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Asymmetric polymerization of diphenyl-2-pyridylmethyl methacrylate leading to optically active polymer with high one-handed helicity

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SUMMARY

Diphenyl-2-pyridylmethyl methacrylate (D2PyMA) was polymerized with organolithium complexes of four novel chiral ligands (1-4) which were prepared from (+)-tartaric acid. The complexes of 3 and 4 gave the optically active poly(D2PyMA) with a highly one-handed helical structure. The fractionation of the polymer afforded the poly(D2PyMA) with almost pure one-handed helicity ($[\alpha]^{25}_{365} \sim -1400^{\circ}$) in good yield.

These chiral lithium complexes were not effective for the asymmetric polymerization of triphenylmethyl methacrylate.

INTRODUCTION

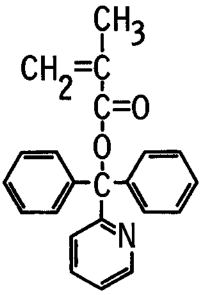
Diphenyl-2-pyridylmethyl methacrylate (D2PyMA) forms a highly isotactic polymer regardless of initiating species (1), as in the case of triphenylmethyl methacrylate (TrMA) (2). These monomers afford optically active helical polymers in the asymmetric polymerization with chiral anionic initiators such as (+)-(2S,3S)-2,3-dimethoxy-1,4-bis(dimethylamino)butane(DDB)-N,N'-diphenylethylenediamine monolithium amide (DPEDA-Li) or (-)-sparteine (Sp)-fluorenyllithium (FlLi) complex (1,3-8). These two chiral initiators are very efficient in the polymerization of TrMA and almost perfectly one-handed helical poly(TrMA) has been obtained. However, these are not effective for D2PyMA. The poly(D2PyMA) obtained is usually a mixture of (+)- and (-)-helices. The ratio of (+)- to (-)-polymer was about 80:20 at the best (3). This ratio has been increased to 85:15 by using a chiral ligand (+)-(3S,4S)-3,4-dimethoxy-N-(2-(dimethylamino)ethyl)pyrrolidine (3).

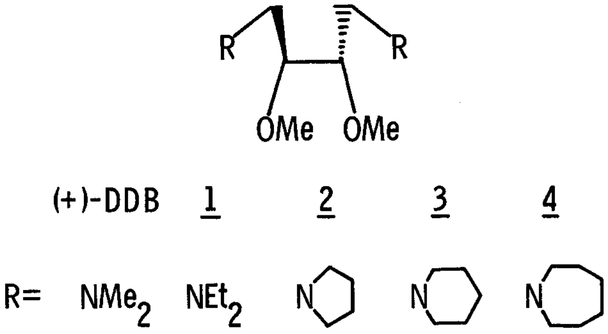
Optically active poly(TrMA) (9-13) and poly(D2PyMA) (3) have unique chiral recognition abilities and can resolve many racemates effectively as chiral stationary phases for high-performance liquid chromatography. The optical resolving power of the chiral stationary phases depends on the helicity of the polymers, and the greater helicity the higher resolving power. Therefore, the efficient preparation of optically active poly(D2PyMA) with a highly one-handed helical content is greatly desirable.

In this paper, we will report the efficient asymmetric polymerization of D2PyMA leading to a highly one-handed helical polymer by using lithium complexes of novel chiral ligands (1-4) derived from tartaric acid.

EXPERIMENTAL

Chiral ligands (+)-(2S,3S)-2,3-dimethoxy-1,4-bis(diethylamino)butane (1), (+)-(2S,3S)-2,3-dimethoxy-1,4-bis(piperidino)butane (3) and (+)-(2S,3S)-2,3-dimethoxy-1,4-bis(1-perhydroazepinyl)butane (4) were prepared from (+)-tartaric acid via (+)-(2S,3S)-2,3-dimethoxysuccinic acid (14). (+)-(2S,3S)-2,3-Dimethoxysuccinic acid was treated with thionyl chloride in benzene to convert acid chloride which was then reacted with corresponding amines. The obtained amides were reduced with lithium aluminum hydride or diborane in THF. The chiral ligands obtained were distilled from calcium hydride or lithium aluminum hydride before use. Chiral ligand (+)-(2S,3S)-2,3-dimethoxy-1,4-bis(1-pyrrolidinyl)butane (2) was prepared by Seebach's method (6,15). These diamines gave satisfactory i.r., n.m.r., and high-resolution mass spectral data. The optical rotation ($[\alpha]_D$ (neat)) of the chiral ligands 1-4 were +26.6°, +5.3°, +2.5°, and +18.2°, respectively. The synthesis and purification of other materials and the polymerization procedure were previously reported (3). The degree of polymerization and the tacticity of polymer were determined by GPC and ^{1}H-NMR, respectively, of the poly(methyl methacrylate) derived from original poly(D2PyMA).


D2PyMA



RESULTS AND DISCUSSION

Table 1 shows the results of the asymmetric polymerization of D2PyMA with (+)-DDB and 1-4 as the chiral ligands. Optical active polymers were obtained quantitatively. The optical rotation of the polymers depended greatly on the chiral ligands. Large influence of the lithium compounds was observed in the polymerization with DDB, 1, and 2, which gave the polymer of relatively low optical activity. However, little influence of the lithium compounds was observed in the polymerization with 3 and 4. Although the ligands 1-4 were derived from (+)-tartaric acid similarly to (+)-DDB, all the new ligands afforded the polymer with negative optical activity opposite to that of the polymer obtained with (+)-DDB.

Table 1

Polymerization of D2PyMA in Toluene at -78°C for 24 h[a]

Initiator	Yield(%)	$[\alpha]^{25}_{365}$[b]
(+)-DDB-FlLi[c]	99	+132
(+)-DDB-DPEDA-Li[d]	100	+757
1-FlLi	100	-264
1-DPEDA-Li	100	-661
2-FlLi	96	-720
2-DPEDA-Li	99	-457
3-FlLi	100[e]	-1232
3-DPEDA-Li	100	-1108
4-FlLi	100[f]	-1233
4-FlLi[g]	100	-1121
4-DPEDA-Li	100	-1170

[a] D2PyMA=1.0 g; toluene=20 ml; [D2PyMA]/[Li]=20.

[b] In $CHCl_3$-2,2,2-trifluoroethanol (9/1).

[c] Polymerized for 15 h; data in ref. 3.

[d] D2PyMA=0.15 g; toluene=3.0 ml; polymerized for 7.6 h.

[e] DP=36; tacticity(%): I 97, H 2, S 1; benzene-hexane (9/1) insoluble part: yield 77%, $[\alpha]^{25}_{365}$ -1472°.

[f] DP=38; tacticity(%): I 97, H 2, S 1; benzene-hexane (9/1) insoluble part: yield 79%, $[\alpha]^{25}_{365}$ -1375°.

[g] [D2PyMA]/[Li]=30.

The efficient chiral ligands were 3 and 4 bearing large cyclic amino groups, and gave the polymers of the higher optical rotation (about -1200°). This high optical rotation was comparable to that of the one-handed helical poly(D2PyMA) isolated by fractionation (3).

Figure 1 shows the change of the optical rotation (α_D^{-78}) in the polymerization of D2PyMA by 4-FlLi, 3-DPEDA-Li, and (+)-DDB-DPEDA-Li in toluene at -78°C. The polymerization carried out in a 1-cm cell to monitor optical rotation directly with a digital polarimeter. The optical rotation of the polymerization mixtures gradually increased with the time, and reached constant values in 1-3 h; the polymer yield was 100%. The activity of 4-FlLi appears higher than those of other two. The $[\alpha]^{25}_{365}$ of the isolated polymers was proportional to the final observed rotation of the mixtures.

Figure 2 shows the GPC curves of the obtained polymers detected by a UV and a polarimetric detector. It has been shown that the polymer obtained with (+)-DDB-DPEDA-Li contained a small portion (∿20%) of (-)-polymer of high molecular weight in addition to a large portion (∿80%) of (+)-polymer of low molecular weight (3). On the contrary, the polymers initiated with 4-FlLi and 4-DPEDA-Li consisted of mostly (-)-polymer of high molecular weight. The ratio of (-)- to (+)-polymer was estimated to be 93:7.

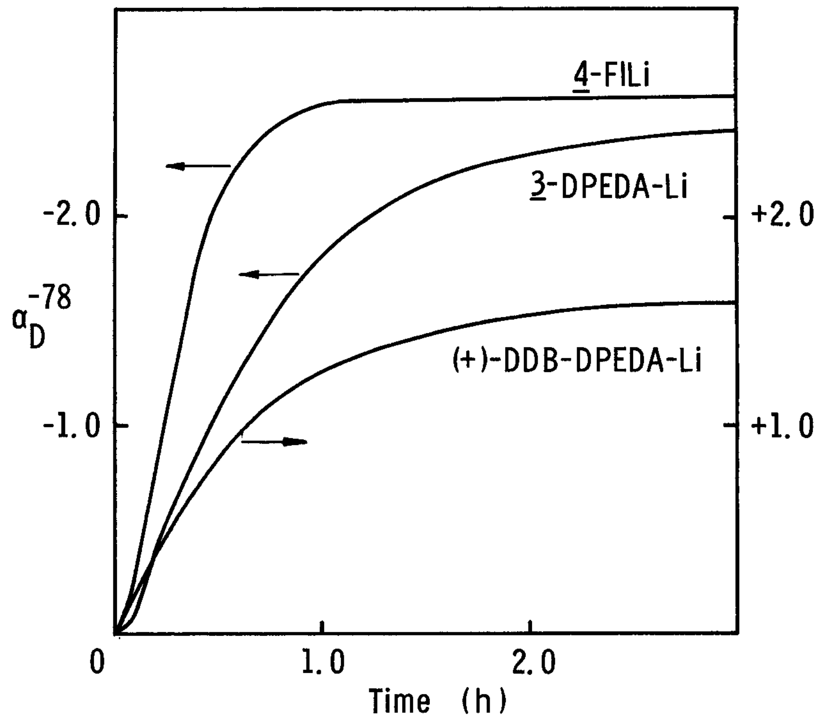


Figure 1. Optical rotation (α_D^{-78}) in the polymerization of D2PyMA in toluene at -78°C.
D2PyMA=0.15 g, toluene=3.0 ml, [D2PyMA]/[Li]=20.

The polymers obtained with 3- and 4-FlLi were fully soluble in the common organic solvents such as chloroform, THF, and benzene and insoluble in methanol and hexane. Fractionation of the polymer prepared with 3- or 4-FlLi by benzene-hexane (9:1) mixture afforded almost pure one-handed helical polymer ($[\alpha]_{365}^{25} \sim -1400^\circ$) in about 80% isolated yield (Table 1). Figure 2-(c) shows the GPC curve of the fractionated (-)-poly(D2PyMA). The UV curve was very similar in shape to the polarimetric curve, indicating that the (-)-polymer was uniform and did not contain (+)-polymer.

We also examined the asymmetric polymerization of TrMA by the DPEDA-Li complexes of chiral ligands 1-4. Although optically active polymers were obtained quantitatively in all cases, the optical rotation ($[\alpha]_{365}^{25}$ +800$\sim$-695°) of the polymers was much lower than that ($[\alpha]_{365}^{25}$ +1227°) (6) obtained with (+)-DDB. These novel chiral ligands 1-4 were not useful for the preparation of poly(TrMA) with high one-handed helicity.

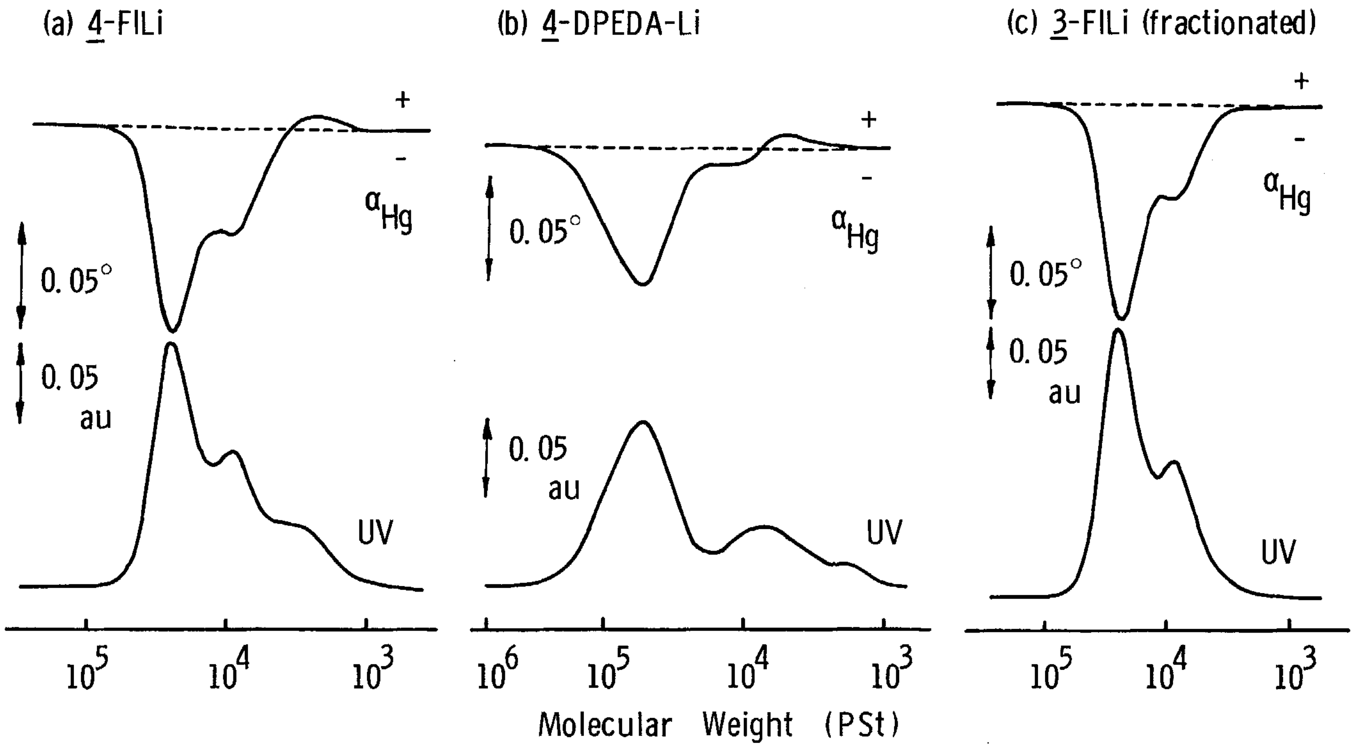


Figure 2. GPC curves of poly(D2PyMA)s obtained with chiral anionic initiators.
Column: Shodex GPC K-802.5 (30 cm)+AC-80M (50 cm), eluent: $CHCl_3$ (1.0 ml/min).

Proper selection of a chiral initiator seems to be required for highly helicity-selective (enantiogenic atropasymmetric) polymerization of these methacrylates.

In conclusion, optically active poly(D2PyMA) with pure one-handed helicity could be obtained in good yield through the asymmetric polymerization of D2PyMA with chiral ligands 3 and 4 followed by fractionation. The chiral ligands are easily obtained from (+)-tartaric acid.

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