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Asymmetric Anionic Polymerization of Triphenylmethyl Acrylate Leading to a Helical Conformation

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The helix is one of the most important and interesting polymer structures, which has chirality due to right- or left-handed helicity.[1] Recently, a one-handed helical polymer has been of much interest in the areas of synthetic polymer chemistry and chiral separation of enantiomers. Triphenylmethyl methacrylate (TrMA) gives a one-handed helical, optically active polymer (PTrMA; $[\alpha]^{25}_{D} = +350-390°$) by anionic polymerization with chiral anionic initiators,[2] and the polymer can separate a variety of racemates as a chiral stationary phase for high-performance liquid chromatography.[3] The helical structure of PTrMA is maintained by sterical repulsion of bulky ester groups of the highly isotactic polymer. However, as far as we know, there is no report that such a stable helix is formed in polyacrylates. This is probably because triphenylmethyl acrylate (TrA) has been known to form a polymer with much less isotacticity in anionic polymerization as well as in radical polymerization.[4] In this paper, we report the asymmetric anionic polymerization of triphenylmethyl acrylate (TrA)[5] which affords an optically active polymer with conformational chirality.

The polymerization was performed in a manner similar to that in the polymerization of TrMA using the complexes of *N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li) with chiral ligands, (−)-sparteine ((−)-Sp), (+)-(2*S*,3*S*)-2,3-dimethoxy-1,4-bis(dimethylamino)butane ((+)-DDB), and (+)-1-(2-pyrrolidinylmethyl)pyrrolidine ((+)-PMP) in toluene at −78 °C for 24 h.[6,8]

The results of polymerization are summarized in Table 1. The polymerization proceeded quantitatively in all cases, and the tacticity and the specific rotation of polymers were greatly affected by the ligands. The specific rotation of the polymers seems to increase with an increase of the isotacticity, and the (+)-PMP system afforded the polymer of the highest specific rotation ($[\alpha]^{25}_{365} = +102°$) and isotacticity ($m = 0.70$). However, these values are much smaller than those ($[\alpha]^{25}_{365} = +1500°$, $mm > 0.99$) of one-handed helical, optically active PTrMA.[2]

The CD spectrum of (+)-PTrA (entry 1 in Table 1) is shown in Figure 1a. The spectrum demonstrates the positive peaks at 210 and 230 nm which may be ascribed to the absorption due to the aromatic and carbonyl groups, respectively. This spectral pattern is quite similar to that of the one-handed helical, optically active PTrMA.[2b] This suggests that the optical activity of the PTrA may be attributed to a partially one-handed helical structure of the polymer chain. The degree of one-handedness must be lower than that of the PTrMA judging from the smaller optical activity and isotacticity of the polymer.

The (+)-PTrA was analyzed by GPC equipped with UV and polarimetric detectors (Figure 2). The polarimetric detection indicates that the polymer contained small amounts of high and low molecular weight fractions and its pattern of the main fraction is similar to that of UV detection, suggesting that the whole polymer including high molecular weight parts is optically active. The partially helical structure must be introduced throughout the polymer chain.

Table 1. Anionic Polymerization of TrA by DPEDA-Li Complexes in Toluene at −78 °C for 24 h[a]

entry	chiral ligand	yield (%)[b]	DP_n[c]	M_w/M_n[c]	tacticity (*m*:*r*)	$[\alpha]^{25}_{365}$ (deg)[d]
1	(+)-PMP	96	46	1.28	0.70:0.30	+102[e]
2	(−)-Sp	98	57	2.94	0.64:0.36	nd[f]
3	(+)-DDB	100	61	1.38	0.49:0.51	−7

[a] [Monomer]/[Initiator] = 20. [b] Methanol-insoluble part. [c] Determined by GPC (polystyrene standard). [d] Measured in $CHCl_3$ at 25 °C (c = ca. 1). [e] $[\alpha]^{25}_{D} = +21.8°$ (c = 1.53). [f] Not determined. The obtained polymer was partly insoluble in common organic solvents.

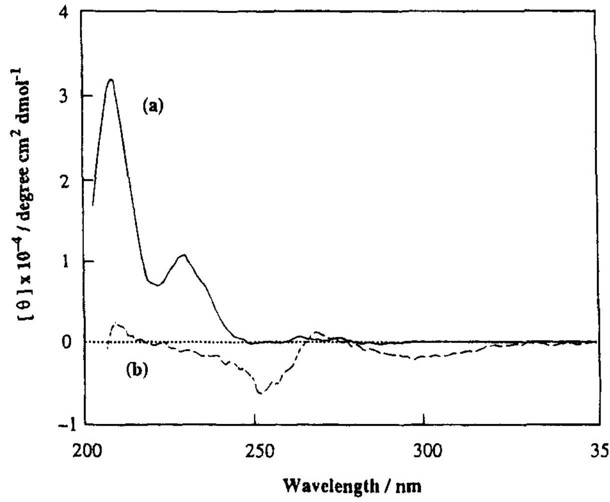

Figure 1. CD spectra of (+)-poly(TrA) (a) and (−)-poly(MA) (b) derived from (+)-poly(TrA) in THF. The molar concentration of (+)-poly(TrA) was calculated on the basis of the monomeric unit (M_w = 314) and that of (−)-poly(MA) on the basis of the polymer molecules (M_w = 4.9 × 10^3).

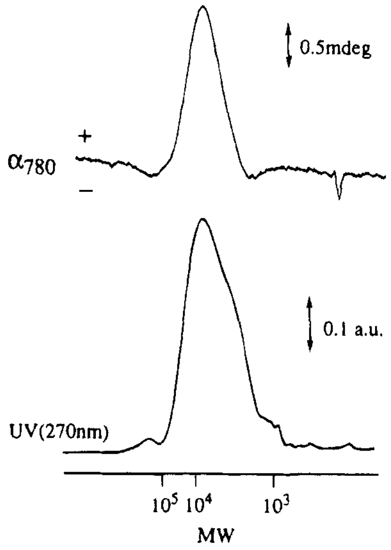

Figure 2. GPC curves of poly(TrA) obtained with (+)-PMP-DPEDA-Li in toluene at −78 °C.

The specific rotation ($[\alpha]^{25}_{365} = +85°$, c = 0.91) of (+)-PTrA in THF did not change in 50 min at 25 °C. However, the optical activity gradually increased at 60 °C and reached about +138° after 20 min. Then the solution became turbid. These results indicate that (+)-PTrA is conformationally stable at room temperature, but some conformational change and association occur at higher temperature. In chloroform, (+)-PTrA precipitated immediately after the dissolution.

To obtain information about the contribution of a configurational factor to the chiroptical property of the polymer, (+)-PTrA (entry 1 in Table 1) was converted to poly(methyl acrylate) (PMA).[8] PMA showed a small negative specific rotation ($[\alpha]^{25}{}_{365} = -18°$), which is opposite in sign to that of (+)-PTrA. The CD spectrum of PMA was quite different in pattern from that for PTrA (Figure 1). The optical activity of PMA may be mainly due to the chirality near polymer ends because the CD peaks of PMA are attributed mainly to the absorption of the initiator residue, an *N,N'*-diphenylethylenediamino group. The induction of the configurational asymmetry clearly occurs at the initial stage of the polymerization and may continue through the polymerization to produce the prevailing conformational asymmetry in the polymer chain.

In conclusion, poly(TrA)s obtained in the asymmetric anionic polymerization using chiral complexes are optically active mainly due to the conformational factor. The isotactic part in the polymer probably has the helical conformation which induces the dextrorotation. Polyacrylates bearing a bulky ester group appear to have stable helical conformation as well as the polymethacrylates.

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References and Notes

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(5) The monomer was synthesized from acrylic acid and trityl chloride with triethylamine in toluene at 80 °C. After crystallization from hexane, the purified monomer was obtained by recrystallization from petroleum ether in 26% yield (mp 70.5–71.5 °C).[4]

(6) The following experiment is typical: TrA (0.50 g, 1.6 mmol) and toluene (10 mL) were placed in a dry glass ampule under a dry nitrogen atmosphere, and the solution was cooled to −78 °C. The initiator solution (0.080 mmol), prepared from DPEDA-Li (1 equiv) and chiral ligand (1.2 equiv) in toluene, was then added to the monomer solution with a syringe. After 24 h, the polymerization was terminated by adding a small amount of methanol. The products were poured into a large excess of methanol, collected by centrifugation immediately, and then dried *in vacuo* at 60 °C for 3 h. The molecular weight and tacticity of the obtained polymer were determined by gel permeation chromatography (GPC) and ^{1}H NMR analysis,[7] respectively, of poly(methyl acrylate) (PMA) derived from the original PTrA.[8]

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(8) The obtained PTrA was converted into PMA by hydrolysis in methanol containing a small amount of hydrochloric acid followed by methylation with diazomethane in the same manner as applied to PTrMA.[2f] The polymer was obtained almost quantitatively.

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