

SHORT COMMUNICATIONS

The NMR Chemical Shifts between the Nonequivalent Methylene Protons of Polymer and Oligomers of Methyl Methacrylate: The Revised *meso/racemo* Assignments for the ω -End Dyad Sequences

Koichi HATADA, Koichi UTE, Tatsuki KITAYAMA,
Katsuji TANAKA, Mamoru IMANARI,*
and Naoyuki FUJII*

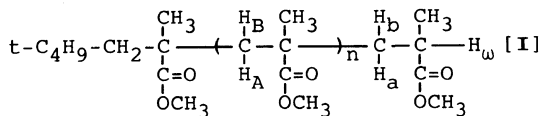
*Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan*

** JEOL Ltd., Akishima, Tokyo 196, Japan*

(Received January 9, 1989)

KEY WORDS ^1H NMR / Two-Dimensional NMR / High Performance Liquid Chromatography / Oligomer / Poly(methyl methacrylate) / X-Ray Crystal Analysis / Tacticity / Living Polymerization /

Polymerization of methyl methacrylate (MMA) initiated with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene proceeds in a living manner, and a highly isotactic PMMA with narrow molecular weight distribution is produced.^{1,2} When the living polymerization is terminated by adding methanol to the polymerization mixture, the polymer molecule having the following chemical structure results. Analysis of chain-end



structures of the PMMA ($\bar{n}=23$) by two-dimensional NMR spectroscopy³ revealed that reaction of the living PMMA anion with methanol is almost non-stereospecific, while that with the monomer is highly isotactic-specific. In addition, we reported the structural analysis of the oligomeric products [I] ($n=0-6$) by HPLC and ^1H NMR spectroscopy.⁴ In the literatures mentioned above,^{3,4} the *meso/racemo* assignments for the monomeric se-

quences in the PMMA and the oligomeric products were made on the basis of the nonequivalency of methylene protons;^{5,6} the chemical shift difference between the ^1H NMR signals of two methylene protons in a given monomeric unit should be larger for a *meso* dyad sequence than for a *racemo* dyad sequence.

Very recently, X-ray analysis of a crystallized MMA trimer was carried out, and the stereostructure of the trimer was found to be *meso-meso*.⁷ This trimer had been erroneously assigned to the *meso-racemo* isomer in our previous papers.^{3,4} The X-ray results indicated that nonequivalency of the methylene protons in in-chain monomeric units (H_A and H_B) is larger for the *meso* dyad sequence than for the *racemo* dyad sequence, while the opposite is true for methylene protons in the ω -end unit (H_a and H_b). This required revision of the former assignments for the ^1H NMR signals due to the monomeric units at the ω -*meso* and ω -*racemo* ends of the isotactic PMMA.³ Figure 1 shows the ^1H NMR

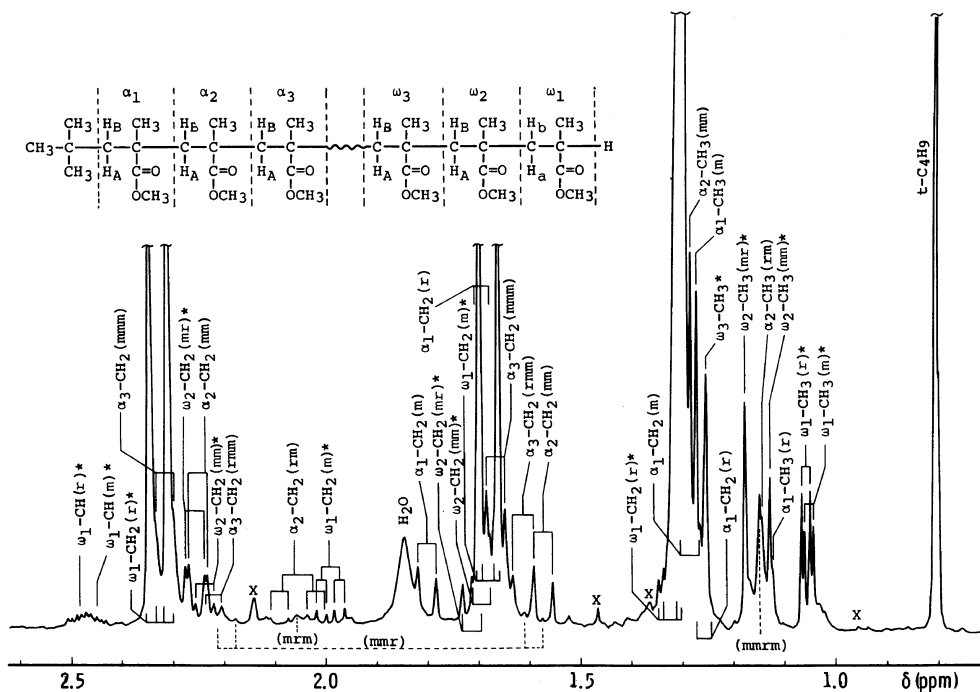


Figure 1. 400 MHz ^1H NMR spectrum of the isotactic PMMA prepared in toluene at -78°C by $t\text{-C}_4\text{H}_9\text{MgBr}$ measured in nitrobenzene- d_5 at 110°C . m = *meso*, r = *racemo*. The revised assignments are indicated by asterisks.

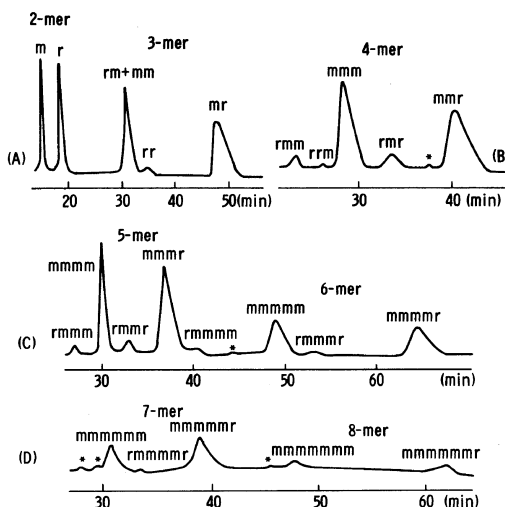
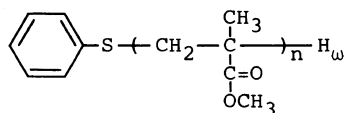


Figure 2. HPLC curves of the MMA-oligomers prepared by $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C for 15 min. Eluent, $n\text{-C}_4\text{H}_9\text{Cl}/\text{CH}_3\text{CN}$ 97.5/2.5 (A), 96/4 (B), 95/5 (C), 88/12 (D); column, Develosil 100-5, 4.6 mm (i.d.) \times 250 mm; detector, RI. Unknown peaks are indicated by asterisks.

spectrum of the PMMA prepared by $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C . The *meso/racemo* assignments for the CH_2 and CH_3 protons in the ω_1 – ω_3 units and the $\omega\text{-CH}$ proton (H_ω) shown in Figure 1 in ref 3 should be corrected as indicated in Figure 1 in this paper.

Corrections should also be made for the *meso/racemo* assignments for the ω -end monomeric sequences of the MMA oligomers. Figure 2 shows the HPLC elution curves of the MMA oligomers with the corrected assignments (*cf.* Figure 1 in ref 4).

A recent publication⁸ dealt with the structural analysis of the MMA oligomers [II] prepared by radical telomerization with thiophenol. The authors determined the stereo-



structures of the di-, tri- and tetra-adducts by ^1H NMR, leading to the conclusion that the propagation step gave preferentially a *racemo* dyad and that the chain-transfer step gave preferentially a *meso* dyad. However, it should be noted that the oligomers [I] and [II] have the same chemical structure at the ω -end monomeric sequences. Reinvestigation similar to that for oligomer [I] should also be conducted for their cases.

REFERENCES

1. K. Hatada, K. Ute, K. Tanaka, T. Kitayama, and Y. Okamoto, *Polym. J.*, **17**, 977 (1985).
2. K. Hatada, K. Ute, K. Tanaka, Y. Okamoto, and T. Kitayama, *Polym. J.*, **18**, 1037 (1986).
3. K. Hatada, K. Ute, K. Tanaka, M. Imanari, and N. Fujii, *Polym. J.*, **19**, 425 (1987).
4. K. Hatada, K. Ute, K. Tanaka, and T. Kitayama, *Polym. J.*, **19**, 1325 (1987).
5. F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.*, **44**, 173 (1960).
6. A. Nishioka, H. Watanabe, K. Abe, and Y. Sono, *J. Polym. Sci.*, **48**, 241 (1960).
7. K. Ute, T. Nishimura, Y. Matsuura, and K. Hatada, *Polym. J.*, **21**, 231 (1989).
8. J.-M. Bessiere, B. Boutevin, and L. Sarraf, *J. Polym. Sci., A*, **26**, 3275 (1988).