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Asymmetric polymerization of cyclopropyldiphenylmethyl and cyclohexyldiphenylmethyl methacrylates and stereomutation of the polymers

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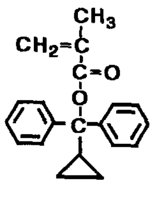
Summary

Cyclopropyldiphenylmethyl and cyclohexyldiphenylmethyl methacrylates were polymerized with chiral anionic initiators in toluene at low temperature. The former monomer gave an atactic polymer and the latter monomer a highly isotactic, optically active polymer of one-handed helical conformation. The optically active polymer underwent a helix-helix transition in chloroform at 60°C.

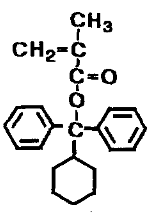
Introduction

Triphenylmethyl methacrylate (TrMA) (1) and diphenyl-2-pyridylmethyl methacrylate (D2PyMA) (2) afford optically active, highly isotactic polymers of one-handed helical structure by asymmetric (helix-sense-selective) polymerization with a chiral anionic initiator. The helical structure of the polymers is considered to be maintained by mutual steric repulsion between the bulky ester groups. The helix of poly(D2PyMA) is less stable than that of poly(TrMA) and undergoes helix-helix transition in solution, in which the one-handed helix changes to a mixture of right- and left-handed helices (3). On the other hand, 1,1-diphenylethyl methacrylate which is less bulky than TrMA and D2PyMA gives an atactic polymer under similar polymerization conditions as those applied to TrMA and D2PyMA (4). Therefore, the stereostructure of ester group greatly affects the formation and stability of the helix.

In the present study, cyclopropyldiphenylmethyl methacrylate (CPDPMA) and cylclohexyldiphenylmethyl methacrylate (CHDPMA) were synthesized and polymerized with chiral anionic initiators to get information on the stereostructure of ester group suitable for obtaining a helical polymethacrylate.



CPDPMA



CHDPMA

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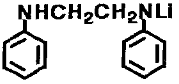
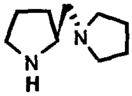
Experimental

CPDPMA was synthesized from sodium salt of cyclopropyldiphenylmethanol (Aldrich) and methacryloyl chloride and recrystallized first from diethyl ether and then from hexane; m.p. 69.7~70.1°C. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.19%; H, 6.85%. Found. C, 82.27%; H, 6.98%. Cyclohexyldiphenylmethanol was synthesized from methyl cyclohexanecarboxylate and phenylmagnesium bromide (PhMgBr). CHDPMA was prepared from the lithium salt of the alcohol and methacryloyl chloride and recrystallized first from ethanol and then from hexane; m.p. 73.6~74.6°C. Anal. Calcd for $C_{23}H_{26}O_2$: C, 82.60%; H, 7.84%. Found. C, 82.40%; H, 7.86%.

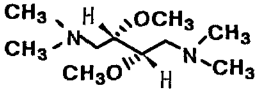
Asymmetric anionic polymerization was carried out in toluene at −78°C and −40°C in a glass ampule or in a 1.0-cm optical cell to monitor the change of optical rotation of the polymerization system. The initiators used for anionic polymerization are the complexes of *N,N'*-diphenylethylenediamine monolithium amide (DPEDA-Li) with (+)-(*S*)-2-(1-pyrrolidinylmethyl)pyrrolidine (PMP), (+)-(2*S*,3*S*)-2,3-dimethoxy-1,4-bis-(dimethylamino)butane (DDB), and (−)-sparteine (Sp). Anionic polymerization was also done with PhMgBr. Polymerization was terminated with a small amount of methanol and precipitated in methanol to be collected by centrifugation. Radical polymerization was done with $(i\text{-PrOCOO})_2$ in toluene at 40°C.



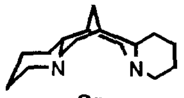
DPEDA-Li



PMP



DDB



Sp

Degree of polymerization (DP) of the polymers was determined by gel permeation chromatography (GPC) of poly(MMA) derived from the original polymers (5). ^{1}H NMR spectra were taken with a JEOL GSX-270 spectrometer. Optical rotation was measured on a JASCO DIP-181 polarimeter. Circular dichroism (CD) spectra were taken on a JASCO J-500 instrument.

Results and Discussion

Polymerization of CPDPMA

The results of polymerization of CPDPMA are shown in Table 1. The polymers obtained with PMP-DPEDA-Li and DDB-DPEDA-Li did not show significant optical activity and were not highly isotactic (Run 1,2 in Table 1). Cyclopropyldiphenylmethyl group seems to be too small as an ester group to form a helical polymethacrylate. CPDPMA afforded a highly isotactic polymer by anionic polymerization with PhMgBr and an atactic polymer by radical polymerization with $(i\text{-PrOCOO})_2$ (Run 3-5 in Table 1). The isotactic polymer was not optically resolved into (+)- and (−)-polymers by chiral HPLC at a temperature range of −30°C~+15°C as poly(D2PyMA) was resolved

Table 1
Polymerization of CPDPMA in Toluene for 24 hr[a]

Run	Initiator	Temp. (°C)	Yield (%)	DP[b]	Mw/Mn[b]	Tacticity(%) *mm*	*mr*	*rr*	$[\alpha]^{25}_{365}$[c]
1	PMP-DPEDA-Li	-78	99	34	1.10	28	31	41	-1°
2	DDB-DPEDA-Li	-78	97	36	3.71	44	32	24	-4°
3	PhMgBr	-78	83	30	3.53	91	8	1	
4	PhMgBr	0	95	65	1.40	94	5	1	
5	(*i*-PrOCOO)$_2$	40	89	103	2.30	22	51	27	

[a]Monomer 0.15 g, toluene 3 ml, [monomer]/[Li]=20 (Run 1,2); monomer 0.4 g, toluene 8 ml, [monomer]/[Mg]=20 (Run 3,4); monomer 0.75 g, toluene 2.5 ml, [monomer]/[initiator]=50 (Run 5). [b]Determined by GPC of poly(MMA)s derived from poly(CPDPMA)s. [c]Measured in $CHCl_3$.

(3), suggesting that the polymers may not take a helical conformation.

Figure 1 shows the change of optical activity of the polymerization systems of CPDPMA with DDB-DPEDA-Li and PMP-DPEDA-Li. Though the polymers isolated in the systems with DDB-DPEDA-Li and PMP-DPEDA-Li were almost optically inactive, the polymerization systems at -78°C showed positive optical activity increasing with the reaction time which reached constant values corresponding to specific rotation $[\alpha]_D^{-78}$

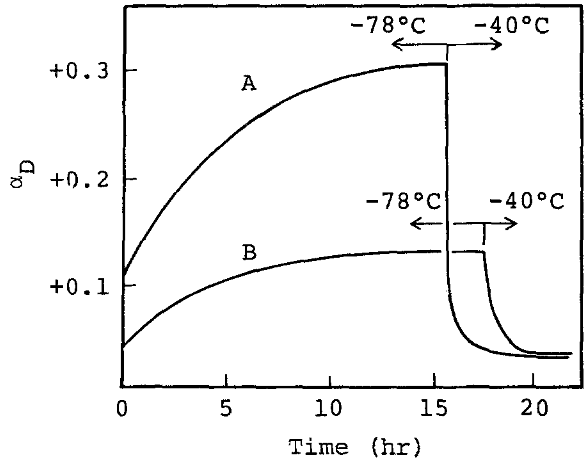


Figure 1. Change of optical rotation of polymerization systems of CPDPMA with DDB-DPEDA-Li (A) and with PMP-DPEDA-Li (B) in toluene at -78°C and -40°C.
CPDPMA 0.15 g, toluene 3 ml, [CPDPMA]/[Li]=20, cell length 1.0 cm.

+64° in DDB-system and +26° in PMP-system. These optical activities decreased quickly to very small values when the temperature of the systems was raised to -40°C. These results suggest that an optically active helical conformation may be partly formed in isotactic sequence of the polymer at -78°C and it changed to an optically inactive random-coil conformation at higher temperature. This possibility is supported by the fact that the final optical activity of the polymerization system at -78°C was higher in the system with DDB-DPEDA-Li which gave the polymer of higher isotacticity.

Polymerization of CHDPMA

The results of polymerization of CHDPMA are summarized in Table 2. All the polymers obtained with the chiral anionic initiators were highly isotactic and the polymers obtained with PMP and DDB complexes showed high dextrorotatory specific rotation. GPC analysis of these (+)-poly(CHDPMA)s with UV and polarimetric detectors did not show the existence of (-)-polymer. These results suggest that the polymers may possess a helical conformation of a single screw-sense. Radical polymerization of CHDPMA also gave a polymer rich in isotacticity (Run 5 in Table 2). Cyclohexyldiphenylmethyl group appears to be suitable as an ester group for the formation of helical polymethacrylate. The molecular weight distribution of the polymers obtained with Sp-DPEDA-Li was much broader than that of the polymers obtained with PMP-DPEDA-Li and DDB-DPEDA-Li and the former polymer contained the polymer of higher DP. This may be the reason for insolubility of the polymer.

The rate of polymerization of CHDPMA with PMP-DPEDA-Li and that with Sp-DPEDA-Li was estimated by monitoring the change of optical activity of polymerization systems during the reaction (Figure 2). Both the systems showed the positive optical rotation which increased with polymerization time. The optical rotation of the system with PMP reached a constant high positive value (α_{435}^{-78} +3.0°) which corresponds to

Table 2
Polymerization of CHDPMA in Toluene[a]

Run	Initiator	Temp. (°C)	Time (hr)	Yield (%)	DP[b]	Mw/Mn[b]	Tacticity(%)			$[\alpha]_{365}^{25}$ [c]
							mm	*mr*	*rr*	
1	PMP-DPEDA-Li	-78	48	99	34	1.10	98	2	0	+758°
2	Sp-DPEDA-Li	-40	48	97	36	3.71	91	6	3	——[d]
3	Sp-DPEDA-Li	-78	168	83	30	3.53	87	7	6	——[d]
4	DDB-DPEDA-Li	-78	48	95	65	1.40	98	1	1	+589°
5	$(i\text{-PrOCOO})_2$	40	24	89	103	2.30	45	36	19	

[a] Monomer 0.5 g, toluene 10 ml, [monomer]/[Li]=20 (Run 1-4); monomer 0.75 g, toluene 2.5 ml, [monomer]/[initiator]=50 (Run 5). [b] Determined by GPC of poly(MMA)s derived from poly(CHDPMA)s. [c] Measured in $CHCl_3$. [d] Insoluble in $CHCl_3$.

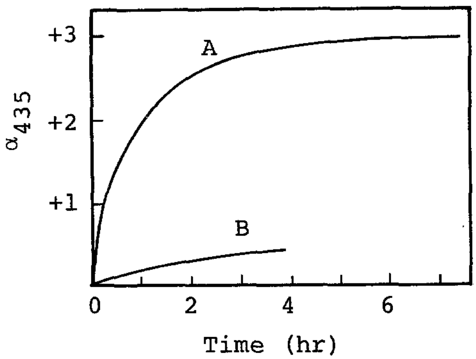


Figure 2. Change of optical rotation of polymerization systems of CHDPMA with PMP-DPEDA-Li at -78°C (A) and with Sp-DPEDA-Li at -40°C (B) in toluene.
CHDPMA 0.15 g, toluene 3 ml, [CHDPMA]/[Li] =20, cell length 1.0 cm.

the specific rotation $[\alpha]^{-78}_{435}$ +622° within about 6 h. This result indicates that the polymerization of CHDPMA is much slower than those of D2PyMA and TrMA. The optical activity of the polymerization systems of D2PyMA (2) and TrMA (6) under the same conditions reached large constant values within 10 min. CHDPMA may be more bulky than D2PyMA and TrMA. The polymerization of CHDPMA with Sp-DPEDA-Li at -78°C was very slow, and the optical activity of the system with Sp-DPEDA-Li at -40°C could not be completely followed because the system gelled in the course of polymerization.

The poly(CHDPMA) of DP = 34 prepared with PMP-DPEDA-Li (Run 1 in Table 2) showed a remarkable change of optical activity in chloroform at 60°C (Figure 3). The optical rotation of the polymer changed rather quickly from a high positive value ($[\alpha]^{60}_{365}$ ~+770°) to a negative one ($[\alpha]^{60}_{365}$ ~-480°). GPC analysis of the levorotatory polymer with UV and polarimetric detectors showed that the polymer consisted of only (-)-polymer. Such a change of optical rotation has been found for optically active poly(D2PyMA) and the change is ascribed to helix-helix transition of the polymer chain (3). The CD and ^{1}H NMR spectra of poly(CHDPMA) were measured under similar conditions to that shown in Figure 3. Figure 4 shows the CD spectra of the poly(CHDPMA). Clear CD band which may be due to carbonyl and phenyl groups was observed in the range of 220~260 nm. Immediately after being dissolved in chloroform, poly(CHDPMA) showed a large positive absorption which rather quickly changed to a negative trough with a similar spectral shape. In the ^{1}H NMR spectrum of the same polymer in $CDCl_3$, almost no change was observed. These findings suggest that the change of optical rotation may be attributable to the helix-helix transition of the polymer. Similarly to the optically active poly(D2PyMA), the helix of poly(CHDPMA) seems to be less stable than that of the optically active poly(TrMA). The change of optical rotation from a positive value to a negative value means that the content of

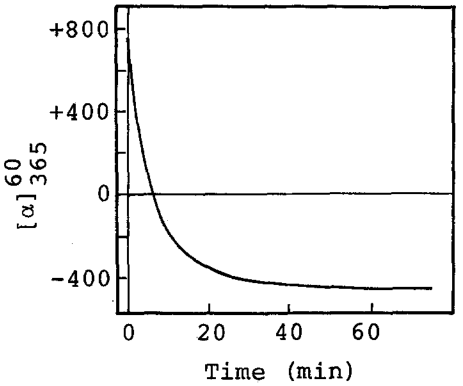


Figure 3. Change of specific rotation of poly(CHDPMA) of DP=34 (Run 1 in Table 2) in $CHCl_3$ at 60°C.

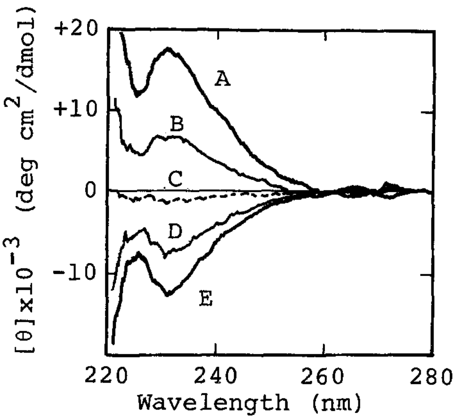


Figure 4. Change of CD spectra of poly(CHDPMA) of DP=34 in $CHCl_3$ at 60°C: 0 min (A), 5 min (B), 10 min (C), 20 min (D), and 60 min (E) after dissolution.

the right- and left-handed helices changed from an excess in one of the two to an excess in the other. Poly(CHDPMA)s of right- and left-handed helical conformations are regarded as enantiomers if ends groups are neglected, and therefore their NMR spectra should be same and CD spectra should be in mirror images. However, poly(CHDPMA)s obtained here are rather low molecular weight and their ends groups may not be neglected. In that case, right- and left-handed helices are a kind of diastereomers with different stabilities. The helix-helix transition observed for poly(CHDPMA) in the present study can be interpreted as a transition from less stable helix which was predominantly formed in the polymerization process at -78°C to a more stable one at 60°C.

References

1. Okamoto Y, Suzuki K, Ohta K, Hatada K, Yuki H (1979) *J. Am. Chem. Soc.* 101: 4763; Okamoto Y, Suzuki K, Yuki H (1981) *J. Polym. Sci. Polym. Lett. Ed.* 19: 451; Okamoto Y, Shohi H, Yuki H (1983) *J. Polym. Sci. Polym. Lett. Ed.* 21: 601; Okamoto Y, Yashima E, Nakano T, Hatada K (1987) *Chem. Lett.* 1987: 759; Wulff G, Sczepan R, Steigel A (1986) *Tetrahedron Lett.* 27: 1991.
2. Okamoto Y, Mohri H, Hatada K (1988) *Chem. Lett.* 1988: 1879.
3. Okamoto Y, Mohri H, Nakano T, Hatada K (1989) *J. Am. Chem. Soc.* 111: 5952.
4. Yuki H, Okamoto Y, Shimada Y, Ohta K, Hatada K (1976) *Polymer* 17: 619; Okamoto Y, Nakano T, Hatada K (1989) *Polym. J.* 21: 199.
5. Katchalski A, Eisenberg H (1951) *J. Polym. Sci.* 6: 145.
6. Nakano T, Okamoto Y, Hatada K, to be published.

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