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# $^1$H NMR spectroscopic differentiation of block copolymer, random copolymer and mixture of the corresponding homopolymers through end group and monomer sequence analyses

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## Summary

Highly isotactic block and random copolymers of methyl methacrylate (MMA) and ethyl methacrylate (EMA) were prepared with *t*-$C_4H_9MgBr$ in toluene at -60°C. $^1$H NMR spectra of the copolymers were measured in nitrobenzene-$d_5$ at 110°C and 500 MHz and analyzed in regard to monomer sequence and the end group. NMR signals due to the monomeric units provide clear indications for distinguishing the block copolymers from the random copolymers. The chemical shift of the initiator fragment signal is so sensitive to the adjacent monomeric unit that PMMA-*block*-poly(EMA) and poly(EMA)-*block*-PMMA can be differentiated spectroscopically. The main part of the spectrum for a mixture of PMMA and poly(EMA) prepared with *t*-$C_4H_9MgBr$ is identical to those for the block copolymers but the mixture shows two *t*-$C_4H_9$- signals arising from both homopolymers and thus can be distinguished from the block copolymers.

## Introduction

NMR spectroscopy is one of the most frequently used tools for the structural analysis of copolymers. In the case of vinyl copolymers, however, the spectrum is often complicated by the existence of not only various monomer sequences but also configurational sequences. Highly stereoregular and living polymerization of methyl methacrylate (MMA) has been realized by the polymerization in toluene at low temperature with *t*-$C_4H_9MgBr$; the polymerization gives highly isotactic poly(methyl methacrylate) (PMMA) with narrow molecular weight distribution (MWD).[1,2] Recently, we examined the possibilities of living and stereospecific copolymerization of MMA and ethyl methacrylate (EMA) by using *t*-$C_4H_9MgBr$ as an initiator.[3] Highly isotactic block copolymers could be prepared by the polymerization of EMA with isotactic PMMA living anion formed with *t*-$C_4H_9MgBr$ or by the polymerization of MMA with isotactic poly(EMA) living anion. Highly isotactic random copolymer of MMA and EMA was obtained from the copolymerization with *t*-$C_4H_9MgBr$ in toluene. High stereoregularity of these copolymers makes their spectra simple and allows more detailed characterization of the structure. In this communication we report $^1$H NMR spectroscopic analyses of the isotactic copolymers of MMA and EMA, from which it is possible to distinguish block copolymers from random copolymers or a mixture of the corresponding homopolymers.

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## Experimental

Monomers were purified by fractional distillation, dried over calcium dihydride and vacuum-distilled just before use. $t$-$C_4H_9MgBr$ was prepared from $t$-$C_4H_9Br$ and Mg in diethyl ether$^{2)}$.

Polymerization was carried out in a glass ampoule filled with dry nitrogen. Block copolymerization was performed in a reaction vessel equipped with a mechanical stirrer. The polymerization reactions were terminated with methanol containing a small amount of HCl at the polymerization temperature. After the solvent and unreacted monomer were removed under high vacuum, the residue was dissolved in benzene. The insoluble materials were removed by centrifugation and the polymeric material was recovered by freeze-drying.

$^1H$ NMR spectra were measured on a JNM-GX500 NMR spectrometer. Molecular weights were determined on a Hitachi 117 vapor pressure osmometer in toluene at 60°C or on a JASCO FLC-A10 GPC chromatograph equipped with Shodex GPC columns KF803 and A-80M using tetrahydrofuran as an eluent. GPC chromatograms were calibrated against standard polystyrene samples.

## Results and Discussion

### *Stereoregular Copolymers of MMA and EMA*

Isotactic PMMA-*block*-poly(EMA) was prepared by the polymerization of EMA with the living PMMA anion formed with $t$-$C_4H_9MgBr$ in toluene at -60°C. The copolymer has the average degree of polymerization (DP) for each block of 59 and fairly narrow MWD.$^{3)}$

Isotactic poly(EMA)-*block*-PMMA was obtained by the polymerization of MMA with poly(EMA) anion formed with $t$-$C_4H_9MgBr$ in toluene at -60°C. The MWD of this block copolymer is bimodal as in the case of the poly(EMA) obtained with $t$-$C_4H_9MgBr$ under the same conditions.$^{3)}$

Conventional copolymerization of EMA and MMA with $t$-$C_4H_9MgBr$ in toluene at -60°C gave highly isotactic copolymer, but its MWD was bimodal; monomer sequence distribution of the copolymer was found to be random from $^{13}C$ NMR analysis of the carbonyl carbon signals.$^{3)}$ Characteristics of the copolymers are summarized in Table 1 together with those of PMMA and poly(EMA).

**Table 1** Characteristics of isotactic copolymers and homopolymers of MMA and EMA prepared with $t$-$C_4H_9MgBr$ in toluene at -60°C

| Polymer | MMA/EMA unit ratio | Mn | | $\overline{Mw}^a/\overline{Mn}$ | Tacticity(%) | | |
|---|---|---|---|---|---|---|---|
| | | NMR | VPO | | *mm* | *mr* | *rr* |
| PMMA-*block*-poly(EMA) | 59/59 | 12700 | 12500 | 1.29 | 97 | 2 | 1 |
| poly(EMA)-*block*-PMMA | 50/55 | 11300 | 11700 | 2.61 | 97 | 3 | 0 |
| poly(MMA-*ran*-EMA) | 53/51 | 11100 | 11300 | 1.53 | 96 | 3 | 1 |
| PMMA | 40/0 | 4090 | — | 1.11 | 97 | 2 | 1 |
| poly(EMA)$^b$ | 0/55 | 6320 | — | 3.49 | 97 | 3 | 0 |

[a] Determined by GPC.

[b] Polymerization at -78°C.

### *$^1$H NMR spectroscopy of copolymer*

Figure 1 illustrates 500 MHz $^1$H NMR spectra, measured in nitrobenzene-$d_5$ at 110°C, of poly(MMA-*ran*-EMA), PMMA-*block*-poly(EMA), poly(EMA)-*block*-PMMA, and a 1:1 mixture of PMMA and poly(EMA) prepared with *t*-$C_4H_9$MgBr. In the spectra of the block copolymers methylene protons showed two sets of AB quartet signals due to PMMA block and poly(EMA) block (Figures 1B and 1C), clearly indicating that the both blocks are highly isotactic. The assignments of these peaks shown in the Figures were made from the comparison of the spectra with those of both the isotactic homopolymers. The corresponding signals of methylene protons in the random copolymer (Figure 1A) showed much complicated splittings (1.75 ppm) or broadening (2.4 ppm) owing to the presence of different types of monomer sequences. $\alpha$-Methyl proton signals of the block copolymers clearly split into two sharp singlets resonating at 1.33 and 1.38 ppm, which were assigned to PMMA block and poly(EMA) block, respectively, while the corresponding signal in the spectrum of the random copolymer was a broad singlet. Similar spectral differences between the block and random copolymers were also observed in the signals due to methyl (1.26 ppm) and methylene (4.13 ppm) protons of ester group in EMA units. Thus, these $^1$H NMR signals are good and clear indications for distinguishing the block and random copolymers of MMA and EMA. Lochmann et al.[4)] reported that block and statistical copolymers of MMA and butyl methacrylate, prepared with ethyl $\alpha$-lithioisobutyrate in the presence of sodium t-butoxide, could be distinguished from the $\alpha$-methyl proton signals in their $^1$H NMR spectra.

NMR spectra of block copolymers are expected to be almost the superimposes of the spectra of the corresponding homopolymers. The signals due to the monomeric units in the isotactic block copolymers (Figures 1B and 1C) are actually very similar to those observed in the spectrum of the mixture of isotactic PMMA and isotactic poly(EMA) (Figure 1D). However, the signals due to initiator fragments (0.8~0.9 ppm) is the exception, which provides the information for distinguishing the block copolymers from the mixture. The PMMA-*block*-poly(EMA) (Figure 1B) and poly(EMA)-*block*-PMMA (Figure 1C) showed single *t*-$C_4H_9$- signals at 0.823 and 0.852 ppm, respectively, which were assigned to the initiator fragments attached to PMMA and poly(EMA) sequences, respectively. On the other hand, the mixture of PMMA and poly(EMA) prepared with the same initiator shows signals of two types of initiator fragments (*t*-$C_4H_9$-) as indicated in Figure 1D. Difference in intensity of the two signals is owing to different DP's of both homopolymers. Thus, the block copolymers can be distinguished from the mixture of the corresponding homopolymers by $^1$H NMR analysis of the end groups, even though the main part of the spectra of the block copolymer and the mixture are almost identical. It is noteworthy that the *t*-$C_4H_9$ signals in the two block copolymers (Figures 1B and 1C) also provides the information whether the block copolymer was prepared from PMMA anion or poly(EMA) anion.

The random copolymer showed two singlet signals at 0.826 and 0.845 ppm due to the initiator fragments, *t*-$C_4H_9$-MMA- and *t*-$C_4H_9$-EMA-, respectively.

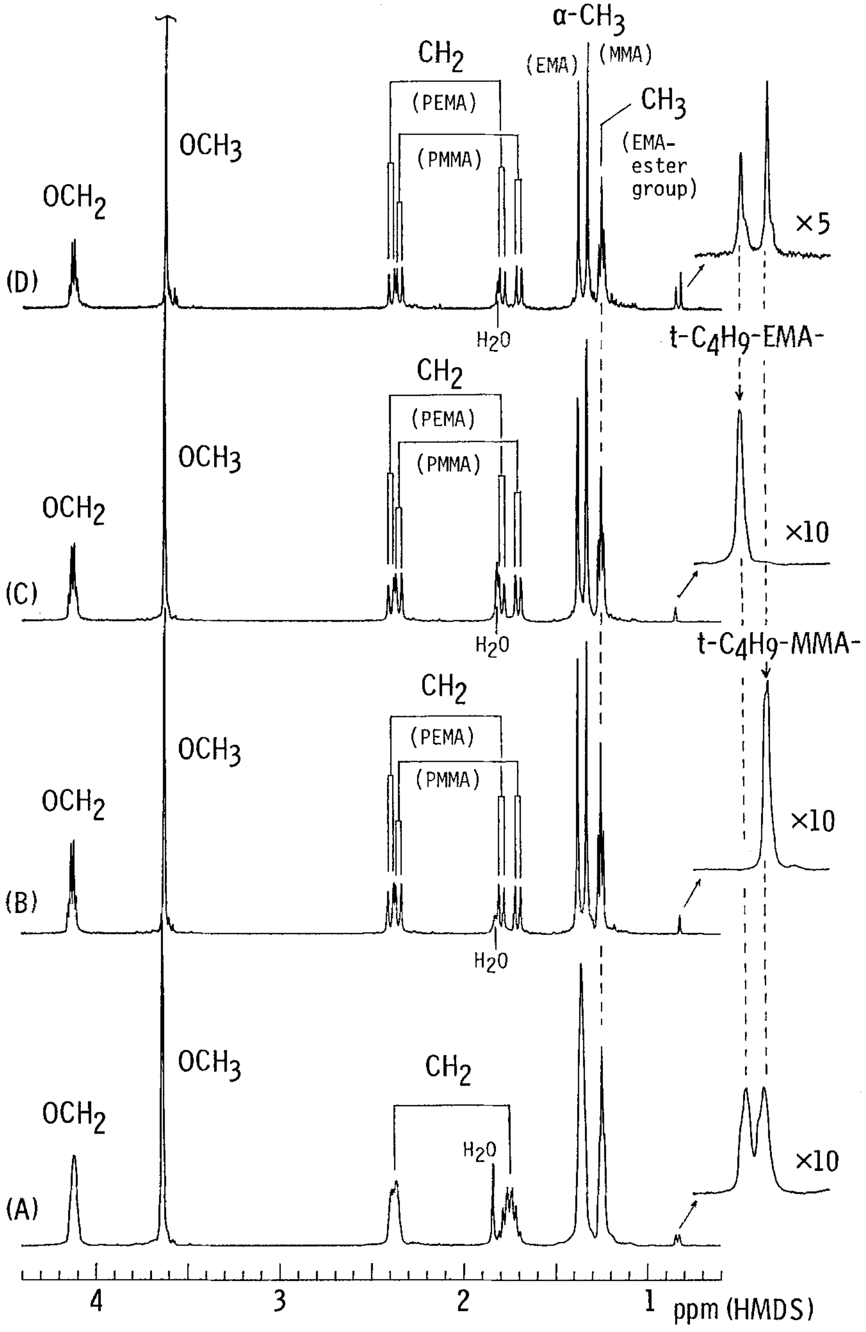

Figure 1 500 MHz $^{1}H$ NMR spectra of highly isotacitic copolymers of MMA and EMA prepared with *t*-$C_4H_9MgBr$ in toluene at -60°C, measured in nitrobenzene-$d_5$ at 110°C.

(A) Poly(MMA-*ran*-EMA). (B) PMMA-*block*-poly(EMA).

(C) Poly(EMA)-*block*-PMMA. (D) PMMA + poly(EMA) (MMA/EMA=1/1).

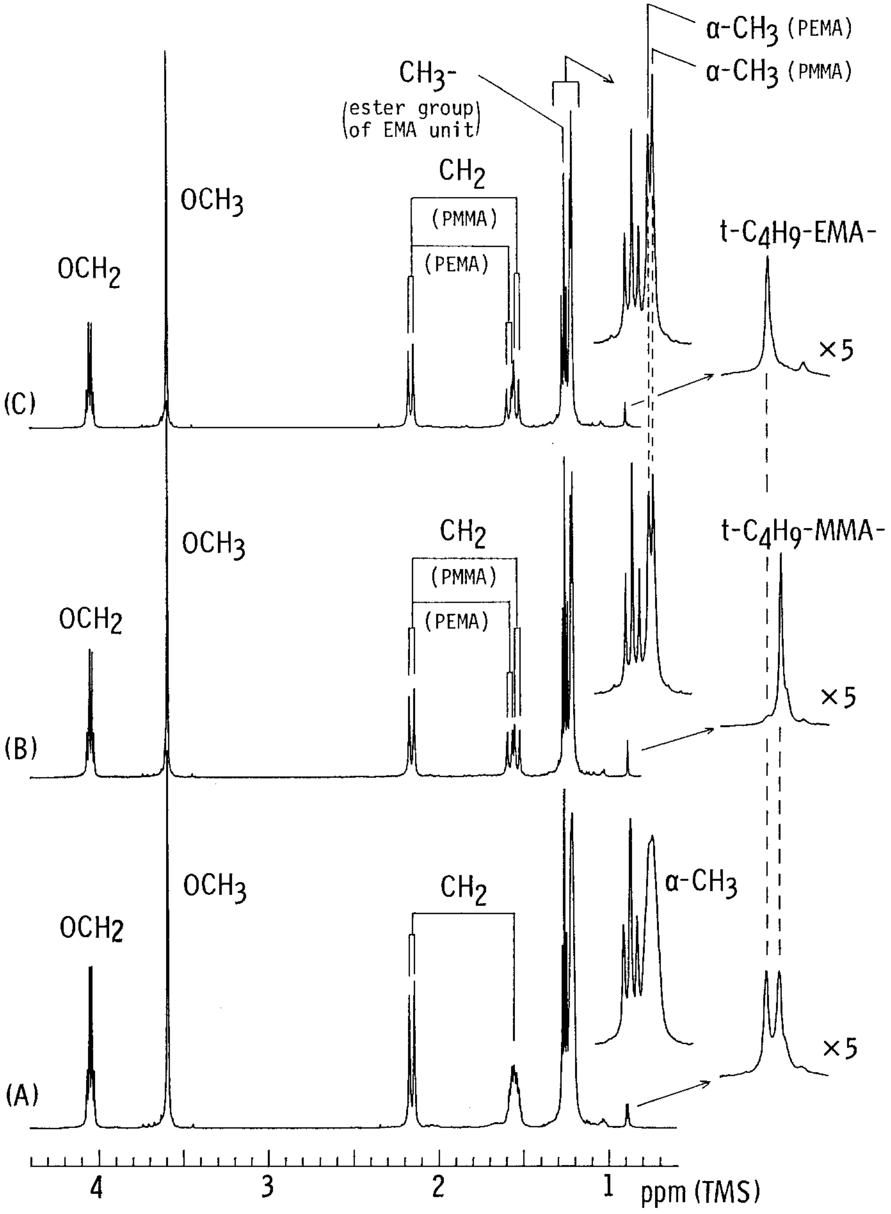

Figure 2 500MHz $^{1}$H NMR spectra of highly isotactic copolymers of MMA and EMA measured in CDCl3 at 55°C.
(A) Poly(MMA-*ran*-EMA). (B) PMMA-*block*-poly(EMA).
(C) Poly(EMA)-*block*-PMMA.

The chemical shift values were not exactly the same as those for the block copolymers (Figures 1B and 1C), due to the difference in monomer sequences following the *t*-$C_4H_9$-MMA- and *t*-$C_4H_9$-EMA- groups. The intensity ratio of these signals is very close to the ratio of the initial concentrations of MMA and EMA monomers (1:1), indicating that the reactivities of these monomers toward *t*-$C_4H_9MgBr$ in the initiation process are almost the same.

We found that the choice of solvent for NMR measurement was very important in the present case. In the $^1H$ NMR spectra of the block and random copolymers measured at 55°C in $CDCl_3$ (Figure 2), instead of nitrobenzene-$d_5$, the methylene (4.05 ppm) and methyl (1.27 ppm) proton signals due to the ester group in EMA unit and one of the main chain methylene proton signals (2.15 ppm) are insensitive to monomer sequence and these signals of the block and random copolymers showed no difference. The chemical shift difference between the $\alpha$-$CH_3$ proton signals for MMA and EMA units in the block copolymers was smaller than that observed in the spectra measured in nitrobenzene-$d_5$. Although the *t*-$C_4H_9$- signal is informative in regard to the first monomer unit at the initiating chain end as seen in Figure 2, it is evident that nitrobenzene-$d_5$ is a better solvent for the structural analysis of these copolymers.

In conclusion, NMR analysis of the end group as well as monomer sequence in copolymers give us information for the detailed understanding of the copolymer structures.

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