Adjusting Conformational Switching Behavior of Helical Polycarbodiimides Through Substituent Induced Polarity Effects

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ABSTRACT: Recent discoveries on the improved versatility of helical polycarbodiimides capable of undergoing low energy reversible conformational changes from realignment of their restricted polyarene pendant groups has led to seven new polycarbodiimides that each present unique information in regards to how the electronics and connectivity of the arene π-system play a crucial role in the behavior of these polymers. In addition to their individual anomalous behavior, this series of functional polymers unlock new answers toward the global understanding of the governing forces behind this complex switching process. Through the incorporation of functional groups covalently attached to the naphthalene pendant, dramatic changes and new application of these systems are realized. Variable temperature polarimetry is used to observe the reversible conformational changes of these chiral polymers. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 719–728, 2011

KEYWORDS: aromatic interactions; carbodiimide; chiral; conformational change; functionalization of polymers; helical; heteroatom containing polymers; molecular machine; optical switching; polarization; polycarbodiimide; polyguanidine; reversible; stimuli-sensitive polymers; tunable

INTRODUCTION Substituent effects on aromatic systems attached to, or along, a polymer backbone present a unique and interesting way of inducing electronic perturbations on a localized region of the polymer repeat unit. Even more interesting is observing how these perturbations translate to the global properties of the polymer system. The substitution of electron withdrawing groups on arene systems, in comparison with electron donating substituents, can give implications toward how noncovalent dipolar π-interactions, conjugation, and/or partial delocalization of these regions play a role on the observed properties of the polymer. We recently published the discovery of a hallmark, versatile, polycarbodiimide (**Poly-1**, Fig. 1) capable of undergoing dynamic changes in conformation through a low-energy concerted realignment of naphthalene pendant groups influenced by solvent and temperature.[1] It has been determined that these observations are not due to polymer aggregation and that this reversible shutter-like reorientation of the aromatic pendant groups occur without inversion of the static helical backbone. Instead, it is a secondary layer of chirality created during the polymerization by these constricted arene pendant groups that gives rise to such dramatic chiro-optical changes. To our knowledge, these polymers remain the only reported examples of synthetic helical macromolecular systems that undergo reversible changes in chiral polarization without inversion of backbone helicity and without the influence of chiral pendant groups, chiral solvent, and/or other chiral perturbations such as chiral guest molecules.[2]

In addition to the potential application of these polymer systems toward tunable polarizers, chirality based chemosensors, biomimetic materials, optical display materials, and data storage devices; we are also invested in the novelty of such a concerted macromolecular expression of chirality transfer. Aromatic π-based interactions are found throughout nature and, in biochemistry, these complex noncovalent interactions are found to play important roles in structural stability, molecular recognition, and the overall properties of biomolecules.[3–6] It is therefore with great interest that we continue our fundamental understanding of the governing forces behind the unique switching behavior of these polycarbodiimide systems. This understanding may prove useful for unlocking new answers toward how noncovalent π-interactions can affect the conformational behavior of complex functional macromolecules. The last few decades have seen prominent advancements toward the understanding of aromatic-aromatic interactions which consist of a complex ballet of solvophobic, Van der Walls, and electrostatic stacking forces.[7–11] The aforementioned **Poly-1** is unique in the sense that it holds a large density of arene substituents affixed to a static chiral scaffolding. This allows the ordered registry of the helix to amplify aromatic interactions and arene conformational transitions to be easily observed through chiro-optical techniques, such as polarimetry. In addition, the long aliphatic alternate polycarbodiimide pendant group allows good polymer solubility in a variety of solvents and dampens aggregation and aromatic interaction

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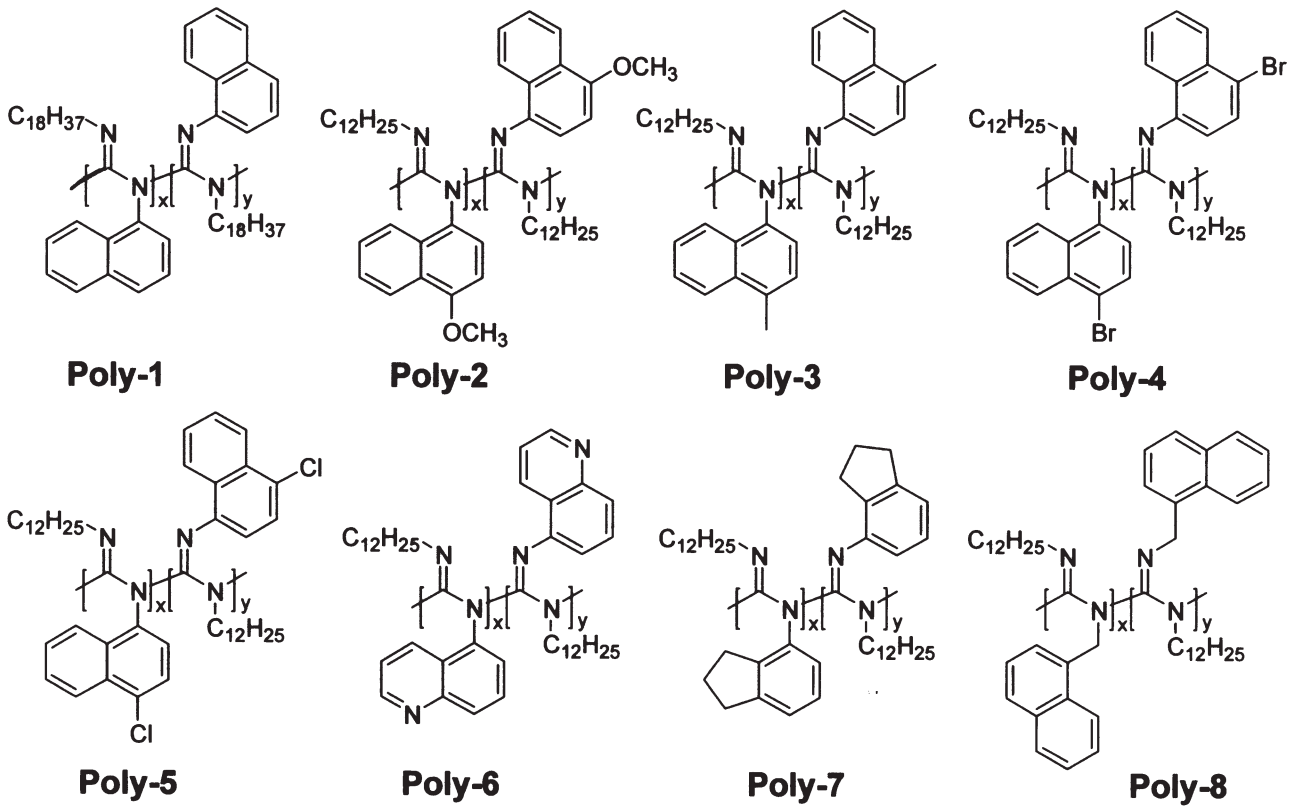


FIGURE 1 Library of Naphthalene Pendant Group Based Helical Polycarbodiimides.

between chains. Due to the buffering of aggregation from this large aliphatic corona, the behavior of this polymer translates directly to how these arene substituents interact along the chain, albeit through aromatic-backbone or aromatic-aromatic interactions, and not due to inter-chain interactions. (i.e., this is a fully intra-molecular phenomenon) This manuscript will take into account the effects that substituents have on the arene pendant groups and how they translate to changes in the conformational switching process of the polycarbodiimide. A secondary study will take into account how disruption of such behavior comes from alteration of the pendant group aromaticity by partial saturation and by changing the proximity of these arene groups to the backbone. A new library of seven select polycarbodiimides (**Poly 2–8**) have been chosen and synthesized to study these effects. Since all of the polymers in Figure 1 are obtained from nonsymmetric carbodiimide monomers having two different pendant groups, we acknowledge the chance for regioirregularity by indicating both regioisomers possible on the resulting polymers.

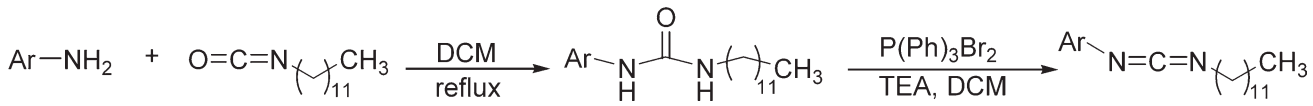
EXPERIMENTAL

Materials

1-aminonaphthalene, 1-methylnaphthalene, 4-methoxy-1-nitronaphthalene, 4-bromo-1-aminonaphthalene, 4-chloro-1-aminonaphthalene, 5-aminoquinoline, 4-aminoindan, 1-naphthylmethylamine, *n*-dodecyl isocyanate, titanium tetraisopropoxide, (R)-(+)-1,1′-bi-2,2′-naphthol (BINOL), palladium (10%) on carbon, acetic anhydride, nitric acid (fuming), and *N*,*N*-dimethylaminoethylamine (DMAEA) were purchased from Aldrich (Sigma-Aldrich, Milwaukee, WI) and used without further purification unless otherwise noted. Triethylamine and common laboratory solvents were purchased from Fisher Scientific, Fair Lawn, NJ. Dibromotriphenylphosphorane salt was purchased from VWR (Suwanee, GA) and used as received. Solvents used for polymerization or catalyst synthesis were dried, distilled, and degassed and stored over molecular sieves prior to use. UV-Vis experiments were performed in spectroscopy grade THF also purchased from Aldrich.

Instrumentation Used for Characterization of Monomers and Polymers

Infrared spectroscopy was performed on a Jasco FT-IR 140 Fourier transform infrared spectrometer using potassium bromide crystal windows purchased from Aldrich. UV-Vis spectroscopy was performed on a Jasco V-550 UV-Vis spectrometer using high clarity quartz cells. Polarimetry was performed on a Jasco P-1010 polarimeter with interchangeable wavelength filters and using a jacketed 0.5 dm cell. Cell temperature was adjusted by a Neslab RTE-140 circulation bath attached to the jacketed cell and the solution temperature within the cell was monitored by an Omega K-Type thermocouple attached to a Barnant digital thermocouple thermometer. ^{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. Mass spectra were obtained at the NCSU



SCHEME 1 General synthesis of carbodiimide monomers.

Department of Chemistry Mass Spectrometry Facility using electrospray ionization (ESI) on an Agilent Technologies 6210 LC-TOF mass spectrometer.

General Preparation of Monomers

Each monomer was synthesized by reacting the appropriate aryl amine with dodecyl isocyanate to form the stable *N,N′*-disubstituted urea precursor which was then dehydrated using dibromotriphenylphosphorane salt and triethylamine (Scheme 1) and purified by column chromatography. Specifics to the procedure have been previously reported.[1] Any additions or changes to the general procedure are listed with each monomer.

N-(1-naphthyl)-N′-(n-octadecyl)carbodiimide (Mono-1)

This has been previously reported and characterized.[1]

N-(4-methoxy-1-naphthyl)-N′-(n-dodecyl) carbodiimide (Mono-2)

5.46 g (27 mmol) of purchased 4-methoxy-1-nitronaphthalene was dissolved in 50 mL toluene and hydrogenated in a Parr reactor using a catalytic amount of 10% Pd/C. After stirring under H_2 pressure at 50 psi and a temperature of 80 °C for 10 h, the resulting pale yellow solution was removed from the reactor and filtered through Celite. (Note: Discoloration of this amine occurs very rapidly and protection of the amine from oxidation by reacting with isocyanate needs to be done directly following filtration) No yield or characterization done due to instability of the amine. Amine was protected by addition of 1.25 molar equivalents of dodecyl isocyanate to form white fluffy urea after recrystallization from 50:50 EtOH: n-BuOH. (85% Yield overall from starting 4-methoxy-1-nitronaphthalene.) Subsequent dehydration and purification resulted in carbodiimide monomer as a pale yellow oil.

Yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.88 (t, 3H), 1.20–1.50 (br, 18H), 1.71 (m, 2H), 3.44 (t, 2H), 3.99 (s, 3H), 6.74 (d, 1H), 7.20 (d, 1H), 7.48–7.55 (m, 2H), 8.22 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.4, 22.9, 27.0, 29.4, 29.6, 29.8 (overlapped), 29.9 (overlapped), 31.7, 32.2, 47.3, 55.9, 103.9, 119.5, 122.2, 123.5, 126.0, 126.2, 126.7, 129.6, 129.7, 137.0, 152.9. IR(cm^{-1}): 3070 and 3043 (w, C—H aryl), 3001 (w, C—H MeO), 2924 (vs., C—H alkyl), 2852 (s, C—H alkyl), 2129 (vs., N=C=N), 1589 (s, C=C), 1267 (s, aryl—O stretch), 1020 (m, H_3C—O stretch) . HRMS-ESI: $M_{theoretical}$ = 367.2744, M_{sample} = 367.2745, ΔM = −0.13 mmass units (−0.37 ppm), $C_{24}H_{34}N_2O$.

N-(4-methyl-1-naphthyl)-N′-(n-dodecyl) carbodiimide (Mono-3)

4-nitro-1-methylnaphthalene was synthesized from purchased 1-methylnaphthalene according to literature.[12]

Yield: 15.46 g (27%). m.p. 61–64 °C (lit. 68 °C) ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.79 (s, 3H), 7.39 (d, 1H), 7.60–7.75 (m, 2H), 8.09–8.17 (m, 2H), 8.61 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 20.5, 123.9, 124.1, 124.9, 125.2, 125.4, 127.4, 129.2, 133.4, 142.6, (ipso-NO_2 carbon was not resolved due to extremely slow relaxation time). IR (cm^{-1}): 3084 (m, C—H aryl), 3057 (m, C—H aryl), 3016 (m, C—H aryl), 2964 (m, C—H methyl), 1599 (m, C=C), 1576 (m, C=C), 1510 (vs., NO_2), 1334 (vs., NO_2 bend).

4-Methyl-1-aminonaphthalene was synthesized from 4-nitro-1-methylnaphthalene through hydrogenation described below:

15.46 g (82.6 mmol) of 4-nitro-1-methylnaphthalene was added to a jar and dissolved in 40 mL of toluene with a stir bar. 277.5 mg of Pd/C (10%) was added to the solution. Jar was lowered into a Parr vessel with a moat of toluene added around the jar to limit toluene from evaporating out of the jar. The Parr reactor was sealed and pressurized with 60 psi of H_2 gas. The Parr reactor was partially submerged in an oil bath on a stir plate and the reaction solution was heated at 100 °C for 24 h with continual H_2 pressure. After cooling, the jar was removed from the vessel and the purple-red solution was filtered through a plug of celite to remove catalyst. After drying over anhydrous sodium sulfate for 15 min, the filtrate was dried to a red oil by vacuum.

Yield: 10.049 g (77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.60 (s, 3H), 4.03 (s, br, 2H), 7.71 (d, 1H), 7.13 (d, 1H), 7.48–7.55 (m, 2H), 7.87 (d, 1H), 7.97 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 19.2, 109.9, 121.6, 124.4, 124.9, 125.1, 125.2, 125.9, 127.0, 133.4, 140.7. IR (cm^{-1}): 3348, 3375 (br, N—H). HRMS-ESI: $M_{theoretical}$ = 157.0964, M_{sample} = 157.0963, ΔM = 0.13 mmass units (0.84 ppm), $C_{11}H_{11}N$.

Reaction of 4-methyl-1-aminonaphthalene with dodecyl isocyanate in DCM refluxed overnight yielded white solid urea which was recrystallized from MeOH. Subsequent dehydration resulted in **Mono-3** as yellow oil after purification.

Yield: 73% ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.88 (t, 3H), 1.20–1.50 (br, 18H), 1.70 (m, 2H), 2.65 (s, 3H), 3.46 (t, 2H), 7.18–7.25 (m, 2H), 7.51–7.56 (m, 2H), 7.94 (d, 1H), 8.31 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):14.4, 19.5, 22.9, 27.1, 29.4, 29.6, 29.8 (overlapped), 29.9 (overlapped), 31.7, 32.2, 47.2, 119.4, 124.3, 124.4, 125.7, 126.4, 126.7, 129.0, 131.0, 133.5, 135.6, 136.4. IR (cm^{-1}): 3066 (w, C—H aryl), 3033 (w, C—H aryl), 2925 (vs., C—H alkyl), 2854 (s, C—H alkyl) 2135 (vs., N=C=N), 1581 (m, C=C). HRMS-ESI: $M_{theoretical}$ = 351.2795, M_{sample} = 351.2796, ΔM = −0.09 mmass units (−0.24 ppm), $C_{24}H_{34}N_2$.

N-(4-bromo-1-naphthyl)-N′-(n-dodecyl) carbodiimide (Mono-4)

Monomer was prepared from commercially available 4-bromo-1-aminonaphthalene and *n*-dodecyl isocyanate as initially described.

Yield: 77% ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.88 (t, 3H), 1.20–1.50 (br, 18H), 1.70 (m, 2H), 3.48 (t, 2H), 7.14 (d, 1H), 7.55 (t, 1H), 7.61 (t, 1H), 7.68 (d, 1H), 8.18 (d, 1H), 8.30 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):14.4, 22.9, 27.0, 29.3, 29.6, 29.7, 29.8, 29.9 (overlapped), 31.6, 32.2, 47.1, 118.1, 120.0, 124.4, 126.8, 127.3, 128.0, 129.9, 130.2, 132.8, 134.9, 137.9. IR (cm^{-1}): 3068 and 3043 (w, C—H aryl), 2924 (vs., C—H alkyl), 2852 (s, C—H alkyl) 2139 (vs., N=C=N), 1583 (s, C=C). HRMS-ESI: $M_{theoretical}$ = 415.1743, M_{sample} = 415.1742, ΔM = −0.07 mmass units (−0.17 ppm), $C_{23}H_{31}BrN_2$.

N-(4-chloro-1-naphthyl)-N′-(n-dodecyl) carbodiimide (Mono-5)

Monomer was prepared from commercially available 4-chloro-1-aminonaphthalene and *n*-dodecyl isocyanate as initially described.

Yield: 82% ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.88 (t, 3H), 1.20–1.50 (br, 18H), 1.72 (m, 2H), 3.48 (t, 2H), 7.20 (d, 1H), 7.48 (d, 1H), 7.53–7.64 (m, 2H), 8.21 (d, 1H), 8.31 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):14.4, 22.9, 27.0, 29.3, 29.6, 29.7, 29.8, 29.9 (overlapped), 31.6, 32.2, 47.1, 119.5, 124.3, 124.6, 126.2, 126.7, 127.7, 130.0, 131.6, 135.0, 137.1. IR (cm^{-1}): 3070 and 3047 (w, C—H aryl), 2925 (vs., C—H alkyl), 2854 (s, C—H alkyl), 2137 (vs., N=C=N), 1585 (s, C=C). HRMS-ESI: $M_{theoretical}$ = 371.2249, M_{sample} = 371.2248, ΔM = 0.06 mmass units (0.17 ppm), $C_{23}H_{31}ClN_2$.

N-(5-quinolyl)-N′-(n-dodecyl)carbodiimide (Mono-6)

Monomer was prepared from commercially available 5-aminoquinoline and *n*-dodecyl isocyanate as initially described.

Yield: 79% ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.88 (t, 3H), 1.20–1.60 (br, 18H), 1.73 (m, 2H), 3.49 (t, 2H), 7.33 (d, 1H), 7.40 (m, 1H), 7.63 (t, 1H), 7.86 (d, 1H), 8.60 (d, 1H), 8.91 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.4, 22.9, 27.0, 29.3, 29.6, 29.7, 29.7–29.8 (overlapped), 29.9, 31.6, 32.1, 47.1, 120.0, 121.0, 124.4, 125.8, 129.4, 132.4, 135.0, 138.0, 149.2, 151.1. IR (cm^{-1}): 3062 and 3030 (w, C—H aryl), 2925 (vs., C—H alkyl), 2854 (s, C—H alkyl) 2133 (vs., N=C=N), 1589 (m, C=C), 1610 and 1570 (s, C=C and C=N ring stretch). HRMS-ESI: $M_{theoretical}$ = 338.2591, M_{sample} = 338.2593, ΔM = −0.23 mmass units (−0.69 ppm), $C_{22}H_{31}N_3$.

N-(4-indanyl)-N′-(n-dodecyl)carbodiimide (Mono-7)

Monomer was prepared from commercially available 4-aminoindan and *n*-dodecyl isocyanate as initially described.

Yield: 73%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.88 (t, 3H), 1.25–1.43 (br, 28H), 1.67 (m, 2H), 2.08 (m, 2H), 2.93 (dd, 4H) 3.38 (t, 2H), 6.87 (d, 1H), 6.98 (d, 1H), 7.08 (t, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.4, 23.0, 25.0, 27.1, 29.4, 29.6, 29.8 (overlapped), 29.9 (br, overlapped), 30.9, 31.5, 32.2, 33.4, 47.3, 120.9, 121.4, 127.5, 136.2 136.7, 138.7, 146.2. IR (cm^{-1}): 3059 (w, C—H aryl), 2925 (vs., C—H alkyl), 2852 (s, C—H alkyl) 2135 (vs., N=C=N), 1587 (s, C=C aryl). HRMS-ESI: $M_{theoretical}$ = 327.2795, M_{sample} = 327.2797, ΔM = −0.25 mmass units (−0.77 ppm), $C_{22}H_{34}N_2$.

N-(1-methylnaphthyl)-N′-(n-dodecyl)carbodiimide (Mono-8)

Dodecyl isocyanate was added to a solution 1-methylnaphthylamine (1:1 molar ratio) in DCM at 0 °C. The urea was recrystallized from MeOH and subsequently dehydrated as previously described to yield a light yellow oil following purification.

Yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.89 (t, 3H), 1.05–1.40 (br, 20H), 2.95 (t, 2H), 4.78 (s, 2H), 7.42–7.59 (m, 4H), 7.81 (d, 1H), 7.88 (d, 1H), 8.06 (d, 1H). IR (cm^{-1}): 3047 (m, C—H aryl), 2924 (vs., C—H alkyl), 2853 (s, C—H alkyl) 2127 (vs., N=C=N), 1693 (m, NCN-CH_2-aryl). HRMS-ESI: $M_{theoretical}$ = 350.2722, M_{sample} = 350.2725, ΔM = −0.3 mmass units (−0.85 ppm), $C_{24}H_{34}N_2$.

Preparation of (R)-BINOL-titanium(IV)-diisopropoxide Catalyst

All polymerizations were performed using (R)-1,1′-binaphth-2,2′-oxy (BINOL) titanium (IV) diisopropoxide catalyst which was synthesized according to previous literature.[1,13]

^{1}H NMR (300 MHz, $CDCl_3$ stored over molecular sieves) δ (ppm): 1.06 (d, 12H), 4.49 (m, 2H), 6.75 (d, 2H), 7.15 (d, 2H), 7.34 (m, 4H), 7.46 (d, 2H), 7.86 (d, 2H).

General Preparation of Polymers

Polymerization and work-up procedures are fully described in previous literature.[1] Unless otherwise noted, polymerizations were performed at room temperature using 1 g portions of monomer and approximately 200:1 molar equivalents of monomer to catalyst predispersed in less than 2 mL of dry $CHCl_3$. Polymerization times ranged from 5–7 days unless otherwise noted. Yields of polymers are reported below. IR and ^{1}H NMR spectra for each polymer are also reported. For IR analysis, thin films of polymer were cast onto a potassium bromide crystal window using $CHCl_3$ as a solvent at room temperature. The loss of the strong carbodiimide (N=C=N) absorption and the arrival of a strong imine (C=N) absorption is indicative of successful polymerization. Due to substantial broadening, little information other than further confirmation of successful polymerization is derived from ^{1}H NMR spectra at this time and this is determined by extreme broadening of signals in addition to anisotropic shielding of some methylene hydrogens into negative ppm values. Due to long delay times, long analysis times, and poor resolution of ^{13}C NMR analyses, this was not performed on these polymers. GPC also results in substantial broadening of eluted peaks. This has been a continual observation of these polymer systems[1] and early experiments performed by Goodwin and Novak[14] using a low-angle light scattering detector proved that polymers of similar molecular weight were eluting over a very long range of elution times. Previously reported data has shown that using >100:1 molar ratio of monomer:catalyst results in a sufficient degree of polymerization for these polymers[1] and, as such, this ratio was kept similar for each polymerization to reduce differences that may result from large variations in molecular weight from **Poly-1** to **Poly-8**.

Poly-N-(1-naphthyl)-N′-(n-octadecyl)carbodiimide (Poly-1)

This polymer has been previously reported and characterized.[1]

Poly-N-(4-methoxy-1-naphthyl)-N′-(n-dodecyl) carbodiimide (Poly-2)

Monomer:catalyst (molar ratio) 200:1. Yield: 77%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): −0.61 (br, overlapping) 0.66

TABLE 1 Experimental Polymerization Parameters for Molecular Weight Study of **Poly-1**

Wt.[a] **Mono-1** (g)	**Mono-1** (mmol)	Cat. (μmol)	Mono:Cat. Ratio	Vol. $CHCl_3$ (mL)	Rxn Time (days)	% Yield	Theo. M_n	Yield Corrected M_n
1.02	2.41	5.7	421:1	2	7	46	177K	81K
1.05	2.48	8.0	309:1	2	7	55	130K	71K
1.04	2.46	11.5	215:1	2	7	88	90K	80K
1.05	2.48	22.9	108:1	2	7	80	45K	35K
1.07	2.53	45.9	55:1	2	7	73	23K	17K

[a] The formula weight for **Mono-1** is (420.7 g/mol).

(br), 0.89 (br) 1.26 (br), 3.64 (br), 6.35 (br), 7.11–8.00 (br, overlapping). IR (cm^{-1}): 3070 and 3047 (w, C—H aryl), 2995 (w, C—H MeO), 2925 (vs., C—H alkyl), 2852 (s, C—H alkyl), 1620 (vs., N=C), 1589 (s, C=C), 1273 (s, aryl—O stretch), 1022 (m, H_3C—O stretch).

Poly-N-(4-methyl-1-naphthyl)-N′-(n-dodecyl) carbodiimide (Poly-3)

Monomer:catalyst (molar ratio) 150:1. Yield: 52%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): −1.27–0.82 (br, overlapping), 0.89 (br), 1.26 (br), 2.26 (br, overlapping), 3.36 (br), 6.70–8.00 (br, overlapping). IR (cm^{-1}): 3056 (w, C—H aryl), 3008 (w, C—H aryl), 2924 (vs., C—H alkyl), 2852 (s, C—H alkyl) 1620 (vs., N=C), 1585 (s, C=C).

Poly-N-(4-bromo-1-naphthyl)-N′-(n-dodecyl) carbodiimide (Poly-4)

Monomer:catalyst (molar ratio) 200:1. Yield: 79%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): −1.20–0.80 (br, overlapping) 0.89 (br), 1.25 (br), 3.49 (br), 4.71 (br), 6.50–8.20 (br, overlapping). IR (cm^{-1}): 3070 and 3043 (w, C—H aryl), 2925 (vs., C—H alkyl), 2852 (s, C—H alkyl) 1633 (vs., N=C), 1563 (m, C=C).

Poly-N-(4-chloro-1-naphthyl)-N′-(n-dodecyl) carbodiimide (Poly-5)

Monomer:catalyst (molar ratio) 200:1. Yield: 82%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): −1.50–0.80 (br, overlapping), 0.89 (br), 1.26 (br), 3.51 (br), 4.77 (br), 6.50–8.30 (br, overlapping). IR (cm^{-1}): 3072 and 3045 (w, C—H aryl), 2925 (vs., C—H alkyl), 2854 (s, C—H alkyl), 1635 (vs., N=C), 1567 (m, C=C).

Poly-N-(5-quinolyl)-N′-(n-dodecyl)carbodiimide (Poly-6)

Monomer:catalyst (molar ratio) 200:1. Yield: 41% ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): −1.93 (br) −1.30–0.65 (br, overlapping), 0.73 (br), 0.88 (br), 1.25 (br), 3.52 (br), 4.79 (br), 6.51 (br), 6.80–8.10 (br, overlapping), 8.68 (br). IR (cm^{-1}): 3062 and 3030 (w, C—H aryl), 2925 (vs., C—H alkyl), 2854 (s, C—H alkyl), 1637 (vs., N=C), 1589 (m, C=C), 1604 and 1570 (s, C=C and C=N ring stretch).

Poly-N-(4-indanyl)-N′-(n-dodecyl)carbodiimide (Poly-7)

Monomer:catalyst (molar ratio) 194:1. Yield: 79%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): −0.50 (br), 0.24–0.80 (br, overlapping), 0.88 (br), 1.26 (br), 1.80–4.00 (br, overlapping), 6.40–7.60 (br, overlapping). IR (cm^{-1}): 3049 (w, C—H aryl), 2923 (vs., C—H alkyl), 2852 (s, C—H alkyl) 1645 (vs., N=C), 1597 (w, C=C aryl).

Poly-N-(1-naphthylmethyl)-N′-(n-dodecyl) carbodiimide (Poly-8)

Monomer:catalyst (molar ratio) 200:1. Yield: 66%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): −0.50–0.50 (br, overlapping), 0.53 (br), 0.69 (br), 0.88 (br), 3.11 (br), 4.53 (br), 5.09 (br), 6.80–8.00 (br, overlapping). IR (cm^{-1}): 3048 (m, C—H aryl), 2924 (vs., C—H alkyl), 2852 (s, C—H alkyl) 1645 (vs., N=C), 1597 (w, C=C aryl).

RESULTS AND DISCUSSION

After the discovery of **Poly-1**,[1] derived from *N*-(1-naphthyl)-*N′*-(*n*-octadecyl) carbodiimide monomer, (**Mono-1**, Table 1), a new study was performed to probe the effects of molecular weight on the observed conformational changes. We were interested to see how molecular weight will affect the optical switching amplitude (OSA), defined as the total difference in specific optical rotation exhibited between the two conformational positions of the naphthalene units. We also wanted to observe any changes that molecular weight has on the temperature at which these realignments occur within a select solvent such as $CHCl_3$. Due to the previously mentioned biased results of gel permeation chromatography,[1,15] this study serves as a foundation for how we can expect molecular weight differences to effect the behavior of these systems. A relatively broad range of molecular weights can be justifiably synthesized by altering the monomer to catalyst ratio of these polymerizations followed by correction of the theoretical number average molecular weight based on the yield of polymer obtained. This series of polymerizations is shown in Table 1. The previously reported (R)-1,1′-binaphth-2,2′-oxy (BINOL) titanium (IV) diisopropoxide catalyst[1,16,17] was used for each polymerization. When performing variable temperature polarimetry on these polymers in $CHCl_3$ (Fig. 2), it can be seen that the OSA is reduced with polymers of substantially low molecular weight (<∼20K). This is believed to be caused by increased chain-end character where helical unraveling is more prominent. Such dramatic decreases in observed specific optical rotations were also observed for helical polyisocyanates at lower molecular weights.[18] More specifically to our case, the lower molecular weight chains are impacted more by this loss of steric constriction which can translate to less restricted realignment of the naphthalene pendant groups and the loss of OSA

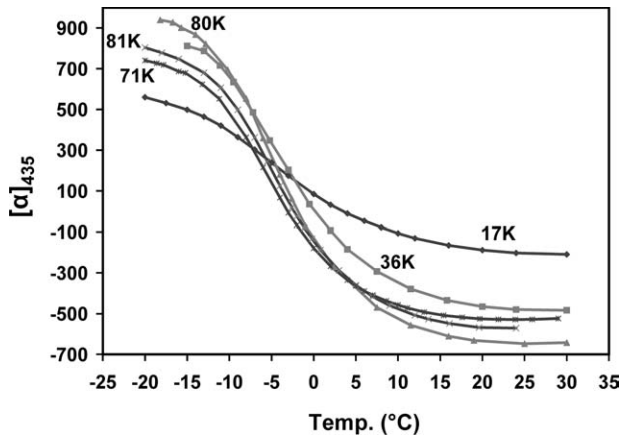


FIGURE 2 Variable temperature polarimetry study of various molecular weight samples of **Poly-1** in $CHCl_3$ (c = 0.20–0.22 g/100 mL). Although the OSA is reduced for low molecular weight polymers, the relative temperature of switching remains the same.

observed. Another important observation is that **Poly-1** undergoes these conformational changes at approximately the same temperature regardless of molecular weight. Therefore, it is concluded that altering the molecular weight of these polymer systems can translate to a change in OSA but not the energy required for switching to occur. It is hypothesized that we must alter the chemical composition and electronic properties of the arene pendant groups in order to observe changes in conformational switching temperatures within a constant solvent.

To date, our working model to explain the reasoning behind this dynamic behavior suggests that the difference in energy associated with the relative positions of the arene pendant groups is dictated by differences in additive polarity by having their dipole moment aligned either with or against the inherent dipole on the polycarbodiimide backbone.[15,19] We now know that solvent plays a crucial role on the relative energy required for these transitions as well.[1] It is therefore plausible that modifying the electronics of the arene π-system through substituent effects and altering the polarity of the pendant groups will change the temperature necessary to observe these realignments with respect to solvent. To further test this hypothesis, the design and synthesis of a series of substituted naphthalene pendant groups (**Poly-2–6**) was performed. The substituents were selectively placed on the "4" position of the 1-naphthyl pendant groups which lies on the same axis of rotation as the aryl-N bond that connects the naphthalene units to the backbone. This positioning should minimize steric interference associated with the rotation and repositioning of the naphthalene core. Additionally, substituents on this position lie in direct resonance with the aryl-N bond, further promoting the desired polarity differences. The substituents range from a strongly donating methoxy group (**Poly-2**), to a weakly donating methyl group (**Poly-3**), to substituents with mixed effects such as halogens (**Poly-4,5**). We also experimented with heteroatom substitution of a ring carbon such as the 5-quinolyl derivative (**Poly-6**). Substituents with mild to strong electron withdrawing character created complications in the synthetic process and are currently under investigation.

Variable temperature polarimetry was performed on each polymer in toluene, THF, and $CHCl_3$, and it was discovered that each polymer behaves anomalously in each solvent (Fig. 3).

The *N*-(4-methoxy-1-naphthyl)-*N*′-(*n*-dodecyl) polycarbodiimide (**Poly-2**) shows profound differences when compared with the previously reported (**Poly-1**).[1] For convenience, a summation of conformational switching temperatures for each polymer with respect to solvent is shown in Table 2. The energy requirements associated with each solvent have been completely reversed for **Poly-2**, with toluene now requiring the lowest energy (~5 °C estimated midpoint temp.) and $CHCl_3$ and THF requiring higher temperatures of 24–27 °C for the observed conformational changes. For **Poly-2**, the OSA in THF reaches 1900° ranging from +1500° to −400°, the largest OSA reported thus far by these polymer systems. These optical rotations are completely reversible upon cooling and no significant helical racemization occurs at these temperatures.

For **Poly-3**, the energy required to observe conformational changes has been greatly increased to the point that the full process cannot be observed within the experimental thermal limits in each solvent. Interestingly, the order of energy required for each solvent (i.e., $CHCl_3$ < THF < toluene) appears to remain the same when compared with **Poly-1** yet the addition of a pedestrian methyl substituent on **Poly-3** has caused a dramatic overall increase in required energy.

The halogen substituted **Poly-4** and **Poly-5** are an interesting case since halogen substituents on an arene system share mixed effects by being σ-withdrawing and π-donating. When comparing **Poly-4** and **Poly-5** to each other, their switching profiles look very similar; higher polarity solvents such as $CHCl_3$ and THF require much lower energy than the less polar toluene. When comparing both of these polymers to the parent **Poly-1**, the energy for toluene has been slightly increased while the energy for THF has been decreased by >15 °C. Another interesting observation from these two polymers is that the more electronegative chlorine substituent has decreased the energy of both the $CHCl_3$ and THF switching profiles proportionally by about 10 °C when compared with bromine and a slight decrease in toluene is seen as well. The full conformational change could not be observed for **Poly-5** in $CHCl_3$ and THF because they are below the thermal limits for the experiment.

Poly-6 presents even more anomalous behavior as a result of the heterocyclic 5-quinolyl pendant group. This pendant group is very similar in size to naphthalene but has very distinct electronics as a result of the nitrogen heteroatom. It is found that $CHCl_3$ is the only solvent that we can observe such conformational changes in and this happens at ~20 °C.

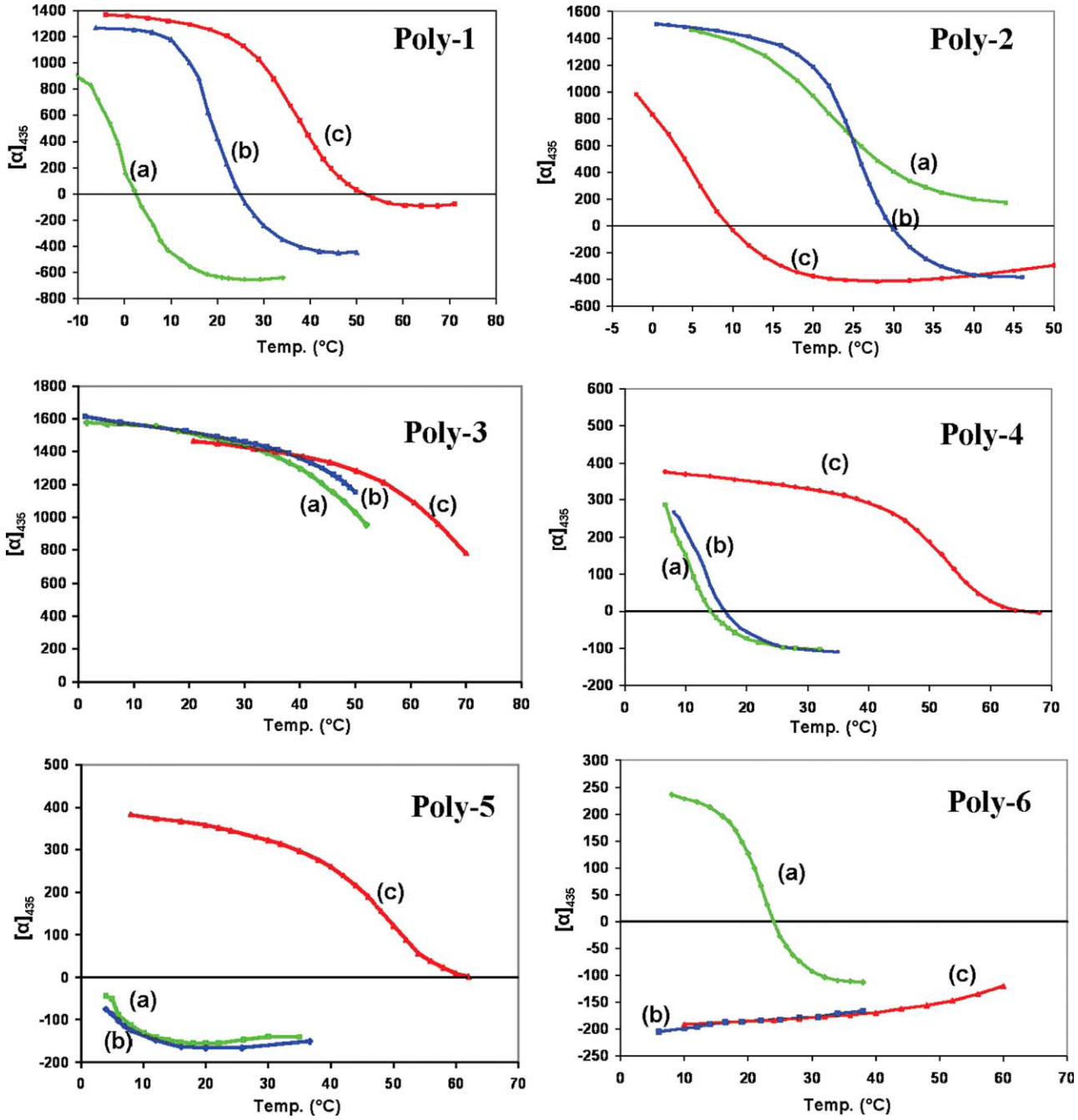


FIGURE 3 Variable temperature polarimetry of **Poly-1–6** showing dramatic conformational switching energy differences between each polymer with respect to solvent. For each plot, the polymer was tested in (a) $CHCl_3$ green (b) THF blue and (c) toluene red. Specific optical rotations were recorded within respective temperature ranges for each solvent using 435 nm light and a concentration range of 0.20–0.22 g/100 mL. Data results for **Poly-1** have been previously reported[1] but are included for clarity of comparison.

Both THF and toluene exhibit negative optical rotations throughout the thermal range, concluding that if conformational changes do occur within these solvents, it requires temperatures less than 0 °C. **Poly-6** presents an exciting new functionality to these reversible switching polycarbodiimides due to the potential chemistry that can be performed on the heterocyclic nitrogen. Recent research by our group has shown evidence that coordination of borane to the nitrogen lone pair of pyridinyl pendant group containing polycarbodiimides allow the use of these polymers as supports for localized chemical transformations.[20] This research can be further extended to include **Poly-6**, potentially allowing a reversibly chiral support for asymmetric catalysis. Such experiments are currently underway.

TABLE 2 UV-Vis and Polarimetry Summation for New Switching Polymers

Polymer ID	Conc. ppm	λ_{max} nm (in THF)	Approx. Switching Temp. (°C)[a]		
			$CHCl_3$	THF	Toluene
Poly-1	4.3	308	1	20	36
Poly-2	4.0	334	23	26	5
Poly-3	4.2	323	>50	>55	>70
Poly-4	4.0	315	10	12	55
Poly-5	4.0	315	<0	<0	52
Poly-6	4.2	314	23	ND[b]	ND[b]

[a] Temperatures taken at the midpoint of the OSA, slight extrapolations were made if necessary.
[b] Not determinable, no evidence of conformational changes are seen within temperature limits.

UV-Vis spectroscopy was performed on each polymer to compare auxochromic effects that each of these new arene substituents have on the polymer absorption bands. Figure 4 shows the overlay of UV-Vis spectra for each polymer dissolved in THF while concentrations and peak absorption maxima can be found in Table 2. The inset shows an enlargement of the naphthyl absorption region between 280 and 380 nm. When compared with the parent **Poly-1**, each of the new substituted polymers exhibit a bathochromic shift at the low energy naphthyl chromophore absorbance region. The donor substituents, methoxide (**Poly-2**) and methyl (**Poly-3**), exhibit the largest shifts of 26 and 15 nm, respectively. Weaker but identical shifts are observed for the halo-substituted **Poly-4, 5** and a similar shift is also realized for **Poly-6**. The resolution of peak maxima below 250 nm is limited by THF; however, these absorptions are also attributed to the naphthyl chromophores as seen by comparison to di-*n*-hexyl polycarbodiimide (**Poly-DnH**), which contains no arene groups. The extinction coefficient for the backbone imine absorption, which is the only chromophore observed for **Poly-DnH**, is significantly less than the higher energy naphthyl absorption and exhibits no significant absorption above 250 nm. This observation leads to the conclusion that the imine absorption for **Poly-(1–6)** is buried underneath the higher energy naphthyl chromophore absorption for these arene based polymers.

In addition to substituent effects on naphthalene, **Poly-7** was synthesized to determine the importance of a fully aromatized pendant group. The 4-indanyl derivative consists of two fused rings (one aromatic and one saturated) and should fulfill the constricted size and spatial requirements as previously investigated.[1] Variable temperature polarimetry of **Poly-7** revealed little to no change in specific optical rotation in toluene, THF, and $CHCl_3$ (Fig. 5). This observation warrants conclusion that π-based interactions on a fully aromatized pendant group play a vital role in the conformational changes observed. In other words, simply having a

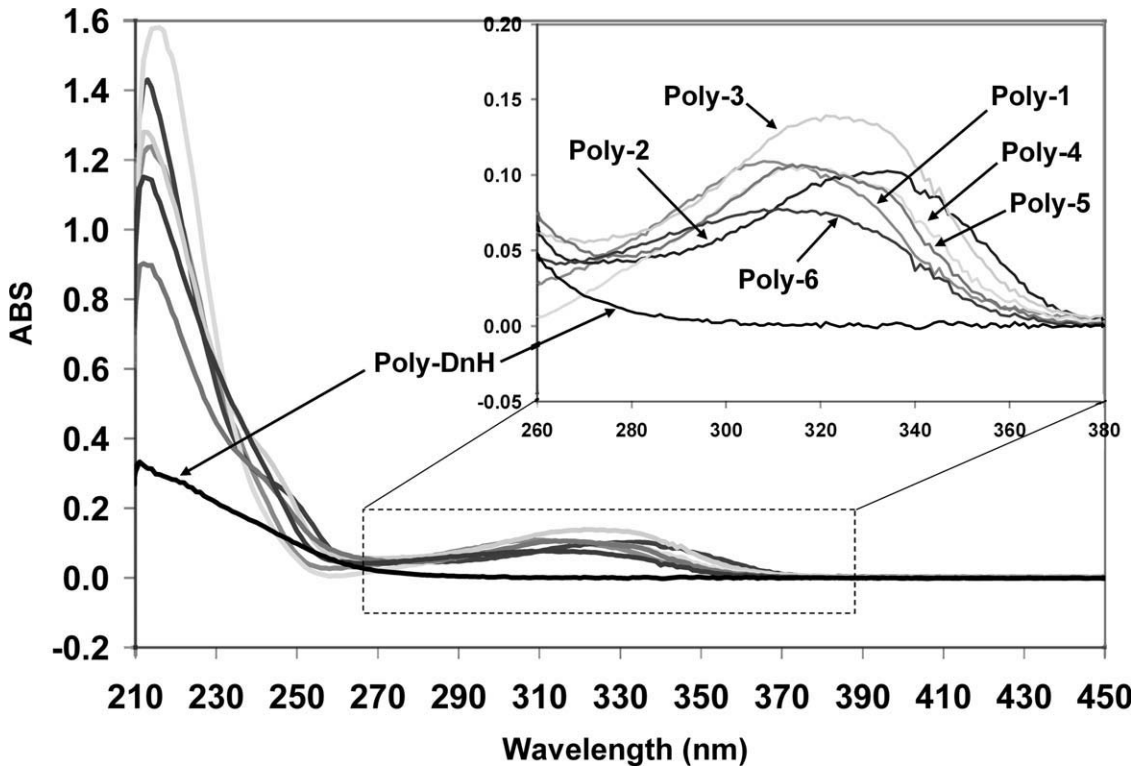


FIGURE 4 UV-Vis spectra overlay of **Poly-(1–6)** in THF at room temperature. Di-*n*-hexyl polycarbodiimide (**Poly-DnH**) is also shown (4.3 ppm in THF) for comparison as a polycarbodiimide without arene chromophores.

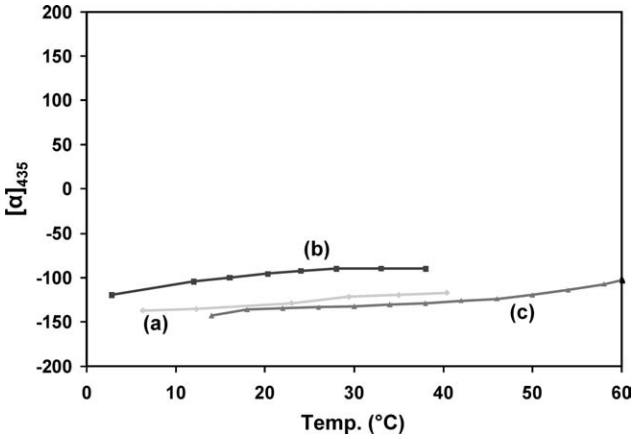


FIGURE 5 Variable temperature polarimetry of **Poly-7** in (a) $CHCl_3$, (b) THF, and (c) toluene. ($c = 0.20$–0.22 g/100 mL) Partial removal of aromaticity from a naphthyl group to an indanyl group results in the complete loss of conformational switching behavior.

constricted bulky pendant group is not enough to allow these transitions.

Poly-8 was synthesized to experiment with the aforementioned second layer of embedded chirality that is sterically affixed around the polymer helical backbone as a result of the direct attachment of these arene systems. For **Poly-8**, mobility and degrees of rotational freedom are introduced to the arene pendant group through spacing from the polycarbodiimide backbone by a methylene unit. Our curiosity is driven by how this increase in pendant group mobility will affect the optical rotations of these polymers and if a second corona of chiral order can still be retained by the 1-naphthylmethyl pendant group. Furthermore, this increase in mobility may promote aromatic-aromatic based interactions by allowing the pendant groups to obtain relative positions that maximize them. **Poly-8** exists as a very tacky polymer after work-up unlike **Poly-(1–7)** which have a fluffy texture. Polarimetry of **Poly-8** reveals a large overall decrease in specific optical rotation ($[\alpha]^5_{435} = -11.2°$, $[\alpha]^{46}_{435} = -18.7°$, $c = 0.23$ g/100 mL in $CHCl_3$), which is comparable with polycarbodiimides that contain only aliphatic pendant groups[21] and little to no change in specific optical rotation throughout the respective temperature ranges. Therefore, a constricted direct attachment of the naphthalene pendant group is required to observe these conformational changes and promotion of a chiral order is not obtained when the addition of a methylene spacer is given.

CONCLUSIONS

We have shown that the energy required for these polycarbodiimide systems to undergo reversible conformational changes is highly influenced by the electronic fingerprint of their arene pendant groups. Substituent induced alterations to the dipolar character of these pendant groups resulted in the first library of switching polycarbodiimides, each of which, exhibit unique energies for these conformational changes with respect to solvent. The dramatic differences in energy associated with each polymer and these conformational changes in $CHCl_3$, THF, and toluene indicate that this behavior is very complex and may be the result of multiple forms of aromatic-aromatic and aromatic-backbone interactions in addition to solvophobic and polarity effects. An attempt to further probe some of these complexities has revealed that complete aromaticity of the pendant group is required for these rearrangements and that a constricted direct attachment of the arene pendant group to the backbone of the polymer is also required. In addition, the incorporation of a heterocyclic nitrogen onto the arene pendant groups, **Poly-6**, presents new functionality, upon which, more utility of this chemistry can be built upon. These results open the door to the possibility that an even larger library of polyarene containing polycarbodiimides with conformational switching behavior is synthetically feasible. Going forward, these substituents can be chemically modified to perform even greater function on a reversibly chiral molecular switch.

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