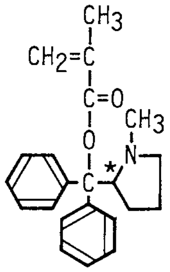
CHEMISTRY LETTERS, pp. 525-528, 1991.

# Synthesis and Reversible Stereomutation of Optically Active Poly[(*S*)-diphenyl(1-methylpyrrolidin-2-yl)methyl methacrylate]

Yoshio OKAMOTO,* Tamaki NAKANO, Etsuko ONO,† and Koichi HATADA†
Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Chikusa-ku, Nagoya 464-01
†Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

Anionic polymerization of (+)-(*S*)-diphenyl(1-methylpyrrolidin-2-yl)methyl methacrylate gave an optically active polymer of helical conformation of single screw-sense. The polymer exhibited a reversible helix-helix transition in a solution of methanol containing an acid.

Methacrylates having bulky achiral ester groups like triarylmethyl afford optically active polymers arising from a one-handed helical structure by asymmetric (helix-sense-selective) polymerization with homochiral anionic initiators.[1,2] Recently, we found that optically active poly(diphenyl-2-pyridylmethyl methacrylate) [poly(D2PyMA)] and poly((+)-phenyl-2-pyridyl-*m*-tolylmethyl methacrylate) [poly((+)-PPymTMA)] undergo a conformational change which induces inversion of the helicity of the polymer chain.[3,4] Stereomutation of one-handed helical poly(D2PyMA) affords a mixture of right- and left-handed helices which are slowly interconvertible and separable by HPLC on a chiral stationary phase.[3] On the other hand, (-)-poly((+)-PPymTMA) which is prepared by helix-sense-selective polymerization of (+)-PPymTMA at -78 °C undergoes irreversible stereomutation to (+)-poly((+)-PPymTMA) due to the chiral side group of the polymer in solution at 60 °C.[4] In the present work, a new optically active polymer, poly[(*S*)-(-)-diphenyl(1-methylpyrrolidin-2-yl)methyl methacrylate] [poly(DMPMA)] was synthesized by anionic polymerization and the stereomutation due to helix-helix transition of the polymer was investigated. The optical rotation of the polymer was reversibly varied by changing the acidity of the solution. This polymer may be the first example of a vinyl polymer which undergoes nearly



DMPMA

perfect slow reversible transition from one helix to the other. Such a transition has been observed for poly-L-proline,[5)] its derivatives,[6)] and polynucleotides.[7)]

Polymerization of DMPMA[8)] was carried out with the complexes of *N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li) with (*S*)-(+)-2-(1-pyrrolidinylmethyl)pyrrolidine (PMP), (+)- and (-)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB), and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in toluene at -78 °C in a glass ampule or a 1-cm optical cell in order to monitor the change of optical rotation of the polymerization systems. The polymerization was terminated with a small amount of methanol and the polymer was precipitated in methanol to be collected by centrifugation.

The polymerization systems directly monitored at -78 °C showed negative optical rotation which increased with polymerization time. However, the isolated polymers were insoluble in common organic solvents, but soluble in methanol containing a small amount of an acid and all samples showed almost the same dextrorotation in methanol containing 20 vol% of $CH_3SO_3H$ (methanol-20%$CH_3SO_3H$) (Table 1). Considering the negative rotation observed during the polymerization, some conformational change must occur during the isolation or dissolution in the solvent. The obtained polymers were highly isotactic. The large optical activity of opposite sign of the polymers to that of the monomer suggests that the polymer may possess an excess of one-handedness of a helical conformation.

Figure 1 shows the change of optical rotation of the polymer (Run 5 in Table 1) dissolved in methanol containing $CH_3SO_3H$ and $CF_3COOH$. The polymer in methanol-0.01%$CH_3SO_3H$ first showed a positive rotation $[\alpha]^{25}_{365}$ +780° which slowly moved with time to a negative value $[\alpha]^{25}_{365}$ -410° (curve A). A further addition of the acid (13.0%) induced the returning of the optical activity

Table 1. Polymerization of DMPMA with DPEDA-Li Complexes in Toluene at -78 °C[a)]

| Run | Ligand | [DMPMA]/[Li] | Yield/% | DP[b)] | Mw/Mn[b)] | Tacticity/%[c)] *mm* | *mr* | *rr* | $[\alpha]^{25}_{365}$/°[d)] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | (+)-DDB | 20 | 100 | 21 | 1.47 | 95 | 4 | 1 | +786 |
| 2 | (-)-DDB | 20 | 98 | 20 | 1.36 | | | | +846 |
| 3 | (+)-PMP | 20 | 100 | 22 | 1.35 | 95 | 4 | 1 | +798 |
| 4 | TMEDA | 20 | 99 | 23 | 1.17 | | | | +809 |
| 5 | TMEDA | 40 | 88 | 37 | 1.32 | 99 | 1 | 0 | +939 |

a) Monomer 0.5 or 1.0 g, toluene/DMPMA = 20/1 (ml/g), time 15-23 days. b) Determined by GPC of poly(methyl methacrylate) derived from poly(DMPMA). c) Determined by $^1H$ NMR of the poly(methyl methacrylate) derived from poly(DMPMA). d) Values observed 2 h after dissolution in methanol-20%-$CH_3SO_3H$.

arriving at $[\alpha]^{25}_{365}$ +779° (curve B). The polymer in methanol-1.5%$CF_3COOH$ also showed a similar change from positive value $[\alpha]^{25}_{365}$ +420° to a negative value $[\alpha]^{25}_{365}$ -890° (curve C), which returned to a positive value $[\alpha]^{25}_{365}$ +770° by the addition of $CH_3SO_3H$ (curves D and E). These optical activities did not move at least for several hours, indicating that the ester groups were not solvolized in these acidic systems.10)

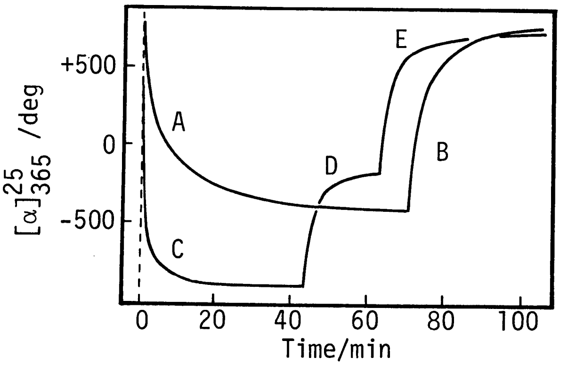


Fig. 1. Change of specific rotation of poly(DMPMA) obtained with TMEDA-DPEDA-Li (Run 5 in Table 1) in the mixtures of methanol and acids; in methanol-0.01%-$CH_3SO_3H$ (curve A), in methanol-13%$CH_3SO_3H$ (curve B), in methanol-1.5%$CF_3COOH$ (curve C), in methanol-0.9%$CF_3COOH$-0.5%-$CH_3SO_3H$ (curve D), and in methanol-0.5%-$CF_3COOH$-9.5%$CH_3SO_3H$ (curve E).

Figure 2 (A) shows the change of the CD spectra of the polymer solutions in methanol-0.01%$CH_3SO_3H$, and Fig. 2 (B) those in the presence of 13.0% of $CH_3SO_3H$ after the completion of the change in Fig. 2 (A). Clear CD bands were observed in the range of 200-240nm. A strong peak at 208 nm and a shoulder at 220 nm may be assigned to the electronic transitions due to the phenyl and carbonyl groups. The intensity of the CD band was almost proportional to the optical activity. The maximum $[\theta]$ values are comparable to those of the purely one-handed helical poly(TrMA) and poly(D2PyMA).11) These results indicate that a reversible stereomutation from one helix to the other was achieved by changing the acidity of the solvent. The protonation of amino groups of poly(DMPMA) with a small amounts of the acid probably induced the first stereomutation due to the repulsion of the charge. The further addition of the acid may weaken the repulsion of the charge by solvating the charge or

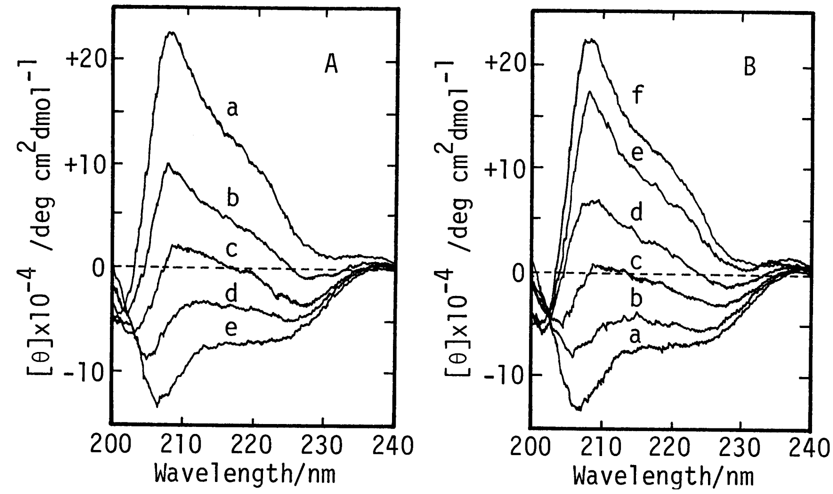


Fig. 2. Change of CD spectra of poly(DMPMA) (Run 5 in Table 1). A: in methanol-0.01%$CH_3SO_3H$; (a) immediately after dissolution ($[\alpha]^{25}_{365}$ +780°), (b) 2 h 5 min (+240°), (c) 4 h 4 min (+81°), (d) 22 h 18 min (-163°), and (e) 70 h (-410°). B: in methanol-13%$CH_3SO_3H$ after completion of the change in A; (a) the last spectrum in A, (b) 5 min after the addition of $CH_3SO_3H$ (13%) (-278°), (c) 52 min (-26°), (d) 2 h 30 min (+252°), (e) 16 h 20 min (+570°), and (f) 30 h (+779°).

by decreasing the degree of dissociation of the ion pair on the side chain which seems to force the helical chain to return to original helix. This may be the first example of reversible stereomutation of a nearly complete one-handed helix to the other in vinyl polymers.

We are deeply grateful to Professor Mark M. Green of the Polytechnic University for helpful discussions and review of the manuscript.

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8) DMPMA was synthesized from (*S*)-(+)-diphenyl(1-methylpyrrolidin-2-yl)methanol[9] and methacryloyl chloride; mp 83.0-84.8 °C, $[\alpha]_D^{25}$ -40.9°, $[\alpha]_{365}^{25}$ -82.2° (benzene), $[\alpha]_D^{25}$ -54.5° (methanol), $[\alpha]_D^{25}$ -40.4° (methanol-0.7%$CH_3SO_3H$).

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10) The results of $^1$H NMR analysis of the polymer also supported this. This stability of ester linkage toward acid is contrast to the weak ester linkage of poly(triphenylmethyl methacrylate) [poly(TrMA)] and poly(D2PyMA). The protonation of amino group of poly(DMPMA) may protect the ester linkage from being attacked by proton.

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(Received January 14, 1991)