C according to the literature.⁸ The polymer obtained by this initiator must contain no ketone units and should have the terminal methine proton in the MMA unit. Figure 1(A) shows the NMR spectrum of the polymer obtained. A broad signal was observed at about 2.45 ppm but not at 2.57 ppm. The polymer obtained with 1,1-diphenylhexyllithium, which scarcely attacks the carbonyl carbon of MMA,^{9,10} also showed its terminal methine proton signal at about 2.45 ppm, as evident from Figure 1(B). This signal disappeared for the most part when the polymerization was terminated with CD₃OD. Thus, the methine proton in terminal MMA unit resonates at about 2.45 ppm and the signal at 2.57 ppm is due only to the methine proton in the terminal BIPK unit.

Figure 2 shows the carbonyl methylene (2.40 ppm) and terminal methine proton (2.57 ppm) region spectra of the polymers and oligomers produced in the polymerization by BuMgCl terminated with CH₃OH or CD₃OD.

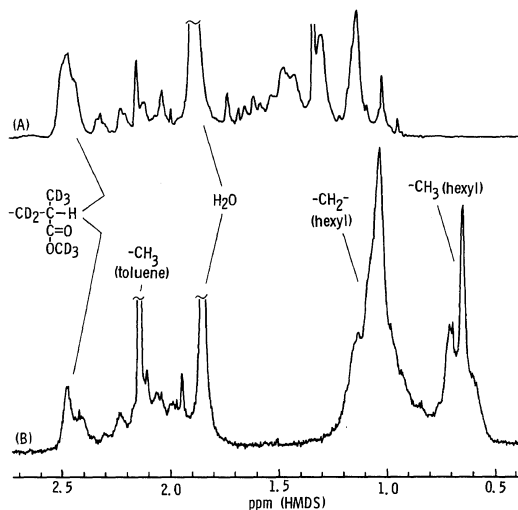


Figure 1. ¹H NMR spectra of the polymers of MMA-*d*₈ prepared by sodium methoxide (A) and 1,1-diphenylhexyllithium (B). (Nitrobenzene-*d*₅, 110°C, 100 MHz).

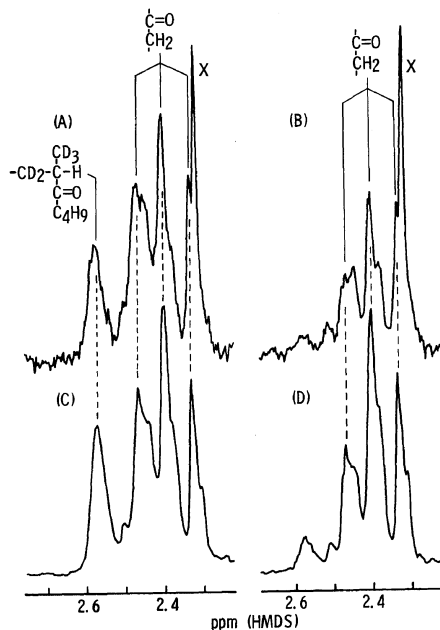
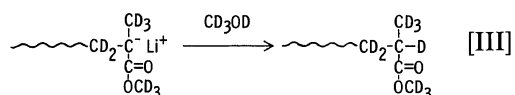
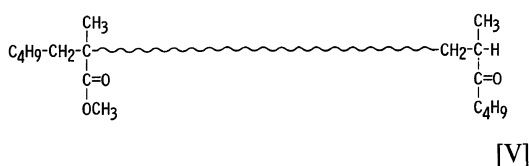
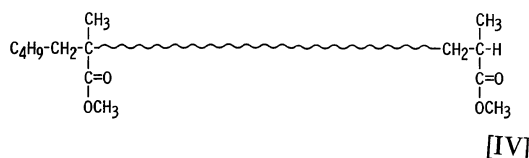


Figure 2. ¹H NMR spectra of the polymers and oligomers of MMA-*d*₈ formed in the polymerization by BuMgCl terminated with CH₃OH or CD₃OD. (A) Polymer, CH₃OH-termination; (B) Polymer, CD₃OD-termination; (C) Oligomer, CH₃OH-termination; (D) Oligomer, CD₃OD-termination. X represents the signal due to the remaining protons in the monomeric units.

When the polymerization was terminated with CD_3OD , the peak at 2.57 ppm nearly disappeared, as expected (Figures 2(B) and 2(D)). However, the intensities of signals around 2.4 ppm also decreased to some extent, indicating that the signal of the methine proton in terminal MMA unit (2.45 ppm) overlapped with the carbonyl methylene signal and disappeared when the polymerization was terminated with CD_3OD .

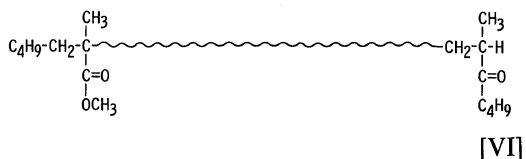


A comparison of the peak intensities around 2.4 ppm of CD_3OD -terminated polymer (Figure 2(B)) and oligomer (Figure 2(D)) with those of CH_3OH -terminated ones (Figures 2(A) and 2(C)) shows that the numbers of the terminal MMA methine proton per polymer and oligomer molecule are 0.4 and 0.4, respectively. This means that 40% of the polymer and oligomer molecules have the structure [IV]. From the intensity measurements of the residual triplet at 2.40 ppm due to the carbonyl methylene protons, the numbers of the BIPK units in a polymer and an oligomer molecule were 0.3 and 0.4, respectively. These values correspond to the number of terminal BIPK methine protons in a polymer (0.3) and an oligomer (0.4) molecule. Thus, at least two types of polymers and oligomers are formed in polymerization by BuMgCl in toluene: one is ended with MMA unit [IV] and the other with BIPK unit [V].



The detailed investigation on other types of terminal structures is in progress.

In polymerization with BuLi , most of polymer molecules each contained one BIPK unit and the terminal methine proton resonated at 2.57 ppm. This signal almost disappeared when the polymerization was terminated with CD_3OD but the intensity of the peak around 2.4 ppm did not decrease. Therefore, the polymer molecules all have terminal BIPK units and contain no terminal MMA units. The following structure should be applicable:



Such a specific location of the BIPK unit in a polymer seems rather strange, since most of the BuLi used was consumed 10 min following initiation, when a BIPK monomer could not be detected and the residual BuLi (ca. 10%)¹¹ did not participate in any reaction. Bywater suggests that the tertiary alkoxide, $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{C}_4\text{H}_9)(\text{OCH}_3)\text{OLi}$, formed by attack of the initiator on the carbonyl group of MMA, might not release lithium methoxide immediately but rather on termination of the reaction to form BIPK.¹² Thus, one possible explanation for the location of the BIPK unit in the structure [VI] is that the tertiary alkoxide coordinates with the propagating chain end, and the ketone is formed on termination to be immediately incorporated into the chain end. A detailed investigation on the polymerization mechanism of MMA with BuLi and BuMgCl is now in progress.

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