

SHORT COMMUNICATIONS

**Optical Activity of Isotactic Oligomers
of Methyl Methacrylate**

Yoshio OKAMOTO, Tamaki NAKANO, and Koichi HATADA

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

(Received September 26, 1988)

KEY WORDS Methyl Methacrylate / Optical Resolution / Oligomer /
Anionic Polymerization / 1-Naphthylmagnesium Bromide / Helicity /

Recently, Cram and Sogah¹ reported that optically active, isotactic oligo- and poly-methacrylates with high optical rotation ($[\alpha]_{578}^{70-350^\circ}$) are obtainable by asymmetric polymerization of methyl methacrylate (MMA) and several other methacrylates with *t*-BuOK-chiral crown ether or *n*-BuLi-chiral diamine complexes in toluene at -78°C . The optical activity has been ascribed to the helical structure of the oligomers and polymers. The activity decreased slowly in solution at room temperature, which has been attributed to uncoiling (mutarotation) of the helix. We reported that such a helical, isotactic polymer can be obtained by the asymmetric polymerization of triphenylmethyl methacrylate with (–)-sparteine (Sp)-*n*-BuLi² or -9-fluorenyllithium (FlLi)³ complex in toluene at -78°C . However, optically active polymers were not obtained from less bulky methacrylates having ester groups such as diphenylmethyl methacrylate and 1,1-diphenylethyl methacrylates.⁴ We believe that the ester groups of these methacrylates are not bulky enough to maintain a helical structure.

In the present study, oligomerization of MMA with 1-naphthylmagnesium bromide (1-NpMgBr) was carried out in toluene at -78°C and the isotactic oligomers obtained were optically resolved immediately after terminating

the reaction in order to get information on the stability and optical activity of the optically pure antipodes of isotactic oligo(MMA).

Oligomerization of MMA by 1-NpMgBr was carried out at a molar ratio $[\text{MMA}]/[1\text{-NpMgBr}]=5$ in toluene at -78°C . A solution of 1-NpMgBr in diethylether/toluene mixture was added to a toluene solution of MMA cooled to -78°C . The reaction was terminated by the addition of a slight excess of methanol at -78°C . The oligomer obtained was first fractionated by GPC in terms of the degree of polymerization,⁵ and was further separated

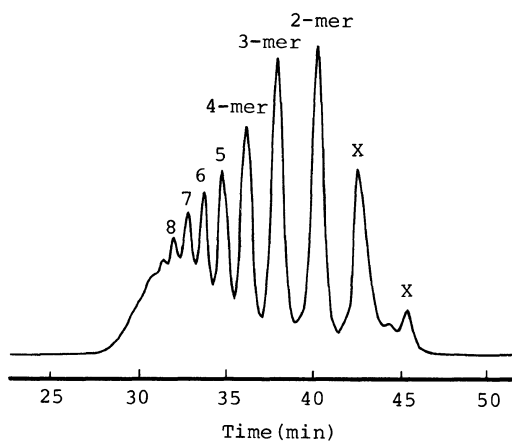


Figure 1. GPC curve of hexane-soluble oligo(MMA) prepared with 1-NpMgBr in toluene at -78°C ($[\text{MMA}]/[1\text{-NpMgBr}]=5$). X, unknown product.

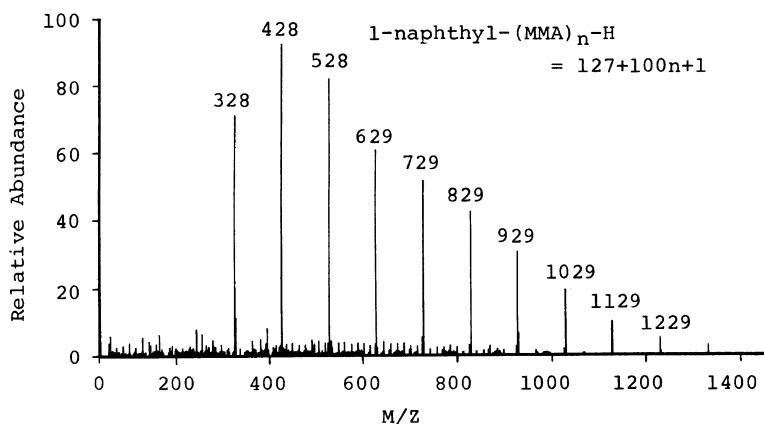


Figure 2. FD mass spectrum of hexane-soluble oligo(MMA) prepared with 1-NpMgBr.

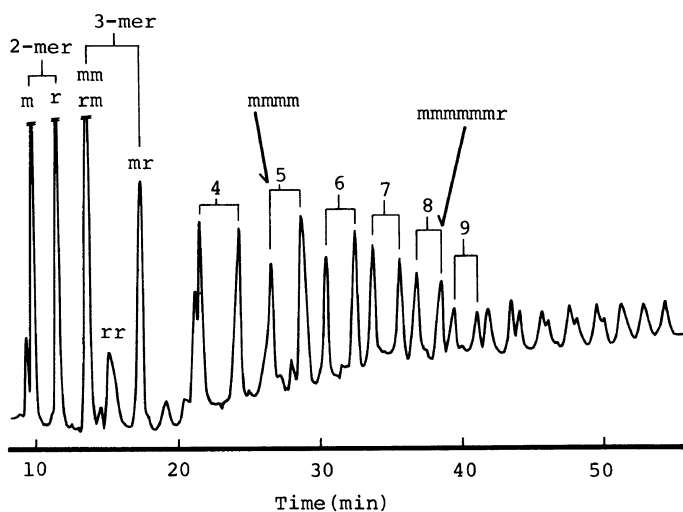


Figure 3. Chromatogram of diastereomeric separation of oligo(MMA) prepared with 1-NpMgBr.

into diastereomers and enantiomers by HPLC using a silica gel column^{3,6} and a chiral column,⁷ respectively.

Figures 1 and 2 show the GPC curve and FD mass spectrum,⁸ respectively, of the hexane-soluble oligo(MMA)s. The mass numbers were observed at m/e 328, 428, 528, ... which correspond to the dimer, trimer, tetramer, ... of MMA ($M_w = 100$) having a 1-naphthyl group ($M_w = 127$). The peaks in the GPC curve were directly assigned as shown in Figure 1 on the basis of similarity in molecular

weight distribution shown in the GPC curve and FD mass spectrum. This is also supported by previous results on MMA dimer and trimer.³

Figure 3 shows the chromatogram of separation of diastereomers of the oligo(MMA). The molecular weight of each peak was determined by FD mass spectroscopy. The oligomers of $DP \geq 4$ consist of two main components of diastereomers. These two components are assigned to the pairs of the isotactic oligomers whose tacticities of ω -end are

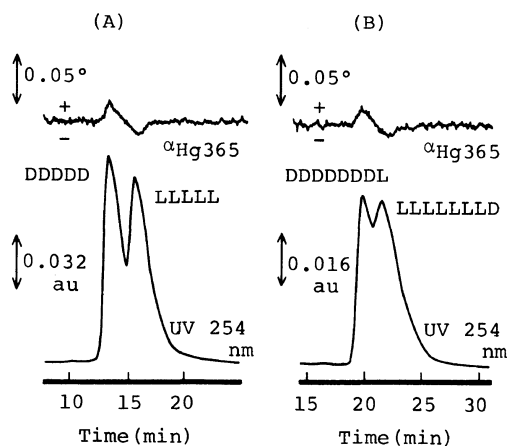


Figure 4. Chromatograms of optical resolution of MMA 5-mer *mmmm* (A) and 8-mer *mmmmmmr* (B) prepared with 1-NpMgBr (sample 2.1 mg (A), 2.0 mg (B)).

racemo(r) and *meso(m)*.^{3,9} This assignment is also supported by the fact that the polymer obtained in 100% yield with 1-NpMgBr was highly isotactic (I:H:S=97:3:0),¹⁰ and the two fractions of pentamer and octamer marked by arrows in Figure 3 were assigned to *mmmm* and *mmmmmmr* isomers by ¹H NMR.^{9,11} The almost equal intensities of the two main peaks indicate that protonation of isotactic oligomer anions with methanol is not stereoselective, while monomer addition occurs mainly in a *meso* fashion.

The *mmmm* pentamer and the *mmmmmmr* octamer were separated from the products obtained by oligomerization immediately after terminating the reaction and were optically resolved by HPLC equipped with UV (254 nm) and polarimetric (Hg 365 nm) detectors. Optical resolution was accomplished within 1.5 h after reaction had stopped. The results are shown in Figure 4. The enantiomers of both 5-mer and 8-mer showed very small rotation though they were sufficiently resolved. Specific rotations ($[\alpha]_{365}$) were estimated to be about 26° (pentamer) and about 23° (octamer).¹² This indicates that the isotactic

oligo(MMA)s isolated in our experiment did not possess such a stable helical conformation as reported by Cram and Sogah,¹ and that methyl ester is too small to maintain such a helical structure.

REFERENCES AND NOTES

- D. J. Cram and D. Y. Sogah, *J. Am. Chem. Soc.*, **107**, 8301 (1985).
- Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, and H. Yuki, *J. Am. Chem. Soc.*, **101**, 4763 (1979).
- Y. Okamoto, E. Yashima, T. Nakano, and K. Hatada, *Chem. Lett.*, **1987**, 759 (1987).
- Y. Okamoto, K. Suzuki, and H. Yuki, unpublished data. In the polymerization of these monomers with the Sp-BuLi complex in toluene at -78°C, the isotacticity of the obtained polymers was low, and a highly isotactic poly(1,1-diphenylmethyl methacrylate) was obtained by using Sp-cyclohexylmagnesium bromide complex. However, the $[\alpha]_D^{25}$ of these polymers was less than two degree.
- GPC separation was performed on a GPC column (maximum porosity 3000) using chloroform as eluent.
- The separation was performed on a silica gel column (Develosil 100-5, 50×0.72 (i.d.) cm) using an acetonitrile-butyl chloride mixture (5:95—50:50) as an eluent under gradient conditions. [G. D. Andrews and A. Vatvars, *Macromolecules*, **14**, 1603 (1981)].
- Optical resolution was carried out on a cellulose tris(3,5-dimethylphenylcarbamate) column (25×0.46 (i.d.) cm) using a hexane-ethanol mixture as an eluent [Y. Okamoto, M. Kawashima, and K. Hatada, *J. Chromatogr.*, **363**, 173 (1986)].
- FD mass spectrum was taken on a JNM-DX303HF spectrometer.
- K. Hatada, K. Ute, K. Tanaka, M. Imanari, and N. Fujii, *Polym. J.*, **19**, 425 (1987).
- Polymerization was carried out at [MMA]/[1-NpMgBr]=20 ($\bar{M}_n=3,800$, $\bar{M}_w/\bar{M}_n=1.65$).
- The *m* and *r* assignment of ω -end dyad is opposite to that reported in ref 9. The present assignment is supported by X-ray analysis of *mm* trimer [K. Hatada, K. Ute, T. Kitayama, K. Tanaka, M. Imanari, and N. Fujii, *Polym. J.*, to be submitted; K. Ute, T. Nishimura, K. Hatada, and Y. Matsuura, *Polym. J.*, **21**, (1989) in press.]
- Values of specific rotation were estimated from the chromatograms shown in Figure 4. Concentration of the sample was calculated from the weight of the sample injected and the volume of the HPLC flow cell (length 5 cm, diameter 0.20 cm). The amounts of racemic samples were 2.1 mg for 5-mer and 2.0 mg for 8-mer.