Polymer Bulletin 23, 157–162 (1990)

Polymer Bulletin

Stereoregular oligomers of methyl methacrylate

4. Supercritical fluid chromatography of the isotactic and syndiotactic oligomers of MMA*

Koichi Hatada[1,], Koichi Ute[1], Tohru Nishimura[1], Masaharu Kashiyama[1], Toshinori Saito[2], and Makoto Takeuchi[2]**

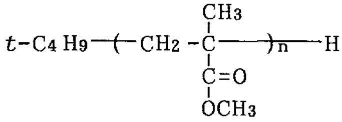
[1]Department of Chemistry, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka 560, Japan
[2]JEOL Ltd., Akishima, Tokyo 196, Japan

SUMMARY

Packed column SFC has been found suitable for the rapid and detailed analysis of the isotactic and syndiotactic oligomers of MMA, when the temperature gradient technique was applied and the modifier was employed. Oligomer components from trimer to 20-mer separated completely. The heptamer fraction collected three times by SFC gave the ^{1}H NMR spectrum of satisfactorily high S/N ratio; the spectrum agreed well with that of the standard sample. Separation by tacticity as well as by molecular weight was observed for the SFC of a mixture of the isotactic and syndiotactic oligomers. The isotactic oligomers had longer retention time than the syndiotactic oligomers of the corresponding degree of polymerization.

INTRODUCTION

Supercritical fluid chromatography (SFC) has been applied to the separation of the homologous species of styrene oligomers (1-3) and other oligomers (4) such as oligosiloxanes (5) and oligoethyleneglycols (6,7). As far as we are aware of, no paper has been published on the separation of stereoisomers of oligomer components by SFC. The usefulness of high performance liquid chromatography (HPLC) in the separation of stereoisomers of MMA oligomers was realized recently (8-12); the stereoisomers of MMA oligomers from dimer to octamer were separated by using silica gel as stationary phase and a mixture of butyl chloride and acetonitrile as mobile phase. In the present work, packed column SFC has been used to the analysis of the isotactic and syndiotactic oligomers of MMA prepared by the stereoregular living polymerizations with t-C_4H_9MgBr (13,14) and t-$C_4H_9Li/(C_2H_5)_3Al$ complex (15,16). These oligomers have the chemical structure as shown below, and differ only in stereoregularity.



$$t\text{-}C_4H_9\text{-}\left(CH_2\text{-}\overset{\displaystyle CH_3}{\underset{\substack{C=O\\ OCH_3}}{C}}\right)_n\text{-}H$$

[I]

Although the propagation process is highly stereospecific for both polymerization systems, the termination reaction (with methanol) is almost nonstereospecific. Thus the isotactic and syndiotactic oligomers consist mostly of the two series of stereoisomers *mm⋯m* and *mm⋯r*, and *rr⋯r* and *rr⋯m*, respectively.

---

*Part 3: cf. Ute K, Nishimura T, Hatada K, Polym J (1989) 21:1027

**To whom correspondence should be addressed

EXPERIMENTAL

Preparation of oligomers: Isotactic-specific polymerization of MMA was initiated with *t*-C_4H_9MgBr ([MMA]/[*t*-C_4H_9MgBr] = 50 mol/mol) in toluene at -78°C, and the reaction was terminated 120 min after the initiation by adding a small amount of methanol to the polymerization mixture (13,14). The yield of the oligomeric products was 20 % (Sample A). Syndiotactic-specific polymerization of MMA was carried out with *t*-$C_4H_9Li/(C_2H_5)_3Al$ complex ([Al]/[Li] = 2/1 mol/mol, [MMA]/[*t*-C_4H_9Li] = 5 mol/mol) in toluene at -78°C (15,16). The polymerization reaction was terminated with methanol 180 min after the initiation to give the oligomer mixture. The mixture was poured into hexane and the insoluble part (57.7%) was subjected to the SFC analysis (Sample B). The standard sample of the purely isotactic heptamer (*mmmmmm* + *mmmmmr*) was isolated by GPC from Sample A. The standard sample of the purely syndiotactic pentamer of MMA (*rrrr*) was isolated by HPLC from the oligomer mixture prepared with *t*-$C_4H_9Li/(C_2H_5)_3Al$ complex and was purified by recrystallization (12).

SFC and GPC measurements: SFC was performed on a JEOL JSF-880 chromatograph equipped with a column (1.7 x 250 mm) packed with octadecylsilane-treated silica gel (particle size 5 μm). The system consists of two computer-controlled pumps (17,18), one is for the delivery of liquefied CO_2 as mobile phase (flow rate = 300 μl/min), and the other for the delivery of ethanol as modifier (flow rate = 25 μl/min). Concentration of the modifier in the mobile phase was kept constant throughout the experiments. The pressure at the bottom of column was regulated by a release valve within ± 1 kg/cm^2 of the desired pressure. An UV detector JEOL CAP-UV01 (detected at 210 nm) fitted with a cell of 1 μl in volume and 5 mm in light path was employed. The amount of sample used for the analysis was 0.3 mg of the oligomer dissolved in 1.0 μl of dichloromethane. The column temperature was initially set 110°C and was cooled down to 50°C at the rate of 4°C/min after injection of the sample.

GPC was performed on a JASCO TRIROTAR-II chromatograph equipped with a GPC column (30 x 500 mm, maximum porosity = 3 x 10^3) and with a Shodex SE-61 RI detector, using chloroform as eluent.

Mass and ^1H NMR spectroscopies: Mass spectra were recorded on a JEOL JMS-DX303HF operated at field-desorption mode. ^1H NMR spectra were measured in chloroform-*d* at 35°C using a JEOL JNM-GX500 spectrometer (90° observation pulse, pulse repetition = 15 s, 3600 scans).

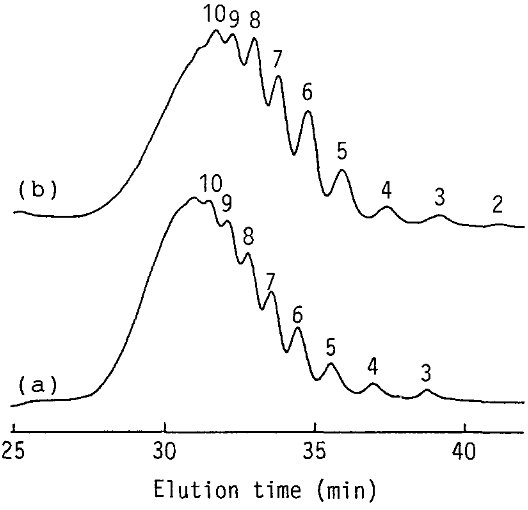


Figure 1 GPC traces of the MMA oligomers prepared with *t*-C_4H_9MgBr (Sample A)(a) and with *t*-$C_4H_9Li/(C_2H_5)_3Al$ (Sample B)(b).

RESULTS AND DISCUSSION

Figure 1 shows the GPC curves of the isotactic oligomer of MMA prepared with *t*-C_4H_9-

MgBr (Sample A) and of the syndiotactic oligomer of MMA prepared with t-$C_4H_9Li/(C_2H_5)_3Al$ complex (Sample B).

The SFC traces of Samples A and B are shown in Figures 2a and 3a, respectively. The pressure at the bottom of column (p_b) was set 198 kg/cm^2 for the measurements. The oligomer components from trimer to 20-mer separated completely. All the analysis finished within 15 min. The standard sample of the syndiotactic pentamer of MMA (*rrrr*), which has a t-C_4H_9- group at its left (initiating) end [1], exhibited the elution peak at the same retention time as the peak numbered 5 in the SFC of Sample B (Figure 3b). Mass spectrum of the fraction #8 isolated from Sample A showed the parent peak at M/Z = 859 (Figure 4), indicating that peak #8 in Figure 2a is attributable to the octamer ($C_{44}H_{74}O_{16}$ = 859.1). The fractions #7 and #9 of Sample A were collected three times, and then analyzed by SFC again; the fractions showed elution peaks at their original positions accompanied by small satellite peaks (Figures 2b and 2c). ^{1}H NMR analysis of the fraction #7 from Sample A yielded the spectrum of good signal-to-noise ratio by an overnight (15 h) measurement as shown in Figures 5a and 5b. In the ^{1}H NMR measurement, the signal at 1.52 ppm due to H_2O was suppressed by the gated homonuclear irradiation. The spectrum agreed well with the spectrum of the isotactic heptamer of MMA (*mmmmmm* + *mmmmmr*)(Figures 5c and 5d). These demonstrate the feasibility of the ^{1}H NMR analysis of the fraction collected by SFC.

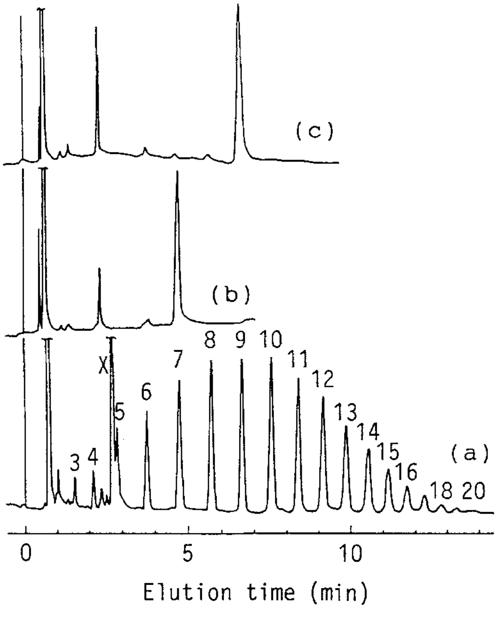


Figure 2 SFC traces of the isotactic oligomer of MMA prepared with t-C_4H_9-MgBr in toluene at -78°C (Sample A)(a) and of the fractions #7 (b) and #9 (c) collected three times from Sample A. Mobile phase: CO_2 0.3 ml/min, C_2H_5OH 0.025 ml/min; column temp: 110°C (initial), 50°C (final); pressure at the bottom of column (p_b): 198 kg/cm^2.

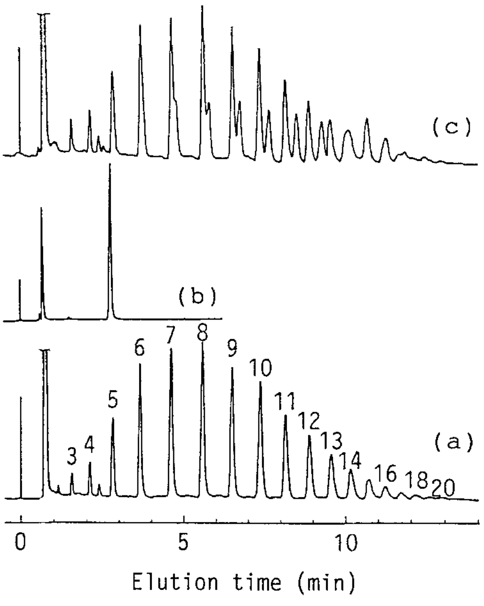


Figure 3 SFC traces of the syndiotactic oligomer of MMA prepared with t-$C_4H_9Li/(C_2H_5)_3Al$ in toluene at -78°C (Sample B)(a), the standard sample of the syndiotactic (*rrrr*) pentamer (b) and of the mixture of Samples A and B (A:B = 1:2)(c). The experimental conditions are the same as in Figure 2.

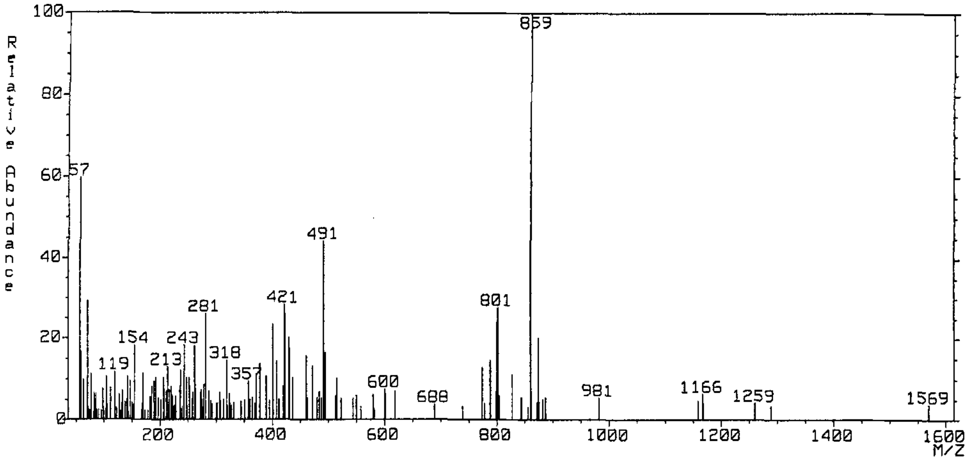


Figure 4 Mass spectrum of the fraction #8 of Sample A collected by SFC.

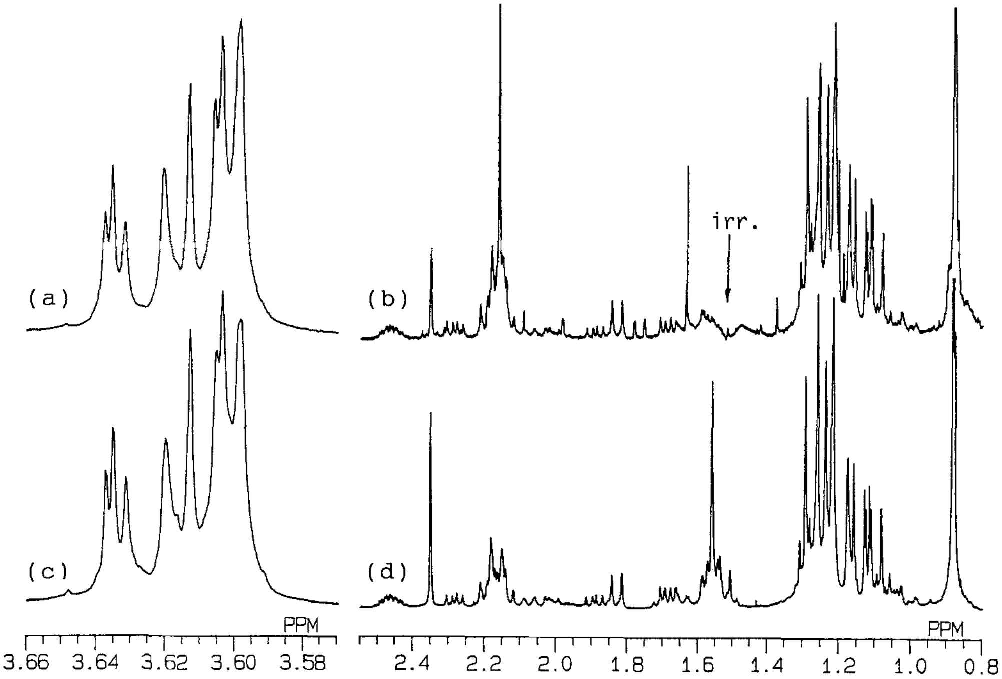


Figure 5 ^1H NMR spectra of the fraction #7 isolated from Sample A using SFC (a and b) and of the isotactic heptamer of MMA (*mmmmm* + *mmmmr*) (c and d). ($CDCl_3$, 35°C, 500 MHz)

Table 1 The *Mn* and *Mw/Mn* values for the MMA oligomers (Samples A and B) determined by GPC and by SFC

Method	Sample A		Sample B	
	Mn	*Mw/Mn*	*Mn*	*Mw/Mn*
GPC	987	1.09	920	1.10
SFC	924	1.05	893	1.11

The complete separation of oligomer components and the rigid assignments for them enabled the determination of *Mn* and *Mw/Mn* for Samples A and B (Table 1). The values determined by SFC and by GPC roughly agreed with each other, however, the values determined by SFC should be considered as more reliable because of the complete separation of the components.

The *mm···m* isomer eluted faster than the *rr···r* isomer in the normal phase HPLC analysis (12). In contrast, the isotactic oligomers had slightly longer retention time in the SFC analysis than the syndiotactic oligomers of the corresponding degree of polymerization. This can be realized more easily in the SFC curve for a 1:2 mixture of Samples A and B (Figure 3c). The difference between the isotactic and syndiotactic oligomers in retention time became obvious over heptamer. The oligomer components from octamer to 12-mer each showed two distinct peaks of nearly 1:2 ratio due to the stereoisomers. The peaks arising from the isotactic 13-mer and the syndiotactic 14-mer joined to give a single broad peak again.

The SFC pattern showed dependency on p_b (Figure 6). In the SFC curve recorded at p_b of 156 kg/cm^2 (Figure 6a), the peaks due to the isotactic 12-mer and the syndiotactic 13-mer overlapped whereas the peaks due to the isotactic 14-mer and the syndiotactic 15-mer overlapped in the SFC recorded at 219 kg/cm^2 (Figure 6b). As p_b increased, separation of the higher molecular weight components was improved and the retention time was shortened.

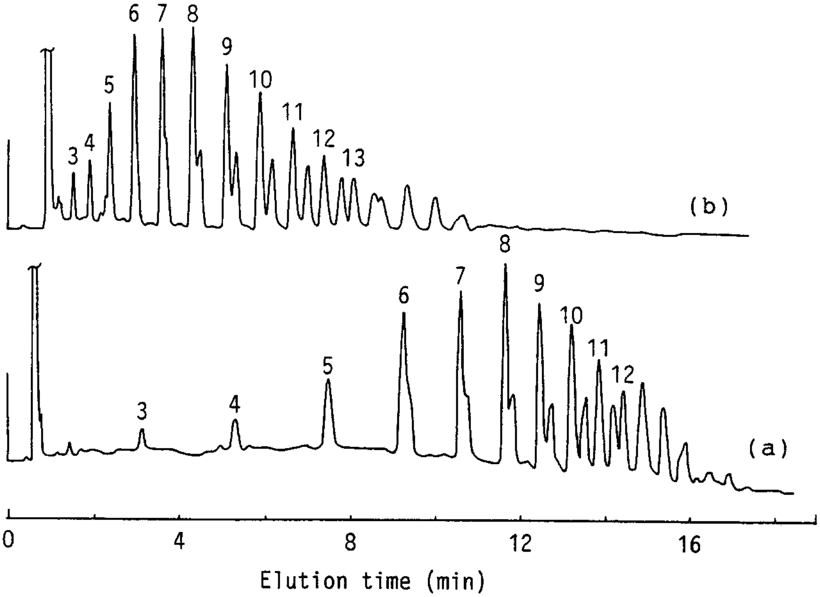


Figure 6 SFC traces for the mixture of the isotactic and syndiotactic oligomers of MMA (Sample A : Sample B = 1 : 2). Pressure at the bottom of column (p_b): (a) 156 kg/cm^2, (b) 219 kg/cm^2.

The elution peak "X" due to an unknown compound was observed between the peaks due to the tetramer and pentamer in the chromatogram recorded at p_b of 198 kg/cm^2 (Figure 2a), whereas it was observed between the peaks due to the pentamer and hexamer in the chromatogram recorded at 219 kg/cm^2 (not shown). This indicates that the unknown compound has the dissolution property much different from that of the MMA-oligomers. The structural analysis of the unknown compound was not possible because of the unexpectedly small amount of the fraction for its strong UV-absorbtion.

The results described above show that SFC is suitable for the rapid and detailed analysis of the MMA oligomers and also for the fractionation of the oligomer components. The stereoregular oligomers of MMA provide good standard materials for SFC analysis because they are free from the peak-broadening due to stereoisomers of the oligomer components.

REFERENCES

1. Jentoft R-E, Gouw T-H (1969) *J Polym Sci* **B7**: 811
2. Klesper E, Hartman W (1977) *J Polym Sci, Polym Lett Ed* **15**: 9; (1977) *ibid* **15**: 713
3. Fjeldsted J-C, Jackson W-P, Peaden P-A, Lee M-L (1983) *J Chromatogr Sci* **21**: 222
4. Schmitz F-P, Gemmel B (1989) Oligomer separation by supercritical fluid chromatography using gradient elution. In: Parvez S, Miyazaki T, Parvez H (eds.) Supercritical Fluid Chromatography and Micro-HPLC. VSP, Utrecht (Progress in HPLC, vol **4**, pp 73-85)
5. Hirata Y, Nakata F (1984) *J Chromatogr* **295**: 315; (1984) *ibid* **315**: 31; (1984) *ibid* **315**: 39
6. Richtar B-E (1985) *J HRC & CC* **8**: 297
7. Matsumoto K, Tsuge S, Hirata Y (1986) *Anal Sci* **2**: 3
8. Okamoto Y, Yashima E, Nakano T, Hatada K (1987) *Chem Lett* **1987**: 759
9. Hatada K, Ute K, Tanaka K, Kitayama T (1987) *Polym J* **19**: 1325
10. Ute K, Nishimura T, Matsuura Y, Hatada K (1989) *Polym J* **21**: 231
11. Hatada K, Ute K, Kitayama T, Tanaka K, Imanari M, Fujii N (1989) *Polym J* **21**: 447
12. Ute K, Nishimura T, Hatada K (1989) *Polym J* **21**: 1027
13. Hatada K, Ute K, Tanaka K, Kitayama T, Okamoto Y (1985) *Polym J* **17**: 977
14. Hatada K, Ute K, Tanaka K, Okamoto Y, Kitayama T (1986) *Polym J* **18**: 1037
15. Kitayama T, Shinozaki T, Masuda E, Yamamoto M, Hatada K (1988) *Polym Bull* **20**: 505
16. Kitayama T, Shinozaki T, Sakamoto T, Yamamoto M, Hatada K (1989) *Makromol Chem, Suppl* **15**: 167
17. Saito T, Takeuchi M (1987) *JEOL News* **23A**: 47
18. Saito T, Takeuchi M (1989) Development of an intelligent cascade pump which can perform microdelivery independent of compressibility of fluid. In: Parvez S, Miyazaki T, Parvez H (eds.) Supercritical Fluid Chromatography and Micro-HPLC. VSP, Utrecht (Progress in HPLC, vol **4**, pp 25-51)

Accepted November 27, 1989 S