

Chiroptical Properties of Oligomers of *m*-Methylphenyl Isocyanate Bearing an Optically Active End-Group

Katsuhiko MAEDA, Masashi MATSUDA, Tamaki NAKANO,
and Yoshio OKAMOTO*

*Department of Applied Chemistry, School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-01, Japan*

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ABSTRACT: Oligomerization of *m*-methylphenyl isocyanate (*m*MePI) with lithium amide of (*S*)-(-)-2-(methoxymethyl)pyrrolidine (MMP) was carried out to obtain oligomers containing a chiral residue at the initial chain end (α -end). The oligomers of degree of polymerization (DP) less than eighteen were separated in terms of DP and the specific rotation of each oligomer was estimated. The oligomers showed the high optical rotation which is ascribed to the structure prevailing in one-screw sense. The specific rotation of the oligomers increased up to DP of twelve and then decreased with an increase in DP. This suggests that the DP corresponding to the average persistence length of single handed helix may be larger than twelve. The specific rotation of the polymers was inversely proportional to the molecular weight. The optical activity of the polymer greatly increased with a decrease in temperature, whereas that of the trimer was not influenced by temperature.

KEY WORDS Oligomer / Aromatic Isocyanate / Helix / Optically Active
Polymer / Anionic Polymerization /

Poly(alkyl isocyanate)s have a rigid rod-like main chain based on the structure of 1-nylon^{1,2} and have extensively been studied from the viewpoints of conformation. Polyisocyanates with optically active side groups can provide important information on a helical structure of the polymers.³⁻⁸ It has been pointed out that poly(aromatic isocyanate)s have much less stiff conformation than that of poly(alkyl isocyanate)s.¹ However, we recently reported that achiral aromatic isocyanates⁹ as well as alkyl isocyanates¹⁰ can afford optically active polymers in the polymerization with chiral anionic initiators such as lithium alkoxides or amides. The obtained polymers showed the optical activity based on the prevailing helicity of a main chain induced by a chiral initiator residue attached to the initial chain end (α -end). The optical activity of the polyisocyanates

decreases with an increase in molecular weight of the polymers. This is because the one-handed helical structure induced by the chiral initiator residue can persist only in a rather short range from the α -end.

In the present study, we synthesized the oligomer of *m*-methylphenyl isocyanate (*m*MePI) with a chiral fragment at the α -end and estimated its specific rotation in order to get information on the helical structure of poly-(aromatic isocyanate)s.

EXPERIMENTAL

Materials

(*S*)-(-)-2-(Methoxymethyl)pyrrolidine [(*-*)-MMP] (Merck, $[\alpha]_D -3^\circ$) was purified by distillation over CaH_2 under reduced pressure. *m*MePI (Aldrich) was distilled over

* To whom all correspondence should be addressed.

CaH₂ under reduced pressure just before polymerization. Tetrahydrofuran (THF) was purified by distillation from Na and CaH₂ and then distilled again from LiAlH₄ under high vacuum just before use.

Preparation of Initiator Solution

Lithium amide of (–)-MMP was prepared by adding an equimolar amount of *tert*-butyllithium solution in pentane to a solution of (–)-MMP in THF at room temperature.

Oligomerization Procedure

Oligomerization was carried out under a dry nitrogen atmosphere. A THF solution of *m*MePI in a glass ampule was cooled to –98°C. The Li-MMP solution was then added to the monomer solution with a syringe. The reaction was terminated by adding a small amount of methanol containing hydrochloric acid after 4 h and the reaction mixture was kept for an hour at the temperature for complete termination. The mixture was added in a large amount of methanol and the polymer precipitated was separated by filtration. The filtrate was concentrated by distillation *in vacuo*, and then chloroform was added to the residue. The solution was washed with water. The chloroform layer was dried over magnesium sulfate and then chloroform was removed by distillation to recover the oligomer.

Fractionation of Oligomer

Fractionation of the oligomer was performed by a high-performance liquid chromatograph (JASCO 880-PU) equipped with a JASCO 875-UV (UV) and a Shodex OR-1 (polarimeter) detectors on a silica gel column (25 × 0.46 (i.d.) cm) using a mixture of hexane and 2-propanol (9:1, v/v) as an eluent. The structure and DP of oligomers were determined by ¹H NMR and FD mass spectroscopies.

Measurements

The molecular weight of the polymer was

determined by GPC measurement on a TOSOH HLC 802A GPC system equipped with an RI detector and a TOSOH LS-8 light scattering detector (He-Ne laser with a detection angle of 5°) by using a Shodex-KF-80M GPC column (eluent: THF). Optical rotation was measured on a JASCO DIP-181 polarimeter. IR spectra were recorded using a JASCO FT-IR-7000 infrared spectrometer. Circular dichroism spectra were taken using a JASCO J-720 spectrometer. ¹H NMR spectra were measured at 60°C using a Varian VXR-500 (500 MHz) spectrometer with tetramethylsilane as an internal standard. FD mass spectra were taken using a JEOL JMS-AX505HA instrument.

RESULTS AND DISCUSSION

Table I shows the results of the oligomerization of *m*MePI with Li-MMP in THF at –98°C. Molar ratios of monomer to initiator were changed from 1 to 10. Methanol-insoluble polymer was not formed at the ratios 1, 3, and 5, but was formed at the ratio 10. The polymer showed a large optical activity ($[\alpha]_{365}^{25} + 1107^\circ$). Figure 1 shows a GPC curve of oligo-I-3 (No. 3 in Table I). The number in the figure corresponds to DPs. MMP and the unimer (1-mer) show negative optical rotation, but the higher oligomers show positive optical

Table I. Oligomerization of *m*MePI with Li-MMP in THF at –98°C^a

No.	[<i>m</i> MePI]/ [Li-MMP]	Yield/% ^b	
		Methanol-insoluble	Methanol-soluble
1	1	0	149
2	3	0	115
3	5	0	102
4 ^c	10	20 ^d	90

^a *m*MePI 0.3 g, THF 5 ml, time 40 h.

^b Based on *m*MePI.

^c *m*MePI 1.0 g.

^d $M_n = 6.6 \times 10^3$, $M_w/M_n = 1.2$, $[\alpha]_{365}^{25} + 1107^\circ$.

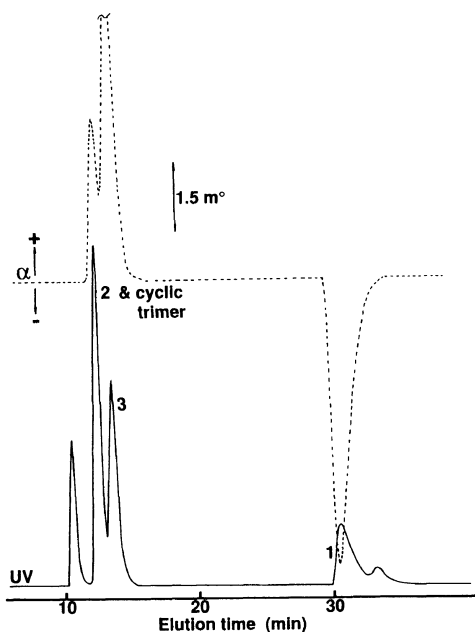


Figure 3. HPLC chromatograms of oligo-I-1 (No. 1 in Table I) (column: silica gel, 25×0.46 (i.d.) cm; eluent: hexane-2-propanol (90:10); 0.5 ml min^{-1}).

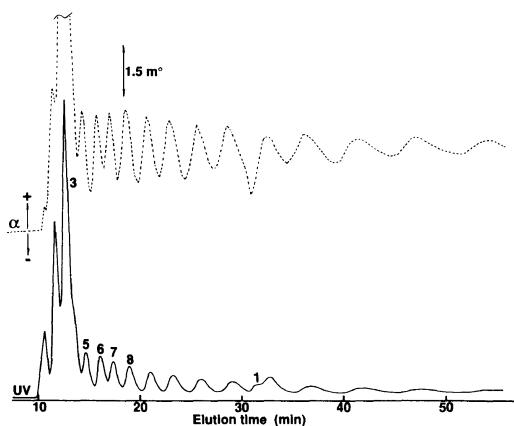


Figure 4. HPLC chromatograms of oligo-I-4 (No. 4 in Table I) (column: silica gel, 25×0.46 (i.d.) cm; eluent: hexane-2-propanol (90:10); 0.5 ml min^{-1}).

> 5 showed little change. The CD spectrum of the 1-mer showed a negative peak around 250 nm, and other's showed positive peaks. The intensity in CD spectra was highest on the 3-mer and decreased with an increase in DP accompanying with the shift to longer wave

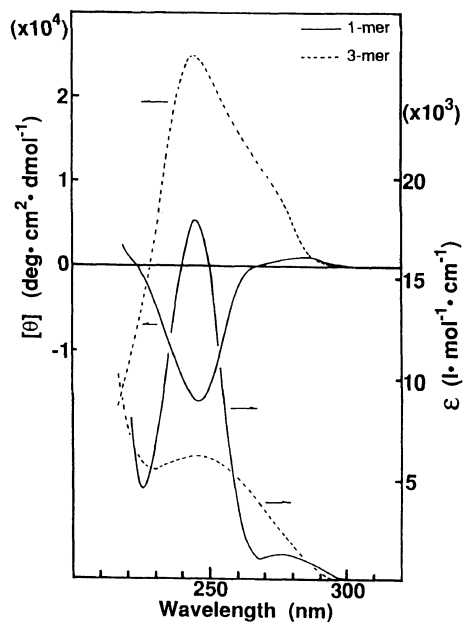


Figure 5. UV and CD spectra of 1-mer and 3-mer in THF.

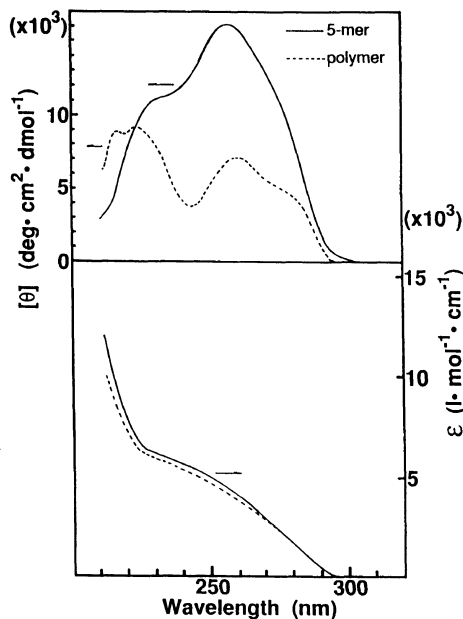


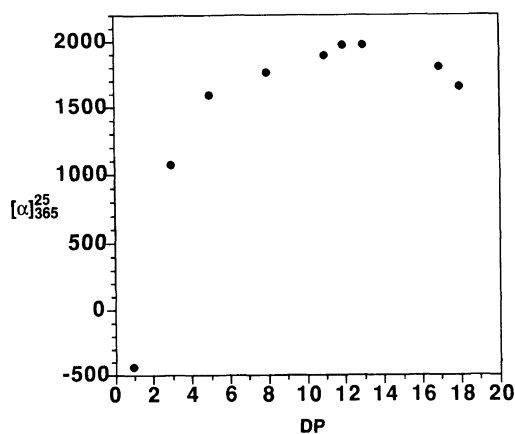
Figure 6. UV and CD spectra of 5-mer and polymer (No. 1 in Table II) in THF.

length.

Table II shows the results of the polymerization at various $[\text{monomer}]/[\text{initiator}]$ ratios.

Table II. Polymerization of *m*MePI with Li-MMP in THF at $-98^{\circ}\text{C}^{\text{a}}$

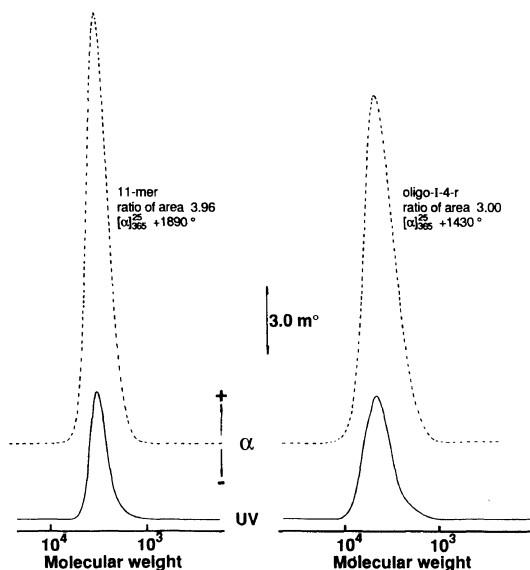
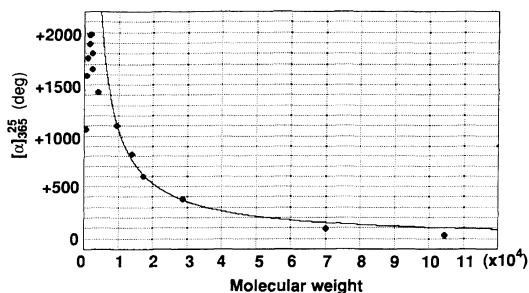
No.	$[\text{mMePI}]/$ $[\text{Li-MMP}]$	Yield ^b %	$[\alpha]_{365}^{25}$ ^c	M_w^{d} (10^4)	M_w/M_n^{d}
1	50	67	+819	1.7	1.2
2	100	73	+584	2.4	1.3
3	200	79	+381	3.8	1.3
4	500	90	+96	7.9	1.2
5	1000	93	+29	12	1.1

^a *m*MePI 0.5 g, THF 5 ml, time 4 h.^b Methanol-insoluble part.^c In THF.^d By light scattering method.**Figure 7.** Specific rotation of oligomers of *m*MePI in THF.

The optical rotation of the polymer decreased with an increase in molecular weight.

The specific rotation of oligomers is plotted against DP in Figure 7. The specific rotation except for that for 1-mer and 3-mer was estimated from the peak area ratio of the chromatograms monitored with polarimeter and UV detectors as exemplified in Figure 8. The specific rotation ($[\alpha]_{365}^{25} + 1430^{\circ}$) and the peak area ratio (3.0) of oligo-I-4-r, which was isolated as a hexane-ethanol (4:1, v/v) insoluble part from oligomer No. 4 in Table I, were selected as the standard.

Figure 9 shows the plots of the specific rotation vs. the molecular weight of oligo-

**Figure 8.** GPC curves of 11-mer and oligo-I-4-r measured with polarimeter and UV (270 nm) detectors.**Figure 9.** Plots of specific rotation vs. molecular weight of poly(*m*MePI) in THF.

mers and polymers. The molecular weight of polymers is M_n estimated by light scattering method. Figures 7 and 9 show that the specific rotation increases with an increase in DP in the range of $3 \leq \text{DP} \leq 12$. This is probably because in this DP range the oligomers have a helical structure without a helix reversal point and optical activity increases as the helical structure persists longer with an increase in DP. The gradual decrease of the specific rotation above $\text{DP} = 12$ may be ascribed to that the oligomer starts to have helix reversals. Therefore, the polymer chain after a certain

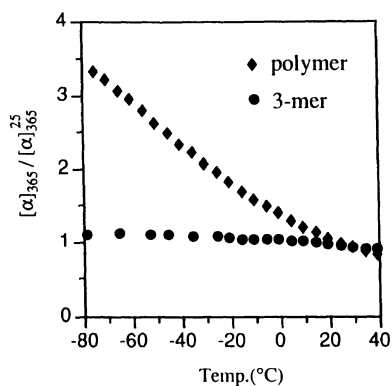


Figure 10. Optical activity of polymer (No. 2 in Table II) and 3-mer in THF at various temperatures.

DP above 12 from α -end should have equal amounts of right- and left-handed helical structures which can not contribute to the optical activity. This means that the specific rotation of the polymer will decrease to a half when the molecular weight increases twice. The curve in Figure 9 was obtained by fitting the points of the polymers above molecular weight 9500 (DP=70) to the equation $[\alpha] = k/M_n$ using a least-squares method. This result shows that the specific rotation is inversely proportional to the molecular weight of the polymer in the range of DP \geq 70, but not in the range of DP \leq 30. This probably indicates that the influence of the chiral end group completely disappears at DP = 30–70.

The specific rotation of the polymer No. 2 in Table II and the 3-mer fractionated by HPLC was measured at various temperatures and the results are shown in Figure 10. The ordinate represents the ratio of the specific rotation at each temperature relative to that at 25°C. The specific rotation of the polymer increased with a decrease in temperature, but the 3-mer showed almost no change. This may be because at lower temperature the one-handed helical structure originated by a MMP residue can be maintained to higher DP. This should result in the higher optical activity. Such

a situation is impossible for the 3-mer.

In this study, we succeeded in the synthesis of the oligomers of an aromatic isocyanate. The chiroptical study of the optically active oligomers with a chiral initiator residue at an α -end indicates that the one-handed helical structure starting from the α -end may persist at least up to DP = 12. This result indicates that in poly(aromatic isocyanate)s helix reversals occur more often than in poly(alkyl isocyanate).⁷ The specific rotation of the polymer with DP \geq 70 is inversely proportional to the molecular weight. It was also found that the specific rotation of the polymer was greater at lower temperature because of the increase in the average length of the helical structure of the polymer chain.

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REFERENCES

1. A. J. Bur and L. J. Fetters, *Chem. Rev.*, **76**, 727 (1976).
2. V. E. Shashoua, W. Sweeny, and R. F. Tietz, *J. Am. Chem. Soc.*, **82**, 866 (1960).
3. M. Goodman and S. Chen, *Macromolecules*, **3**, 398 (1970).
4. M. Goodman and S. Chen, *Macromolecules*, **4**, 625 (1971).
5. M. M. Green, C. Andreola, B. Munoz, and M. P. Reidy, *J. Am. Chem. Soc.*, **110**, 4063 (1988).
6. M. M. Green and M. P. Reidy, *J. Am. Chem. Soc.*, **111**, 6452 (1989).
7. S. Lifson, C. Andreola, N. C. Peterson, and M. M. Green, *J. Am. Chem. Soc.*, **111**, 8850 (1989).
8. M. M. Green, S. Lifson, and A. Teramoto, *Chirality*, **3**, 285 (1991).
9. Y. Okamoto, M. Matsuda, T. Nakano, and E. Yashima, *J. Polym. Sci., A, Polym. Chem.*, **32**, 309 (1994).
10. Y. Okamoto, M. Matsuda, T. Nakano, and E. Yashima, *Polym. J.*, **25**, 391 (1993).