

# Synthesis and propeller-propeller transition of optically active poly(diphenyl-*o*-methoxyphenylmethyl methacrylate)

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Diphenyl-*o*-methoxyphenylmethyl methacrylate was polymerized with several organolithium complexes of chiral ligand such as (–)-sparteine (Sp) and (S,S)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB). (+)-DDB was effective in preparing a polymer of high optical rotation, whereas (–)-Sp only gave oligomers with low optical rotation for the repulsive hindrance between the bulky ester group and the rigid ligand. The optical rotation of the polymer decreased rapidly to a constant value due to the propeller-propeller transition, which has been demonstrated by <sup>1</sup>H n.m.r. and circular dichroic spectra.

(Keywords: poly(diphenyl-*o*-methoxyphenylmethyl methacrylate); chirality; propeller-propeller transition)

## INTRODUCTION

Bulky triphenylmethyl methacrylate (TrMA) and analogues are special monomers which can give isotactic, one-handed-screw-type helical polymers by asymmetric polymerization<sup>1</sup>. The helical structures are stable even in solution because of the bulkiness of the ester groups. Optically active poly(triphenylmethyl methacrylate) (PTrMA) is known to be useful in resolving many racemic compounds which are usually difficult to resolve by conventional methods<sup>2</sup>.

Recently, a novel optically active poly(diphenyl-*o*-tolylmethyl methacrylate) (PDPTMA) was synthesized and a stereomutation due to the propeller-propeller transition was found for the first time<sup>3</sup>. In order to clarify this kind of mutarotation, we synthesized a new optically active poly(diphenyl-*o*-methoxyphenylmethyl methacrylate) (PDPMA) and found direct evidence for the transition by <sup>1</sup>H n.m.r.

## EXPERIMENTAL

Diphenyl-*o*-methoxyphenylmethyl methacrylate (DPMMA) was synthesized by the reaction of methacrylic acid with diphenyl-*o*-methoxyphenylmethyl chloride<sup>4</sup> which was prepared from methoxyphenyl magnesium chloride and benzophenone and purified by recrystallization from a mixture of ether and petroleum (1:1). M.p. 110–111°C; <sup>1</sup>H n.m.r. (C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 25°C): 1.936 (s, 3H, C=C–CH<sub>3</sub>), 3.266 (s, 3H, OCH<sub>3</sub>), 5.463 and 6.212 (m, 2H, C=CH<sub>2</sub>), 6.649–7.470 (m, 14H, aromatic-H). The other materials were obtained by the procedures reported previously<sup>3</sup>.

Polymerization was carried out in dry toluene at –74°C under nitrogen in a glass ampoule. An anionic initiator such as fluoryllithium-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane or butyllithium-(–)-sparteine, was added to the monomer solution. The polymerization

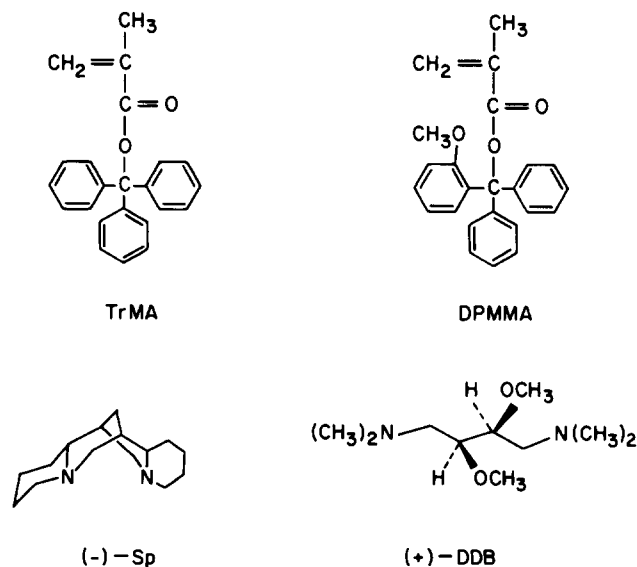
was terminated with a small amount of methanol and the polymer was precipitated in methanol and collected by centrifugation.

Optical rotation was measured in dry tetrahydrofuran (THF) on a Perkin-Elmer 241 polarimeter at 20°C. Circular dichroic spectra were recorded in dry THF using Jasco J500C apparatus. <sup>1</sup>H n.m.r. spectra were obtained in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> or dry CD<sub>2</sub>Br<sub>2</sub> by a Unity 400 spectrometer at 25°C.

## RESULTS AND DISCUSSION

### Polymerization

Table 1 shows the results of the asymmetric polymerization of DPMMA with (S,S)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB) or (–)-sparteine (Sp) as the chiral ligand. Optically active



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**Table 1** Asymmetric polymerization of DPMMA in toluene at  $-74^{\circ}\text{C}^{\text{a}}$ 

No.	Initiator	Time (h)	Yield (%)	$[\alpha]_{\text{D}}^{25\text{b}}$ (deg)	
				B-P <sup>c</sup> insoluble	B-P <sup>c</sup> soluble
1	FILi-(+)-DDB	4.5	100	+339	+295 <sup>d</sup>
2	Ph <sub>2</sub> NLi-(+)-DDB	6	60	+256	+25
3	BuLi-(+)-DDB	6	60	+265	–
4	t-BuLi-(+)-DDB	6	30	+256	+57
5	BuLi-(+)-Sp	9	15	–	+23
6	FILi-(–)-Sp	9	15	–	+33

<sup>a</sup> Monomer 1 g, toluene, 20 ml,  $[\text{M}]/[\text{I}] = 20$ ,  $[\text{ligand}]/[\text{Li}] = 1.2$

<sup>b</sup> In THF

<sup>c</sup> Mixture of benzene and petroleum (1:1, v/v)

<sup>d</sup> Mixed with some high-molecular-weight polymer

polymers were obtained in each case. The chirality of DPMMA must arise from the prevailing one-handed helical conformation of the main chain as well as the chiral propeller structure of the ester group, as observed for PTrMA and PDPTMA.

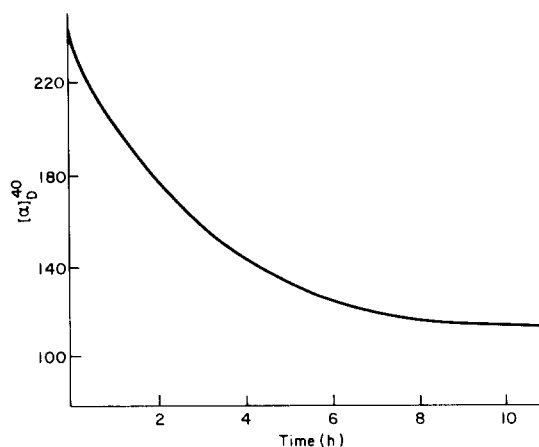
The optical rotation of PDPMMA depended greatly on the chiral ligand used. (+)-DDB gave polymers with high optical rotation, whereas when (–)-Sp was used, only low-molecular-weight polymers soluble in a mixture of benzene and petroleum were formed in rather low yield. This suggested that the introduction of a methoxy group to the phenyl ring increased the repulsive hindrance between the bulky triarylmethyl group and the rigid ligand, especially for (–)-Sp, and thus prevented the molecular weight of the polymer from increasing. A similar situation has been observed for PDPTMA<sup>3</sup>. Based on the signs of the rotation, PDPMMA showed the same screw-sense helical conformation as PTrMA and PDPTMA when (+)-DDB or (–)-Sp was used as the chiral ligand.

#### Propeller–propeller transition

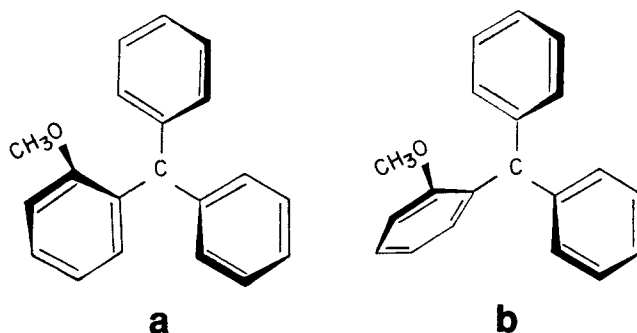
In contrast to PTrMA, which has been proved to show good stability of optical activity<sup>5</sup>, the specific rotation of PDPMMA in THF solution changed greatly, even more than that of PDPTMA<sup>3</sup>. Figure 1 shows the change of optical rotation of polymer no. 3 (Table 1). The THF solution first showed  $[\alpha]_{\text{D}}^{40} = +246^{\circ}$ , then the value decreased rapidly during the early period. A constant value was reached after about 10 h.

This change in rotation must be attributed to a conformational change in either the helical chain or the propeller structure. Apparently, the possibility of helix–coil or helix–helix transition could be ruled out, since after the change, the optical rotation of the polymer was neither zero nor a negative value. Thus, the only reason for the rotational change must be the propeller–propeller transition of the ester group, just as we have discussed for the case of PDPTMA.

The triphenylmethyl group in (+)-PTrMA can be assumed to be a left-handed helical structure, which was determined by the chiral ligand<sup>6</sup>. Such a chiral propeller structure has been demonstrated by empirical force field calculation<sup>7,8</sup> and the dihedral angle formed by the planes of the phenyl rings was calculated to be  $35.7^{\circ}$  for the most stable structure of triphenylmethane<sup>7</sup>. During the polymerization of DPMMA, the existence of the chiral ligand tended to give a propeller structure with equal

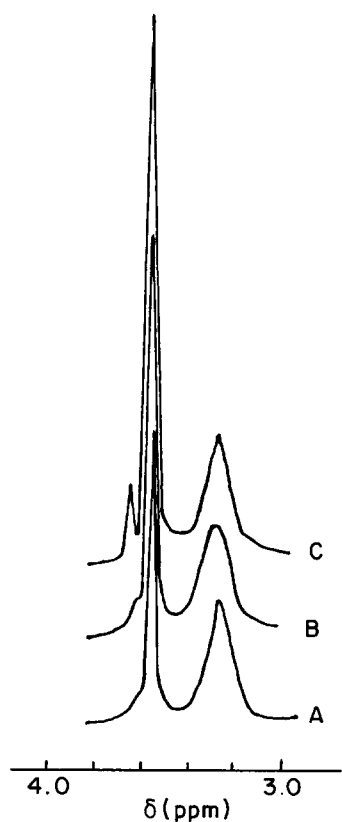


**Figure 1** Change of optical rotation of PDPMMA (no. 3 in Table 1) in dry THF at  $40^{\circ}\text{C}$



**Figure 2** Two possible propeller structures of the triarylmethyl group in PDPMMA: (a) kinetically favoured isomer, A; (b) thermodynamically preferred isomer, B

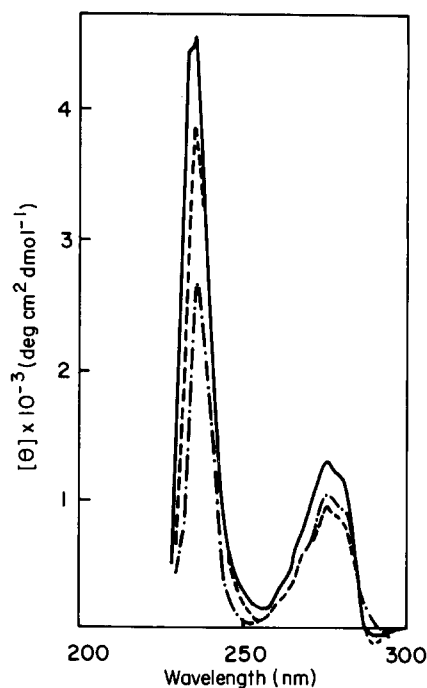
dihedral angles, similarly to that of PTrMA<sup>9</sup>. Such a conformational isomer was kinetically favoured during chain propagation. However, the thermodynamically preferred conformation of the propeller structure for PDPMMA must be a more upright position of the methoxy-substituted phenyl ring, for the steric hindrance of the methoxy group, as illustrated in Figure 2. This conformational isomer would lead to a decrease in the observed optical rotation, which can be deduced from Figure 1. Therefore, when PDPMMA was dissolved in THF solution free of chiral ligand, the kinetically favoured propeller would be transformed to the



**Figure 3**  $^1\text{H}$  n.m.r. spectra of PDPMMA (no. 1 in Table 1) in the range of 3–4 ppm in  $\text{CD}_2\text{Br}_2$  at  $25^\circ\text{C}$ . The ratio of the strength of the peak at low field to that up-field was: A, 0.63; B, 0.70; C, 0.73

thermodynamically preferred isomer; it was this kind of propeller–propeller transition which caused the change of the specific rotation of PDPMMA.

The propeller–propeller transition of PDPMMA was monitored by means of  $^1\text{H}$  n.m.r. spectra. The results are shown in Figure 3. There were two peaks, at 3.55 ppm and 3.27 ppm, arising from the methoxy connected to the phenyl ring, as observed in poly(4-methoxyphenyl isocyanide)<sup>10</sup>. With time, the signal at 3.55 ppm increased while that at 3.27 ppm decreased. The ratio of the strength of the peak at 3.55 ppm to that at 3.27 ppm increased from 0.63 to 0.73 with time. As can be seen in Figure 2, the methoxy proton in the thermodynamically stable propeller structure (B) was less shielded by the other phenyl ring than that in the kinetically favoured isomer (A). So the peak at low field can be assigned to the methoxy protons in the B isomer and the up-field peak to the methoxy protons in the A isomer. The change in strength of the peaks reflected the equilibrium shift of the two isomers. This has been considered as direct evidence for propeller–propeller transition.



**Figure 4** Change of circular dichroic spectra of PDPMMA (no. 1 in Table 1) in dry THF at  $40^\circ\text{C}$ . —, As soon as the polymer dissolved; ---, 20 min later; - · - ·, 14 h later

The circular dichroic spectra of PDPMMA further confirmed the propeller–propeller transition. The peak at around 240 nm, arising from the adsorption of the phenyl ring, decreased with time (Figure 4). However, the spectral pattern was not reversed, so only the propeller conformation was changed.

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