

Helix-Sense Selective Polymerization of Carbodiimides: Building Permanently Optically Active Polymers from Achiral Monomers

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The helix, a ubiquitous motif in biological polymers, is also an important structure in synthetic materials.¹ Many applications of helical polymers emanate from the disymmetric nature of a single helical sense, and these include chiral separations medium,² display materials,³ sensors,⁴ selective Bragg reflectors,⁵ amplifiers,⁶ and optoelectronic materials.⁷ While single screw-sense polymers can be formed from optically active, homochiral monomers,¹ this approach is limited by both the small number of viable monomers and expense. To address this limitation, we have been interested in developing helix-sense selective polymerizations of achiral monomers using chiral catalysts.⁸ For this approach to be viable, the helical conformation of the polymer must be under kinetic, rather than thermodynamic, control, and the helix inversion barrier must be sufficiently high to retain the single-handed screw sense. Herein, we wish to report the polymerization of achiral carbodiimides with optically active catalysts to yield stable helical materials with persistent optical activities.

We previously reported the synthesis of optically active, helical polyguanidines from a chiral monomer, *N*-(*R*)-2,6-dimethylheptyl)-*N'*-hexylcarbodiimide, **1**.⁹ Poly-**1** displayed mutarotation with a change in both magnitude and sign when polymer solutions were annealed at elevated temperature (e.g., $[\alpha]_{365} = +7.5^\circ$ to $[\alpha]_{365} = -157.5^\circ$). We have now found that even more dramatic changes are observed when the hexyl group of **1** is replaced by a phenyl. For example, upon annealing poly(*N*-(*R*)-2,6-(dimethylheptyl)-*N'*-phenylcarbodiimide), poly-**2**, at temperatures between 50 and 85 °C, the specific rotation, $[\alpha]_{435}$, changes from -209° to $+255^\circ$ ($c = 0.2$ g/100 mL in toluene) (Figure 1).

By measuring the kinetics of these transitions at different temperatures, we have estimated the helix inversion barriers for these polymers to be 21.6 and 29.2 kcal/mol, respectively. This unusual behavior can be ascribed to an evolution of the polymer chains from kinetically controlled to thermodynamically controlled conformations.⁹

The fact that the polyguanidines could be isolated in kinetically controlled conformations bolstered our hopes for developing helix-sense selective polymerizations. Our first attempts polymerizing carbodiimides with optically active catalysts produced only modest results.¹⁰ Far better results, however, were obtained using (*S*-BINOL)Ti(OiPr)₂, **S-I** (or **R-I**).¹¹ The monomers (*N*-hexyl-*N'*-(X)carbodiimides (where X = isopropyl (**3**), hexyl (**4**), or phenyl (**5**)) were polymerized with **S-I** in good yields (86–95%) and showed varying degrees of asymmetric induction (eq 1).

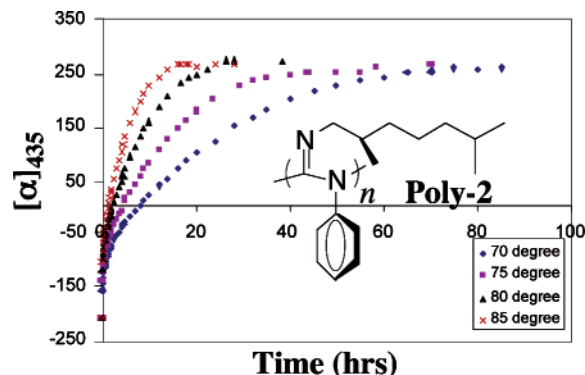
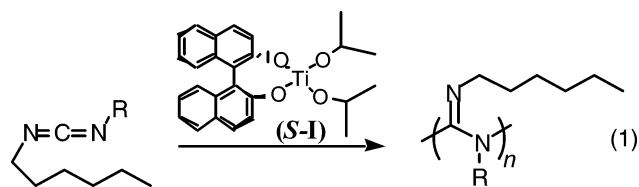


Figure 1. Evolution of the optical rotation of poly-2 as a function of time and temperature.

All of the polymers produced were found to be optically active, verifying that the chiral ligand indeed dictates the conformation of polymer chain. Optical rotations ($[\alpha]_{435}$, $c = 0.2$ in toluene) were measured to be -15° , -44° , and -753° for poly-**3**, **4**, and **5**. **R-I** produces essentially mirror image results (e.g., poly-**5**, ($[\alpha]_{435}$, $c = 0.2$ in toluene).

The optical rotations of poly-(**3**–**5**) were found to be temperature-dependent and diminished to zero at elevated temperatures. We ascribe this behavior to conversion of chains with a predominate screw sense to a racemic mixture of chains through a helix inversion processes. For example, the optical activity of poly-**5** was relatively stable at 25 °C ($k_{\text{obs}} = 3.96 \text{ s}^{-1}$, $t_{1/2} = 631 \text{ h}$). However, the optical rotation decreased rapidly and approached 0° after 15 h when the polymer solution in toluene was heated at 70 °C ($k_{\text{obs}} = 920 \text{ s}^{-1}$, $t_{1/2} = 2.7 \text{ h}$).

For poly-**4** and poly-**5**, plots of $\ln\{([\alpha] - [\alpha]_{\infty})/([\alpha]_0 - [\alpha]_{\infty})\}$ versus time yielded linear lines at different temperatures, which suggested that the helix inversion is the first order to polymer concentration. From Arrhenius plots, the activation energy barriers of helix inversion were estimated to be 22.8 and 25.6 kcal/mol for poly-**4** and poly-**5**, respectively. Accurate kinetic data could not be determined for poly-**3** due to the relatively low optical rotation, slow inversion rate, and polymer decomposition, but a lower limit of approximately 28 kcal/mol could be established from the limited data collected at 70–80 °C.

For many applications, stable, nonracemizable helices are required. To accomplish this, we investigated increasing the sterics of the side chains using 2,6-substituted aromatic substituents, and during this study we came across a remarkable polymer that permanently maintains its chiral conformation even at elevated temperatures. Of the various substituted derivatives investigated, *N*-methyl-*N'*-(2-methyl-6-isopropylphenyl)carbodiimide, **6**, proved to be both polymerizable and produced a soluble polymer in high yields. The *N*-methyl group was selected to improve the polymerizability of the carbodiimide monomer, and the 2,6-substitution pattern was used to further break the symmetry of the repeating

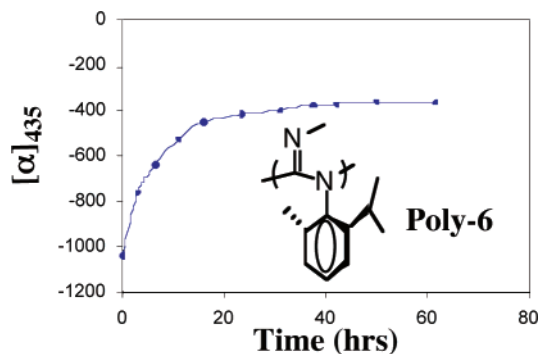


Figure 2. Optical rotation of poly-6 in chloroform as a function of time at 50 °C.

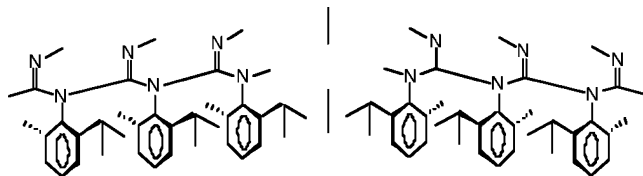


Figure 3. Mirror images of poly-6 illustrating the asymmetry resulting from the regioregular alignment of the aryl substituents and the regular registry of the imine groups.

unit. Poly-6 showed an even higher specific rotation than poly-5 ($[\alpha]_{435} = -867^\circ$ in toluene, ($c = 0.093$) and -1034° in CHCl_3 ($c = 0.33$).

Surprisingly, when poly-6 was annealed its optical rotation never went to zero, i.e., it would not racemize. Instead, the optical rotation reached a plateau value ($[\alpha]_{435} = -360^\circ$, $c = 0.33$ in CHCl_3) that was indefinitely stable (Figure 2). Arrhenius analysis yielded an activation barrier $E_a = 23$ kcal/mol for the initial process.

We believe the observed mutarotation is again associated with the racemization of the helical backbone. However, maintaining optical activities under these racemizing conditions requires that a higher level asymmetry be built into the polymer structure that involves both regioregular placement of the aromatic substituents and regular registry of the imine groups (Figure 3).

This proposal is supported by the observation of two signals for the isopropyl methyl groups at δ 25 and 21 ppm in the ^{13}C NMR spectrum of poly-6, which indicates that *N*-aryl rotation and the syn/anti-topomerization of $\text{C}=\text{N}$ double bond are both inhibited in the polymer chain. The spectrum does not change upon annealing. The close packing of adjacent groups along the polymer chain requires these normally low-energy processes¹² to occur with a level of cooperativity, such as all *N*-aryl bonds rotating in concert, that cannot be achieved.

Building on this concept of breaking the symmetry of the aromatic ring, we synthesized and polymerized *N*-dodecyl-*N'*-(1-naphthyl)carbodiimide, **7**, using *S*-**I**. Again, high enantioselectives were observed. Poly-7 proved to be an interesting material. Among its unusual properties, the optical rotation of poly-7 shows a strong solvent dependence varying from -256° in heptane to $+302^\circ$ in dichloromethane. These dramatic differences suggest extensive, but reversible, changes in the helical conformation of poly-7 that do not induce racemization. These changes do not track with the dipole moment or dielectric constant of the solvent, implying deep-seated, specific solvent-polymer interactions un-

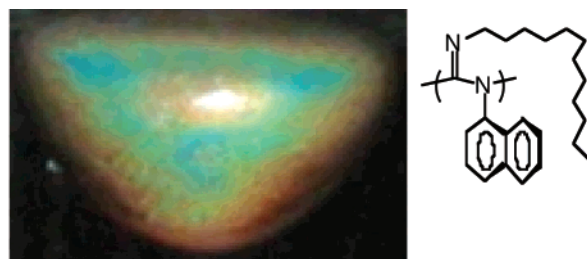


Figure 4. Opalescent cholesteric films of poly-7 prepared using chiral catalyst *S*-**I**.

derlie this phenomenon. Although no evidence exists to suggest this, aggregation cannot be ruled out at this time.

The single-handed nature of these chiral polymers translates from the independent chains to their bulk properties. Poly-7 displays birefringent, cholesteric mesophases. Most interesting, however, is when the solvent is removed by simple evaporation, the resultant films of poly-7 are highly opalescent (Figure 4) due to the Bragg reflection of visible light from the pitch of the frozen cholesteric domains.¹³ Our previous examples of opalescent solids required locking-in the cholesteric mesophases by cross-linking reactions.⁵

In conclusion, asymmetric complexes of the type illustrated by *S*- and *R*-**I** are effective at catalyzing the helix-sense selective polymerization of achiral carbodiimides. Furthermore, by controlling the substitution pattern, permanent asymmetry can be induced into these polymers, and unusual properties result.

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Supporting Information Available: Experimental details for the monomer synthesis, polymerization, and other related characterizations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Green, M. M.; Cheon, K.-S.; Yang, S.-Y.; Park, J.-W.; Swansburg, S.; Liu, W. *Acc. Chem. Res.* **2001**, *34*, 672.
- (2) (a) Tsuchida, A.; Hasegawa, T.; Kobayashi, K.; Yamamoto, C.; Okamoto, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 2681. (b) Shinohara, K.; Aoki, T.; Kaneko, T. *J. Polym. Sci., Polym. Chem. Ed.* **2002**, *40*, 1689.
- (3) Dyer, D. J.; Schroeder, U. P.; Chan, K.-P.; Twieg, R. J. *Chem. Mater.* **1997**, *9*, 1665.
- (4) (a) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860. (b) Kubota, T.; Yamamoto, C.; Okamoto, Y. *J. Polym. Sci., Polym. Chem. Ed.* **2003**, *41*, 3703. (c) Ashida, Y.; Sato, T.; Morino, K.; Maeda, K.; Okamoto, Y.; Yashima, E. *Macromolecules* **2003**, *36*, 3345.
- (5) Maxein, G.; Keller, H.; Novak, B. M.; Zentel, R. *Adv. Mater.* **1998**, *3*, 341.
- (6) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3139.
- (7) (a) Koeckelberghs, G.; Sioncke, S.; Verbiest, T.; Persoons, A.; Samyn, C. *Polymer* **2003**, *44*, 3785. (b) Kauranen, M.; Verbiest, T.; Meijer, E. W.; Havinga, E. E.; Teerenstra, M. N.; Schouten, A. J.; Nolte, R. J. M.; Persoons, A. *Adv. Mater.* **1995**, *7*, 641.
- (8) (a) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013. (b) Demins, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 7962.
- (9) Schlitzer, D. S.; Novak, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 2196–2197.
- (10) Heintz, A. M.; Novak, B. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 429.
- (11) Balsells, J.; Davis, T. J.; Carroll, P.; Walsh, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 10, 336.
- (12) Kessler, H.; Leibfritz, D. *Chem. Ber.* **1971**, *104*, 2143–2157.
- (13) Ferguson, J. L. *Mol. Cryst.* **1966**, *1*, 293.

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