Asymmetric Polymerization and Oligomerization of 3-Phenylpropanal with Grignard Reagent−(−)-Sparteine Complexes with Termination by Tishchenko Reaction

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ABSTRACT: 3-Phenylpropanal (3-PPA) was polymerized with Grignard reagent−(−)-sparteine complexes, such as ethylmagnesium bromide−(−)-sparteine (EtMgBr−Sp) and *n*-octylmagnesium bromide−(−)-sparteine (OctMgBr-SP) complexes, in toluene at low temperature. The poly(3-PPA) obtained showed optical activity with negative rotation ($[\alpha]^{25}_{365}$ −33° to −56°), which may be based on a predominant one-handed helical conformation of the main chain, and also exhibited a signal due to an ester carbonyl group at 1738 cm^{-1} in its IR spectrum. This means that the polymer has an ester group at the ω-end which is formed by a Tishchenko-type termination reaction between the growing chain end and the 3-PPA monomer. The poly(3-PPA) is stable at room temperature, whereas the poly(3-PPA) obtained with EtMgBr alone at −78 °C degrades slowly even in the solid state to 3-PPA monomer at room temperature. ^{1}H and ^{13}C NMR spectra of the poly(3-PPA) showed rather sharp resonances, suggesting that the polymer may be stereoregular, although the tacticity is not clear. In order to determine the stereostructures of the poly(3-PPA) and the polymerization mechanism, the oligomerization of 3-PPA was carried out with the EtMgBr−Sp and OctMgBr−Sp complexes in toluene at −78 °C. The oligomers of 3-PPA were isolated by fractionation using GPC, HPLC, and supercritical fluid chromatography techniques. The main fraction was 3-phenylpropyl 3-phenylpropanoate, and the other oligomers were found to have a 3-phenylpropoxy group at the α-end and a (2-phenylethyl)carbonyl group at the ω-end, while a very small amount of oligomers contained an octyl group at the α-end. These results clearly indicate that the Grignard reagents are not the real initiator of most of the molecules but that the (1-phenylpropoxy)magnesium bromide formed by the Tishchenko-type termination reaction between the oligomeric growing chain end and the 3-PPA monomer mainly initiated the polymerization of 3-PPA. The propagation should be terminated by the Tishchenko reaction again to afford the poly(3-PPA) having the ester terminal ω-end and (3-phenylpropoxy)magnesium bromide as a cyclic mechanism. The 2-mer consisted of meso and racemo diastereomers, and the ratio was determined to be 85/15 by ^{1}H and ^{13}C NMR spectroscopies. Both the 1- and 2-mers were successfully resolved into optical isomers by chiral HPLC separation using cellulose tris[(3,5-dimethylphenyl)carbamate] as a chiral stationary phase. On the basis of these results, the mechanism of the polymerization of 3-PPA was elucidated.

Introduction

The synthesis of optically active helical polymers is of great interest from stereochemical and functional standpoints.[1] Poly(triarylmethyl methacrylate)s,[2] poly(triarylmethyl acrylate),[3] and some other synthetic polymers such as polychloral,[4] polyisocyanates,[5] polyisocyanides,[6] and poly(2,3-quinoxaline)s[7] are known to exist in a helical structure. The helical structures are stable even in solution owing to the bulkiness of the side group, except for polyisocyanates. The optically active poly(triarylmethyl methacrylate)s and polyisocyanides with a predominant one-handed screw sense can be prepared by asymmetric polymerization using chiral initiators or catalysts. Previously, we reported that triphenylmethyl methacrylate (TrMA) forms a highly isotactic and one-handed helical polymer with several chiral anionic initiators such as the complexes of organolithiums with (−)-sparteine (Sp) and (+)- or (−)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB).[1a,2] The chiral ligands play an essential role in controlling the helical sense. The mechanism of the asymmetric polymerization of TrMA was successfully elucidated by isolating oligomers of TrMA from unimer to octamer followed by the detailed analysis of their stereochemistry including the absolute configuration of the oligomers.[2c]

Sparteine is also an excellent ligand in asymmetric synthesis[8] and the enantiomer-selective polymerization of racemic methacrylates.[9] For instance, the complex with EtMgBr preferentially polymerizes one enantiomer of α-methylbenzyl methacrylate, and the enantiomeric excess (ee) of the polymerized monomer in the initial stage ranged up to 95%.[9] The mechanism of this extremely high selectivity was discussed on the basis of the structures of the complex and the methacrylates.

Polychloral prepared with chiral alkoxides showed a large specific rotation in the solid state.[4] However, because of its insolubility, it is not clear whether such polychlorals would have a stable one-handed helical structure in solution. Recently, a series of isotactic oligomers of chloral were isolated by using GPC and SFC, and their helical structure in both solid and solution was confirmed by X-ray and NMR analyses, respectively.[10] Generally, polymerization of aldehydes must be terminated with acid anhydrides or acid chlorides to end cap the terminal alkoxide anions because polyaldehydes readily degrade to aldehyde monomer at room temperature.[11]

In the present study, we performed the asymmetric polymerization of 3-phenylpropanal (3-PPA) with Grignard reagent−Sp complexes as chiral anionic initiators in order to investigate the possibility of obtaining the poly(3-PPA) with a predominantly one-handed helical conformation. In the course of this study, we have found that the EtMgBr−Sp and OctMgBr−Sp complexes afford an optically active polymer having an ester linkage

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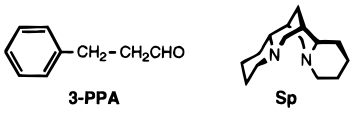
Table 1. Polymerization of 3-PPA wth the EtMgBr−Sp Complex in Toluene[a]

run	toluene (mL)	temp (°C)	time (h)	yield[b] (%)	$\bar{M}_n \times 10^{-3}$ [c]	$\bar{M}_w/\bar{M}_n$[c]	$[\alpha]^{25}_{365}$[d] (deg)
1	1	−78	2	36.3	6.3	1.53	−46.0
2	3	−78	2	39.1	6.2	1.50	−55.6
3	10	−78	2	44.2	6.1	1.47	−33.0
4	3	−98	2	12.8	7.3	1.34	−42.7
5[e]	3	−78	100	13.9[f]			

[a] 3-PPA, 1.0 g (7.5 mmol); EtMgBr, 0.15 mmol; Sp, 0.18 mmol. [b] MeOH-insoluble fraction. Most of the MeOH-soluble part was 3-phenylpropyl 3-phenylpropanoate (see text). [c] Estimated by GPC (polystyrene standards). [d] In THF. [e] Without Sp. [f] Not soluble in common organic solvents.

at the ω-end through the Tishchenko reaction. The ester terminal end helped to stabilize the polymer obtained. Based on the detailed analysis of the oligomers of 3-PPA obtained in the oligomerization with the Grignard reagent−Sp complexes, the stereostructure of the oligomers and the mechanism of the asymmetric polymerization are discussed.



Results and Discussion

Asymmetric Polymerization of 3-Phenylpropanal and Stereostructure of Polymers. Table 1 shows the results of the asymmetric anionic polymerization of 3-PPA with the EtMgBr−Sp complex in toluene at −78 or −98 °C together with those of polymerization by uncomplexed EtMgBr at −78 °C. The polymer obtained with the EtMgBr−Sp complex was soluble in THF and chloroform and showed a negative rotation ($[\alpha]^{25}_{365}$ −33° to −56°), while the polymer obtained with EtMgBr alone was scarcely soluble in common organic solvents, and the polymer yield was low even after 100 h. The degree of polymerization (DP) of poly(3-PPA)s obtained with the complex was from 40 to 50 by GPC based on polystyrene standards. The optical activity of the polymer depended on the temperature and the concentration of 3-PPA in the polymerization mixture. The highest optical activity was observed on the polymer obtained in toluene (3 mL) at −78 °C (run 2). At −98 °C, the yield and specific rotation of the polymer were lower. Most of the methanol-soluble part was 3-phenylpropyl 3-phenylpropanoate, and unreacted monomer was scarcely noted in the ^{1}H NMR spectra. The mechanism for the formation of the ester is described later.

Figure 1 shows the GPC curves of poly(3-PPA) obtained with the EtMgBr−Sp complex (run 2 in Table 1) monitored by UV (254 nm) and polarimetric detectors. The UV and polarimetric detectors showed a similar GPC curve, although a polarimetric detector displayed a large negative peak in the higher molecular weight region and a small positive peak in the lower molecular weight region. The intensities of these curves are comparable to each other in the higher molecular weight region, indicating that the polymer seems to have similar specific rotation independent of the molecular weight in the higher molecular weight region.

The poly(3-PPA)s obtained with the EtMgBr−Sp complex were stable at room temperature, while poly(3-PPA) obtained with EtMgBr alone slowly decomposed even in the solid state to 3-PPA monomer at room

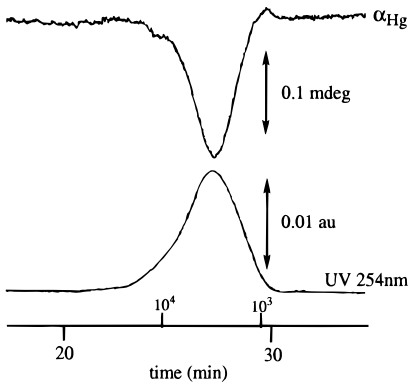


Figure 1. GPC curves of poly(3-PPA) (run 2 in Table 1) obtained with the EtMgBr−Sp complex in toluene at −78 °C.

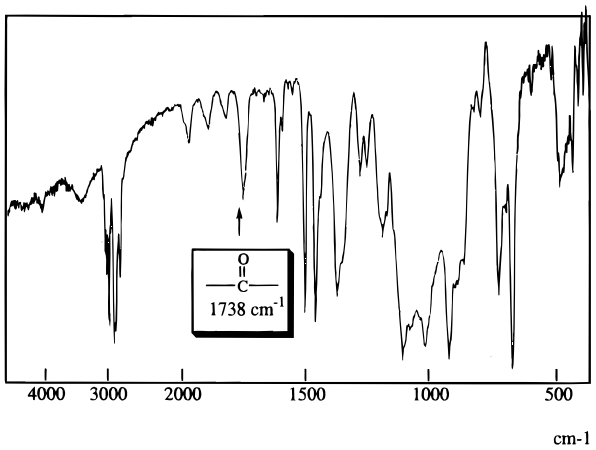


Figure 2. IR spectrum of poly(3-PPA) (run 2 in Table 1) obtained with the EtMgBr−Sp complex in toluene at −78 °C.

temperature. Figure 2 shows the IR spectrum of poly(3-PPA) obtained with the EtMgBr−Sp complex (run 2 in Table 1). The spectrum exhibits a characteristic band at 1738 cm^{-1}, while poly(3-PPA) obtained with uncomplexed EtMgBr did not show such a band. This may suggest that the poly(3-PPA) obtained with the EtMgBr−Sp complex may have an ester group at a terminal end, which must contribute to its stabilization. One possible route for the ester formation is the Tishchenko reaction by which 3-PPA is catalytically converted into the ester form.

The condensation of aldehydes to produce esters is known as the Tishchenko reaction,[12] which is catalyzed by, for instance, aluminum alkoxides[12a] and ruthenium complexes.[12c] Here, we found that a novel Tishchenko-type ester formation proceeds in 3-PPA anionic polymerization catalyzed by Grignard reagent−Sp complexes.

Figure 3 shows the ^{1}H (a) and ^{13}C (b) NMR spectra of poly(3-PPA) (run 2 in Table 1) obtained with the EtMgBr−Sp complex in toluene at −78 °C. The peaks were assigned as shown in Figure 3. The ^{1}H and ^{13}C NMR spectra showed clear resonances ascribed to the polymerized monomer units. Particularly, α-proton and α-carbon resonances at around 5.2 and 97 ppm, respectively, showed very sharp peaks. This suggests that the polymer may be stereoregular, although the tacticity is not clear. We could not observe a clear peak due to the carbonyl group in the ^{13}C NMR spectrum. The concentration of the carbonyl group at the ω-end seems to be quite low because of the high molecular weight of the polymer (*ca.* 6000; DP = *ca.* 45). However, the IR spectrum (Figure 2) may suggest the existence of the ω-end ester group as previously shown. Moreover, in

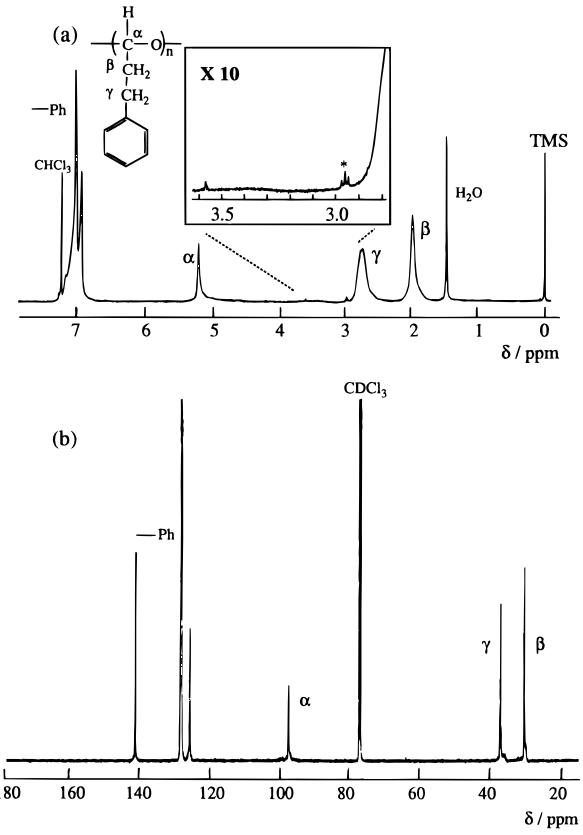


Figure 3. ^{1}H (a) and ^{13}C (b) NMR spectra of poly(3-PPA) (run 2 in Table 1) obtained with the EtMgBr−Sp complex at −78 °C.

Table 2. Polymerization of 3-PPA with Various Initiators in Toluene at −78 °C[a]

run	initiator	yield[b] (%)	$\bar{M}_n \times 10^{-3}$ [c]	$\bar{M}_w/\bar{M}_n$[c]	$[\alpha]^{25}_{365}$[d] (deg)
1	*t*-BuMgBr−Sp	36.0	6.9	1.29	−54.3
2	PhMgBr−Sp	48.0	6.0	1.30	−55.3
3	3-PPOMgBr−Sp[e]	46.0	5.7	1.38	−49.0
4	*c*-HexMgBr−Sp	42.0	7.2	1.54	41.0
5	*c*-HexMgCl−Sp	41.0	7.3	1.49	−43.0
6	OctMgBr−Sp	49.2	7.6	1.51	−46.0
7[f]	OctMgBr−Sp	48.3	7.1	1.58	−48.8
8	*n*-BuLi−Sp				

[a] 3-PPA, 1.0 g (7.5 mmol); Grignard reagent, 0.15 mmol; Sp, 0.18 mmol; toluene, 3 mL; polymerization time, 2 h. Most of the MeOH-soluble part was 3-phenylpropyl 3-phenylpropanoate. [b] MeOH-insoluble fraction. [c] Estimated by GPC based on polystyrene standards. [d] In THF. [e] (3-Phenylpropoxy)magnesium bromide−Sp complex. [f] Terminated with CH_3OD.

the expanded spectrum in Figure 3a, there exist peaks of low intensity marked by an asterisk, which may be due to resonances derived from an end group. Oligomerization studies with the same catalysts support the structure (see below). No signals due to the ethyl group of the initiator were observed in the ^{1}H NMR spectrum.

The results of polymerization of 3-PPA with other various Grignard reagent−Sp complexes are summarized in Table 2. The polymerization was carried out in toluene at −78 °C by using the complexes of Sp and *tert*-butylmagnesium bromide (*t*-BuMgBr), phenylmagnesium bromide (PhMgBr), cyclohexylmagnesium bromide (*c*-HexMgBr), cyclohexylmagnesium chloride (*c*-HexMgCl), octylmagnesium bromide (*n*-OctMgBr), and butyllithium (*n*-BuLi). (3-Phenylpropoxy)magnesium bromide (3-PPOMgBr) prepared by the reaction of an equimolar amount of 3-phenylpropanol and EtMgBr was also used. Most polymers obtained showed optical activity with negative rotations as similarly seen in Table 1. All polymers showed an absorption at around 1740 cm^{-1} in their IR spectra. This may suggest that the polymers may have the terminal ester group at the ω-end regardless of which Grignard reagent was used. The *n*-BuLi−Sp complex did not afford a polymer.

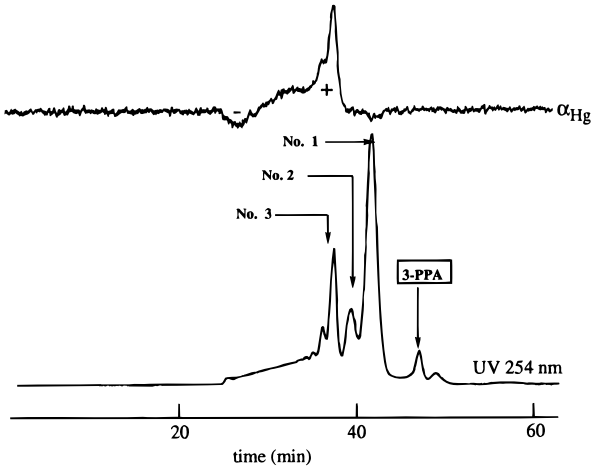
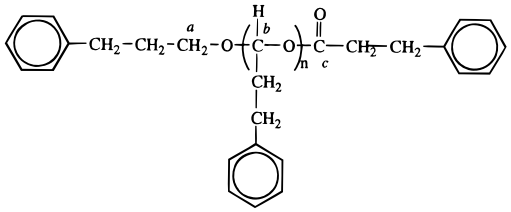


Figure 4. GPC curves of oligo(3-PPA) obtained with the EtMgBr−Sp complex in toluene at −78 °C. [3-PPA]/[EtMgBr−Sp] = 5.

Oligomerization of 3-PPA. In order to gain insight into the stereostructure of poly(3-PPA) obtained with the EtMgBr−Sp complex and the polymerization mechanism, oligomerization of 3-PPA was carried out with 5/1 molar ratio of 3-PPA to the EtMgBr−Sp complex in toluene at −78 °C. Figure 4 shows the GPC curves of the resulting oligo(3-PPA) monitored with UV and polarimetric detectors, and the change in optical rotation with DP was followed. The oligo(3-PPA) having a lower DP showed positive rotation, which may be based on the configurational chirality of the asymmetric centers. The optical rotation changed from positive to negative values as DP increased. The comparison between the UV and polarimetric chromatograms indicates that the oligo(3-PPA) having a higher DP shows relatively high optical rotation. The results of Figures 1 and 4 suggest that the optical activity of the poly(3-PPA) may be ascribed to main chain chirality, probably due to a predominant one-handed helical structure, since the polymer seems to be stereoregular and the configurational chirality of asymmetric centers for optical activity may be negligible in this case.

The oligomers could be separated into three fractions: no. 1, 2, and 3 in Figure 4, by GPC. However, the separation efficiency by GPC was not enough to isolate each oligomer in a pure form. Therefore, SFC was employed for further purification of the fractionated oligomers (see the Experimental Section). The isolated oligomers were assigned by measuring two-dimensional ^{1}H NMR spectra (COSY), ^{13}C NMR spectra, and FD mass spectra. Figure 5 shows the ^{1}H NMR spectra of the isolated oligomers, whose signals were reasonably assigned. The characteristic spectroscopic data of the oligomers are summarized in Table 3. All oligomers showed a strong absorption at around 1740 cm^{-1} in their IR spectra and exhibited a peak at 172 ppm in their ^{13}C NMR, clearly indicating the existence of the carbonyl group. The methine protons (Hb; d and g in Figure 5c) and asymmetric carbons (footnote b in Table 3) of the compound **3** split into two pairs of resonances. These may be assigned to diastereomers (meso and racemo), and the diastereomer ratio was estimated to be 85/15,

Table 3. Characteristic Spectroscopic Data of Oligomers



				^{13}C NMR (ppm)		
oligomer	FD-MS (*m*/*z*)	IR (C=O, cm^{-1})	^{1}H NMR (H_b, ppm)	C_a	C_b	C_c (C=O)
1 ($n = 0$)	268.2 (M^+)	1736		63.74		172.43
2 ($n = 1$)	402.2 (M^+)	1736	5.825	68.39	98.14	172.43
3[a] ($n = 2$)	535.2 ($M^+ - 1$)	1738	4.660 (4.590), 6.081 (5.976)	65.71 (66.47)	95.28 (94.85), 101.93 (103.11)	172.42 (172.25)

[a] In parentheses are shown data for the diastereomers.

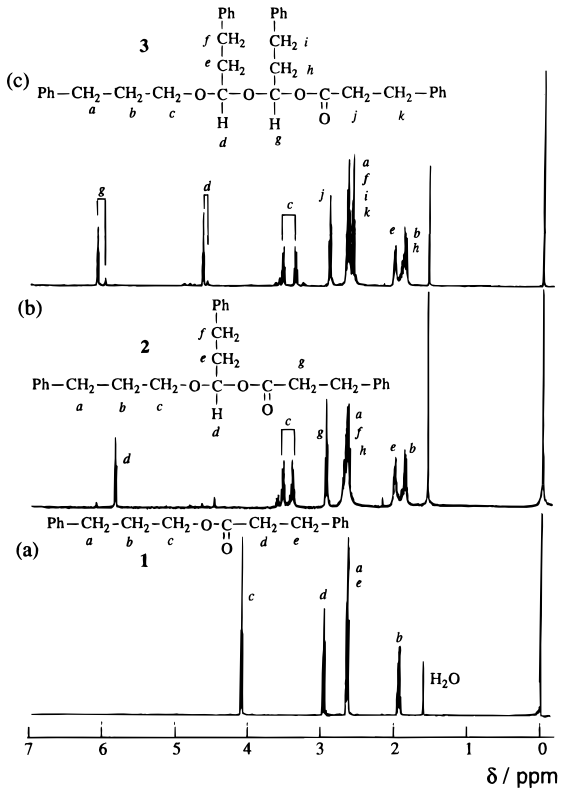


Figure 5. ^{1}H NMR spectra of the isolated oligo(3-PPA)s for fraction no. 1 (a), 2 (b), and 3 (c) in Figure 4.

although the assignment of the diastereomers could not be done.

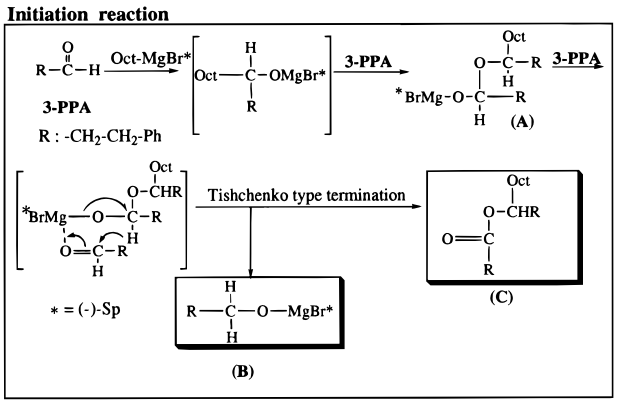
The FD mass spectra of the oligomers showed main peaks of *m*/*z* 268.2 (M^+), 402.2 (M^+), and 535.2 ($M^+ - 1$) for the oligomers **1**−**3**, respectively, corresponding to the molecular mass of the oligomers with the structures shown in Figure 5. The main fraction (no. 1) was 3-phenylpropyl 3-phenylpropanoate (**1**), and the other oligomers were found to have a 3-phenylpropoxy group at the α-end and a (2-phenylethyl)carbonyl group at the ω-end, while the oligomers, at least the isolated oligomers, did not contain an ethyl group at the α-end. These results clearly indicate that the oligomerization was mainly initiated by (3-phenylpropoxy)magnesium bromide instead of ethylmagnesium bromide; the former species must be produced by the Tishchenko-type termination reaction between 3-PPA and the growing chain end which may be initiated with the EtMgBr−Sp complex in the early stage of the oligomerization. From these ^{1}H NMR spectra of the oligomers, the peaks of relatively low intensity marked by an asterisk in the expanded ^{1}H NMR spectrum (Figure 3a) may be assigned to resonances derived from the ω-end group corresponding to *j* for the oligomer **3** in Figure 5c. The resonances for the α-end group (*i.e.*, c for **3**) could not be clearly found in the expanded spectrum, although there exists a very broad resonance at around 3.3−3.7 ppm. This may be due to a resonance from the α-end protons. Consequently, it may be concluded that the poly(3-PPA) obtained with the EtMgBr−Sp complex may have a similar structure to **3**.

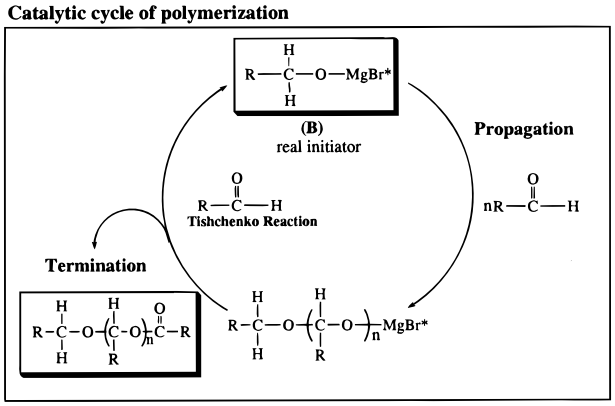
As described previously, we could not detect any polymers and oligomers having an ethyl group at the α-end. This means that very few units of the EtMgBr−Sp complex may actually participate in the initiation reaction. However, there seems to be another route to the formation of the 3-(phenylpropoxy)magnesium bromide, that is, reduction of 3-PPA by the EtMgBr through a β-hydride transfer reaction. If this is the case, the products in the polymerization reaction would not contain the ethyl group at the α-end.

In order to investigate the possibility of such a reaction, 3-PPA was oligomerized with the OctMgBr−Sp complex giving optically active poly(3-PPA) as well as the EtMgBr−Sp complex (Table 2). The octyl group may be suitable for detection by NMR and mass spectroscopy. After the oligomerization was terminated with methanol containing a small amount of HCl or methanol-d_1 (CH_3OD), unreacted monomer, solvent, and compounds derived from the OctMgBr were recovered by distillation under high vacuum. The distillate was directly analyzed by GC mass spectroscopy. The GC mass spectra showed a peak *m*/*z* 114 for the distillate terminated with methanol and 115 for methanol-d_1 corresponding to octane and octane-d_1, respectively, while a peak of *m*/*z* 112 corresponding to 1-octene was not confirmed in both the distillates, indicating that such a β-hydride transfer reduction of 3-PPA by the OctMgBr did not occur and part of the Grignard reagent remained in the solution as an active form. A quite small amount of the OctMgBr therefore must initiate the polymerization of 3-PPA.

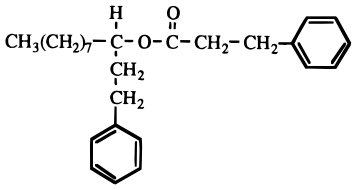
The GPC curve of oligo(3-PPA) obtained with the OctMgBr−Sp complex showed a similar pattern to that of the oligo(3-PPA) obtained with the EtMgBr−Sp complex. The ^{1}H NMR spectrum of the oligo(3-PPA) showed that a major product was 3-phenylpropyl 3-phenylpropanoate. However, there existed clear resonances corresponding to an octyl group centered at 0.9 and 1.2 ppm, suggesting that part of the oligomers contained an octyl group at the α−end. It should be noted that

Chart 1





poly(3-PPA) obtained with the OctMgBr−Sp complex (run 6 in Table 2) did not exhibit such resonances at around 0.8−1.3 ppm in its ^{1}H NMR spectrum. The oligo(3-PPA) was further separated by GPC and HPLC on a silica gel column using chloroform as the eluent to remove 3-phenylpropyl 3-phenylpropanoate and fractionate low molecular weight oligomers. The FD mass spectrum of the low molecular weight fraction showed a peak at m/z 380 ($M^+ - 1$) corresponding to the molecular weight of the oligomer with the structure shown below, suggesting that the oligomer contained an octyl group at the α-end and the ester terminal at the ω-end. Other low molecular weight oligomers detected included **1**−**3** in Figure 5.



From the results obtained above, the mechanism of polymerization with the OctMgBr−Sp complex can be described as in Chart 1. A small amount of the OctMgBr−Sp complex initiates the polymerization of 3-PPA to afford an oligomer anion (A), which is terminated by the Tishchenko-type reaction with 3-PPA to give an oligomer having the ester terminal at the ω-end (C) and 3-(phenylpropoxy)magnesium bromide−Sp complex (B). The resulting 3-(phenylpropoxy)magnesium bromide−Sp complex initiates the polymerization to give optically active poly(3-PPA). The propagation will be terminated by the Tishchenko-type reaction again to afford poly(3-PPA) having the 3-phenylpropoxy group at the α-end and the ester terminal at the ω-end and also (3-phenylpropoxy)magnesium bromide−Sp (B) in a cyclic mechanism. This cyclic mechanism may also operate for the EtMgBr−Sp system.

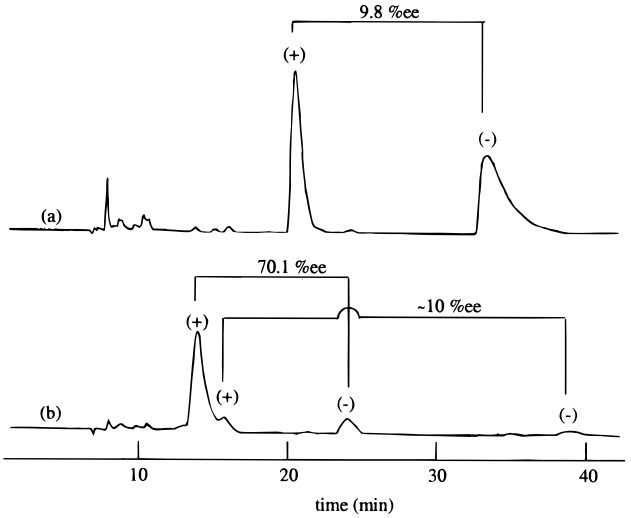


Figure 6. Resolution of **2** (a) and **3** (b) in Figure 5 on cellulose tris[(3,5-dimethylphenyl)carbamate]. Column, 25 × 0.46 (i.d.) cm; eluent, hexane/2-propanol = 90/10; flow rate, 0.5 mL/min.

Resolution of Oligomers. Figure 6 shows the chromatograms for the resolution of the oligomers (**2** and **3** in Figure 5) obtained from the oligomerization. The oligomers **2** and **3** were successfully separated into optical isomers by using a chiral HPLC column packed with cellulose tris[(3,5-dimethylphenyl)carbamate].[13] The oligomer **2** having an asymmetric carbon was completely resolved into two enantiomers and **3** into four isomers. Although the absolute configuration has not been determined, the enantiomeric pairs of **3** can be assigned based on the sign of rotation and peak areas of four isomers because the ratio of meso and racemo diastereomers was 85/15 as described previously. Enantiomeric excess (ee) of **1** was low (*ca.* 10%; rich in (−)-isomer), while the ees of the diastereomers (meso and racemo) were 70.1% and 10% (rich in (+)-isomer). The high ee of a diastereomer may suggest that a certain oligomer anion with a configuration, for instance, *SS* or *RR*, may propagate preferentially to higher molecular weight oligomers and polymers to show optical activity. Such a mechanism has been realized in the asymmetric polymerization of TrMA by the complexes of organolithiums with Sp or other chiral ligands.[2c] For further discussion, full assignments of the configuration of oligomers by means of X-ray[10] may be useful.

Experimental Section

Materials. 3-Phenylpropanal (Tokyo Kasei) was dried over CaH_2 for 2 h with stirring and distilled under reduced pressure (bp 104−105 °C/13 mmHg). The purity was determined to be more than 99.8% by gas chromatography. EtMgBr was prepared by a usual method using magnesium and ethyl bromide in dry ether under nitrogen, and its concentration was determined to be 0.92 M by acid and base titration. Other Grignard reagents used in this study were also prepared by a similar method. Toluene was purified in the usual manner, mixed with a small amount of butyllithium, and distilled under high vacuum just before use. Sparteine (Sigma) was dried over CaH_2 for 2 h with stirring and distilled under reduced pressure (bp 92.0−93.5 °C/0.06 mmHg). The Grignard reagent−Sp complexes were prepared by mixing the Grignard reagent with 1.2 equiv of Sp in toluene at room temperature under dry nitrogen, and the concentration of the Grignard reagent was adjusted to 0.30 M.

Polymerization Procedure. Polymerization was carried out in a glass ampule under dry nitrogen atmosphere. After

the ampule was evacuated on a vacuum line and flushed with dry nitrogen, a three-way stopcock was attached to the ampule, and toluene (1−10 mL) and 3-PPA (1.0 g, 7.5 mmol) were added with a hypodermic syringe. The monomer solution was then cooled to −78 or −98 °C, and the prescribed initiator solution was added to the mixture to initiate the polymerization with a syringe; the molar ratio of monomer to EtMgBr was 50. The reaction was terminated with a few drops of methanol containing a small amount of HCl. The polymer was precipitated in a large amount of methanol, separated by centrifugation, and dried in vacuo at 50 °C for 3 h.

Measurements. One-dimensional ^{1}H- and ^{13}C NMR and two-dimensional COSY spectra were taken on a Varian XL500S (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) spectrometer in $CDCl_3$. Tetramethylsilane (TMS) was used as an internal standard. IR spectra were recorded using a Jasco fourier transform IR-7000 spectrophotometer with a Jasco PTL-396 data processor. Field desorption (FD) and GC mass spectra were recorded on a Jeol JMS-AX505HA spectrometer. Optical rotation was measured with a Jasco DIP-181 polarimeter. UV spectra were recorded in THF solutions on a Jasco Ubest-55 spectrophotometer. Gel permeation chromatography (GPC) was performed using a Jasco 880-PU chromatograph equipped with UV−visible (254 nm; Jasco 875-UV) and polarimetric (Jasco DIP-181C) detectors. GPC columns, Shodex KF-802.5 (30 × 0.72 (i.d.) cm) and AC-80 (50 × 0.72 (i.d.) cm), or a column packed with poly[styrene-*co*-(*p*-divinylbenzene)] gel (50 × 0.72 (i.d.) cm, maximum porosity 3000) was connected in series, and chloroform was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with standard polystyrenes or oligostyrenes (Tosoh). Supercritical fluid chromatography (SFC) was performed on a Jasco Super-200 chromatograph equipped with a column oven and two pumps: one for the delivery of liquefied CO_2 as a mobile phase (flow rate, 2.4 mL/min), and the other for the delivery of ethanol as a modifier (flow rate, 0.4 mL/min). A column (25 × 0.46 (i.d.) cm) packed with silica gel (Develosil 100-5, Nomula Chemical Co., particle size 5 μm) was used. The fluid pressure was controlled by a back-pressure regulator to 204 kg/cm^2. The column temperature was adjusted to 40 °C. Chromatograms were recorded with a UV detector operated at a wavelength of 220 or 240 nm. Resolution of oligomers was carried out on a Jasco Trirotar-II liquid chromatograph equipped with UV−visible and polarimetric detectors by using a chiral column packed with cellulose tris[(3,5-dimethylphenyl)carbamate]-coated macroporous silica gel,[13] and a hexane-2-propanol mixture was used as the eluent.

Spectroscopic Data of Oligomers of 1−3 Shown in Figure 5. 1: ^{1}H NMR ($CDCl_3$, TMS) δ 7.35−7.26 (m, 10H, Ph), 4.05 (t, 2H, -CH_2-O-), 2.98 (t, 2H, CO-CH_2-), 2.61 (m, 4H, Ph-CH_2-), 1.98 (m, 2H, -CH_2-); ^{13}C NMR ($CDCl_3$) δ 172.43, 141.74, 141.29, 128.46, 128.38, 128.35, 128.25, 126.23, 125.95, 63.74, 35.83, 32.10, 30.93, 30.13; IR (KBr) 1736 (CO) cm^{-1}; FD-MS *m*/*z* 268.2 (M$^+$), 134.1.

2: ^{1}H NMR ($CDCl_3$, TMS) δ 7.35−7.26 (m, 15H, Ph), 5.82 (t, 1H, -O-CH-O-), 3.58 and 3.40 (t, 2H, -CH_2-O-), 2.98 (t, 2H, -CO-CH_2-), 2.61 (m, 6H, Ph-CH_2-), 2.01 (m, 2H, -CH_2-), 1.98 (m, 2H, -CH_2-); ^{13}C NMR ($CDCl_3$) δ 172.43, 141.57, 141.05, 140.20, 128.49, 128.44, 128.41, 128.34, 128.31, 128.29, 126.30, 125.98, 125.85, 98.14, 68.39, 35.94, 35.87, 32.28, 31.06, 30.81, 30.22; IR (KBr) 1736 (CO) cm^{-1}; FD-MS *m*/*z* 402.2 (M$^+$), 252.2, 134.1.

3: ^{1}H NMR ($CDCl_3$, TMS; the chemical shifts due to a minor diastereomer are shown in parentheses) δ 7.35−7.26 (m, 20H, Ph), 6.08 (5.98) (t, 1H, -O-CH-O-), 4.66 (4.59) (t, 1H, -O-CH-O-), 3.58 and 3.40 (t, 2H, CH_2-O-), 2.98 (t, 2H, CO-CH_2-), 2.61-(m, 8H, Ph-CH_2-), 2.01 (m, 2H, -CH_2-), 1.98 (m, 4H, -CH_2-); ^{13}C NMR ($CDCl_3$) δ 172.42 (172.25), 141.73 (141.77), 141.57 (141.37), 141.05 (140.92), 140.21 (140.22), 128.52, 128.44, 128.40, 128.38, 128.36, 128.35, 128.32, 128.27, 126.35, 125.98, 125.88, 125.85, 10l.93 (103.11), 95.28 (94.85), 65.71 (66.47), 36.05 (36.17), 35.89, 35.86, 32.32 (32.40), 31.37 (31.20), 30.72 (30.70), 30.44 (30.53), 30.04 (30.09); IR (KBr) 1738 (CO) cm^{-1}; FD-MS *m*/*z* 535.2 (M$^+$ − 1), 388.2, 252.1, 134.1.

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