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Induction of Helicity in Poly(*n*-hexyl isocyanate) with Terminal Chiral Residues

G. Yogendra Nath,[†] Shashadhar Samal,[†]
Sang-Yoon Park,[†] C. N. Murthy,[‡] and Jae-Suk Lee*,[†]

Department 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,
and Applied Chemistry Department, Faculty of Technology
and Engineering, The M. S. University of Baroda,
Vadodora 390001, India

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The polyisocyanates are fascinating polymers in that they have a dynamic right- (P) or left-handed (M) helical conformation.[1,2] The groups of Green,[3] Okamoto,[4] and Zentel,[5] among others,[6] have made a number of elegant studies on these polymers. Optically active polyisocyanates with one-handed helical conformation can be obtained by using chiral initiators (Figure 1a),[7] monomers (Figure 1b),[8] and solvents.[9] Single helical screw sense in the isocyanates through chiral inductions by these routes is marked with fascinating concepts such as the sergeants-and-soldiers principle[3,10] and the majority rule.[11] The chiral inductions of such types, called the domino effect, are also achieved in peptides by noncovalent interactions.[12] There have been no studies so far on helicity induction by introducing a terminal chiral moiety in the polyisocyanates largely because quantitative termination of the living polyisocyanate has not been achieved until recently. Herein, we report the covalent domino effect of the terminal chiral residues in the living poly(*n*-hexyl isocyanate) (PHIC) by reacting the polymer with a number of chiral acid chlorides in the presence of pyridine (Figure 1c).

Termination of the living PHIC with a functional moiety is not efficient due to low reactivity of the living anion at −98 °C. Increasing the temperature does not help either, as a competing backbiting reaction leads to rapid degradation of the polymer. Introduction of the terminal group in polyisocyanates at room temperature via coordination polymerization[13−15] was not very efficient even after 24 h of reaction. For quantitative termination of the living PHICs, long-living nature of the polymer is crucial. However, during polymerization PHIC undergoes rapid trimerization unless an additive is used.[16] We recently achieved the polymerization of *n*-hexyl isocyanate (HIC) using sodium benzanilide as the initiator which does the dual function of initiation as well as the chain-end protection.[17] The living nature of PHIC was as high as 60 min which allowed enough leverage to carry out termination reaction very effectively using a number of acid chlorides. Since at −98 °C the living PHIC is still very quiescent, the reaction with an acid chloride required catalyzing by pyridine. The reaction mediated by the pyridinium ion[18] augmented the nucleophilicity of the PHIC anion, leading to introduction of the terminal residues most efficiently with polymer yields as high as 100%.

In this work we study the induction of chirality in the polyisocyanates through termination by reacting the living PHICs with chiral (*R*)- and (*S*)-2-bromo-3-methylbutyryl chloride ([α]^{22} = ±21°) (Figure 1, see also Figure S1, Supporting Information). The chiral PHICs of different molecular weights (MWs) in the range 2.5−9 kg mol^{-1} (Table S1, Supporting Information) were synthesized to study the effect of MW and temperature on circular dichroism (CD). For chiral studies involving polyisocyanates, where small variations in MW can have profound bearing on the optical activity, it is essential that the molecular weight distribution (MWD) of the polymers should be narrow. The low molecular weight chiral PHICs synthesized for the present study were of very narrow MWD (<1.1). The ^{1}H NMR spectra of all the synthesized polymers did not show any NH peak, indicating that the introduction of the chiral moiety to the N-terminal was 100% (Figures S2, Supporting Information).

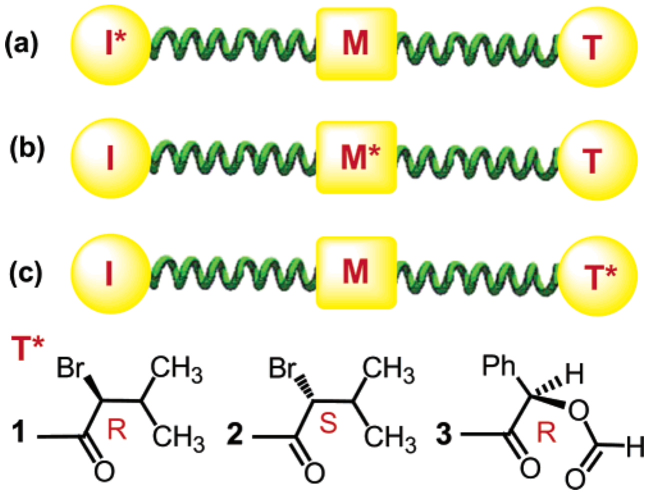

Figure 1. Schematics of the chiral PHICs obtained by (a) chiral initiator (ref 7), (b) chiral monomer (refs 8, 10, 11), and (c) chiral terminal moieties, **1**−**3** (this work). I, M, and T represent the achiral initiator, monomer, and terminal groups, respectively, I*, M*, and T* being the corresponding chiral species.

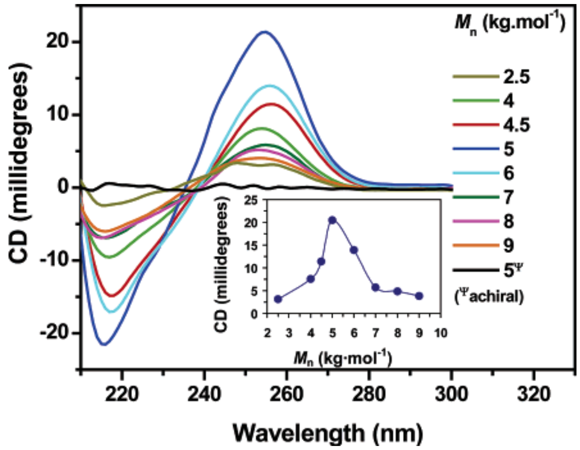

Figure 2. CD spectra of chiral PHICs of varying molecular weight with *R*-BMB terminal group in hexane (1 mg/mL, path length 0.01 cm) at 25 °C. Inset: MW of the chiral PHICs vs CD intensity at 257 nm.

The CD of the chiral oligoisocyantes of varying MW in the range 2.5−9 kg mol^{-1} with (*R*)-2-bromo-3-methylbutanoyl (*R*-BMB) terminal group (**1**) is shown in Figure 2. The chiral low MW polymers showed a CD maximum at 257 nm, characteristic of the polyisocyanate backbone.[9] The intensity of CD absorption steadily increased up to MW of 5 kg mol^{-1} and thereafter it

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[†] Gwangju Institute of Science and Technology.
[‡] The M. S. University of Baroda.
* Corresponding author. E-mail: jslee@gist.ac.kr.

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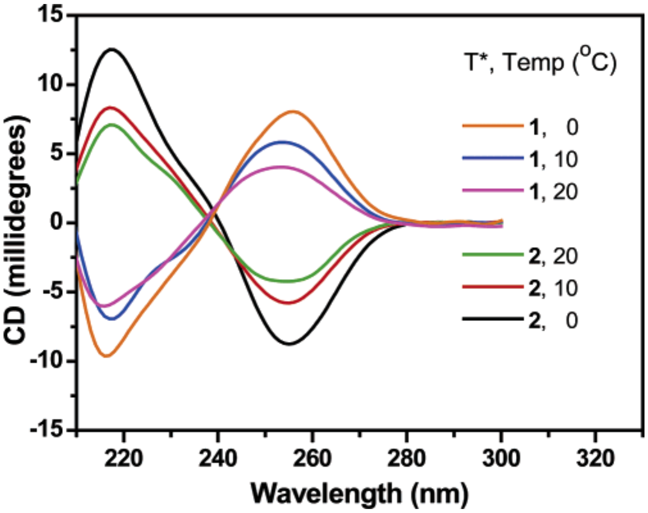

Figure 3. CD spectra of PHICs with terminal chiral groups T*, **1** and **2**, in hexane (1 mg/mL, path length 0.01 cm) at three different temperatures, 0, 10, and 20 °C.

decreased (Figure 2, inset). This MW of the PHIC means a DP of ∼36, which is more than twice reported for oligomers from aryl isocyanates prepared by chiral initiator and obtained by fractionation.[19] That the compensation of the CD by HIC segments of opposite helicity is quantitative was demonstrated when a mixture of two PHIC samples of equal MW (9 kg mol^{-1}) and concentration but opposite helicity showed no CD. This was further confirmed when addition of 10 M excess of (*R*)-2-bromo-3-methylbutyric acid (*R*-BMBA) to chiral PHIC of MW 9 kg mol^{-1} with *R*-BMB terminal groups showed no effect on CD in agreement with earlier observations in chiral initiator system.[20]

Chiral PHICs of similar MW but of opposite helicity with *R*- and *S*-BMB terminal chiral species were used to study the effect of temperature on helicity (Figure 3). As shown above, the chiral PHIC of MW 9 kg mol^{-1} has a low CD, almost close to that of the sample of MW 2.5 kg mol^{-1} at ambient temperature. When the temperature of the chiral PHIC of MW 9 kg mol^{-1} in solution was decreased, the CD steadily increased, indicating enhanced induction of helicity at lower temperature. Expectedly, for the polymer of MW 5 kg mol^{-1}, which has no kinks at ambient temperature there was no change in CD upon decreasing the temperature. Both the PHICs with opposite helicity showed identical CD behavior toward variation in temperature.

The covalent domino effect demonstrated here through termination route has a distinct aspect in that it is possible to introduce functional groups to the chiral PHIC chain in the anionic polymerization environment, an added advantage not realized with other methods such as using the chiral initiators or the chiral monomers. For example, through termination we could synthesize the chiral PHIC with the terminal group **3** containing the CHO group. In the presence of pyridine, the COCl group was highly reactive to such an extent that the formyl CHO group remained unaffected. This reactive chiral polymer should be suitable for further reactions. It would be possible to introduce other functional groups by using suitable chiral acid chlorides.

In principle, a chiral moiety at either termini of the polyisocyanate should have similar helicity manifestations. The factors that could be responsible for the protracted induction length are attributed to the optical property of the chiral moiety and the appended group on the amide nitrogen, in addition to the temperature and solvent effects. In our case narrow polydispersity (<1.1) and high purity were distinctive contributing factors. A chiral oligohexylisocyanate with a broad polydispersity means a mixture of oligomers of varying sizes. While this would not be of much concern for high molecular weight PHICs, small variations in MW of oligomers can significantly influence the CD.

We have successfully demonstrated significant helicity induction by appending terminal chiral residues to the living PHICs. Helicity is induced up to ∼36 monomer units at room temperature. In contrast to the limited number of chiral initiators and monomers known, there is a long list of the chiral acid chlorides of varying optical activity to choose from. Using this protocol, functional chiral polyisocyanates can be accessible with applications envisaged in such diverse areas as chiral separation, catalysts for asymmetric synthesis, information storage, chiral sensing, etc.

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Supporting Information Available: Experimental procedure and results. These materials are available free of charge via the Internet at http://pubs.acs.org.

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