

Induction of Single Helical Screw Sense in Poly (*n*-Hexyl Isocyanate) by End-capping with a Chiral Moiety

G. Yogendra Nath,¹ Shashadhar Samal,¹ Sang-Yoon Park,¹ C. N. Murthy,² Jae-Suk Lee^{*1}

¹Department of Materials Science and Engineering and Center for Advanced Materials Research and Education (CAMRE), Gwangju Institute of Science and Technology (GIST), 1 Oryong-dong, Buk-gu, Gwangju 500-712, Korea. *jslee@gist.ac.kr

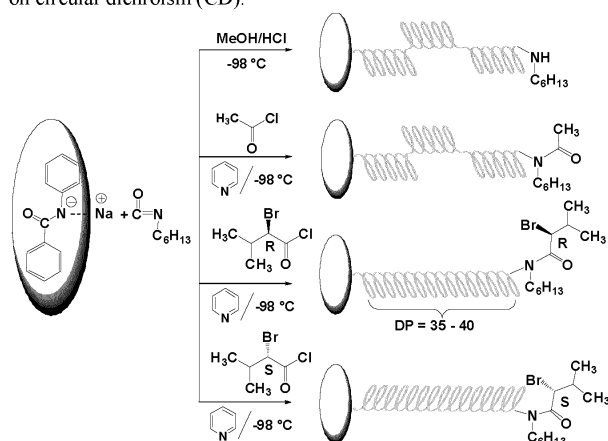
²Applied Chemistry Department, Faculty of technology and engineering, The M. S. University of Baroda, Vadodara 390001, Gujarat, India.

Introduction

Polyisocyanates are a kind of polymers with a helical conformation that is intercepted by mobile helical reversal defects, allowing the helical chains to interconvert dynamically between left- and right-handed conformations. These polymers give opportunity to observe the effect of helical sense induced by chiral moiety in the chain end. Optically active polyisocyanates with one-handed helical conformation can be obtained by using chiral monomers [1], initiators [2], and solvents [3]. Herein, we report chiral induction in poly(*n*-hexyl isocyanate) (PHIC) by covalently appending a chiral residue to the end of the polyisocyanate chain.

We have been involved in controlled synthesis of PHICs by anionic polymerization using additives [4]. We recently achieved the polymerization of HIC using sodium benzanilide (Na-BA) as the initiator that does the dual function of initiation as well as chain-end protection [5]. The living nature of PHIC was as high as 60 minutes that allowed us to end-cap PHIC using a number of acid chlorides in the presence of pyridine leading to 100% end capping.

In this work we study the induction of chirality in PHIC synthesized by Na-BA and end-capped with chiral R- and S-2-bromo-3-methylbutyryl chloride (R-, S-BMBC) (Scheme 1). Chiral PHICs of different molecular weights in the range 2.5 - 9 kg·mol⁻¹ were synthesized to study the effect of molecular weight and temperature on circular dichroism (CD).



Scheme 1. PHIC end-capping with different acid chlorides in the presence of pyridine at -98 °C.

Experimental

All polymerizations were carried out under high vacuum in a glass apparatus equipped with break-seals. In a typical polymerization procedure, the initiator solution, Na-BA in THF, was transferred into the reaction flask through the break-seal and the solution temperature was then equilibrated to the reaction temperature of -98 °C. The polymerization was carried out by adding the HIC in THF to the initiator solution. End capping of the polymer chain was successfully done by the introduction of pyridine as a catalyst along with acid chloride into the polymerization reaction. After 50 min of polymerization, pyridine and acid chloride R-BMBC (or S-BMBC) were added in sequence. Termination occurred immediately seen from the color change of the amidate anion from greenish yellow to colorless. Polymers were precipitated into methanol, filtered, and

dried *in vacuo*. Low molecular weight polymers were separated by centrifuge. The yield of the polymer was ~100%. For circular dichroism studies the polymers were reprecipitated several times in methanol and freeze-dried under vacuum at 10⁻⁶ torr.

Results and discussion

Polymers with low molecular weight in the range 2.5 - 9 kg·mol⁻¹ were synthesized by using the protocol we developed. The polydispersities were also very narrow (<1.1). These chiral low molecular weight polymers showed a CD maximum at 257 nm, characteristics of the polyisocyanate backbone. The intensity of CD absorption steadily increased up to molecular weight of 5 kg·mol⁻¹ and thereafter it decreased (Figure 1). This molecular weight of the PHIC means a DP value of ~36 after accounting for the molecular weight of the initiator and the end group. When the temperature chiral PHIC of molecular weight 9 kg·mol⁻¹ in solution was decreased the CD steadily increased indicating that at low temperature the helix induction length increased beyond a DP of 36. A mixture of two PHIC samples of equal molecular weight and concentration but opposite helicity showed no CD.

Enhanced induction length could be attributed to the optical property of the chiral moiety, the appended group on amide nitrogen, temperature and solvent effects, as well as narrow polydispersity. Control of polydispersity to values less than 1.1 makes it almost a monodisperse system and hence CD values were high.

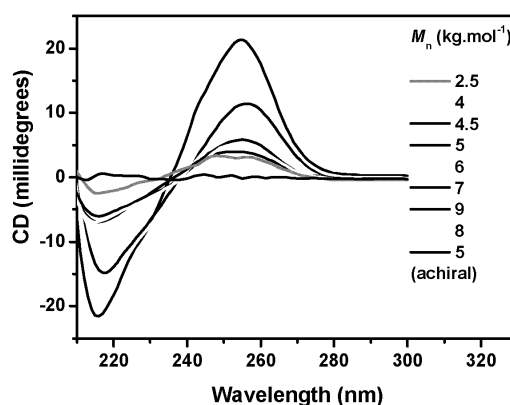


Figure 1. Circular dichroism spectra of PHIC of varying molecular weights end-capped with R-BMBC in hexane (1 mg/mL, path length 0.01 cm) at 25 °C.

Conclusions

We have shown that a control over living anionic polymerisation of HIC by using a suitable initiator affords an opportunity to introduce chiral end-groups with 100% yield and in high purity. The chiral end-groups could induce helicity up to ~40 monomer units at room temperature, which is quite high in comparison to previously known chiral isocyanates. In contrast to the limited number of chiral initiators known, there is a long list of the chiral acid chlorides of varying optical activity to choose from. Using this protocol a number of functional chiral polyisocyanates can be accessible for tailored applications in such diverse areas as chiral separation, catalysts for asymmetric synthesis, information storage, chiral sensing, etc.

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