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ASYMMETRIC POLYMERIZATION OF N-DIPHENYLMETHYLMALEIMIDE WITH CHIRAL ANIONIC INITIATORS

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ABSTRACT

Asymmetric polymerization of *N*-diphenylmethylmaleimide was performed with chiral anionic initiators in toluene at -78 and 0°C to obtain optically active polymer. The polymer obtained with (–)-sparteine-fluorenyllithium complex [(–)Sp-FILi] showed high positive specific rotation ($[\alpha]_{\text{D}}^{20} = +64^{\circ}$ in chloroform), and the polymer obtained with (S)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine-*N,N'*-diphenylethylenediaminelithium [(+)PMP-DPEDALi] complex showed negative specific rotation ($[\alpha]_{\text{D}}^{20} = -37.2^{\circ}$ in chloroform). The polymers obtained with (–)Sp-FILi and (+)PMP-DPEDALi were characterized by circular dichroism and NMR spectra. The optical activity of the polymer might be mainly attributed to the chiral *trans* structure of the main chain.

INTRODUCTION

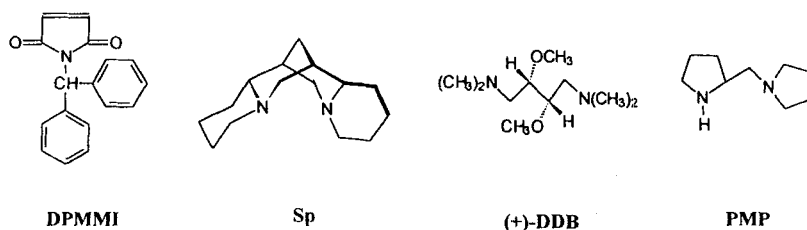
Various optically active polymers with chirality mainly due to the helical conformation have been attracting great attention [1]. The helical polymers have been obtained through asymmetric polymerizations of many nonchiral monomers [1, 2] such as methacrylates, acrylate, acrylamides, isocyanides, isocyanotes, chloral, propylene, and phenylacetylene. Helical polymers were also recently obtained by

radical polymerization of nonchiral monomers in chiral solvent [3] as well as by radical polymerization and copolymerization of chiral monomers [4]. Several kinds of helical polymers show excellent chiral recognition ability for many racemic compounds and have been used as a chiral stationary phase for high-performance liquid chromatography (HPLC) [5–8]. The optically active poly(*N*-substituted maleimide)s have been obtained by polymerization and copolymerization of optically active *N*-substituted maleimide monomers (RMI) [9, 10], radical copolymerizations of nonchiral RMI monomers with styrene in chiral solvents [11], and asymmetric polymerization of nonchiral RMI monomers performed with *n*-butyllithium (*n*BuLi)/(–)-sparteine (Sp) [12, 13]. In the second case, the optical activity is attributed to asymmetric induction to the copolymer main chain, and the specific rotation of the copolymers obtained is generally low. In the third case, the optical activity of the RMI polymers may be ascribed not only to the helical structure but also to the excessive chiral centers of (*S,S*) or (*R,R*) formed by *trans* opening of the double bond. Up to now, the detailed mechanism by which stereoselective polymerization occurs has not been very clear. In order to investigate the influence of initiators and structure of monomers on the optical activity of polymers, we intend to synthesize a series of monomers containing different bulky side group such as *N*-benzylmaleimide, *N*-diphenylmethylmaleimide, and *N*-triphenylmethylmaleimide. In the present study a novel monomer, *N*-diphenylmethylmaleimide (DPMMI), is synthesized from maleic anhydride and diphenylmethylamine. The asymmetric polymerization is performed with complexes of organolithiums with (–)-sparteine [(–)Sp], (*S,S*-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butanes [(+)-DDB] and (*S*)-(+)-1-(2-pyrrolidinylmethyl) pyrrolidine [(+)-PMP] to obtain optically active polymers. See Scheme 1.

EXPERIMENTAL

Materials

Sp (Sigma Chemical Co.), DDB (Aldrich Chemical Co.), and PMP (Aldrich Chemical Co.) were dried over calcium hydride and distilled under reduced pressure. Fluorene (Fl) (Aldrich Chemical Co.) was used as commercially available. *N,N'*-Diphenylethylenediamine (DPEDA) (Aldrich Chemical Co.) was recrystallized from hexane.



SCHEME 1.

Synthesis of DPMMI Monomer

DPMMI was prepared from maleic anhydride and diphenylmethylamine according to the usual methods described in the literature [14] as shown in Scheme 2. The crude product was recrystallized three times from ethanol to obtain pure DPMMI; yield, 36%; mp, 150–151°C. The DPMMI monomer was identified on the basis of elemental analysis and also IR and ¹H-NMR spectra.

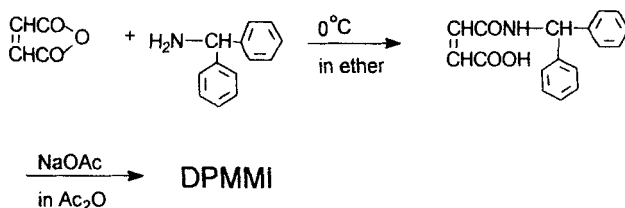
Elemental analysis. Found for C₁₇H₁₃NO₂: C 77.46%, H 5.18%, N 5.26%. Calculated: C 77.57%, H 4.94%, N 5.32%. ¹H NMR [δ in ppm from Si(CH₃)₄ in CDCl₃]: 7.30 (m, 10H in phenyl group), 6.75 (s, 2H, –CH=CH–), 6.50 (s, 1H, –CH–). IR spectrum (KBr pellet) [wave number (cm⁻¹): 3100, 1780, 1700, 1600, 1490, 1450, 820, 750, 700.

Polymerization Procedure

Fluorenyllithium (FLi) prepared from FI and butyllithium was mixed with (–)Sp in toluene to prepare the complex at room temperature. DPEDALi, prepared from DPEDA and butyllithium, was mixed with (+)DDB and (+)PMP, respectively [15]. The polymerization was carried out in toluene under dry nitrogen. An initiator solution was added to the monomer solution cooled to –78 or 0°C. The reaction was terminated with a small amount of methanol. The polymer was precipitated in a large amount of methanol containing a small amount of hydrochloric acid, collected by filtration or centrifugation, washed with methanol three times, and dried under vacuum at 55°C.

Measurements

Optical rotation was measured with a Perkin-Elmer 141 MC polarimeter using the 589 nm wavelength of a sodium lamp at 20°C. UV spectrum was recorded at room temperature in chloroform solution on a Shimadzu UV-3000 spectrophotometer. Circular dichroism (CD) spectra were recorded in a 0.1-cm cell at room temperature on a JASCO J-500C spectropolarimeter. ¹H-NMR spectra were measured in deuterium chloroform at room temperature with a Varian XL-200 spectrometer. The gel permeation chromatographic (GPC) analysis was accomplished on a Waters 201 with a μ-Styragel column and tetrahydrofuran as solvent, and the molecular weight was calibrated with standard polystyrene. The x-ray diffraction pattern was obtained on a Rigaku D/max-3B diffractometer with the 0.154 nm wavelength of CuKα radiation.



SCHEME 2.

RESULTS AND DISCUSSION

Table 1 shows the results of the asymmetric polymerization of DPMMI with the complexes of (–)Sp-FILi, (+)DDB-DPEDALi, and (+)PMP-DPEDALi, as well as radical polymerization with α,α' -azobisisobutyronitrile (AIBN). The polymerizations are homogeneous throughout at 0°C, but the polymerization becomes heterogeneous because of poor solubility of the monomer when polymerization is carried out at –78°C and the polymerization reaction is very slow. The conversion of monomer is relatively low and the polymers obtained show no optical activity. Okamoto et al. [12] reported that the polymerization of *N*-phenylmaleimide with (–)Sp-BuLi initiator complex in toluene gave levorotatory polymer. Contrary to the result of *N*-phenylmaleimide in stereoselectivity, dextrorotatory DPMMI polymer is obtained with a similar initiator system. When the polymerizations are carried out with (+)DDB and (+)PMP complexes in toluene, levorotatory polymers are obtained. The polymers are soluble in chloroform, tetrahydrofuran, and toluene. The specific rotation of the polymer in chloroform solution does not change with time.

The molecular weights of the polymers calibrated by polystyrene standards are rather low as shown in Table 1, and the molecular weight distributions are substantially broad. This result is similar to that of anionic polymerization of *N*- α -methylbenzylmaleimide [10]. The polymers obtained with (+)DDB-DPEDALi and (+)PMP-DPEDALi have somewhat higher molecular weights than the polymers obtained with (–)Sp-FILi. The results of the obvious low molecular weight and broad distribution could arise from some side reactions such as an attack of the propagating carbanions on the carbonyl groups. Besides, it is estimated that the calibration method of GPC by using a polystyrene standard is not very appropriate for these RMI polymers and results in some deviations.

UV spectrum for poly(DPMMI) was measured in chloroform solution and shown in Fig. 1. The UV curve shows a broad absorption from 240 to 280 nm which may be due to carbonyl groups in the imide ring and phenyl groups.

CD spectrum for the (–)poly(DPMMI) obtained with (+)PMP-DPEDALi was measured in chloroform, and a broad negative absorption was observed at about 247 nm, as shown in Fig. 1. The CD spectra for the (+)poly(DPMMI) obtained with (–)Sp-FILi were also measured in different solvents, and a broad positive absorption at about 248 nm opposite the absorption of (–)poly(DPMMI) was observed in tetrahydrofuran, chloroform, and dichloromethane. The absorptions are attributable to the $n \rightarrow \pi^*$ transition of two carbonyl groups in the imide ring and the $\pi \rightarrow \pi^*$ transition of the phenyl groups.

The DPMMI polymers obtained in toluene with chiral anionic and radical initiators indicate different ¹H-NMR spectra in deuterium chloroform as shown in Fig. 2. The signals assigned to H in the main chain for the (a) polymer obtained with (–)Sp-FILi and the (b) polymer obtained with (+)PMP-DPEDALi show a sharp absorption at 3.70 ppm, but that for (c) polymer obtained with radical initiator shows a broad absorption at about 3.50 ppm. This suggests that (+)poly(DPMMI) and (–)poly(DPMMI) have the same main chain structures, and the polymer obtained by anionic polymerization has a higher stereoregularity than that obtained by radical polymerization. According to Cubbon's report [16], three types of polymer can be formed due to *trans* opening of the double bonds: 1) all the rings

TABLE 1. Polymerization of DPMMI in Toluene^a

Run	Initiator	[DPMMI]/ [Initiator]	Temperature, °C	Time, hours	Yield, %	$M_w \times 10^{-3}$	M_w/M_n	$[\alpha]_D^{20}$ ^b
1	(-)Sp-FILi	20	-78	24	24	2.59	4.0	0°
2	(-)Sp-FILi	40	-78	2	16	—	—	0°
3 ^c	(-)Sp-FILi	20	0	0.5	32	3.68	4.1	+7.5°
4	(-)Sp-FILi	10	0	24	93	4.25	3.6	+28°
5	(-)Sp-FILi	20	0	24	60	4.40	3.4	+32°
6	(-)Sp-FILi	30	0	48	40 ^d	4.50	2.9	+64°
7	(+)DDB-DPEDALI	20	0	24	68	—	—	+5.7°
8	(+)PMP-DPEDALI	20	0	24	68	12.32	3.8	-8.2°
9	AIBN	100	60	24	12	8.96	4.1	-37.2°

^a Conditions: DPMMI, 0.5 g; toluene, 10 mL; [ligand]/[Li] = 1.2.^b Measured in chloroform.^c Polymerization was initiated at -78°C and maintained at this temperature for 2 hours. The temperature of polymerization was then increased to 0°C.^d Chloroform-methanol (2/8, v/v) insoluble and soluble part, respectively.

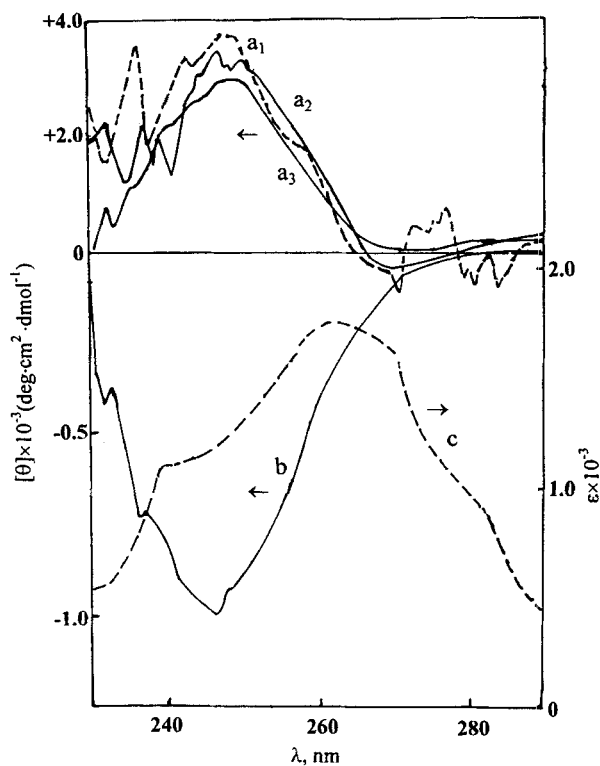


FIG. 1. CD spectra for (+)poly(DPMMI) (Expt. 6): (a₁) $c = 0.10 \text{ g} \cdot \text{L}^{-1}$ in THF, (a₂) $c = 0.10 \text{ g} \cdot \text{L}^{-1}$ in CHCl_3 , (a₃) $c = 0.10 \text{ g} \cdot \text{L}^{-1}$ in CH_2Cl_2 ; (b) Expt. 8, $c = 2.5 \text{ g} \cdot \text{L}^{-1}$ in CHCl_3 ; and (c) UV spectrum for the polymer in CHCl_3 .

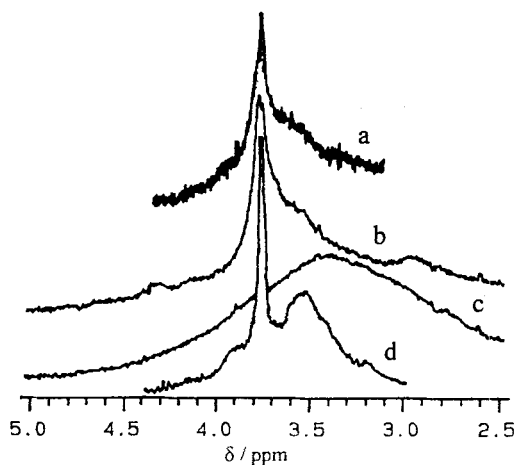


FIG. 2. ^1H -NMR spectra of poly(DPMMI) obtained with chiral anionic initiator: (a) Expt. 5; (b) Expt. 8, radical initiator; (c) Expt. 9; and (d) the soluble part of the polymer (Expt. 6e) in chloroform-methanol (2/8 v/v).

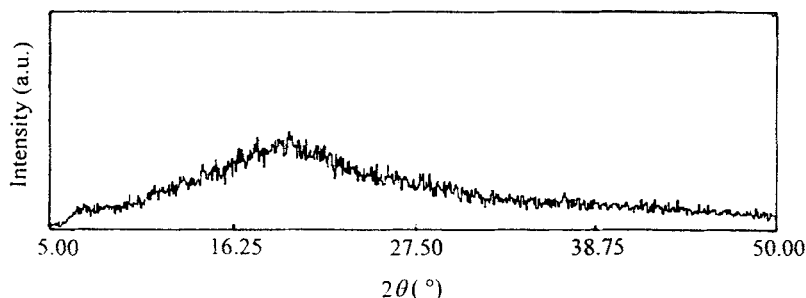


FIG. 3. X-ray powder pattern of poly(DPMMI) (Expt. 4).

are on the same side of the backbone chain (threo-diisotactic polymer), 2) the rings are on alternate sides of the backbone chain (threo-disyndiotactic polymer), and 3) the rings may be randomly distributed on either side of the backbone chain. The (+)poly(DPMMI) and (–)poly(DPMMI) might be formed with threo-diisotactic or threo-disyndiotactic stereostructure, and the polymer obtained by radical polymerization could be atactic.

The x-ray diffraction pattern of powder samples of (+)poly(DPMMI) is shown in Fig. 3. The (+)poly(DPMMI) was found to be amorphous. It seems likely that the polymer is predominantly threo-disyndiotactic because threo-disyndiotactic placements might disrupt the crystallinity [16].

The structure of the soluble part of the polymer (Expt. 6e) in chloroform-methanol (2/8 v/v), which shows low optical activity ($[\alpha]_D^{20} = +5.7^\circ$ in CHCl_3) was assigned by ^1H NMR. As shown in Fig. 2(d), this oligomer shows not only a sharp absorption at 3.70 ppm but also a broad absorption at about 3.50 ppm. This suggests that this oligomer as formed in anionic polymerization is partly of atactic structure, similar to that obtained by radical polymerization. Oishi et al. reported that degrees of polymerization of *N*-2-fluorenyl maleimide (FMI) ($\text{DP} = 7$) and *N*-1-naphthyl maleimide (NMI) ($\text{DP} = 9$) obtained with (–)Sp-BuLi may not be enough to form a helical structure or these polymers may contain the chiral centers of (*S,S*) almost similar to those of (*R,R*), so both specific rotations of FMI and NMI polymers were almost zero [13]. In the case of DPMMI polymerization with (–)Sp-FiLi, the polymers obtained still exhibit some optical activities in spite of their low degree of polymerization. The possibility of chirality formed by asymmetric conformation seems to be low because the degree of polymerization may not be enough to form a perfect helical structure. The chirality is considered in this case to be mainly attributable to the excessive chiral center of (*R,R*) or (*S,S*) formed in the main chain by asymmetric *trans* opening of double bond.

Optically active RMI polymers have recently been used in our laboratory as a chiral stationary phase for high-performance liquid chromatography (HPLC). The poly(DPMMI) shows a good chiral recognition ability for many racemic compounds, but the poly(*N*-phenylmaleimide) shows no chiral recognition ability. The details will be reported elsewhere.

REFERENCES

- [1] M. Farina, *Top. Stereochem.*, **17**, 1 (1987); G. Wulff, *Angew. Chem. Int. Ed. Engl.*, **28**, 21 (1989); Y. Okamoto and E. Yashima, *Prog. Polym. Sci.*, **15**, 263 (1990); Y. Okamoto and T. Nakano, *Chem. Rev.*, **94**, 349 (1994).
- [2] E. Yashima, S. Huang, and Y. Okamoto, *J. Chem. Soc. Chem. Commun.*, p. 1811 (1994); T. Aoki, M. Kokai, K. Shinohara, and E. Oikawa, *Chem. Lett.*, p. 2009 (1993); S. Habue, T. Tanaka, and Y. Okamoto, *Macromolecules*, **28**, 5973 (1995); T. Nakano, Y. Okamoto, and K. Hatada, *Polym. J.*, **27**, 882 (1995).
- [3] Y. Okamoto, T. Nakano, Y. Shikisai, and A. Mutsuda, *Polym. Prepr.*, **35**, 591 (1994).
- [4] Y. Okamoto, M. Nishikawa, T. Nakano, E. Yashima, and K. Hatada, *Macromolecules*, **28**, 5135 (1995); T. Nakano, Y. Okamoto, D. Y. Sogah, and S. Zheng, *Ibid.*, **28**, 8705 (1995).
- [5] Y. Okamoto and K. Hatada, *J. Liq. Chromatogr.*, **9**, 369 (1986); Y. Okamoto and K. Hatada, in *Chromatographic Chiral Separations* (M. Zief and L. J. Crane, Eds.), Dekker; New York, NY, 1988, p. 199.
- [6] Y. Okamoto, S. Honda, I. Okamoto, H. Yuki, S. Murata, R. Noyori, and H. Takaya, *J. Am. Chem. Soc.*, **103**, 6971 (1981).
- [7] Y. Okamoto, H. Mohri, and K. Hatada, *Polym. J.*, **21**, 439 (1989).
- [8] C. Ren, C. Chen, F. Xi, T. Nakano, and Y. Okamoto, *J. Polym. Sci., Part A, Polym. Chem.*, **31**, 2721 (1993).
- [9] T. Oishi, N. Okamoto, and M. Fujimoto, *Ibid.*, **24**, 1185 (1986); *J. Macromol. Sci.—Chem.*, **A25**, 1039 (1988); H. Yamaguchi and Y. Minoura, *J. Polym. Sci., Part A*, **8**, 929 (1970); T. Oishi and M. Fujimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1821 (1992); K. Kagawa and T. Oishi, *Polym. J.*, **27**, 579 (1995); T. Oishi, K. Kagawa and M. Fujimoto, *J. Polym. Sci., Polym. Chem.*, **33**, 1341 (1995).
- [10] T. Oishi and M. Fujimoto, *J. Polym. Sci., Polym. Chem.*, **22**, 2789 (1984).
- [11] M. Yoshihara, J. Asakura, H. Takahashi, and T. Maeshima, *J. Macromol. Sci.—Chem.*, **A20**, 123 (1983).
- [12] Y. Okamoto, T. Nakano, H. Kobayashi, and K. Hatada, *Polym. Bull.*, **25**, 5 (1991).
- [13] T. Oishi, H. Yamasaki, and M. Fujimoto, *Polym. J.*, **23**, 795 (1991).
- [14] L. E. Coleman Jr., J. F. Bork, and H. Dunn Jr., *J. Org. Chem.*, **24**, 135 (1959); N. B. Mehta, P. A. Phillips, F. F. Liu, and R. E. Brooks, *Ibid.*, **25**, 1012 (1960).
- [15] T. Nakano, Y. Okamoto, and K. Hatada, *J. Am. Chem. Soc.*, **114**, 1318 (1992).
- [16] R. C. P. Cubbon, *Polymer*, **6**, 419 (1965).

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