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A New, More Versatile, Optical Switching Helical Polycarbodiimide Capable of Thermally Tuning Polarizations ±359°

Justin G. Kennemur, J. B. Clark, IV, Gonglu Tian, and Bruce M. Novak*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695

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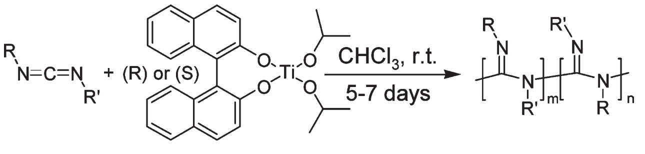
ABSTRACT: An in depth study of newly synthesized polycarbodiimides containing asymmetric aryl pendant groups has been performed. The focus of this study was to create new polymers capable of the low-energy, reversible, solvo-, and thermocontrollable conformational switching phenomenon previously discovered. Of the polymers synthesized, one polymer, *N*-(1-naphthyl)-*N*′-(*n*-octadecyl) polycarbodiimide, **Poly-5**, has been found to undergo reversible optical switching in various solvents, each of which alter the temperature at which the switching is observed. The switching is not due to helical inversions, but instead due to synchronous rearrangement of polyarene pendant groups around the helical backbone. This is further shown by anisotropic changes of the aromatic chemical shifts using variable temperature ^{1}H NMR through the observed thermal switching range in THF-d_8. The net change in specific optical rotation reaches a remarkable 1700° and changes in the direction of rotation. The polymer system is tunable and capable of holding the polarization output constant at constant temperature anywhere within the switching profile. Polarimetry and electronic circular dichroism (ECD) studies were performed to observe these conformational changes. Additionally reported are new polycarbodiimides that probe the effects of size and geometry of various arene pendant groups on the switching behavior of these polymer systems.

Introduction

Polycarbodiimides (or polyguanidines), a static class of helical polymers with dynamic features, have continued to evolve since the discovery of the ability to polymerize carbodiimides in a living fashion via titanium or copper amidinate complexes.[1,2] These systems can be polymerized with an excess helical sense through the use of carbodiimide monomers containing chiral pendant groups[3−5] as well as with achiral carbodiimides through the use of chiral catalyst systems (Scheme 1).[6,7] Of the many interesting properties exhibited by these helical polymers, such as chain stiffness,[8] high racemization barriers,[5] liquid crystalline cholesteric, lyotropic, and thermotropic phases,[6,9,10] and large optical rotatory dispersion (ORD),[5] focus has been placed on a unique thermo- and solvocontrollable switching phenomenon that has been previously discovered after the synthesis of *N*-(1-anthryl)-*N*′-(*n*-octadecyl)polycarbodiimide, **Poly-1** (Chart 1).[11,12]

The development of synthetic helical polymers capable of exhibiting conformational changes through the influence of external forces, such as solvent, pH, and temperature, has been a growing area of interest.[13] Of this class of polymers, some have been reported to exhibit large changes and reversals in the direction of ORD and ECD Cotton effects. To date, most of these conformational changes reported by synthetic helical polymers such as polyisocyanates,[14−17] poly(phenylacetylene)s,[18−22] and polysilylenes[23,24] have been attributed to helix−helix transitions of their relatively flexible backbone through the influence of chiral pendant groups and/or chiral guest molecules. Potential applications of such systems include optical sensors, optical displays, chemosensors, biomimetic materials, data storage devices, and chiral separations, to name a few. In light of this, **Poly-1** is unique in the sense that it is polymerized with an excess helical sense using achiral monomers, and similar ORD and CD changes are observed without the influence of other chiral species, meaning that the only chiral presence in this system is due to the helical backbone. **Poly-1** exhibits a large reversible change in optical rotation and ECD Cotton effects when dissolved in toluene and fluctuated within a relatively low-temperature range ($[\alpha]^{31}_{D} = +300°$, $[\alpha]^{44}_{D} = -205°$).[11] Through a series of ECD, polarimetry, and VCD studies, it was discovered that these large changes in **Poly-1** were not caused by imine or helical inversions but instead by synchronous realignment of the anthracene pendant groups, which span around the fixed polycarbodiimide helical backbone.[12] The basis for this behavior lies within the fact that the large, "shutter-like", anthracene pendant groups form an embedded second-level of chirality around the helical backbone and are too restricted for free rotation, hence allowing them to lie collectively in only two positions relative to the helical director. It is the switching between these two positions that gives rise to the change in ORD observed. Although interesting, **Poly-1** was found to switch by thermal influence in toluene alone. Other solvents, such as $CHCl_3$ and THF, could be doped in toluene to induce the switching, but the phenomenon was not observed by thermal influence in these solvents.[11] Such limitations prevented a more in depth study toward the influential forces, albeit solvation, polarity, and weak noncovalent interactions that may govern these conformational changes. With this in mind, we set out to synthesize new polycarbodiimides that exhibit this switching capability with the hopes of further deducing trends within this unique behavior.

Scheme 1. General Synthesis of Helical Polycarbodiimides Using Achiral Asymmetric Monomers and a Chiral (*R*) or (*S*)-BINOL-diisopropoxy-titanium(IV) Catalyst



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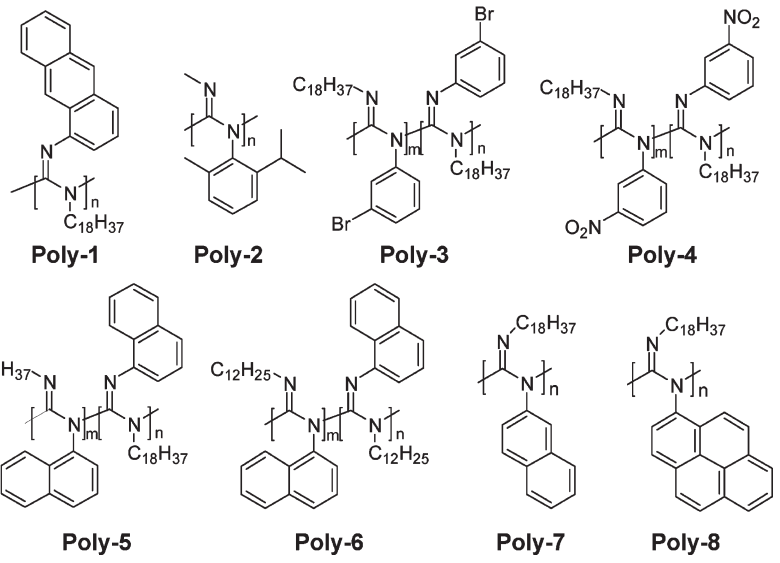
*Corresponding author: Bruce_Novak@ncsu.edu.

Chart 1. Previously and Newly Synthesized Polycarbodiimides Containing Asymmetric Polyarene Pendant Groups[a]



[a] Previously reported **Poly-1**[11] and **Poly-2**[6] are shown with their originally designated regiostructure.

Experimental Section

Materials. 3-Nitroaniline, 3-bromoaniline, *n*-octadecyl isocyanate, 1-aminonaphthalene, 1-aminopyrene, 2-aminonaphthalene, bromine, titanium tetraisopropoxide, (*R*)-(+)-1,1′-bi-2,2′-naphthol (BINOL), (*S*)-BINOL, decalin, *N*,*N*-dimethylaminoethylamine (DMAEA), and ethylbenzene were purchased from Aldrich (Sigma-Aldrich, Milwaukee,WI) and used without further purification unless otherwise noted. Triethylamine, triphenylphosphine, and other discussed laboratory solvents were purchased from Fisher Scientific, Fair Lawn, NJ. Solvents used for polymerization or catalyst synthesis were dried, distilled, and degassed and stored over molecular sieves prior to use. ECD and UV−vis experiments were performed in spectroscopy-grade THF also purchased from Aldrich.

General Preparation of Monomers. Appropriate amine and isocyanate (1:1 mol equiv) were combined and refluxed in DCM overnight. The resulting solid urea was separated by filtration, recrystallized in mixtures of ethanol and methanol, and dried under vacuum. To a charged DCM solution of triphenylphosphine, bromine, and triethylamine (1:1.1:2.2 mol equiv based on urea) at 0 °C, the urea is added in portions, and the reaction is allowed to warm to room temperature. The dehydration of urea into carbodiimide can be monitored by infrared spectroscopy by the formation of a strong N=C=N absorption band at ~2100 $\mathrm{cm^{-1}}$. Once complete, the resulting monomer is purified by quenching the reaction solution with pentane and filtering away unwanted triphenylphosphine oxide and triethylammonium bromide salt. The filtrate, containing the dissolved monomer, is then reduced via rotary evaporation, and the pentane quenching cycle is repeated up to three times to remove as much unwanted byproducts as possible. Final purification of the monomer can be performed by column chromatography using silica gel as the stationary phase and mixtures of DCM/hexanes as the mobile phase. Once collected, the pure monomers are dried by high vacuum and backfilled with dry nitrogen several times using Schlenk techniques prior to polymerization.

Preparation of (*R*)-BINOL-titanium(IV)-diisopropoxide Catalyst.[25] Titanium tetraisopropoxide is dried, distilled, and degassed prior to use. (*R*)-BINOL is kept in an MBraun Unilab drybox under a dry nitrogen atmosphere and used as received. In the drybox, 1:1 mol equiv of titanium tetraisopropoxide and (*R*)-BINOL are slightly diluted in dry, degassed toluene and added to a 50 mL top-sealing Schlenk flask. The flask is sealed, removed from the drybox, and stirred at room temperature for 3−5 h. Using a Schlenk line equipped with high vacuum and dry nitrogen, toluene and liberated isopropanol are removed from the flask, and the resulting red-orange catalyst is recrystallized in dry, degassed, diethyl ether (DEE). After cooling in an ice bath, the DEE is carefully removed from the orange crystals using a dry syringe. The crystals are then fully dried by reduced pressure and transferred back into the drybox for storage. The same procedure is followed if using the (*S*)-BINOL ligand instead.

General Preparation of Polymers. Polymers are prepared according to Scheme 1. In a drybox, monomer is added to a clean vial and weighed (typically ~1 g of monomer is used for polymerizations). To the monomer is added the appropriate amount of catalyst dissolved in dry, degassed $\mathrm{CHCl_3}$ at a known concentration. The monomer-to-catalyst molar ratio is typically 200:1 unless otherwise noted. The polymerization vial is capped tightly and stirred within the drybox for 3−5 days. Depending on the nature of the monomer, solidification and seizing of the stir bar could occur within 3 days or up to 5 days. Once the stir bar is seized, the polymer gel is allowed to diffuse further for 1−3 days in the vial. The polymer is purified by dissolving in wet $\mathrm{CHCl_3}$ and precipitated by dropping the solution into stirring methanol, ethanol, or *n*-butanol. The choice of alcohol depends on the miscibility of the residual monomer within it. The polymer is filtered, collected, and redissolved/reprecipitated up to three times for further purity. Polymers are then dried under vacuum.

Instrumentation Used for Characterization of Monomers and Polymers. Infrared spectroscopy is performed on a Jasco FT-IR 140 Fourier transform infrared spectrometer using potassium bromide crystal windows purchased from Aldrich. UV−vis spectroscopy is performed on a Jasco V-550 UV−vis spectrometer using high-clarity quartz cells. Polarimetry is performed on a Jasco P-1010 polarimeter with interchangeable wavelength filters and using a jacketed 0.5 dm cell. Cell temperature is adjusted by a Neslab RTE-140 circulation bath attached to the jacketed cell, and the solution temperature within the cell is monitored by an Omega K-Type thermocouple attached to a Barnant digital thermocouple thermometer. ECD experiments are performed in high clarity quartz cells with a Jasco J-600 spectropolarimeter equipped with a variable temperature (VT) circulation bath. GPC analyses are performed using two sequential PL-Gel 5 μm Mixed-C columns 300 × 7.5 mm (Polymer Laboratories, Amherst, MD) that are kept isothermal in an Eppendorf CH-500 column heater. A mixture of 0.5% DMAEA in HPLC grade THF is used as a mobile phase, and standards of poly-2-vinylpyridine (PSS-USA, Silver Spring, MD) are used for universal calibration. A Jasco PU-1580 intelligent HPLC pump and a Jasco RI-1530 refractive index detector are also used. ^{1}H and ^{13}C NMR analyses were performed on a Mercury 300 or 400 spectrometer using deuterated solvents (Cambridge Isotope Laboratories) with tetramethylsilane internal standard. VT ^{1}H NMR was performed on a Mercury 300 spectrometer. Mass spectra were obtained at the NCSU Department of Chemistry Mass Spectrometry Facility using electrospray ionization (ESI) on an Agilent Technologies 6210 LC-TOF mass spectrometer.

Results and Discussion

Before the discovery of **Poly-1**, unique behavior from polycarbodiimides containing an asymmetric arene pendant group had already been observed. Previously reported **Poly-2** exhibited incomplete racemization, even upon annealing at higher temperatures for many hours.[6] It was concluded that steric hindrance caused by the bulky and asymmetric 2-isopropyl-6-methylphenyl pendant group induced a permanent asymmetry to the polymer system that disallowed full racemization. Building on ideas from these combined discoveries, we initiated a series of structure−property relationship studies to elucidate the important elements that are responsible for the observed optical switching process. Our first set of potentially switching polycarbodiimides was to contain a phenyl pendant group with different substituents placed in the meta position, **Poly-3,4**. These substituents could provide asymmetry, steric restriction on *N*-Aryl bond rotations, and, through inductive effects, would diversify the polarity of the arene group. The other pendant group, *n*-octadecyl, is used primarily for improving the polymer solubility in various solvents and also to stay structurally consistent with **Poly-1**. It was discovered that neither of these phenyl derivatives exhibited any significant change in optical rotation as a function of temperature in various solvents. For **Poly-3** in toluene, c = 0.104 (g/100 mL), $[\alpha]^{10}_{D} = +65°$, and $[\alpha]^{60}_{D} = +65°$, and in $CHCl_3$, c = 0.132, $[\alpha]^{0}_{D} = +83°$, and $[\alpha]^{50}_{D} = +73°$. For **Poly-4** in toluene, c = 0.108, $[\alpha]^{10}_{D} = +129°$, and $[\alpha]^{60}_{D} = +133°$, and in $CHCl_3$, c = 0.108, $[\alpha]^{0}_{D} = +151°$, and $[\alpha]^{50}_{D} = +127°$. Speculation is made that the substituted phenyl groups may not have sufficient size to prevent them from freely aligning around the helical backbone and therefore eliminating synchronous realignments.

Our next course of action was to increase the arene pendant group size and move to a larger 1-naphthyl pendant group, **Poly-5**. A similar polymer, **Poly-6**, had been previously synthesized, but much of the focus was placed on its ability to form highly opalescent films due to frozen cholesteric domains.[6] However, **Poly-6** did show unusual ORD behavior having a negative optical rotation when dissolved in heptanes and a positive optical rotation when dissolved in DCM.[6] This gave us great optimism that **Poly-5** would be a good candidate for observing new optical switching properties.

It was soon discovered that in addition to **Poly-5** undergoing reversible optical switching in toluene, for the first time, we observe unique thermally induced switching profiles in other solvents such as $CHCl_3$ and THF (Figure 1). Resulting effects from switching in these different solvents include a change in the switching temperature (~0.5 °C in $CHCl_3$, 19.5 °C in THF, and 36 °C in toluene, taken at the $\Delta[\alpha]$ midpoint) and a shift in the min/max of the ORD plateaus. The net change in specific optical rotation for this polymer reaches 1700° and changes in rotational direction. Because **Poly-5** contains a significant amount of π-character, it is worth noting that we are confident these observed changes are not due to aggregation of the polymer chains. Large conformational changes observed by ECD because of supramolecular aggregation of chiral polythiophenes based on interchain $\pi-\pi$ interactions and solvation efficiency have been reported.[26] Our confidence toward the absence of such aggregation lies within four observations: (1) Aggregation is very sensitive to concentration, and the optical switching properties observed do not change at various concentrations. (2) The polymers are easily passed through a 0.2 μm PTFE syringe filter in all reported solvents, most notably $CHCl_3$ and toluene, which exhibit opposite switching positions at room temperature. (3) The optical rotation outputs are stable, which would not be the case if aggregates of the polymer were crossing in and out of the path of plane polarized light. (4) The large *n*-octadecyl pendant groups surrounding the π-rich polymer backbone provide a "sheath" of aliphatic character, allowing good solvation between chains and a dampening of interchain interactions. To our knowledge, this is the first polymer system that undergoes a thermally induced conformational change in multiple solvents without supramolecular aggregation or the influence of chiral pendant groups and/or chiral perturbations. It is also the largest change in ORD observed for these polycarbodiimide systems thus far.

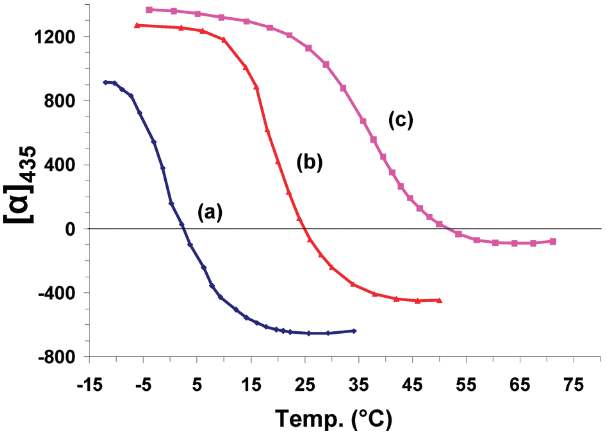


Figure 1. Specific optical rotation measurements as a function of temperature for **Poly-5** in (a) chloroform, (b) THF, and (c) toluene (λ = 435 nm, c = 0.20 to 0.22 g/100 mL).

Many heat−cool cycles can be performed with repeatable ORD switching and without significant racemization of the helix. This is especially true in $CHCl_3$ and THF, where the switching occurs at lower temperatures and further supports previously made conclusions that these transitions are too low in energy to involve imine inversions and helix inversions.[12] Quick heating of the polymer solution with a preheated circulation bath shows evidence of these changes occuring very rapidly. Unlike **Poly-1**, the blue-shifted naphthyl group permits optical rotation experiments at 435 nm, which benefits the amplification in ORD observed. Switching properties are independent of the alkyl pendant group, and this was confirmed by polarimetry comparison of **Poly-5** and **Poly-6**. These two polymers, one containing an *n*-octadecyl pendant group and the other containing an *n*-dodecyl pendant group, switch at the same temperature in $CHCl_3$. ECD experiments of **Poly-5** were performed at various temperatures in THF (Figure 2). As a result of the switching process, observed Cotton effects move from a positive to a negative direction and are reversible. In addition, blue/red shifts of the peak maxima are observed during this process, especially at the E_2 band (301 $\leftrightarrow$ 293 nm) absorption of the naphthyl group, suggesting that the polymer backbone has an auxochromic effect that changes during their repositioning.[27] It should be noted that the imine on the helical backbone exhibits a Cotton effect that is hidden beneath the larger amplitude chromophoric pendant group absorption. UV−vis absorption of di-*n*-hexyl polycarbodiimide (a polycarbodiimide derivative with no arene chromophores) has a λ_{max} of 239 nm. Assurance that the imine cotton effect remains fixed lies within the fact that racemization would occur if helical inversions were occurring, which would result in an irreversible loss of all observed Cotton effects.

To support further that these observed changes are a result of realignment of the polyarene pendant groups, VT ^{1}H NMR was performed on **Poly-5** in THF-d_8. Spectra were taken in 10 °C intervals that scope the thermal range where optical switching is observed for this solvent (Figure 3). Between the temperatures of 20 and 30 °C, the appearance of two new chemical shifts near 6.5 ppm along with the emergence and sharpening of the broad peak at 7.0 ppm is seen. This observation falls in line with expected changes in anisotropic behavior that would be experienced by the aryl protons from the repositioning of the arene pendant groups relative to one another and the polymer backbone.

Another interesting property of this polymer system is that the specific optical rotation can be tuned and held to any value within the range of optical switching under isothermal conditions. This permits the polymer system to function as a tunable polarizer capable of spanning the full arc values ±359° and maintaining the desired ORD without significant racemization of the helical backbone. Figure 4 shows an isothermal study performed on **Poly-5** in THF. Over the course of 16 h, the polymer solution temperature was changed every 4 h, and the resulting optical rotation exhibited was held with relative stability. The gradual slopes of the first three increments are due to slow deviations in solution temperature resulting from changes in ambient temperature competing with the circulation bath throughout the day. During the last 4 h of the experiment, the solution temperature held constant at 19.6 °C and the resulting optical rotation also remained constant. The spike at just over 12 h is from an overshot caused by the cooling process of the circulation bath.

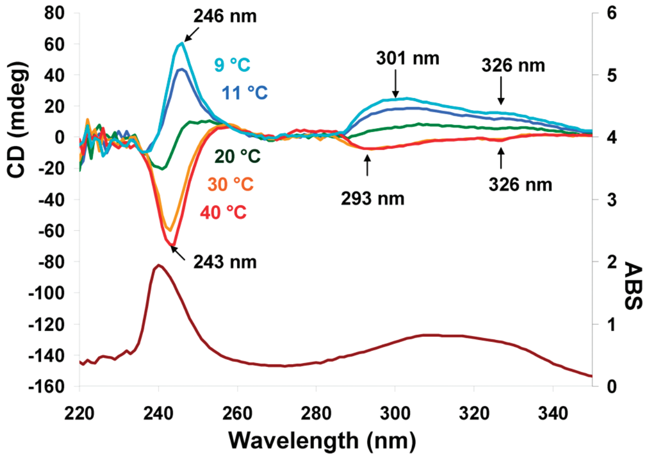


Figure 2. ECD at various temperatures (top) and UV−vis at r.t. (bottom) of **Poly-5** in THF (40 μg/mL). The ECD solution was heated from 11 to 40 °C and then cooled back to 9 °C. Red/blue shifts along with directional switching of Cotton effects are observed and coincide with polarimetry switching temperatures.

Characterization of **Poly-5** by infrared spectroscopy reveals two imine absorptions at 1641 and 1620 cm^{-1}, which is interpreted as regioirregularity of the polymer. This is not an uncommon observation for polymerizations using the (*R*)-BINOL-diisopropoxy-titanium(IV) catalyst and is believed to be primarily caused by different aggregation states of the active catalyst.[28] Unfortunately, catalysts previously reported by us that provided improved regioregularity with other monomers[11] exhibited no significant improvement to the regioregularity of **Poly-5**. Although polymerizations with electron deficient d^0 titanium catalysts have been shown to be living for these systems,[1] **Poly-5** (M_w = 78 000, M_w/M_n = 4.2) elutes over a broad range, resulting in high PDI during GPC analysis. This is another previously seen characteristic of polycarbodiimide systems.[1,11] Polarimetry annealing studies of **Poly-5** in decalin at temperatures of 65, 75, and 80 °C reveal this polymer to have a barrier to racemization of 25 kcal/mol. Although this barrier is not as high as 36 kcal/mol reported for **Poly-1**,[5] the fact that switching can now be observed at much lower temperatures overcomes this slight loss in helical stability.

As previously stated, the monomers used for these polymerizations are achiral; therefore, the resulting chirality of these polymer systems rests solely on the helical nature of the backbone. As such, monomers polymerized into opposite helices should result in enantiomeric polymers and exhibit the same physical properties, only varying in their direction of polarization.[29] To confirm this, we polymerized **Poly-5**(S) (Figure 4) using the opposite handed (*S*)-BINOL-diisopropoxy titanium(IV) catalyst and found that the switching profile of this polymer

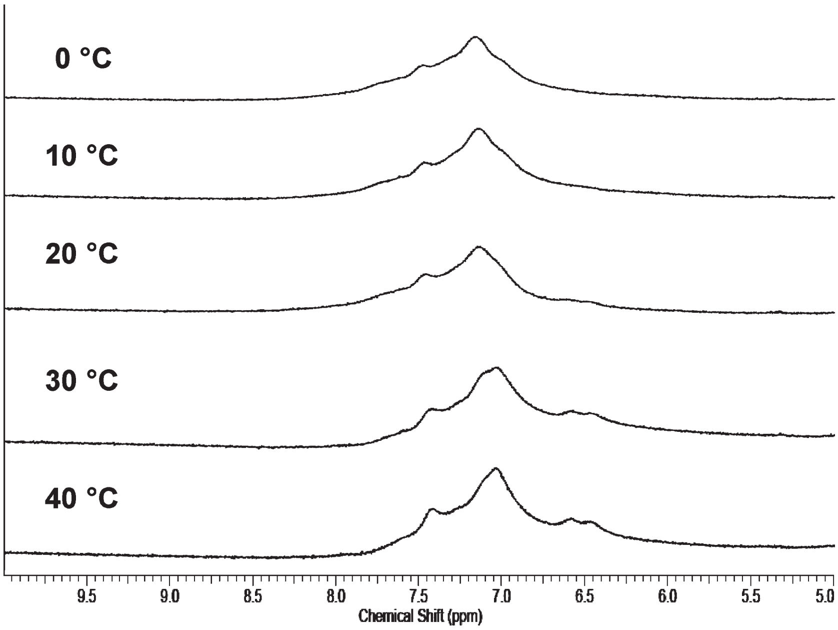


Figure 3. VT-^{1}H NMR of **Poly-5** in THF-d_8. Changes in the aryl proton chemical shifts are seen as a result of anisotropic differences during the switching process of the naphthyl groups.

behaves oppositely to that of **Poly-5(R)**. Figure 5 shows a polarimetry study overlay of the (*R*)- versus (*S*)-BINOL-catalyzed polymers and their enantiomeric switching behavior in CHCl$_3$ and toluene as a function of temperature. To ensure that these polymers would be as similar as possible (with the exception of the catalyst chirality), a new batch of **Poly-5(R)** was created at the same time as **Poly-5(S)** using the same monomer batch, dilution/catalyst solvent, temperature, and polymerization time. This is worth noting because the **Poly-5(R)** data in Figure 4 has slightly less amplitude in ORD switching than shown for previously reported **Poly-5** in Figure 1. This is sometimes seen between polymer samples that are prepared during different runs, allowing the possibility of slightly different variables in the polymerization process to lend slightly different properties to the resulting polymers. An in-depth synthetic optimization study of these polymerizations and the variables that affect the resulting polymers is currently underway.

Synthetic investigations focused on the effects of size and geometry of these polyarene pendant groups were performed. The repeat unit of **Poly-7** is constitutionally the same as **Poly-5**, the only difference being the attachment of the 2-naphthyl versus the 1-naphthyl pendant group. As a consequence of this difference, the spatial arrangement of the naphthalene groups around the helical scaffold is altered. Interestingly, this spatial alteration caused **Poly-7** to exhibit no significant changes in ORD as a function of temperature in toluene, $c = 0.213$ (g/100 mL), $[\alpha]^{10}_{435} = +247°$, and $[\alpha]^{70}_{435} = +180°$. The slight decrease in ORD at higher temperatures was not reversible, making it likely due to partial racemization of the helix. This discovery elucidates the necessity for these polyarene pendant groups to have a sufficient "kink" in their geometry relative to the helical director, making them more prone to restricted rotation through "shutterlike" interactions.

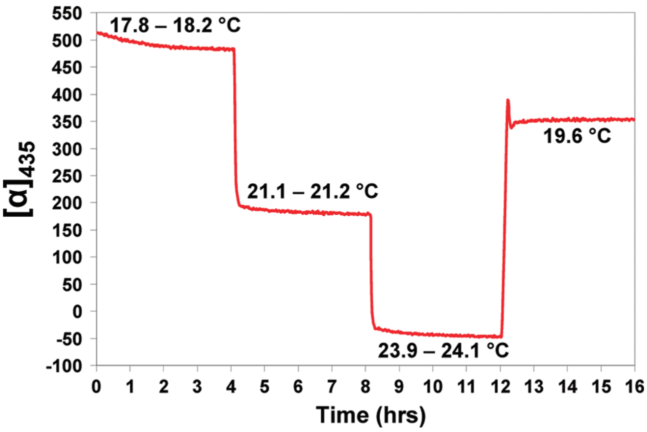


Figure 4. Specific optical rotation of **Poly-5** in THF held isothermal at four different temperatures during 4 h increments ($\lambda = 435$ nm, $c = 0.200$ g/100 mL). Slight increases in cell temperature are evident; however, the specific optical rotation remains constant at isothermal conditions.

Poly-8 was created to understand further the upper size limit of these polyarene flaps. The 1-pyrenyl pendant group is the largest polyarene pendant group made thus far. When testing the switching capabilities of **Poly-8** in toluene (Figure 6a), we observed a large reversible change in optical rotation; however, the switching behavior was broadened and occurs at a much higher temperature than that seen for **Poly-1** and **Poly-5**. Because of concerns with toluene vapor pressure within the cell at temperatures > 80 °C, another polarimetry test was performed in ethylbenzene (bp 136 °C). To our surprise, the switching process in ethylbenzene occurred at a much lower temperature than that observed for toluene (Figure 6b). This is an extreme example of the importance solvation plays in this switching process. The addition of a single methylene carbon to the side chain of the aromatic solvent lowers the switching temperature by ~40 °C.

Characterization of **Poly-7** and **Poly-8** by IR surprisingly revealed them both to be highly regioregular. For **Poly-7**, a large imine absorption was observed at 1618 cm^{-1} with a very small shoulder at 1633 cm^{-1}. According to previous research, the lower imine wavenumber coincides with the *n*-octadecyl pendant group being attached to the imine.[30] **Poly-8** also favors this regioisomer with a single sharp imine stretch at 1614 cm^{-1}. Although this regioisomer is the opposite of that reported for the initially observed **Poly-1**, it can be concluded that switching can occur regardless of the regioposition of the polyarene pendant group. These structure–property relationships have allowed us to determine: (a) the alkyl group plays no role in the optical switching; it is solely a function of the aromatic pendant group; (b) the optimum size of the aromatic pendant group is the two fused-ring naphthyl derivative; (c) the attachment of the polymer to the aromatic group is required to be at the 1-carbon position; and (d) regioirregularities among the side chains do not inhibit the optical switching.

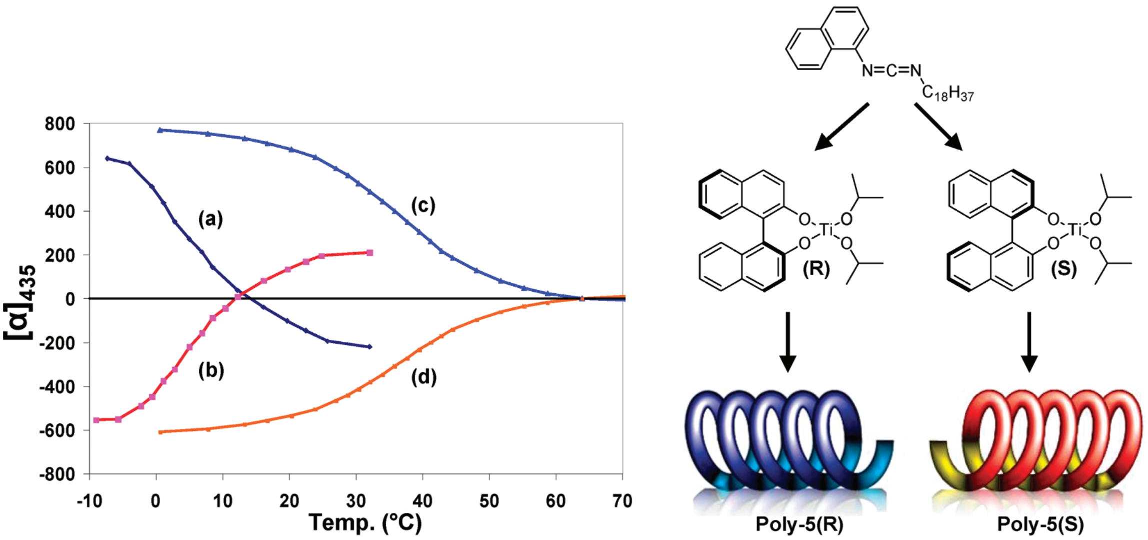


Figure 5. Polarimetry analysis of **Poly-5(R)** ((a) in CHCl$_3$, (c) in toluene) and **Poly-5(S)** ((b) in CHCl$_3$, (d) in toluene). Polymerizing identical achiral monomers into opposite helices results in enantiomeric switching behavior. ($\lambda = 435$ nm, $c = 0.20$ to 0.22 g/100 mL).

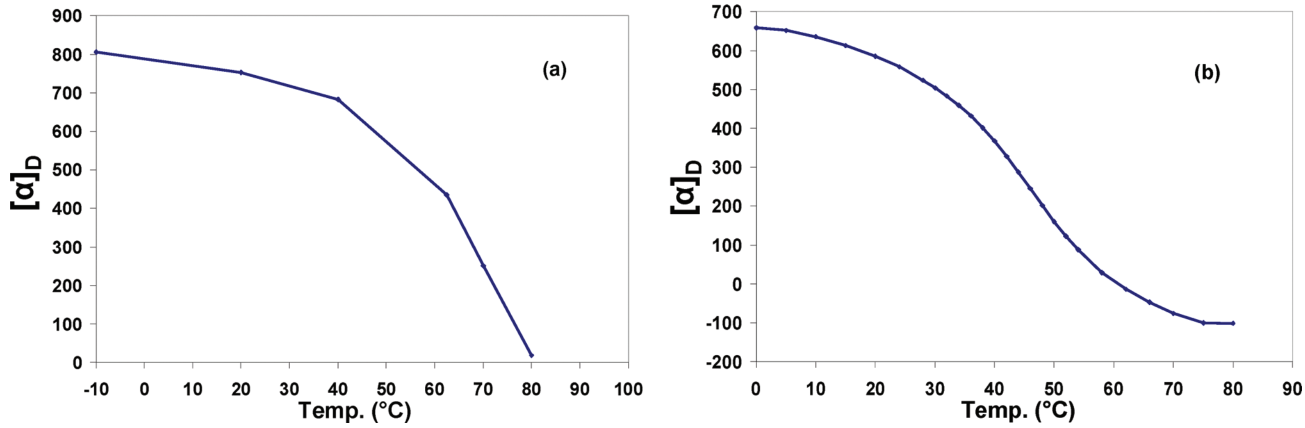


Figure 6. (a) Specific optical rotation versus temperature of **Poly-8** in toluene (c = 0.212 g/100 mL, λ = 589 nm) and (b) ethylbenzene (c = 0.204 g/100 mL, λ = 589 nm).

GPC characterization of regioregular **Poly-7** (M_w = 13 000, $M_w/M_n = 1.3$) and **Poly-8** (M_w = 12 600, $M_w/M_n = 1.7$) revealed sharp elution peaks and highly improved polydispersity values compared with those of **Poly-5**. Because these polymers are derived from the same catalyst, the reason for improved elution of these polymers, and therefore better polydispersity values may be attributed to the improved regioregularity of **Poly-7** and **Poly-8**.

Conclusions

We have discovered two new polymers, **Poly-5** and **Poly-8**, capable of undergoing low-energy, reversible, conformational changes due to realignments of their polyarene pendant groups. Of these two, **Poly-5** exhibits improvement in amplification and a higher level of versatility by switching in a variety of solvents at lower temperatures with net reversible changes in specific optical rotation reaching 1700°. ECD Cotton effects also reversibly change in direction during this switching process, and red/blue shifts are observed for the naphthyl chromophore. We have also shown that these large ORD changes are tunable by maintaining isothermal conditions anywhere within the thermal switching profiles and that the ORD output remains constant. Through VT ^{1}H NMR, changes in the naphthyl proton chemical shifts due to changes in anisotropy during the switching process are observed. As expected, opposite-handed helices of **Poly-5** behave enantiomerically, and this was confirmed by observing identical but opposite switching profiles for these stereoisomers. **Poly-8** switches in toluene and ethylbenzene; however, the larger 1-pyrenyl pendant groups behave more cumbersome, requiring relatively higher temperatures, and result in broadening of the switching profile. **Poly-3**, **-4**, and **-7** did not exhibit any significant changes in specific optical rotation as a function of temperature and solvent. From these, we were able to understand further the importance of size and spatial arrangement required for the polyarene pendant groups to undergo these conformational changes. New techniques are currently being explored to determine why certain solvents affect the switching temperature the way they do and how they dictate the desired positioning of the polyarene pendant groups. In addition, experiments are currently underway to elucidate further optimization strategies for these polymer systems as well as synthetic explorations toward even more optical switching polycarbodiimides.

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Supporting Information Available: Further experimental details and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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