J. Am. Chem. Soc. **1992**, *114*, 1318–1329

Asymmetric Polymerization of Triphenylmethyl Methacrylate Leading to a One-Handed Helical Polymer: Mechanism of Polymerization

Tamaki Nakano,[†] Yoshio Okamoto,*[,†] and Koichi Hatada[‡]

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan, and Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received March 1, 1991*

Abstract: Asymmetric oligomerization of triphenylmethyl methacrylate (TrMA) was carried out with complexes of 9-fluorenyllithium and chiral ligands in toluene at −78 °C, and the oligomers obtained were converted into methyl esters. The resulting oligo(methyl methacrylate)s were first fractionated by gel permeation chromatography in terms of degree of polymerization and further separated into diastereomers and optical isomers by high-performance liquid chromatography. The distribution of oligomers and the ratio of isomers in each oligomer gave important information on the mechanism of the asymmetric (helix sense selective) polymerization of TrMA. The reactivity of each oligomer anion depended greatly on its degree of polymerization and stereostructure. The oligomer anions whose asymmetric centers have *R* configuration in the system with the complex of 9-fluorenyllithium and (−)-sparteine and those of *S* configuration in the systems with (+)-(2*S*,3*S*)-2,3-dimethoxy-1,4-bis(dimethylamino)butane and (+)-(*S*)-1-(2-pyrrolidinylmethyl)pyrrolidine as chiral ligands predominantly propagated to a one-handed helical polymer. A stable helix starts at degree of polymerization 9 in the former system and at degree of polymerization 7 in the latter two systems. One helix turn seems to consist of three or four monomeric units. The main chain of the resulting polymer in the former system possessed *RRR*--- absolute configuration and that in the latter systems *SSS*---, though both polymers are considered to be of the same helicity, *P* or *M*. These results indicate that the helicity of the polymer is not governed by the configuration of the main chain but by the chirality of the ligands.

Introduction

The helix is one fundamental structure for macromolecules. Many stereoregular macromolecules including naturally occurring and synthetic ones are known to take helical conformation in the solid state.[1] A polymer with right- or left-handed helical conformation can be optically active without any chiral component because it is chiral. However, most isotactic vinyl polymers such as polystyrene and polypropylene without chiral pendant groups cannot be optically active in solution because the dynamics of polymer chains is extremely fast at room temperature in solution and therefore the polymers cannot maintain a helical conformation.[2] However, there exists the possibility of obtaining optically active polymers if the polymer backbone is very rigid or sterical repulsion of side groups is large enough to maintain a stable conformation. These possibilities have been realized in a few synthetic polymers: polyisocyanides,[3] polyisocyanates,[4] polychloral,[5] and poly(triarylmethyl methacrylate)s.[6] The first example of this kind of optically active polymer is poly(*tert*-butyl isocyanide). This was confirmed by chromatographic optical resolution of the polymer synthesized with an achiral initiator system,[3a,b] and recently direct asymmetric synthesis with optically active Ni(II) complexes was realized.[3e] The presence of the bulky *tert*-butyl group appears necessary to maintain the helical conformation. Optically active polyisocyanate can be obtained by anionic copolymerization of achiral isocyanates with a small amount of an optically active isocyanate.[4] Its optical activity is much greater than the activity of the chiral isocyanate. One-handed helical structure is induced by incorporation of a small amount of the chiral isocyanate. Although polychloral prepared by an enantiomerically pure initiator is considered to possess one-handed helical conformation, the very large optical activity of the polymer has been confirmed only in film because the polymer is insoluble.[5a,b] Several optically active poly(triarylmethyl methacrylate)s have been directly synthesized by asymmetric (helix sense selective) anionic polymerization.[6] The helices of polychloral and poly(triarylmethyl methacrylate)s are considered to be maintained by the steric repulsion between the bulky side groups.

Triphenylmethyl methacrylate (TrMA) is the first example of a vinyl monomer which directly affords an optically active, highly isotactic polymer by polymerization with chiral initiators.[6a–c] The optical activity of the polymer arises mainly from a stable one-handed helical conformation because poly(methyl methacrylate) derived from the poly(triphenylmethyl methacrylate) (poly(TrMA)) shows very low optical activity. Optically active poly(TrMA) shows high chiral recognition ability as a chiral stationary phase for optical resolution by high-performance liquid chromatography (HPLC), and many racemic compounds have been resolved on the phase.[7] Therefore, clarification of the

---

[†] Nagoya University.

[‡] Osaka University.

(1) (a) Tadokoro, H. *Structure of Crystalline Polymers*; Wiley: New York, 1979. (b) Vollmert, B. In *Polymer Chemistry*; Springer-Verlag: New York, 1973; pp 593–597.

(2) (a) Frisch, H. L.; Schuerch, C.; Szwarc, M. *J. Polym. Sci.* **1953**, *11*, 559. (b) Pino, P. *Adv. Polym. Sci.* **1965**, *4*, 393.

(3) (a) Nolte, R. J. M.; van Beijnen, A. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1974**, *96*, 5932. (b) Drenth, W.; Nolte, R. J. M. *Acc. Chem. Res.* **1979**, *12*, 30. (c) van Beijnen, A. J. M.; Nolte, R. J. M.; Naaktgeboren, A. J.; Zwikker, J. K.; Drenth, W. *Macromolecules* **1983**, *16*, 1679. (d) Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, F., III. *Macromolecules* **1988**, *21*, 1839. (e) Kamer, P. C.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 6818.

(4) (a) Green, M. M.; Andreola, C.; Munoz, B.; Reidy, M. P.; Zero, K. *J. Am. Chem. Soc.* **1988**, *110*, 4063. (b) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. A.; Willson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452.

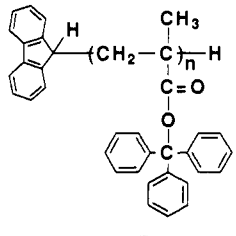
(5) (a) Corley, L. S.; Vogl, O. *Polym. Bull.* **1980**, *3*, 111. (b) Vogl, O.; Corley, L. S.; William, J. H.; Jaycox, J. D.; Zhang, J. *Makromol. Chem. Suppl.* **1985**, *13*, 1. (c) Zhang, J.; Jaycox, G. D.; Vogl, O. *Polym. J.* **1987**, *19*, 603. (d) Ute, K.; Nishimura, T.; Hatada, K.; Xi, F.; Vass, F.; Vogl, O. *Makromol. Chem.* **1990**, *191*, 557.

(6) (a) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979**, *101*, 4796. (b) Okamoto, Y.; Suzuki, K.; Yuki, H. *J. Polym. Sci. Polym. Chem. Ed.* **1981**, *18*, 3043. (c) Okamoto, Y.; Shohi, H.; Yuki, H. *J. Polym. Sci. Polym. Lett. Ed.* **1983**, *21*, 601. (d) Okamoto, Y.; Mohri, H.; Hatada, K. *Chem. Lett.* **1988**, 1879. (e) Okamoto, Y.; Yashima, E.; Hatada, K. *J. Polym. Sci. Polym. Lett. Ed.* **1987**, *25*, 297. (f) Okamoto, Y.; Nakano, T.; Asakura, T.; Mohri, H.; Hatada, K. *J. Polym. Chem. Part A: Polym. Chem. Ed.* **1991**, *29*, 287. (g) It was reported that oligo- and polymethacrylates such as poly(MMA) and poly(benzyl methacrylate) maintain their helical conformation in solution: Cram, D. J.; Sogah, D. Y. *J. Am. Chem. Soc.* **1985**, *107*, 8301. However, we believe that such ester groups are not bulky enough to maintain their helical conformation: Okamoto, Y.; Nakano, T.; Hatada, K. *Polym. J.* **1989**, *21*, 199.

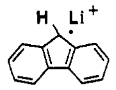
(7) (a) Yuki, H.; Okamoto, Y.; Okamoto, I. *J. Am. Chem. Soc.* **1980**, *102*, 6356. (b) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H.; Murata, S.; Noyori, R.; Takaya, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971. (c) Okamoto, Y.; Okamoto, I.; Yuki, H. *Chem. Lett.* **1981**, 853. (d) Okamoto, Y.; Yashima, E.; Ishikura, M.; Hatada, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 255. (e) Okamoto, Y.; Yashima, E.; Hatada, K.; Mislow, K. *J. Org. Chem.* **1984**, *49*, 557. (f) Chance, J. M.; Geiger, J. H.; Okamoto, Y.; Aburatani, R.; Mislow, K. *J. Am. Chem. Soc.* **1990**, *112*, 3540. (g) Okamoto, Y.; Hatada, K. *J. Liq. Chromatogr.* **1986**, *9*, 369.

0002-7863/92/1514-1318$03.00/0 © 1992 American Chemical Society

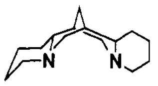
detailed mechanism of this unique asymmetric polymerization is an attractive and challenging problem. Previously, we reported the preliminary results of asymmetric oligomerization of TrMA with a complex of 9-fluorenyllithium (FlLi) and (−)-sparteine (Sp) as an initiator.[8] TrMA gives an optically active polymer with several chiral initiators such as the complexes of Sp and butyllithium (*n*-BuLi),[6a,b] Sp and FlLi,[8] Sp and (1,1-diphenylhexyl)lithium (DPHLi),[8,9a] and (+)-(2*S*,3*S*)- or (−)-(2*R*,3*R*)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB) and (*N*,*N*′-diphenylethylenediamine)monolithium amide (DPEDA-Li).[6c] However, in most cases, the products of the polymerization were a mixture of a polymer (80–90 wt %) of high optical activity and an oligomer (10–20 wt %) of low optical activity. The oligomer of low optical activity was considered to be produced from the species with lower activity than the species for the one-handed helical polymer; that is, the oligomer anions of certain specific stereostructure would propagate to the polymer, and the others would remain as oligomers until completion of the polymerization.[6b] Therefore, the composition of stereoisomers in the oligomer anions should change in the process of polymerization. Wulff and co-workers also reported similar oligomerizations of TrMA with Sp–DPHLi[9a] and Sp–(diphenylmethyl)lithium (DPMLi) complexes.[9b] They separated the oligomers in terms of degree of polymerization (DP) and analyzed the oligomers (DP = 1–4) by ^{1}H and ^{13}C NMR spectroscopies as a mixture of diastereomers.



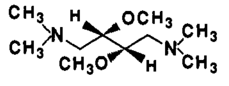
poly(TrMA)



FlLi

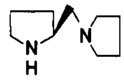


Sp

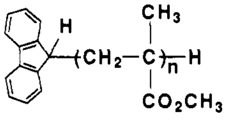


DDB

In the present paper, we report the detailed results of the asymmetric oligomerization of TrMA and the complete separation and assignment of resulting oligomers. With the obtained results, the mechanism of the asymmetric polymerization of TrMA is discussed in detail. Oligomerization of TrMA was carried out by the complexes of FlLi with three chiral ligands in toluene at −78 °C at the several [TrMA]/[Li] ratios and terminated by protonation with CH_3OH to give the oligomers having a fluorenyl group at the initiation end (α end) and a hydrogen at the termination end (ω end).[10] The chiral ligands employed were Sp, DDB, and (+)-(*S*)-1-(2-pyrrolidinylmethyl)pyrrolidine[6d] (PMP). The resulting oligomers were converted into their methyl esters (oligo(MMA)) and fractionated by gel permeation chromatography (GPC) in terms of DP. Each oligomer was further separated into diastereomers and optical isomers by HPLC using columns packed with silica gel and polysaccharide derivative coated silica gel, respectively. The assignments of diastereomers were accomplished by ^{1}H NMR analyses. The absolute configurations of oligomers were determined on the basis of an optically active MMA dimer having a fluorenyl group at the α end derived from (2*R*,4*R*)-2,4-dimethylglutaric acid.



PMP



oligo(MMA) (n=2~8)

Experimental Section

Materials. Toluene was purified in the usual manner, mixed with a small amount of *n*-BuLi, and distilled under high vacuum just before use. Tetrahydrofuran (THF) was refluxed over CaH_2 and distilled over $LiAlH_4$.

n-BuLi was synthesized from butyl chloride (BuCl) and Li powder in heptane under argon atmosphere[11] and was used as a 0.756 M solution for preparation of an initiator solution.

Fluorene (Nacalai Tesque) was first recrystallized from ethanol and then from hexane; mp 104.5–105.0 °C.

Chiral ligands, Sp (Sigma), (+)-DDB (Aldrich), and PMP (Aldrich), were dried over CaH_2 and distilled under reduced pressure.

TrMA was synthesized from methacrylic acid and triphenylmethyl chloride in the presence of triethylamine[12] and was first recrystallized from diethyl ether and then from hexane; mp 101.9–102.9 °C (lit.[13] mp 102–103 °C).

Oligomerization and Polymerization Procedure. FlLi was prepared by adding 1 equiv of *n*-BuLi to a solution of fluorene in toluene at room temperature. This was mixed with 1.2 equiv of a chiral ligand. The mixture was left for 10 min at room temperature for the formation of a complex.

The oligomerization was carried out in a dry glass ampule under a dry nitrogen atmosphere. TrMA (1.0 g, 3.05 mmol) was placed in a glass ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this procedure was repeated three times, a three-way stopcock was attached to the ampule and toluene or THF (20 mL) was added with a hypodermic syringe to dissolve TrMA. Then, the monomer solution was cooled to −78 °C, and a prescribed amount of an initiator solution was added to the monomer solution with a syringe. The reaction was terminated by the addition of a small amount of CH_3OH. After termination, the solvent was evaporated and a part of resulting oligomer was solvolyzed by refluxing in CH_3OH containing a small amount of hydrochloric acid. The resulting oligo(methacrylic acid) was suspended in benzene and methylated by CH_2N_2 in ether solution to give oligo(MMA).[14]

Polymerization was carried out in the same way as the oligomerization described above. The polymerization was also done in a quartz optical cell to monitor the optical activity of the reaction system.[6c] In the case of polymerization, the products were poured into a large amount of CH_3OH after termination and collected by centrifugation as quickly as possible. The polymer was dried under high vacuum at 60 °C for 3 h. The polymer was once dissolved in THF or in a mixture of THF and CH_2Br_2 and poured into a large amount of a mixture of benzene and hexane (1/1, v/v). The insoluble part was collected by centrifugation and the soluble part by evaporation under high vacuum. Conversion of the polymer into the methyl ester (poly(MMA)) was done in the same way as applied for the oligomers.

Preparation of MMA Dimer Having a 9-Fluorenyl Group at the α End from 2,4-Dimethylglutaric Acid. 9-(Iodomethyl)fluorene was synthesized from 9-fluorenylmethanol. 9-Fluorenylmethanol (Aldrich; 4.98 g, 25.4 mmol) and aqueous HI (Nacalai Tesque; 55% v/v, 16.0 mL) were mixed in a round-bottomed flask, and the resultant mixture was heated to 90 °C with vigorous stirring for 26 h. A deep red mixture was extracted with diethyl ether. The ethereal layer was washed with water, dried over magnesium sulfate, and evaporated under high vacuum. The crude product was a mixture of the iodide and the unreacted alcohol at a molar

---

(8) Okamoto, Y.; Yashima, E.; Nakano, T.; Hatada, K. *Chem. Lett.* **1987**, 759.

(9) (a) Wulff, G.; Sczepan, R.; Steigel, A. *Tetrahedron Lett.* **1986**, *27*, 1991. (b) Wulff, G.; Vogt, B.; Petzoldt, J. *ACS Polym. Mat. Sci. Eng.* **1988**, *58*, 859.

(10) According to the IUPAC structure-based nomenclature for polymers, the polymer obtained in the present study is named α-hydro-ω-9-fluorenylpolymethacrylate in which the process of the formation of polymer chain is irrespective. However, in the present paper, the α and ω ends are designated as prefixes of the beginning (the side of fluorenyl group) and the terminal (the side of methine hydrogen originated from termination reagents) of the chain, respectively, on the basis of the formation process of the polymer.

(11) Ziegler, K.; Gellert, H. G. *Ann.* **1950**, *567*, 179.

(12) Yuki, Y. Japan Kokai 560-8117, 1981.

(13) (a) Adrova, N. A.; Prokhorova, L. K. *Vysokomol. Soedin.* **1961**, *3*, 1509. (b) Okamoto, Y.; Yuki, H. In *Macromolecular Syntheses*; Stille, J. K., Ed.; Robert E. Kreiger Publishing: FL, 1990, Vol. 10, pp 41–44.

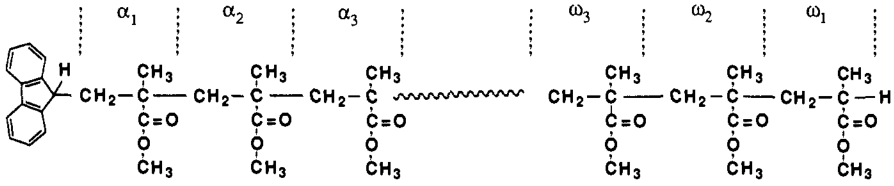
(14) Katchalski, A.; Eisenberg, H. *J. Polym. Sci.* **1951**, *6*, 145.

Table I. Asymmetric Polymerization of TrMA with Sp–, DDB–, and PMP–FlLi Complexes in Toluene at –78 °C^a

				B/H^b-insoluble part						
run	initiator	time (h)	yield^c (%)	yield (%)	$[\alpha]^{25}{}_D{}^d$ (deg)	$[\theta]^e \times 10^{-4}$ (235 nm)	$[\theta]^e \times 10^{-5}$ (210 nm)	DP^f	$M_w/M_n{}^f$	tacticity^g (%) mm
1	Sp–FlLi	24	99	82	+383	+9.42	+2.32	60	1.31	>99^h
2	DDB–FlLi	24	100	93	+344	+8.45	+1.86	47	1.10	>99^h
3	PMP–FlLi	3	100	94	+334	+7.78	+1.76	39	1.12	>99^h

^{a}Conditions: TrMA, 1.0 g (3.05 mmol); toluene, 20 mL; [TrMA]/[Li] = 20. ^{b}A mixture of benzene and hexane (1/1, v/v). ^{c}CH_3OH-insoluble part. ^{d}*c* 0.5 (THF). ^{e}CD spectrum was measured in THF at ca. 25 °C. Units: cm^2 $dmol^{-1}$. ^{f}Determined by GPC of poly(MMA) derived from poly(TrMA). ^{g}Determined by ^1H NMR of poly(MMA) derived from poly(TrMA). ^{h}The signals due to the racemo sequence were found only in the ω end.

Chart I. Structure and Numbering System of Monomeric Units of Oligo- and Poly(MMA)



ratio of 52/48 by ^1H NMR analysis. The alcohol was removed by silica gel column chromatography with a mixture of diethyl ether and hexane (1/1, v/v) as eluent to give red crystals. The crystal obtained was dissolved in diethyl ether. The solution was washed with a saturated water solution of Na_2SO_3 to remove iodine and dried over $MgSO_4$ to give 2.48 g (31.9%) of the iodide free from alcohol and iodine. Further purification was done by recrystallization twice from diethyl ether and once from hexane to give 0.61 g (7.9%) of white crystals: mp 89.7–90.7 °C; ^1H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 7.30–7.75 (m, 8 H, aromatic), 4.17 (t, 1 H, CH), 3.71 (d, 2 H, CH_2). Anal. Calcd for $C_{14}H_{11}I$: C, 54.93; H, 3.62; I, 41.45. Found: C, 54.97; H, 3.67; I, 41.26.

2,4-Dimethylglutaric acid (Aldrich; a mixture of (±) and meso isomers) was methylated with CH_2N_2. The resulting dimethyl 2,4-dimethylglutarate was reacted with 1 equiv of lithium diisopropylamide (LDA) in dry THF at 0 °C for 0.5 h under a dry nitrogen atmosphere in a round-bottomed flask equipped with a three-way stopcock. Then, 1 equiv of 9-(iodomethyl)fluorene in dry THF was added with a syringe. The solution was stirred for 3 h at 0 °C. A large excess of hydrochloric acid in CH_3OH was then added to the solution. After the solvent was evaporated, the crude product was extracted with diethyl ether. The ethereal layer was washed with water and dried over $MgSO_4$. HPLC separation of the product was done by using an HPLC column (50 × 0.72 (i.d.) cm) packed with silica gel (Nomura Chemicals, Develosil 100-5). A mixture of BuCl and CH_3CN (97/3, v/v; flow rate 2.4 mL/min) was used as an eluent.[8,15]

Preparation of Optically Active MMA Dimer Having a 9-Fluorenyl Group at the α End from (–)-(2*R*,4*R*)-2,4-Dimethylglutaric Acid. 2,4-Dimethylglutaric acid (a mixture of (±) and meso isomers) was converted into its acid chloride with 1.2 equiv of $SOCl_2$, and the product was distilled under reduced pressure to give 2,4-dimethylglutaroyl dichloride, bp 77–85 °C (3 mmHg). The acid chloride was reacted with benzyl alcohol in the presence of excess triethylamine to give the dibenzyl ester, which was separated into optical isomers by HPLC. Optical resolution was done with a chiral HPLC column (50 × 2.0 (i.d.) cm) packed with amylose–tris(3,5-dimethylphenylcarbamate)-coated macroporous silica gel[16] by using a mixture of hexane and 2-propanol (98/2, v/v; flow rate 9.9 mL/min) as eluent. The (–) isomer eluted at 27.2 min, the meso isomer at 29.0 min, and the (+) isomer at 30.4 min. The (–) isomer ($[\alpha]^{25}_D$ –31° (*c* 2.54, hexane)) was hydrolyzed by hydrochloric acid to give an optically active acid: $[\alpha]^{25}_D$ –21° (*c* 0.88, CH_3OH) (lit.[17] $[\alpha]^{25}_D$ –40° (water)). Then, the optically active acid was methylated with CH_2N_2, giving the dimethyl ester, $[\alpha]^{25}_D$ –31° (*c* 0.93, CH_3OH). This optically active (*R*,*R*)-dimethyl ester was used for preparation of the MMA dimer in the same way as described above for the synthesis of the racemic MMA dimer.

Measurements. ^1H NMR spectra were measured on JEOL GX-500 (500-MHz), JEOL GSX-270 (270-MHz), and Varian VXR-500 (500-MHz) spectrometers. Measurements were done in $CDCl_3$ at 35 °C or in nitrobenzene-d_5 at 110 °C. Two-dimensional spectra were taken under the same spectral conditions as described before.[18] Optical rotation was measured with a Jasco DIP-181 polarimeter. Circular dichroism (CD) spectra were obtained with a Jasco J-720 spectrometer. Field desorption (FD) mass spectra were measured on a JEOL DX-HF303 spectrometer.

The molecular weights of the polymers were determined by GPC measurement of poly(MMA) derived from the original polymer on a Jasco Trirotar II^P chromatograph equipped with a Jasco RI-SE64 (reflective index) detector. Two commercial columns (Shodex KF-802.5, 30 × 0.72 (i.d.) cm; Shodex AC-80M, 50 × 0.72 (i.d.) cm) were connected in series, and $CHCl_3$ was used as the eluent. A calibration curve was obtained with standard polystyrene.

Separation by HPLC was done by using Jasco Trirotar II and BIP-I chromatographs equipped with one or two of the following: Jasco UVIDEC-100-III (UV), UVIDEC-100-V (UV), MULTI-320 (UV), and DIP-181C (polarimetry) detectors. An automatic eluent mixer, Jasco GR-A50, was employed for the diastereomeric separation of oligomers. Columns used and chromatographic conditions were as follows. For the GPC analysis of the oligomers, a column packed with poly(styrene-*co*-*p*-divinylbenzene) gel (50 × 2.2 (i.d.) cm, maximum porosity 3000) or two commercial columns connected in series (Shodex Gel-101, 50 × 0.72 (i.d.) cm) were used with $CHCl_3$ as an eluent (flow rate 3.0 mL/min for the former column and 0.5 mL/min for the latter ones). For the separation of diastereomers, columns (25 × 0.46 (i.d.) cm, 50 × 0.72 (i.d.) cm) packed with silica gel (Nomura Chemicals, Develosil 100-5) were used with a mixture of BuCl and CH_3CN as the eluent[8,15] in programmed ratios: from 95% BuCl to 60% BuCl during a 60-min period (flow rate 0.5 mL/min for the former column and 2.4 mL/min for the latter column). Optical resolution of oligo(MMA)s was done on chiral columns (25 × 0.46 (i.d.) cm) packed with cellulose derivatives using a hexane–alcohol eluting system (flow rate 0.5 mL/min).[19] For optical resolution of the MMA dimer prepared from 2,4-dimethylglutaric acid, a column packed with cellulose–tris(3,5-difluorophenylcarbamate)-coated macroporous silica gel[20] was used with a mixture of hexane and 2-propanol (95/5, v/v) as the eluent. For optical resolution of the MMA dimer obtained from oligomerization systems, a column packed with cellulose–tris(3,5-dichlorophenylcarbamate)-coated macroporous silica gel[19b] was used with a mixture of hexane and 2-propanol (95/5, v/v) as the eluent. For optical resolution of the mixture of MMA trimers mm and rm, a column packed with cellulose–tris(3,4-dichlorophenylcarbamate)-coated macroporous silica gel[19b] was used with a mixture of hexane and 2-propanol (90/10, v/v) as the eluent. For optical resolution of MMA trimers rr and mr, a column packed with cellulose–tris(3,5-dichlorophenyl/dimethylphenylcarbamate)-coated macroporous silica gel[19b] was used with a mixture of hexane and 2-propanol (90/10, v/v) as the eluent. For optical resolution of the MMA pentamer, hexamer, heptamer, or octamer, a column packed with cellulose–tris(3,5-dimethylphenylcarbamate)-coated macroporous silica gel[19b] was used with a mixture of hexane and ethanol (80/20, v/v) as the eluent.

---

(15) Andrews, G. D.; Vatvars, A. *Macromolecules* **1981**, *14*, 1603.

(16) Okamoto, Y.; Aburatani, R.; Fukumoto, T.; Hatada, K. *Chem. Lett.* **1987**, 1857.

(17) Fredga, A. *Arkiv Kemi* **1947**, *24A*, No. 32.

(18) (a) Ute, K.; Nishimura, T.; Matsuura, Y.; Hatada, K. *Polym. J.* **1989**, *21*, 231. (b) Ute, K.; Nishimura, T.; Hatada, K. *Polym. J.* **1989**, *21*, 1027. (c) Hatada, K.; Ute, K.; Tanaka, K.; Kitayama, T. *Polym. J.* **1987**, *19*, 1325. (d) Hatada, K.; Ute, K.; Tanaka, K.; Imanari, M.; Fujii, N. *Polm. J.* **1987**, *19*, 425.

(19) (a) Okamoto, Y.; Kawashima, M.; Hatada, K. *J. Am. Chem. Soc.* **1984**, *106*, 5357. (b) Okamoto, Y.; Kawashima, M.; Hatada, K. *J. Chromatogr.* **1986**, *363*, 173.

(20) Okamoto, Y.; Aburatani, R.; Hatada, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 955.

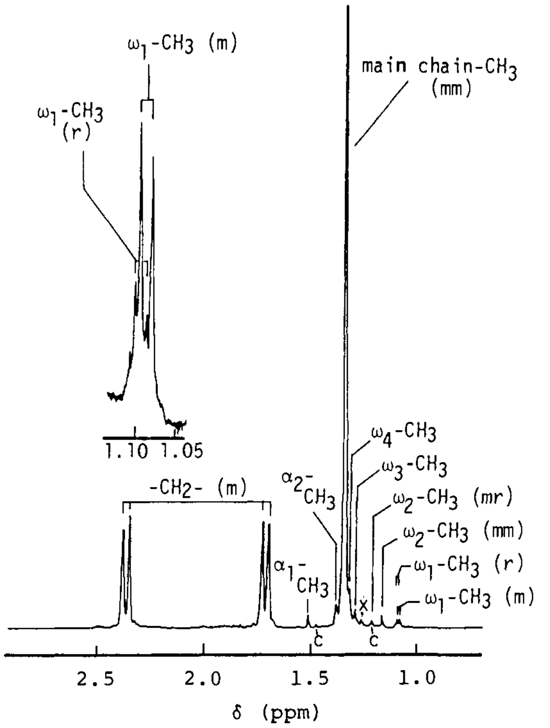


Figure 1. 500-MHz ^{1}H NMR spectrum of poly(MMA) derived from benzene–hexane-insoluble poly(TrMA) of DP = 60 (1 in Table I) (nitrobenzene-d_5, 110 °C). c and × denote ^{13}C satellite bands of the main-chain CH$_3$ signal and impurity, respectively.

Results and Discussion

Asymmetric Polymerization of TrMA with Three Initiator Systems. The results of asymmetric polymerization of TrMA with Sp–FlLi, DDB–FlLi, and PMP–FlLi are shown in Table I. The three initiators gave highly isotactic, optically active polymers which showed almost the same positive rotation, indicating that the polymers possess a one-handed helical conformation of the same screw sense. The polymers obtained with the three initiators showed large positive CD absorption bands with identical spectral patterns, which were similar to that of the poly(TrMA) prepared with the Sp–*n*-BuLi complex.[6b] This also indicates that the three polymers possess the same helicity. The CD spectra showed two peaks at 235 and 210 nm, which may be ascribed to the absorption based on carbonyl and phenyl groups, respectively. The molecular ellipticity ([θ]) values are shown in Table I. The ellipticity values are approximately proportional to the specific rotation of the polymers.

Triad tacticity of the polymer was determined by ^{1}H NMR of poly(MMA) derived from the original polymer. As an example, the spectrum of the poly(MMA) of DP 60 derived from the poly(TrMA) obtained with Sp–FlLi (run 1 in Table I) is shown in Figure 1. In the spectrum, most peaks could be assigned to those of isotactic sequence including the methyl groups in the vicinity of the α and ω ends. Racemo sequence was obviously found only for the ω end. Assignments of the small peaks in the α-methyl region were done on the basis of detailed studies on the ^{1}H NMR assignments of isotactic oligo- and poly(MMA) having a *tert*-butyl group at the α end[18] and the assignments of isotactic oligo(MMA)s having a 9-fluorenyl group at the α end which will be described later. The structure and the numbering system of the monomeric units of the oligo- and poly(MMA) are illustrated in Chart I. Slightly lower isotacticity of poly(TrMA) in the previous reports[6a,b] may be due to the fact that no correction was made for the end groups of the polymer chain.

GPC curves of poly(TrMA)s obtained with Sp and DDB complexes showed two peaks.[6b] However, poly(MMA) derived from these polymers showed only one GPC peak with a narrow distribution. Part of poly(TrMA) may exist in association form as in the case of poly(diphenyl-2-pyridylmethyl methacrylate).[6d]

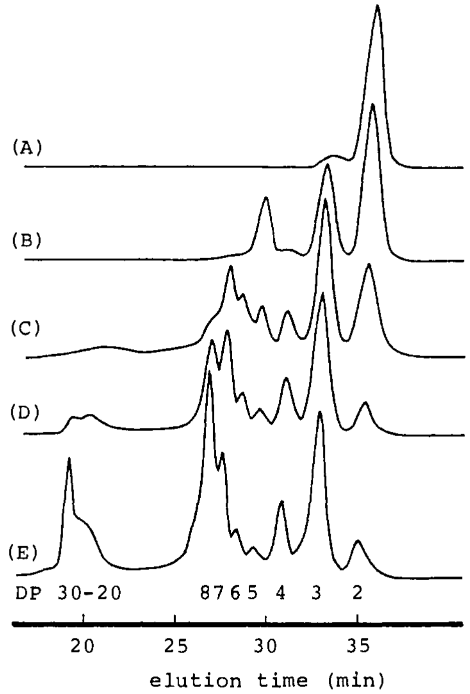


Figure 2. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp–FlLi at [TrMA]/[Li] = 2 (A), 3 (B), 5 (C), 10 (D), and 20 (E).

In all the polymerizations shown in Table I, the products could be separated into two fractions: a polymer of high optical rotation which was insoluble in a mixture of benzene and hexane (1/1, v/v) and an oligomer of low optical activity which was soluble in the solvent as mentioned in the previous paper.[6b] The amount of oligomer was larger and DP of the polymer was higher in the system with Sp–FlLi than in the systems with DDB–FlLi and PMP–FlLi at the same [TrMA]/[Li] ratio. In the system with Sp–FlLi, the relative amounts of less active oligomer anions may be larger and those of active oligomer anions which can propagate to the polymer may be smaller. This should result in the formation of a polymer of higher DP.

It has been reported that the polymerization of TrMA with DDB–*n*-BuLi is much faster than that with Sp–*n*-BuLi.[6c] This was based on measurement of the change of optical activity of the polymerization system during reaction. Optical activity of the systems increased with polymerization time and reached a final constant value within 16 h after initiation in the system with Sp–*n*-BuLi and within 2 h in the system with DDB–*n*-BuLi.[6c] The rate of polymerization with PMP–FlLi was examined in the present study in the same way as described before.[6c] The optical rotation reached at a large positive value ($\alpha^{-78}{}_D$ +3.2°) within 10 min. The value is comparable to the final values observed in the systems with Sp–*n*-BuLi and DDB–*n*-BuLi.[6c] The rate of polymerization with PMP–FlLi may be much higher than those with Sp–FlLi and DDB–FlLi.

Distribution of Oligomers. In all the oligomerizations, the reaction of TrMA with the initiators seems to proceed almost quantitatively to give oligomers with a 9-fluorenyl group at the α end and a hydrogen at the ω end because no clear sign of unreacted monomer and side products which might be produced by the attack of the carbonyl group of TrMA with FlLi was found on the IR and ^{1}H NMR spectra of reaction mixtures. GPC analysis also supported this.

Figures 2–4 show the GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp–FlLi, DDB–FlLi, and PMP–FlLi as initiators, respectively, at [TrMA]/[Li] = 2, 3, 5, 10, and 20. In these GPC curves, the ratio of the peak intensity approximately corresponds to the molar ratio of oligomers because UV detection at 254 nm is mainly due to a fluorenyl group at the α end of each oligomer. The chromatographic patterns of the original oligo(TrMA)s were similar to those of the corresponding

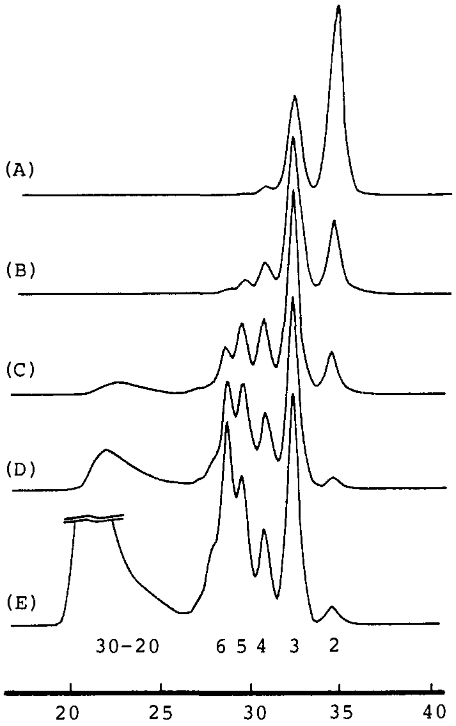


Figure 3. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with DDB-FlLi at [TrMA]/[Li] = 2 (A), 3 (B), 5 (C), 10 (D), and 20 (E).

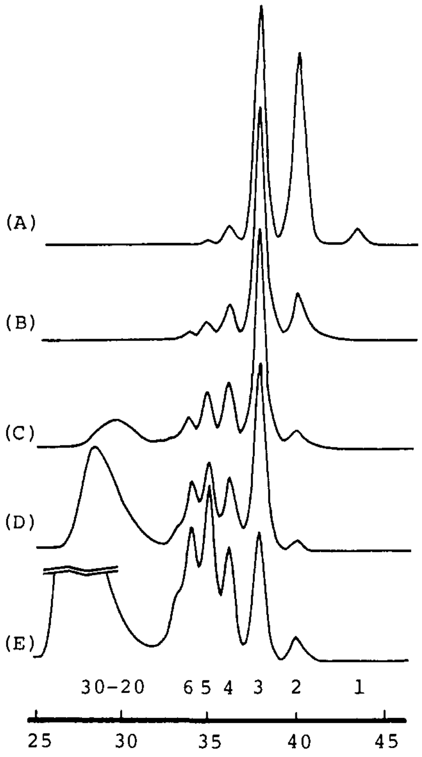
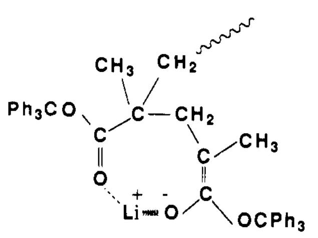


Figure 4. GPC curves of oligo(MMA)s derived from oligo(TrMA)s prepared with PMP-FlLi at [TrMA]/[Li] = 2 (A), 3 (B), 5 (C), 10 (D), and 20 (E).

Chart II. Intramolecular Solvation of the ω-End Anion



oligo(MMA)s. The peaks in the GPC curves were assigned by FD mass spectroscopy. The mass spectrum of oligo(MMA) derived from oligo(TrMA) prepared with Sp–FlLi and terminated by methanol at [TrMA]/[Li] = 5 showed main peaks of m/z 366, 466, 566, 666, 766, 866, and 967 corresponding to the molecular weights of the oligomers of DP 2–8 with the structure shown in Chart I. The spectrum also showed another series of smaller peaks of m/z 350, 450, 550, 650, 750, 850, and 951, though the definite structure of the oligo(MMA)s corresponding to these molecular weights is unknown at the present time. Oligo(MMA)s with a structure other than that shown in Chart I may be formed in the process of conversion of oligo(TrMA) into methyl esters.[21] The intensity ratio of the main peaks was similar to that of the GPC curve. In the GPC curves, the peak corresponding to a unimer (DP 1) was not clearly observed except for oligo(MMA) obtained with PMP–FlLi at [TrMA]/[Li] = 2 and, even in that case, it was much smaller than the other peaks. The existence of a unimer was not confirmed even in the equimolar reaction of TrMA and Sp–FlLi,[8] indicating that the unimer anion is much more reactive than the initiator complex and dimer anion. The high activity of the unimer anion may be due to the effect of "intramolecular solvation" proposed for anionic polymerization of methacrylates.[22] As illustrated in Chart II, the ω-end anion of the propagating species is stabilized by complex formation between the Li cation and the carbonyl group of the penultimate monomeric unit. This stabilization is not possible for a unimer anion. On the other hand, Wulff and co-workers reported that a significant amount of unimer was found in the system with Sp–DPHLi at [TrMA]/[Li] = 5[9a] and in the systems with Sp–DPMLi at [TrMA]/[Li] = 0.5 and 1.[9b] The activity of the unimer anion in their systems may be much lower than that in our systems. The α end group of an oligomer anion may affect its activity in the oligomerization. The oligomer distributions at [TrMA]/[Li] = 5 in all the systems were not simple. Although the oligomers of DP <9 in the systems with Sp–FlLi and the oligomers of DP <7 in the other two systems were observed in addition to the polymer (DP 20–30), the oligomers of intermediate DPs were not obviously detected. Original poly(TrMA)s (DP 20–30) showed high positive rotation in the GPC analysis with a polarimetric detector. Similar results were also found in the oligomerizations at [TrMA]/[Li] = 10 and 20. Wulff and co-workers also observed a similar irregular distribution in the oligomerization with Sp–DPHLi at [TrMA]/[Li] = 5.[9a] The oligomer distribution at [TrMA]/[Li] = 3 in the system with Sp–FlLi was also apparently irregular, and the relative content of tetramer was unnaturally low. These unusual oligomer distributions indicate that the reactivity of each oligomer anion depends greatly on its degree of polymerization. This is likely correlated with the specific conformation of the oligomer anions; that is, three or four monomeric units may form one turn of the helix. An analogous possibility has been discussed by Wulff and co-workers.[9] Theoretical analysis of conformation of isotactic poly(TrMA) shows that 3.6 monomeric units may form one turn of the helix.[23] A stable one-handed helix may start at DP $\simeq$9

---

[21] These oligo(MMA)s with an unknown structure other than that shown in Chart I were not found in the analyses of oligo(MMA)s derived from oligo(TrMA)s prepared with the complexes of (9-alkylfluorenyl)lithiums. The detailed results of oligomerization of TrMA with the complexes of (9-alkylfluorenyl)lithiums with Sp will be reported elsewhere.

[22] (a) Fowells, W.; Schuerch, C.; Bovey, F. A.; Hood, F. P. *J. Am. Chem. Soc.* **1967**, *89*, 1396. (b) Kraft, R.; Muller, A. H. E.; Warzelhan, V.; Hocker, H.; Schulz, G. V. *Macromolecules* **1978**, *11*, 1093. (c) Lochmann, L.; Trekoval, J. *Makromol. Chem.* **1982**, *183*, 1361. (d) Tsvetanov, Ch. B.; Dotscheva, D. T.; Panayotov, I. M. *Makromol. Chem.* **1982**, *183*, 517. (e) Tsvetanov, Ch. B.; Muller, A. H. E.; Schulz, G. V. *Macromolecules* **1985**, *18*, 863.

[23] Cavallo, L.; Corradini, P.; Vacatello, M. *Polym. Commun.* **1989**, *30*, 236.

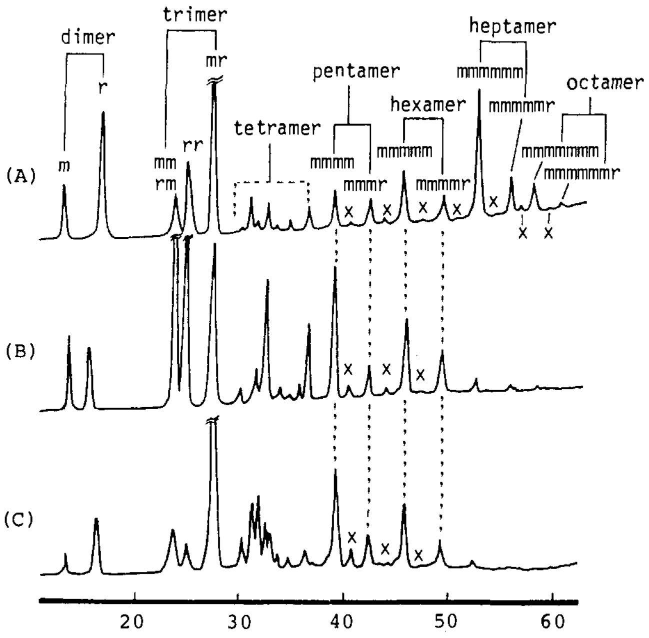


Figure 5. Chromatograms of separation of diastereomers of oligo(MMA)s derived from oligo(TrMA)s prepared with Sp–FlLi (A), DDB–FlLi (B), and PMP–FlLi (C) at [TrMA]/[Li] = 5.

in the system with Sp–FlLi and at DP $\simeq 7$ in the other two systems. Once an oligomer anion grows to DP $\simeq 9$ or 7, it adds TrMA more readily than other oligomer anions of lower DP probably because of its stable helical conformation suitable for the addition of TrMA. The much lower content of heptamer (DP 7) and octamer (DP 8) in the systems with DDB–FlLi and PMP–FlLi[24] than in the system with Sp–FlLi at [TrMA]/[Li] = 5 suggests that the formation of the third turn of a helix may be easier in these systems compared with the system with Sp–FlLi.

Separation and Assignment of Diastereomers. In order to get deeper information on the stereochemistry of the oligomerization, the oligomers were separated into diastereomers by HPLC on a silica gel column using a mixture of BuCl and CH_3CN as an eluent.[8,15] Figure 5 shows the chromatograms of the separation of oligo(MMA)s derived from oligo(TrMA)s obtained with Sp–FlLi, DDB–FlLi, and PMP–FlLi as initiators at [TrMA]/[Li] = 5. The dimer was fractionated into two components, assigned as meso (m) and racemo (r), and the trimer into three components, a mixture of mm and rm, rr, and mr. The tetramer consisted of many components whose assignments have not yet been completed. In contrast to these results on the trimer and tetramer, in the system with Sp–DPHLi, 90% of the trimer consisted of the mm isomer and most of tetramer consisted of mmm and mmr.[9a] In all the systems, oligomers of DP ≥5 consisted of two main diastereomers which were assigned to the pair of isotactic oligomers having m and r ω-end configuration, indicating that the predominantly propagating oligomer anions are isotactic and its protonation with CH_3OH is not highly stereospecific. The definite structure of the oligomers of small peaks marked by × in Figure 5 is unknown. Molecular weights of these oligomers were of the series of 550, 650, 750, ... These may be formed in the process of conversion of oligo(TrMA) into oligo(MMA) as mentioned in the preceding section.[21]

Assignments of the diastereomers of oligo(MMA) were accomplished by measuring two-dimensional ^1H NMR and FD mass spectra of the fractions of the oligomers in Figure 5. The present

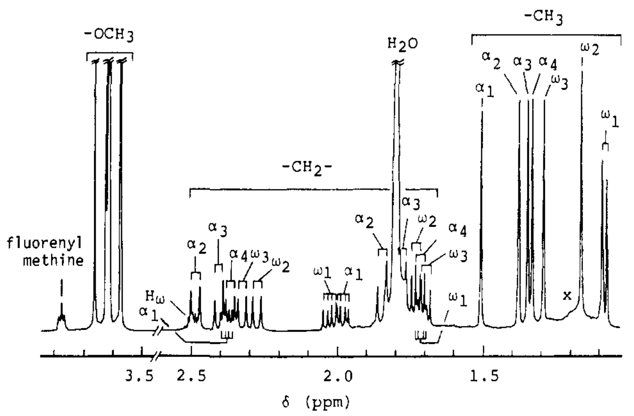


Figure 6. 500-MHz ^1H NMR spectrum of MMA heptamer mmmmmm (nitrobenzene-d_5, 110 °C). × denotes impurity.

assignment is based on those of pure isotactic and pure syndiotactic oligo(MMA)s (DP 2–8) having a *tert*-butyl group at the α end and a hydrogen at the ω end by two-dimensional NMR and X-ray analyses.[18] The configurational relationship between two neighboring asymmetric centers in the α_n and α_{n+1} monomeric units (dyad) of an oligomer, m or r (Scheme I), was judged by the difference in chemical shift of nonequivalent methylene protons of the α_{n+1} monomeric unit in these studies. The assignment of m and r of each dyad in an oligomer was performed on the basis of the fact that the difference in chemical shifts of the nonequivalent methylene protons is larger in the m dyad than in the r dyad except for the dyad at the ω end. This has been confirmed by X-ray crystal analysis of an MMA trimer having a *tert*-butyl group at the α end.[18a] Values of the difference in chemical shifts were reported to be 0.48–0.64 ppm for the m dyad and 0.00–0.17 ppm for the r dyad except for that at the ω end and for isotactic oligomers, 0.20–0.27 ppm for the m dyad and 0.42–0.48 ppm for the r dyad at the ω end of the chain.[18b] Assignments of the trimer, pentamer, hexamer, heptamer, and octamer obtained in the present study were also done in the same way by referring to these values. Assignment of diastereomers of a dimer having a fluorenyl group at the α end has already been accomplished by X-ray crystal structure analysis and ^1H NMR spectroscopy.[25] The spectra of the isomers of the trimer were taken in $CDCl_3$ and those of the isomers of pentamer, hexamer, heptamer, and octamer in nitrobenzene-d_5. As an example, the ^1H NMR spectrum of MMA heptamer mmmmmm is shown in Figure 6. All the signals except for those of the methoxy protons shown in Figure 6 were reasonably assigned by using a two-dimensional technique. The values of difference in chemical shifts of the methylene protons of the α_2–ω_2 monomeric units of the main isomers of pentamer, hexamer, heptamer, and octamer were in the range 0.54–0.66 ppm, indicating that these isomers were isotactic. These values agree well with that of the isotactic polymer. The chemical shift differences of the ω-end methylene protons of these isomers were 0.31–0.32 ppm for m and 0.95–1.01 ppm for r, and those of the α-end methylene protons were almost constant at 0.40–0.41 ppm. The difference in the chemical shift of the methylene protons of the central (α_2) monomeric unit of the trimer was 0.48 or 0.52 ppm for m and 0 ppm for r, and that of the ω-end methylene protons was 0.29–0.45 ppm for m and 0.87–1.03 ppm for r. It has been found for the dimer that the differences in the chemical shifts of the nonequivalent methylene protons of the ω-end monomeric unit were 0.92 ppm for the r isomer and 0.23 for the m isomer.[25]

Ratios of diastereomers in each oligomer obtained with the three FlLi initiator systems are summarized in Table II. The ratio of m to r of the ω end of the oligomers implies the stereospecificity of protonation of the anion with CH_3OH. This is not as high as the stereospecificity of addition of TrMA favoring exclusively the m sequence. In all the systems protonation in r fashion is favored

---

(24) The existence of heptamer and octamer in systems with DDB–FlLi and PMP–FlLi is not clear in the GPC curve (Figures 3 and 4) because the separation of the peaks is not sufficient. However, these oligomers were clearly observed in the separation by supercritical fluid chromatography of the oligo(MMA) derived from oligo(TrMA) obtained with PMP–FlLi at [TrMA]/[Li] = 10. Okamoto, Y.; et al. Unpublished results.

(25) Nakano, T.; Ute, K.; Okamoto, Y.; Matsuura, Y.; Hatada, K. *Polym. J.* **1989**, *21*, 935.

Scheme I. Meso and Racemo Dyads in the Main Chain of Oligo- and Poly(MMA)

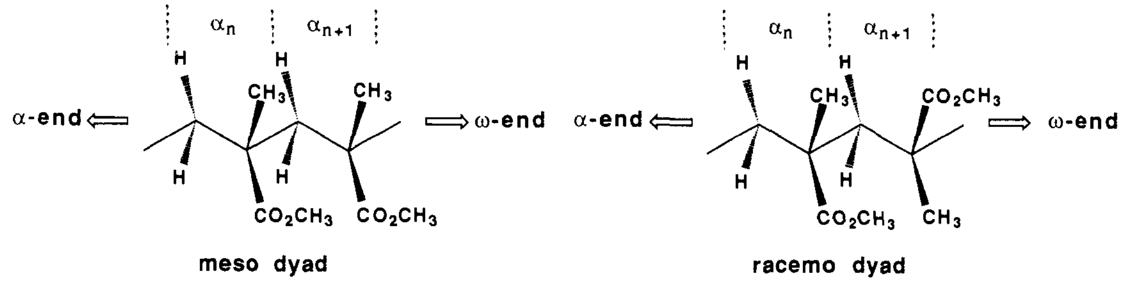


Table II. Ratios of Diastereomers of Oligo(MMA)s Derived from Oligo(TrMA)s Obtained with Sp–FlLi, DDB–FlLi, and PMP–FlLi at [TrMA]/[Li] = 2, 3, 5, 10, and 20[a]

initiator	[TrMA]/[Li]	dimer m/r	trimer mm + rm/rr/mr	pentamer mmmm/mmmr[b]	hexamer mmmmm/mmmmr[b]	heptamer mmmmmm/mmmmmr[b]	octamer mmmmmmm/mmmmmmr[b]
Sp–FlLi	2	14/86	14/35/51	*c*	*c*	*c*	*c*
	3	25/75	15/37/48	65/35	74/26	83/17	*c*
	5	28/72	16/26/58	60/40	67/33	88/12	86/14
	10	13/87	7/14/79	83/17	22/78	78/22	91/9
	20	21/79	8/14/78	88/12	13/87	68/32	88/12
DDB–FlLi	2	23/77	39/30/31	*c*	*c*	*c*	*c*
	3	37/63	45/28/26	78/22	64/36	85/15	*c*
	5	40/60	52/32/16	83/17	65/35	87/13	*c*
	10	40/60	54/31/15	73/29	63/37	65/35	*c*
	20	43/57	56/36/8	72/28	66/34	74/26	*c*
PMP–FlLi	2	18/82	7/14/79	*c*	*c*	*c*	*c*
	3	23/77	9/14/78	69/31	67/33	(66/34)	*c*
	5	28/72	13/6/81	74/26	71/29	(71/29)	*c*
	10	34/66	18/2/80	72/28	66/34	(63/37)	*c*
	20	43/57	18/4/78	70/30	60/40	(64/36)	*c*

[a] Determined by HPLC analysis with UV detection at 254 nm. [b] The ratio of isotactic oligomers having m ω-end configuration to those having r ω-end configuration. The other oligomers were neglected here since the amounts of those were very low. [c] Not obviously detected.

for dimer and trimer anions, while protonation in m fashion is favored for the isotactic oligomer anions of DP ≥5 except for the hexamer anion obtained with Sp–FlLi at [TrMA]/[Li] = 10 and 20. The ratio of m to r of the ω end of a polymer obtained with Sp–FlLi was found to be 6/1 by ^1H NMR analysis (Figure 1), though the polymer could not be separated by HPLC as oligomers were separated. The stereospecificity of protonation of the polymer anion in the system with Sp–FlLi is similar to that of the isotactic pentamer, hexamer, heptamer, and octamer anions in this initiator system except for that of the hexamer anion at [TrMA]/[Li] = 10 and 20. This suggests that these isotactic oligomer anions may resemble the polymer anion. The unnaturally high content of diastereomers whose ω ends have r configuration in hexamer in the system with Sp–FlLi at [TrMA]/[Li] = 10 and 20 will be explained later by considering the change in relative amount of the two optical isomers of isotactic hexamer anion with the progress of the reaction.

Optical Resolution of Dimer and Assignments of Four Isomers. The diastereomers separated above were optically resolved by HPLC on a chiral stationary phase, and the absolute configurations of optical isomers were determined. In the notation of isomers, meso addition is represented as *RR* and *SS* in the present paper in which the left side is the α-end side. Therefore, the isotactic sequences are represented as ---*RRR*--- and ---*SSS*---.

Figure 7 shows chromatograms of the optical resolution of the MMA dimer derived from the TrMA dimer prepared with Sp–FlLi at [TrMA]/[Li] = 2, 3, 10, and 20. The dimer was completely separated into four isomers (*SS*, *RR*, *RS*, *SR*) by using a chiral HPLC column packed with cellulose-tris(3,5-dichlorophenylcarbamate)-coated silica gel.[19b] Content of the optical isomers was determined by this separation.

The assignment of the four isomers of the dimer was done by analyzing an optically active dimer synthesized from (−)-(*R*,*R*)-2,4-dimethylglutaric acid[17] (Scheme II). This optically active acid was prepared by hydrolyzing optically active dibenzyl 2,4-dimethylglutarate (ee 85%), which was obtained by chromatographic separation of a mixture of (±)- and *meso*-dibenzyl ester. The (−)-acid thus obtained was methylated by CH_2N_2 followed

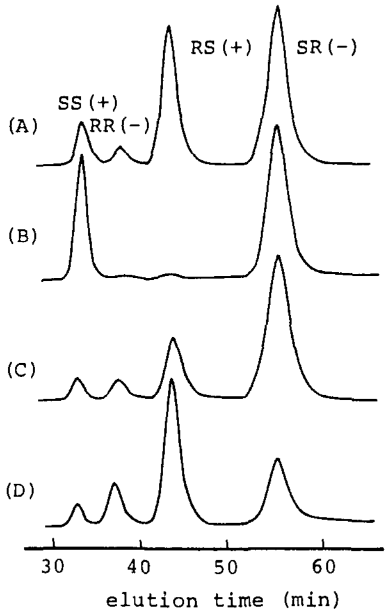
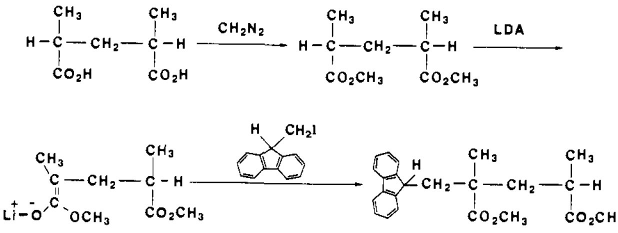


Figure 7. Chromatograms of optical resolution of MMA dimer derived from TrMA dimer prepared with Sp–FlLi at [TrMA]/[Li] = 2 (A), 3 (B), 10 (C), and 20 (D).

Scheme II. Synthesis of MMA Dimer from 2,4-Dimethylglutaric Acid



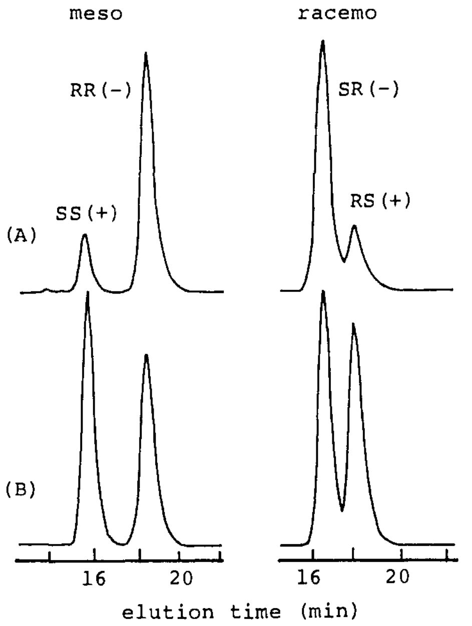


Figure 8. Chromatograms of optical resolution of MMA dimers prepared from (−)-(2*R*,4*R*)-dimethylglutaric acid (A) and (±)- and *meso*-dimethylglutaric acid (B).

by lithiation with 1 equiv of lithium diisopropylamide (LDA). The lithiated methyl ester was allowed to react with 9-(iodomethyl)fluorene to introduce a fluorenylmethyl group at the 2-position of the ester. This afforded a mixture of *RR* and *SR* dimers. The possibility of lithiation at both the 2- and 4-positions of the ester in this process was found to be negligible by the following experiment. Dibenzyl ester rich in (−)-(*R*,*R*) isomer was lithiated with 1 equiv of LDA and quenched by CH_3OH. The resulting dibenzyl ester consisted mainly of (−)-(*R*,*R*) and meso isomers, and no increase of (+)-(*S*,*S*) isomer against (−)-(*R*,*R*) isomer was observed by HPLC analysis. This indicates that only one of the 2- and 4-positions of the benzyl ester is lithiated with 1 equiv of LDA, and no exchange reaction between the lithiated esters proceeds.

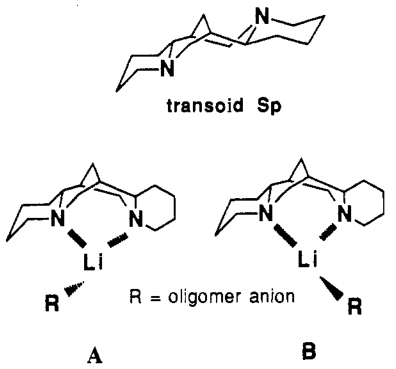
The optically active MMA dimer thus obtained was separated by HPLC using a silica gel column, and the structures of m and r isomers were confirmed by FD mass and ^{1}H NMR spectroscopic analyses. The analytical data were identical to those of the MMA dimer obtained from oligomerization of TrMA. The m and r isomers of the optically active dimer were optically resolved by chiral HPLC in order to learn the content of the optical isomer. The chromatograms are shown in Figure 8 together with the results of analyses of the dimer prepared from a mixture of (±)- and *meso*-2,4-dimethylglutaric acid. Enantiomeric excess (ee) values of both m and r isomers obtained from the (*R*,*R*)-acid were lower than that of the original acid (65% ee for m and 58% ee for r), suggesting that some racemization occurred in the process of hydrolyzing the ester group and introducing the fluorenylmethyl group. However, in both chromatograms of resolution of m and r isomers, one antipode of negative rotation predominated over the other. This indicates that the optical isomer of negative rotation is the isomer whose asymmetric center of the ω end has *R* configuration, that is, *RR* isomer for m and *SR* isomer for r. This assignment is consistent with the previous tentative assignment based on optical rotation of the model compounds.[8,25,26]

Table III. Ratios of the Four Optical Isomers of MMA Dimer Derived from TrMA Dimer Prepared with Sp–FlLi, DDB–FlLi, and PMP–FlLi[a]

initiator	[TrMA]/[Li]	m (%) *SS* (+)	m (%) *RR* (−)	r (%) *RS* (+)	r (%) *SR* (−)	*S*−/*R*−[b]
Sp–FlLi	2	9	4	32	55	64/36
	3	25	1	3	71	96/4
	10	7	6	22	65	72/28
	20	8	13	49	30	38/62
DDB–FlLi	2	16	8	27	49	65/35
	3	27	10	19	44	71/29
	5	30	11	17	42	72/28
	10	27	13	18	42	69/31
	20	32	12	18	38	70/30
PMP–FlLi	2	14	4	23	59	73/27
	3	15	8	29	48	63/37
	5	19	9	22	50	69/31
	10	25	9	22	45	70/30
	20	32	11	18	39	71/29

[a] Determined by HPLC optical resolution of the dimer with UV detection at 254 nm. The dimers were separated from the mixture of oligo(MMA)s by GPC. The range of error at the 99% confidence level for the percentage of *S*-isomer at [TrMA]/[Li] = 2 in the Sp–FlLi system was found to be ca. ±3% in 10 repeated runs. [b] *S*− = *SS* + *SR*; *R*− = *RR* + *RS*.

Chart III. Transoid Sp and the Two Types of Complexes of Cisoid Sp with Oligomer Anion



The ratios of the four isomers obtained in the three initiator systems are summarized in Table III. In the system with Sp–FlLi, the contents of MMA dimer depended greatly on the [TrMA]/[Li] ratio. The relative total amounts of *RR* and *RS* isomers, generically named *R*– isomer in this paper, greatly decreased with increasing [TrMA]/[Li] ratio from 2 to 3. This is ascribed to the predominant propagation of *R*–$^-$ dimer anion with high stereoselectivity to trimer anion in the early stage of polymerization. In the present paper, *R*–$^-$ and *S*–$^-$ anions represent the dimer anions which give *RR* and *RS* dimers and *SS* and *SR* dimers, respectively, by protonation with CH_3OH. Although the *R*–$^-$ dimer anion gives *RR* and *RS* dimers by protonation with CH_3OH, the configuration of the chiral center of the ω end is not important from the viewpoint of stereochemistry of propagation because it is determined by a termination reaction with CH_3OH and has no concern with the propagation stereochemistry.

In contrast to the change in the ratio ([*S*–]/[*R*–]) of the isomers at [TrMA]/[Li] ratios of 2 and 3, as the [TrMA]/[Li] ratio increased from 3 to 20, the amount of *S*– isomer (*SS* + *SR*) decreased and reached a ratio of *R*– to *S*– of 62/38 at [TrMA]/[Li] = 20 where 82% of the product was a polymer of DP 60 (Table I). This indicates that a significant amount of *S*–$^-$ dimer anion propagated to trimer anion until completion of polymerization leaving the less reactive *R*–$^-$ anion. To explain this, the existence of two *R*–$^-$ dimer anion species with different activities is assumed. Two conformers, transoid and cisoid, are possible for Sp, and when Sp forms a bidentate complex with a metal cation, the cisoid structure is preferred (Chart III).[27a,b] NMR analyses of the complexes of Sp and magnesium dialkyl- and butyllithium show that the alkyl group of the metal compound can exist in two different magnetic environments and the exchange between the two positions is slow.[27c,d] On the basis of this ob-

---

(26) Jacques, J.; Gros, C.; Bourcier, S. In *Stereochemistry*; Kagan, H. B., Ed.; Georg Thieme: Stuttgart, 1977; Vol. 4, pp 80–84.

(27) (a) Bohlmann, F.; Zeisberg, R. *Chem. Ber.* **1975**, *108*, 1043. (b) Bohlmann, F.; Shumann, D.; Arndt, C. *Tetrahedron Lett.* **1965**, 2705. (c) Fraenkel, G.; Cottrell, C.; Ray, G. J.; Russell, J. *J. Chem. Soc., Chem. Commun.* **1971**, 273. (d) Fraenkel, G.; Appleman, B.; Ray, J. G. *J. Am. Chem. Soc.* **1974**, *96*, 5113.

Table IV. Ratios of the Eight Optical Isomers of MMA Trimer Derived from TrMA Trimer Prepared with Sp–FlLi, DDB–FlLi, and PMP–FlLi[a]

	[TrMA]/	mm (%)		rm (%)		rr (%)		mr (%)		
initiator	[Li]	*SSS* (+)	*RRR* (−)	*SRR* (−)	*RSS* (+)	*SRS* (+)	*RSR* (−)	*RRS* (+)	*SSR* (−)	*SS*−/*RR*−/*SR*−/*RS*−[b]
Sp–FlLi	2	~0	11	~0	3	2	23	56	5	5/67/2/26
	3	4	6	1	4	1	36	28	20	24/34/1/41
	5	15	~0	~0	3	3	20	~0	59	74/0/3/23
	10	6	~0	~0	1	1	13	~0	79	85/0/1/14
	20	7	~0	~0	1	1	13	~0	78	85/0/1/14
DDB–FlLi	2	18	6	~0	14	6	25	5	26	44/11/6/39
	3	21	8	1	16	4	24	4	22	43/12/5/40
	5	19	9	1	23	2	30	3	13	32/11/3/54
	10	13	13	~0	27	1	30	5	11	24/18/1/57
	20	7	11	1	37	1	34	4	5	12/15/2/71
PMP–FlLi	2	5	~0	~0	~0	4	11	~0	80	85/~0/4/11
	3	7	1	~0	1	3	10	~0	78	85/1/3/11
	5	11	1	~0	~0	2	5	3	78	89/4/2/5
	10	15	2	~0	1	~0	2	5	75	90/7/~0/3
	20	11	5	2	~0	1	3	8	70	81/13/3/3

[a] Calculated from the ratio of diastereomers shown in Table II and the ratio of optical isomers determined by HPLC optical resolution of each diastereomer with UV detection at 254 nm. [b] *SS*− = *SSS* + *SSR*; *RR*− = *RRR* + *RRS*; *SR*− = *SRS* + *SRR*; *RS*− = *RSR* + *RSS*.

servation, two types of complexes of Sp and TrMA oligomer anion (A and B) are postulated, in which the anion is located in different positions with respect to the Sp backbone with a skewed shape as shown in Chart III. The shape of the chiral cavity which determines stereospecificity and activity of the complex should be different in complexes A and B. This assumption is supported by the fact that a slight difference in Sp backbone showed remarkable influence on the stereospecificity and activity of the initiator complex in the enantioselective (stereoelective) polymerization of racemic α-methylbenzyl methacrylate with the complexes of ethylmagnesium bromide with Sp and its derivatives.[28]

As for the other two initiator systems, *S*− isomer predominated over *R*− isomer at all [TrMA]/[Li] ratios, indicating that the propagating dimer anion always contains a larger amount of *S*− anion than *R*− anion. However, the change in the amount of *S*− and *R*− isomers was not obvious compared with that in the Sp–FlLi system. The two isomeric dimer anions seem to possess similar reactivity in these two systems.

Optical Resolution of Trimer and Assignments of Eight Isomers. To examine the stereochemistry of propagation from trimer anion to higher oligomer anions, trimers were analyzed in the same manner used for the dimer. Eight isomers exist for the trimer, and these were almost completely resolved by chiral HPLC. As an example, the chromatograms of resolution for the MMA trimer derived from the TrMA trimer prepared with Sp–FlLi at [TrMA]/[Li] = 3 are shown in Figure 9. Relative amounts of the isomers obtained in the three initiator systems are summarized in Table IV.

The eight isomers were assigned on the basis of the content of isomers obtained in the system with Sp–FlLi at [TrMA]/[Li] = 2. Under this condition with Sp–FlLi, the product was mainly dimer (~93%) in addition to a small amount of trimer (Figure 2A), suggesting that the small amount of trimer should be produced from the more active dimer anion. The predominantly propagating dimer anion in the early stage of polymerization was shown to be $R-^{-}$ from the results in Table III as described above. Actually, all diastereomers of the trimer consist of predominantly one antipode of the enantiomers at [TrMA]/[Li] = 2. Therefore, the predominant optical isomers of trimer were assigned to the ones whose asymmetric carbon at the α end has *R* configuration. This assignment agreed with that based on the optical rotation, referring to the model compounds.[8,25,26] In our previous assignment, we assumed that the optical rotation of an isomer of trimer depends on the configuration of the asymmetric carbon of the ω end.

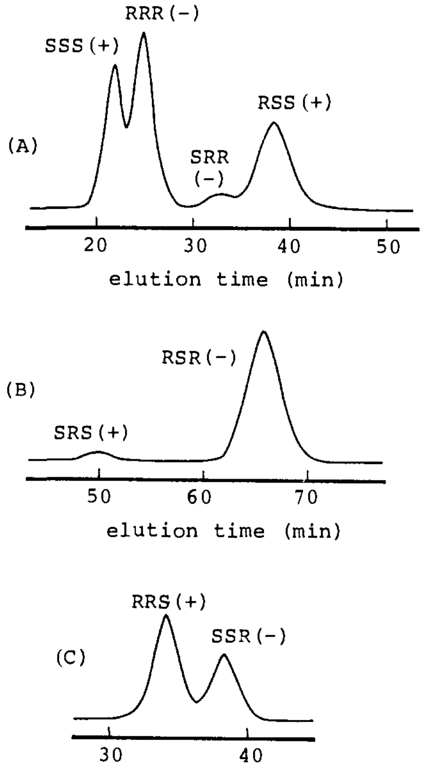


Figure 9. Chromatograms of optical resolution of MMA trimers mm and rm (A), rr (B), and mr (C) derived from the TrMA trimer prepared with Sp–FlLi at [TrMA]/[Li] = 3.

Similar to the dimer, isomers of the trimer are named by omitting the ω-end configuration, such as *RR*−, which represents *RRR* and *RRS*. In the system with Sp–FlLi, as the [TrMA]/[Li] ratio increased, the amount of *SS*− (*SSR* + *SSS*) increased and that of *RR*− (*RRR* + *RRS*) decreased to zero at [TrMA]/[Li] = 5 (Table IV). The amount of *RS*− (*RSR* + *RSS*) first increased with an increase of [TrMA]/[Li] ratio from 2 to 3 and then decreased with further increase of [TrMA]/[Li] ratio, though the degree of decrease was not as obvious as that of *RR*−. The change in the amount of *SR*− (*SRS* + *SRR*) was not as remarkable as that of the other isomers. These results indicate that, in the system with Sp–FlLi, the $RR-^{-}$ trimer anion is much more reactive than the other isomeric anions, particularly the $SS-^{-}$ anion. Though the $RS-^{-}$ trimer anion is also rather reactive in the latter stage of polymerization, this anion should not grow to the higher isotactic oligomer or polymer, because the isomers having r configuration at the α end of the main chain were obviously not detected in the separation of diastereomers of pentamer to octamer (Figure 5A) and NMR analysis of the polymer (Figure

---

(28) (a) Okamoto, Y.; Suzuki, K.; Kitayama, T.; Yuki, H.; Kageyama, H.; Miki, K.; Tanaka, N.; Kasai, N. *J. Am. Chem. Soc.* **1982**, *104*, 4618. (b) Kageyama, H.; Miki, K.; Tanaka, N.; Kasai, N.; Okamoto, Y.; Yuki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1319.

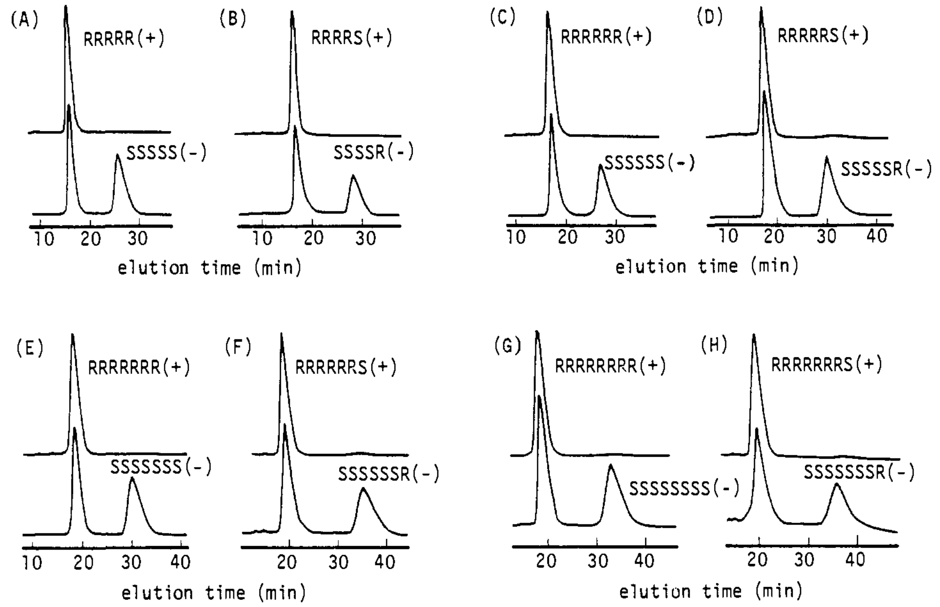


Figure 10. Chromatograms of optical resolution of MMA pentamers mmmm (A) and mmmr (B), MMA hexamers mmmmm (C) and mmmmr (D), MMA heptamers mmmmmm (E) and mmmmmr (F), and MMA octamers mmmmmmm (G) and mmmmmmr (H) derived from the corresponding TrMA oligomers prepared with Sp–FlLi and the corresponding racemic MMA oligomers prepared with FlLi in THF: top, optically active oligomers; bottom, racemic oligomers. Pentamers and hexamers were isolated from the products of oligomerization at [TrMA]/[Li] = 3, and heptamers and octamers were isolated from those at [TrMA]/[Li] = 5.

Table V. Ratios of Optical Isomers of Isotactic Oligo(MMA)s Derived from Oligo(TrMA)s Obtained with Sp–FlLi, DDB–FlLi, and PMP–FlLi[a]

		pentamer		hexamer		heptamer		octamer	
initiator	[TrMA]/[Li]	mmmm *RRRRR*/*SSSSS*	mmmr *RRRRS*/*SSSSR*	mmmmm *RRRRRR*/*SSSSSS*	mmmmr *RRRRRS*/*SSSSSR*	mmmmmm *RRRRRRR*/*SSSSSSS*	mmmmmr *RRRRRRS*/*SSSSSSR*	mmmmmmm *RRRRRRRR*/*SSSSSSSS*	mmmmmmr *RRRRRRRS*/*SSSSSSSR*
Sp–FlLi	3	~100/~0	~100/~0	~100/~0	98/2	~100/~0	~100/~0	*b*	*b*
	5	95/5	85/15	97/3	54/46	~100/~0	97/3	~100/~0	~100/~0
DDB–FlLi	3	2/98	2/98	3/97	1/99	10/90	9/91	*b*	*b*
	5	3/97	7/93	1/99	2/98	1/99	~0/~100	*b*	*b*
PMP–FlLi	3	~0/~100	18/82	~0/~100	13/87	*b*	*b*	*b*	*b*
	5	~0/~100	10/90	~0/~100	5/95	*b*	*b*	*b*	*b*

[a] Determined by HPLC optical resolution of the diastereomers with UV detection at 254 nm. [b] Not obviously detected in the separation of diastereomers (Table II).

1). The *RS*–$^-$ trimer anion may grow to the tetramer anion and remain without further propagation. The trimer anions at [TrMA]/[Li] = 10 and 20 with Sp–FlLi are considered to be the less reactive anions remaining after polymer formation.

In the system with DDB–FlLi, the amount of *SS*– decreased and that of *RS*– increased with increasing [TrMA]/[Li] ratio, though the change was not as obvious as in the system with Sp–FlLi. This indicates that the *SS*–$^-$ trimer anions predominantly propagate to the higher ones with less stereospecificity than that in the system with Sp–FlLi.

In the system with PMP–FlLi, the change in amount of isomers was much smaller than in the other two systems. However, here, the information on stereospecific propagation can be drawn from the amounts of isomers. The oligomer obtained at [TrMA]/[Li] = 3 consisted mainly of trimer (~67%) (Figure 4B), and *SS*–isomer comprises 85% of the trimer. This indicates that the *SS*–$^-$ anion is the predominant propagating trimer anion in this system.

Optical Resolution of Higher Oligomers. Separation of diastereomers showed that oligomers of DP ≥5 in all the systems consisted mainly of isotactic ones whose ω ends have m and r configurations (Figure 5). The isotactic oligomers were optically resolved by HPLC. Figure 10 shows chromatograms of optical resolution of the isotactic oligomers obtained in the system with Sp–FlLi: pentamers and hexamers obtained at [TrMA]/[Li] = 3 and heptamers and octamers obtained at [TrMA]/[Li] = 5. Racemic oligomers were obtained by oligomerization of TrMA with FlLi in THF without a chiral ligand. As shown in the figure, all the isotactic oligomers were perfectly resolved. Ratios of the enantiomers obtained in the three systems are summarized in Table V.

Isotactic oligomers obtained in the three systems consisted mostly of one antipode of enantiomers except for the hexamer mmmmr in the system with Sp–FlLi at [TrMA]/[Li] = 5. The antipodes in excess in the system with Sp–FlLi are the opposites of those in the systems with DDB– and PMP–FlLi. This indicates that the isotactic oligomer anions of opposite absolute configuration predominantly propagate to the polymer in the system with Sp–FlLi and the other two systems. Assignments of the isomer were done as follows. In the system with Sp–FlLi at [TrMA]/[Li] = 3, pentamer and hexamer are the highest oligomers in the products; that is, those oligomers were produced from the dimer and trimer anions of higher activities. The results in Tables III and IV showed that the *R*–$^-$ dimer anion and *RR*–$^-$ trimer anion were much more reactive than the other isomeric anions in the early stage of polymerization. Therefore, these antipodes were assigned to the oligomers whose asymmetric centers of the main chains had *R* configurations. Antipodes of the heptamer and octamer were also assigned to *RRR*––– isomers in this system since they were produced from the smaller oligomer anions including hexamer and pentamer anions which consisted purely of one antipode. *Consequently, the results of optical resolution of isotactic oligomers indicate that the isotactic oligomer anions of RRR––– configuration in the system with Sp–FlLi and those of SSS––– configuration in the systems with DDB–FlLi and PMP–FlLi predominantly propagate to the polymer of one-handed helicity, and the polymer obtained in the former system possesses RRR––– configuration and that in the latter two systems SSS––– configuration, although these polymers have the same helicity.* The exceptional existence of the significant amount of *SSSSSR* hexamer in the system with Sp–FlLi at [TrMA]/[Li] = 5 may

Table VI. Ratios of Isomers Whose ω Ends Possess m Configuration to Those Whose ω Ends Possess r Configuration[a]

		dimer		trimer				pentamer[b]		hexamer[b]		heptamer[b]		octamer[b]	
initiator	[TrMA]/[Li]	*SS*/*SR*	*RR*/*RS*	*SSS*/*SSR*	*RRR*/*RRS*	*SRR*/*SRS*	*RSS*/*RSR*	–*SS*/–*SR*	–*RR*/–*RS*	–*SS*/–*SR*	–*RR*/–*RS*	–*SS*/–*SR*	–*RR*/–*RS*	–*SS*/–*SR*	–*RR*/–*RS*
Sp–FlLi	2	14/86	12/88	*c*	16/84	*c*	12/88								
	3	26/74	25/75	17/83	18/82	*c*	10/90	*c*	65/35	*c*	75/25	*c*	83/17		
	5			20/80	*c*	*c*	13/87	40/60	62/38	11/89	78/22	*c*	88/12	*c*	86/14
	10	13/87	21/79	7/93	*c*	*c*	7/93								
	20	21/79	21/79	8/92	*c*	*c*	7/93								
DDB–FlLi	2	25/75	23/77	41/59	55/45	*c*	36/64								
	3	38/62	34/66	49/51	67/33	20/80	40/60	78/22	83/17	63/37	83/17	85/15	86/14		
	5	42/58	39/61	59/41	75/25	33/67	43/57	83/17	71/29	65/35	*c*	87/13	*c*		
	10	39/61	42/58	54/46	72/28	*c*	47/53								
	20	45/55	40/60	58/42	73/27	*c*	52/48								
PMP–FlLi	2	19/81	15/85	6/94	*c*	*c*	*c*								
	3	24/76	22/78	8/92	*c*	*c*	9/91	73/27	*c*	70/30	*c*				
	5	28/72	29/71	12/88	25/75	*c*	*c*	76/24	*c*	72/28	*c*				
	10	36/64	30/70	17/83	30/70	*c*	27/73[c]								
	20	45/55	38/62	14/86	39/61	*c*	*c*								

[a] Calculated from the data in Table II–V. The ranges of error at the 99% confidence level for the percentages of *SR* isomer and *RS* isomer in the Sp–FlLi system at [TrMA]/[Li] = 2 were found to be ca. ±4% and ±3%, respectively, in 10 repeated runs. [b] –*SS* and –*SR* denote the isotactic oligomers whose asymmetric centers in the main chain have *S* configuration, and –*RR* and –*RS*, those of *R* configuration. [c] The ratio could not be calculated precisely because the amount of one of or both of the isomers was very low.

mean that the S–$^-$ dimer anion which predominantly propagated in the rather final stage of polymerization grew to a hexamer anion which remained until completion of the polymerization.

Stereochemistry of Protonation of Oligomeric Anions. The results shown above give us information on the stereochemistry of the protonation of oligomer anions with CH_3OH. From the results of separation of the isomers of dimer, trimer, pentamer, hexamer, heptamer, and octamer, ratios of the isomers which differ only in configuration of the asymmetric center at the ω end (–m isomer and –r isomer) were calculated. The results are summarized in Table VI.

In the system with Sp–FlLi, for all the isomeric anions of dimer and trimer, protonation was mainly in r fashion and the ratios of –m isomer to –r isomer were not obviously dependent on the [TrMA]/[Li] ratio. As for the higher oligomers, the stereospecificity of protonation differed depending on the absolute configuration of the main chain of the isomeric anion. Protonation of m fashion (m protonation) was major for the isomeric anions of *RRR*--- configuration and that of r fashion (r protonation) for the isomeric anions of *SSS*--- configuration. This reasonably explains the unnaturally high content of mmmmr isomer in hexamer in the system with Sp–FlLi at [TrMA]/[Li] = 10 and 20 (Table II). The hexamer at [TrMA]/[Li] = 10 and 20, which is considered to be the *remaining* oligomer, may consist mainly of *SSSSSR* isomer produced from the relatively less reactive *SSSSS*–$^-$ anion.

It was confirmed that, for the dimer anion in the system with Sp–FlLi at [TrMA]/[Li] = 2, the stereospecificity of protonation was not affected by reaction time in the range 1 min to 24 h after the reaction starts.

The ω-end configuration, ---*R* and ---*S*, may be determined by protonation of the enolate anion (Chart II). This assumption is also supported by the fact that the stereospecificity of protonation of oligo(TrMA) anions was strongly affected by the stereostructure of the protonating reagent.[29] For several α-metalated carbonyl compounds whose structure resembles that of the oligomethacrylate anion, the enolate structure has been proved by NMR spectroscopic and X-ray crystallographic analyses.[30]

In the system with DDB–FlLi, r protonation predominated for the dimer anions and *SR*–$^-$ trimer anion and m protonation for *RR*–$^-$ trimer and the isotactic anion of pentamer, hexamer, and heptamer. In the system with PMP–FlLi, r protonation predominated for all the isomeric anions of dimer and trimer and m protonation for the higher isotactic oligomer anions.

In both the systems with DDB–FlLi and PMP–FlLi, m protonation for most dimer and trimer anions seems to increase with [TrMA]/[Li] ratio, even taking into account experimental error. This change in stereospecificity of protonation may be ascribed either to structural factors or to aggregation of oligomer anions. The existence of different complexing forms between chiral ligands and oligomer anions such as that postulated for the dimer anion in the Sp–FlLi system (Chart III) may be less plausible in the systems with DDB and PMP because almost no change was observed in activities of dimer and trimer anions in the reaction with TrMA monomer with the change of [TrMA]/[Li] ratio (Tables III and IV). Aggregation of oligomer anions seems to be a more plausible postulate as the reason for the change in stereospecificity of protonation. Since reaction volume was kept constant for all reactions, the concentration of oligomer anions decreases as [TrMA]/[Li] increases. The degree of aggregation of oligomer anions may be influenced by concentration. It has been reported that lithium compounds with structures similar to that of methacrylate aggregate in a concentration range which is close to that adopted in our experiment both in hydrocarbon solvents and in polar solvents.[31] The oligomer anions with Sp may not aggregate. Since Sp is much bulkier than the other two ligands, it may prevent aggregation.

Mechanism of Polymerization. From the results obtained above, the mechanism of asymmetric polymerization can be described as follows. Oligomer anions in the early stage of polymerization consist of species of different activity. The highly active oligomer anion predominantly propagates to the helical polymer, and the less active species remain as oligomers until completion of polymerization. The activity of oligomer anions depends on stereostructure and the complexing form between the anion and chiral ligand.

In all the systems, propagation of unimer anion to dimer anion is very fast. In the early stages of polymerization with Sp–FlLi, the R–$^-$ dimer anion predominantly propagates to trimer anion, and in the latter stages of polymerization, the S–$^-$ dimer anion predominantly propagates to trimer anion. However, the S–$^-$ dimer anion does not grow to a polymer and remains as trimer, tetramer, and hexamer anions until completion of polymerization. In the next step, the *RR*–$^-$ trimer anion is more reactive than the other isomeric anions and is used for formation of the higher isotactic oligomer anion with *RRR*--- configuration. Once an isotactic oligomer anion grows to DP ~9, reaction of the anion with TrMA monomer is accelerated to afford an optically active, one-handed helical polymer of *RRR*--- configuration. In the

---

(29) The detailed results will be reported in a separate paper.

(30) (a) Seebach, D.; Amstutz, R.; Laube, T.; Schweizer, W. B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5403. (b) Vancea, L.; Bywater, S. *Macromolecules* **1981**, *14*, 1321. (c) Vancea, L.; Bywater, S. *Macromolecules* **1981**, *14*, 1776.

(31) (a) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972. (b) Halaska, V.; Lochmann, L. *Collect. Czech. Chem. Commun.* **1973**, *38*, 1780. (c) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 3345. (d) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 462.

system with DDB–FlLi, reactivities of *S*–$^-$ and *R*–$^-$ dimer anions are similar. However, the propagating dimer anion contains a larger amount of *S*–$^-$ dimer anion than *R*–$^-$ dimer anion. In the next step and thereafter, *SS*–$^-$ trimer anion and the higher isotactic oligomer anions with *SSS*––– configuration predominantly propagate to a polymer of *SSS*––– configuration. In the system with PMP–FlLi, the propagation of unimer anion to dimer anion is slower than in the other two systems. The stereochemistry of propagation in this system is similar to that in the DDB–FlLi system, and a polymer of *SSS*––– configuration is produced. In the systems with DBB–FlLi and PMP–FlLi, acceleration of polymerization occurs when the oligomer anion grows to DP ~7. The difference in the stereochemistry of propagation with the three initiator systems must be related to the stereostructure of the complexes of oligomer anions with chiral ligands.

Though the absolute configuration of asymmetric carbons in the main chain of the polymer obtained with Sp–FlLi is opposite that of the polymers obtained with DDB–FlLi and PMP–FlLi, all the polymers possess the same helicity. The two isotactic polymer chains of the same helicity with opposite absolute configurations are regarded as diastereomers, particularly when DP is low, because the influence of the α and ω end groups cannot be ignored. Therefore, the stereostructure of the helices in the vicinity of the chain ends may slightly differ depending on the absolute configuration. This may be the reason why a stable helix starts at different DP in the above polymerization systems. The helix with *SSS*––– configuration may be more stable than that with the opposite configuration, since the helix starts at lower DP (~7), and polymerization is much faster in the systems with DDB–FlLi and PMP–FlLi than in the system with Sp–FlLi.

There exist few examples of studies on polymerization with stereochemical investigation of each addition step of a monomer including the absolute configuration of the main chain as done in the present study. Pino and co-workers briefly reported such a study of polypropylene produced with an optically active zirconium catalyst.[32] The present report may be the first example of assignment of absolute configuration of the main chain of polymethacrylate, and we could show that th polymer chains produced with the chiral initiator systems have exclusively either *RRR*––– or *SSS*––– absolute configuration.

Acknowledgment. We thank Dr. K. Ute and Mr. Y. Terawaki (Osaka University) for their help in measuring two-dimensional NMR spectra and Dr. E. Yashima (Nagoya University) for fruitful discussions.

Registry No. (±)-MMA, 138180-98-0; (±)-*m*-MMA (dimer), 138181-02-9; (±)-*r*-MMA (dimer), 125078-68-4; (±)-*mm*-MMA (trimer), 138181-03-0; (±)-*rr*-MMA (trimer), 138256-49-2; (±)-*mr*-MMA (trimer), 138181-04-1; (*S*,*S*)-MMA (dimer), 138256-50-5; (*R*,*R*)-MMA (dimer), 138256-51-6; (*R*,*S*)-MMA (dimer), 138257-63-3; (*S*,*R*)-MMA (dimer), 138256-52-7; FlLi·SP, 138180-99-1; FlLi·DDP, 138181-00-7; FlLi·PMP, 138181-01-8; TrMA (homopolymer), 27497-74-1; (*R*,*R*)-$HO_2CCH(CH_3)CH_2CH(CH_3)CO_2H$, 24018-75-5; *meso*-$HO_2CCH(CH_3)CH_2CH(CH_3)CO_2H$, 2121-67-7; (±)-$MeO_2CCH(CH_3)CH_2CH(CH_3)CO_2Me$, 2121-68-8; (*R*,*R*)-$MeO_2CCH(CH_3)CH_2CH(CH_3)CO_2Me$, 85717-93-7; 9-(iodomethyl)fluorene, 73283-56-4; 9-fluorenylmethanol, 24324-17-2.

Supplementary Material Available: Tables of ^1H NMR chemical shifts of MMA dimer, trimer, pentamer, hexamer, heptamer, and octamer (4 pages). Ordering information is given on any current masthead page.

---

(32) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189.

Generation of 2-Azaallyl Anions by the Transmetalation of *N*-(Trialkylstannyl)methanimines. Pyrrolidine Synthesis by [3 + 2] Cycloadditions with Alkenes

William H. Pearson,* Daniel P. Szura, and Michael J. Postich

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055. *Received July 12, 1991*

Abstract: Treatment of *N*-(trimethylstannyl)methanimines or *N*-(tri-*n*-butylstannyl)methanimines with methyllithium or *n*-butyllithium, respectively, affords 2-azaallyl anions by tin–lithium exchange. These anions undergo intermolecular or intramolecular [π4s + π2s] cycloadditions with alkenes and alkynes to generate pyrrolidines or pyrrolines after quenching with water or other electrophiles. The tin–lithium exchange method allows unstabilized 2-azaallyl anions to be generated for the first time. The lifetime of the anions is limited by a competing intermolecular side reaction. Therefore, relatively reactive alkenes and alkynes must be used, such as stilbene, styrenes, enynes, diphenylacetylene, vinyl sulfides, vinyl selenides, and vinyl silanes. The latter three types of anionophiles afford functionalized cycloadducts which may be transformed into more useful pyrrolidines by reduction, elimination, or oxidation. A synthesis of the alkaloid (±)-mesembrane was accomplished using an intramolecular 2-azaallyl anion cycloaddition.

The pyrrolidine ring is a common feature of many interesting natural and unnatural compounds. Synthetic methods which allow the rapid construction of the pyrrolidine ring would be very useful. In particular, methods which make more than one ring bond in a single operation would be the most efficient, and such reactions generally fall into the cycloaddition category. Whereas the Diels–Alder reaction has been of major importance in the synthesis of both carbocyclic and heterocyclic six-membered rings,[1] cycloaddition reactions which form five-membered heterocyclic rings have only recently gained similar popularity. Of particular utility is the cycloaddition of 1,3-dipolar species, leading to a variety of five-membered ring heterocycles.[2] The cycloaddition of azomethine ylides **1** with alkenes has proven to be effective for the assembly of a variety of pyrrolidines **2**.[3] A related, but less well

---

(1) (a) Boger, D. L.; Weinreb, S. N. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic Press: San Diego, 1987. (b) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1990.

(2) Padwa, A. *1,3-Dipolar Cycloaddition Chemistry*; Wiley-Interscience: New York, 1984; Vols. 1 and 2.

(3) (a) Lown, J. W. in ref 2, Vol. 1, Chapter 6. (b) Pearson, W. H. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1988; Vol. 1, pp 323–358. (c) Vedejs, E. In *Advances in Cycloaddition*; Curran, D. P., Ed.; JAI: Greenwich, CT, 1988; Vol. 1, pp 33–51. (d) Achiwa, K.; Terao, Y.; Aono, M. *Heterocycles* **1988**, *27*, 981. (e) Padwa, A. In *Advances in Cycloaddition*; Curran, D. P., Ed.; JAI: Greenwich, CT, 1990; Vol. 2, Chapter 1.

0002-7863/92/1514-1329$03.00/0 © 1992 American Chemical Society