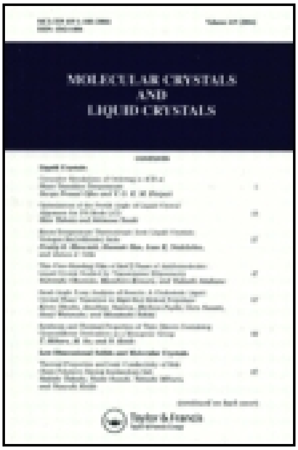

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Anionic Polymerization of Isocyanates with Optically Active Properties

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Anionic Polymerization of Isocyanates with Optically Active Properties

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Abstract Random copolymers, an optically functionalized isocyanate containing disperse red 1 (DR1NCO) with a chiral isocyanate containing (*s*)-(-)-2-methylbutanol (MBI), were prepared by anionic polymerization in THF at –98°C with Na-Naph as a two-directional initiator. As the contents of MBI in the copolymer increased, the optical rotation of the polymer was also increased. To study about the optical activity change with initiator systems, homo polymer of MBI was synthesized with one-directional and two-directional initiator. The difference of optical activity in both systems was investigated using Circular Dichroism (CD) spectroscopy and optical rotation.

Keywords Anionic polymerization; Optical activity; Polyisocyanate

INTRODUCTION

Polyisocyanates are stiff polymers due to amide bond in the polymer main chain. These amide bonds have partially double bond character and tend to be planar. However the polyisocyanate chains are twisted into helical conformation because of steric reason [1]. Due to this strucural property, polyisocyanates have been studied in many applications such as chiral recognition materials, optical switch and liquid crystal materials [2-4].

In this study, we synthsized the random copolymers of isocyanate containing nonlinear optical functionality (DR1NCO) with isocyanate chirality (MBI) via the anionic polymerization using sodium naphthalenide (Na-Naph) as the two-directional initiator. To inspect the effect of polymeric backbone structure on the optical activity, poly(MBI)s with diphenylmethyl sodium (Na-DPM) as the one-directional initiator were synthesized and the optical activity of the polymers was compared with the poly(MBI) from Na-Naph.

EXPERIMENTAL

2-[4-(4-Nitrophenylazo)-N-ethylphenyl amino]ethoxy carbonyl amino hexyl isocyanate (DR1NCO): 1,6-Diisocyanatohexane (7.8 ml) was introduced to a reactor at 25 °C. And then, solution of Disperse Red 1 (DR1, 1.7 g) in THF (60 ml) was added dropwise with vigorous stirring. The reaction mixture was vigorously stirred for another 12 h. Large amount of dry *n*-hexane was added into the mixture to get precipitation under nitrogen atmosphere, and the precipitate was obtained by filtering the solution and washed by dry n-hexane.

(*s*)-(-)-2-Methyl-1-butyloxy carbonyl amino hexyl isocyanate (MBI): This monomer was prepared from the reaction of 1,6-diisocyanatohexane and (*s*)-(-)-2-methylbutanol by the similar procedures as above.

All the polymerizations were carried out under high-vacuum conditions (10^{-6} mmHg) in an all-glass apparatus equipped with break-seals. CD/ORD spectra (JASCO 715) were taken using quartz cell (0.1 dm length) under nitrogen at room temperature.

RESULTS AND DISCUSSION

Table 1 shows the results of random copolymer of DR1NCO with MBI. Due to the optical activity of MBI, polymers with optical activity were obtained and optical activity increases as the composition of MBI increases.

TABLE 1 Poly(DR1NCO-r-MBI)s with Na-Naph at –98°C

Composition [a], %					
Oct-NCO[b]	MBI	DR1NCO	Mn[c]	Mw/Mn[c]	$[\alpha]_D^0$
8.0	< 1.0	91.0	11,000	1.10	0
23.0	10.0	77.0	15,000	1.85	+10
35.0	29.0	36.0	14,900	1.32	+17
58.0	34.0	8.0	27,000	1.89	+27

[a] Determined by ^{1}H NMR and UV. [b] Oct-NCO was used as additive to stabilize the anion in the initiation step. [c] Determined by SEC using polystyrene standard in THF at 35°C.

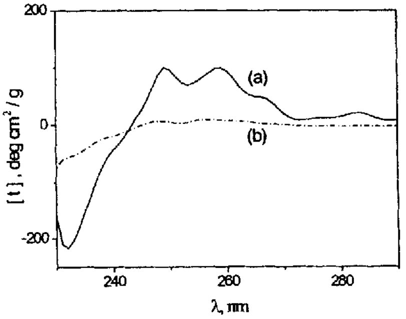

FIGURE 1 CD spectra of poly (MBI)s, (a) with one-directional, (b) two-directional initiator

To inspect the effect of polymeric structure on the optical activity, homo polymer of MBI was synthesized with Na-Naph or diphenyl methyl sodium (Na-DPM) as a two or one-directional initiator respectively. Sodium tetraphenyl borate as the ligand was also added to the polymerization with Na-Naph to get the well-controlled polymer. Figure 1 shows the CD spectra of poly(MBI)s in each case. In the case of polymer only with one-directional initiator, it shows preferred helix conformation in CD spectrum and its optical rotation is higher than that of the other case.

The optical rotation measurement also shows the same results. Especially, in the case of polymer with $NaBPh_4$, the polymer shows very low optical activity (nearly zero degree at 589 nm). Thus, it can be explain that the polymer from bi-directional initiator has the kink like a helix reversal at the middle of the backbone (double carbonyl bond) so that the polymer has low optical activity and no preferred helix conformation.

CONCLUSIONS

This study shows that optical activity of poly(MBI)s depends on the initiator system and backbone structure. Thus, it can be concluded that the kink duc to two-directional initiated system serves as helix reversal and it prohibit the formation of one-handed helical conformation in two-directional initiated system.

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REFERENCES

1. Bur, A. J.; Fetters, L. J. *Chem. Rev.*, **76**, 727 (1976).
2. Maeda, K.; Matsunaga, M.; Yamada, H.; Okamoto, Y. *Polym. J.*, **29**, 333 (1997).
3. Muller, M.; Zentel, R. *Macromolecules*, **27**, 4404 (1994).
4. Goodman, M.; Chen, S. *Macromolecules*, **4**, 625 (1971).