

Asymmetric polymerization of *N*-phenylmaleimide*

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Summary

Asymmetric polymerization of *N*-phenylmaleimide was carried out with the complexes of butyllithium and chiral ligands and optically active polymers were obtained. The optical activity of the polymers should be based on the chiral trans structure of the main chain.

Introduction

There are many reports on the asymmetric polymerization and copolymerization of cyclic olefins (1). However, most of the studies on homopolymerization deal with the monomers which have no C_2 axis of symmetry such as benzofuran (2,3). Studies on the polymerization of monomers with a C_2 axis of symmetry are limited to copolymerization with other monomers, although the possibility of the formation of an optically active homopolymer from a monomer with a C_2 axis of symmetry has been pointed out (4). In the present study, anionic homopolymerization of *N*-phenylmaleimide (PMI) was carried out with the complexes of butyllithium (*n*-BuLi) with chiral ligands to obtain an optically active polymer. This may be the first clear example of optically active homopolymer from a cyclic olefin which has a C_2 axis of symmetry. PMI is known to be polymerized with an anionic initiator (5). Recently, Oishi and co-workers also briefly reported on the asymmetric polymerization of the *N*-substituted maleimides including PMI with the complex of *n*-BuLi and (-)-sparteine (Sp) (6).

Experimental

PMI (Aldrich) was recrystallized from a 1:1 (vol/vol) mixture of hexane and toluene; m.p. 89-90°C. *n*-BuLi was prepared from butyl chloride and lithium powder in heptane. Vitride (sodium bis(2-methoxyethoxy)aluminum hydride) (Nacalai Tesque) was obtained as a toluene solution and used without further purification. Sp (Sigma) ($[\alpha]_D^{20}$ -17.8° (c 3.9, ethanol)) and (+)-(2S,3S)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB) (Aldrich) ($[\alpha]_D^{20}$ +23.4° (c 3.0, benzene))

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were dried over calcium hydride and distilled under reduced pressure. Preparation and purification of (-)-6-ethylsparteine (EtSp) ($[\alpha]_D^{20}$ -6.9° (c 1.7, ethanol) were described previously (7). *n*-BuLi was mixed with these ligands (1.2 equivalent of *n*-BuLi) in toluene to prepare complexes at room temperature. *n*-BuLi-Sp-CuI complex was prepared by adding CuI to the above complex. The polymerization was carried out in toluene or tetrahydrofuran under dry nitrogen. An initiator solution was added to the monomer solution cooled to -78°C. The reaction was terminated with a small amount of methanol. The polymer was precipitated in a large amount of methanol containing small amount of hydrochloric acid, separated by filtration, washed with methanol, and dried. GPC measurement of the polymer was done with a Shodex AC80M column, and the molecular weight was calibrated with standard polystyrene. ¹H NMR spectrum of the polymer was measured in chloroform-d₁ at 55 °C on a JNM-MH-100 (100MHz) spectrometer.

Results and discussion

The results of polymerization of PMI are shown in Table 1. In every case, an optically active polymer was obtained. The polymer was soluble in tetrahydrofuran and chloroform and insoluble in diethyl ether and toluene. The ¹H NMR of the polymer (No. 2) showed no peak at δ 1-2 ppm, indicating that the sample did not contain Sp. The GPC analysis of the polymer indicated the absence of low-molecular-weight oligomers. The polymer (No. 2) purified by reprecipitation from a chloroform

Table 1
Polymerization of PMI^a

Run No.	Initiator	Solvent	Temp. (°C)	Time (hr)	Yield (%)	$[\alpha]_{435}^{25}$ ^b
1	<i>n</i> -BuLi-Sp	toluene	-78	24	11	-9.4°
2	<i>n</i> -BuLi-Sp	toluene	0	1	17 ^c	-16.9°
3	<i>n</i> -BuLi-Sp	THF	0	1	79	-1.5°
4	<i>n</i> -BuLi-Sp-CuI	toluene	0	1	5	-23.7°
5	Vitride ^d -Sp	toluene	0	1	14	+1.6°
6	<i>n</i> -BuLi-EtSp	toluene	0	1	11	-16.2°
7	<i>n</i> -BuLi-DDB	toluene	0	1	13	+1.2°

^aPMI 1.0 g (5.8 mmol), initiator 0.12 mmol, solvent 20ml.

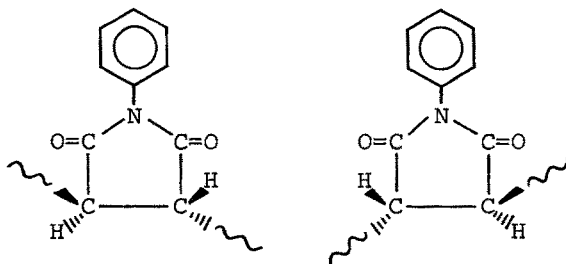
^bMeasured in chloroform, (c 1.0, 1 dm).

^cDegree of polymerization was 43.5 (M_n = 7530, M_w = 10460).

^dSodium bis(2-methoxyethoxy)aluminum hydride.

solution into methanol showed almost the same optical activity $[\alpha]_{435}^{25} -17.2^\circ$. These results indicate that the optical activity of the polymer sample was not due to the contamination of small molecules such as Sp. When the polymerization was carried out with Sp and EtSp complexes in toluene, levorotatory polymers with relatively high optical activity were obtained in rather low yields. Among these polymers, the one obtained with *n*-BuLi-Sp-CuI complex showed the highest optical rotation. Vitride-Sp initiator system did not afford the polymer with a high optical activity. Polymerization temperature also affected the optical rotation of the obtained polymer. The polymerization with *n*-BuLi-Sp complex in tetrahydrofuran afforded the polymer in a high yield, but optical rotation of the polymer was much smaller than that of the polymer obtained in toluene. *n*-BuLi-DDB complex was not effective.

The optical activity of the polymer obtained here is assumed to be due to mainly the chirality of the asymmetric center of the main chain. In the case of a polymer prepared from a cyclic olefin which has no C_2 symmetry axis, all the asymmetric centers of the main chain are the real chiral center, because the polymer has no plane of symmetry. But in the case of poly(PMI), if the double bond opens in "cis-fashion" in the process of the formation of polymer, a local plane of symmetry generates in the center of the monomeric unit, which may scarcely contribute to optical activity of the polymer. The chirality of asymmetric centers can contribute to the optical activity only if the double bond opens in "trans-fashion". Consequently, the probability of generation of an optically active polymer is lower in the case of PMI than in the cases of the other cyclic olefins without a C_2 axis of symmetry. The polymer obtained in the present study should have in excess one of two structures shown below. The ^1H NMR spectrum of the polymer (No. 2) showed broad peaks due to phenyl protons at δ 7.2 ppm and methine protons of main chain at δ 4 ppm, and detailed analysis of the polymer structure has not yet been attained. Chiral conformation such as helicity may contribute to the optical activity of the polymer, if the polymer has predominantly one of the two trans structures.



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