Stimuli-Responsive Polymers VI. Azobenzene Modified Copolyaramides with Chiral Helical Geometries: Influence of Rigid, Helix-Disrupting Segments on Physiochemical and Chiroptical Behavior^{††}

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ABSTRACT: Polymers comprised of alternating *trans*-4,4'-azobenzene and helix directing (*R*)-2,2'-binaphthylene backbone linkages adopt single handed helical conformations in solution that are reversibly distorted by light and heat regulated *trans* $\leftrightarrow$ *cis* isomerization processes. The replacement of (*R*)-binaphthylene backbone groups with helix-disrupting 4,4'-diphenylfluorene segments affords permanent changes in some of the properties exhibited by this family of optically active materials. Polymer solubilities in organic solvents like THF and acetone are significantly diminished while thermal stabilities and photophysical behavior remain largely unchanged. Optical rotation magnitudes measured at the sodium D-line drop in a linear manner with the loss of the atropisomeric binaphthylene linkages. However, all of the polymer variants exhibit stimuli-responsive chiroptical behavior when evaluated in DMAC or THF solution environments. Specific rotation magnitudes are reversibly diminished by the near-UV light induced *trans* $\rightarrow$ *cis* isomerization reaction. Optical rotatory power is restored by reverse *cis* $\rightarrow$ *trans* isomerization processes triggered by heat or by visible light illumination. That stimuli-responsive chiroptical properties are exhibited by all polymer variants regardless of their monomer compositions indicates that global helical order along the polymer backbone is not necessarily required for this effect. Rather, isomerization induced perturbations to the local dihedral angles residing in the atropisomeric binaphthylene main chain segments likely serve as the genesis for photo- and thermo-regulated behavior in these materials.

KEY WORDS Stimuli-Responsive Chiroptical Behavior / *trans*–*cis* Azobenzene Isomerization / Helical Polymers / Circular Dichroism / Optical Rotation / Exciton Coupling / Cardo Polymers /

Macromolecules endowed with single-handed helical geometries can be prepared by a variety of synthetic methods. Monomers based on chiral 1,1'-binaphthylenes, 1,1'-biphenylenes and other axially dissymmetric ring systems provide convenient access to condensation polymers with chiral helical motifs. The polycondensation of (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine with terephthaloyl chloride was first reported by Schulz and Jung over thirty years ago.¹ The resulting polyaramide exhibited significant optical rotatory power that was attributed to the presence of a single helical screw sense along the polymer's conformationally restricted backbone. In the decades that have followed, a variety of other optically active macromolecules have been assembled from atropisomeric, helix-directing monomers using this same generalized approach.²

Earlier, this laboratory reported the preparation of a number of helical *trans*-azobenzene modified polyaramides from both (*R*)- and (*S*)-1,1'-binaphthyl-2,2'-diamine.^{3,4} Some of these materials were specifically designed to undergo reversible helix order $\leftrightarrow$ disorder transitions in response to multiple *trans* $\leftrightarrow$ *cis* azobenzene isomerization reactions triggered within the poly-

mer's main chain.^{5–8} When evaluated in polar solvent media, the helical polyaramides *trans*-1(*R*) and *trans*-1(*S*) were found to possess specific rotations (sodium D-line) near (–) 500 and (+) 500 deg dm^{–1} g^{–1} cm³, respectively. This optical rotatory power was reduced by a full order of magnitude when the polymer solutions were briefly exposed to near ultraviolet (UV) light to drive the *trans* $\rightarrow$ *cis* photoisomerization process. Optical rotation magnitudes were returned to their original values by a series of thermally or photochemically me-

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^{††}Dedicated to Professor Otto Vogl on the occasion of his 75th birthday.

diated *cis* $\rightarrow$ *trans* isomerization reactions which served to restore helical backbone motifs in these systems. Similar findings have been communicated by Takeishi *et al.*, for two other series of helical polyamides fitted with chiral 2,2'-biphenylene or 6,6'-binaphthylene main chain linkages.^{9, 10}

The helical molecular architectures adopted by polymeric constructs like *trans*-**1(R)** and *trans*-**1(S)** can also be permanently altered or modified by randomly coupling helix-disrupting monomer segments into their polyaramide backbones. Molecular modeling studies carried out in this laboratory more recently have shown that at low levels of incorporation, these surrogate monomer linkages can give rise to localized bulges, kinks or other point-defects within the polymer's ordered helical screw. With higher molar loadings of the non helicogenic segment, backbone structures become progressively more distorted and global helical geometries ultimately collapse along the polymer chain. Conformational perturbations of this type might be expected to have an impact on the physical properties and the stimuli-responsive chiroptical behavior exhibited by this class of materials.

In an effort to further extend our studies in this area and to explore some of the predictions gleaned from our molecular modeling efforts, we have now prepared a new family of azobenzene modified copolyaramides. These materials contain both helix-directing 2,2'-binaphthylene linkages and helix-disrupting diphenylfluorene segments that, together, provide for more complex backbone architectures. The syntheses, physical properties and photo-physcial behavior of these new constructs are described herein along with a detailed account of their stimuli-responsive chiroptical behavior in dilute solution environments.

EXPERIMENTAL

Materials

Anhydrous *N,N*-dimethylacetamide (DMAC) and anhydrous tetrahydrofuran (THF) were both supplied by Aldrich and were stored over 4 Å molecular sieves under an Ar atmosphere. (*R*)-(+)- and (*S*)-(–)-1,1'-binaphthyl-2,2'-diamine (99%, 99% ee, Aldrich) were both recrystallized from warm methanol and then rigorously dried *in vacuo* before use. *trans*-Azobenzene-4,4'-dicarbonyl chloride^{11, 12} and model compound *trans*-**7(R)**⁸ were each synthesized as previously reported. All other reagents and solvents (> 97%) were obtained from Aldrich and were used without further purification.

Preparation of Polymers

In a typical polymerization reaction, a mechanically stirred solution of *trans*-azobenzene-4,4'-dicarbonyl chloride (1.55 mmol) and diamine (or mixture of two diamines) (1.50 mmol) in DMAC (30 mL) was stirred at room temperature under Ar for 4 to 6 h. The viscous red solution that resulted was then poured into water (300 mL), giving a stringy orange solid. The solid was vigorously extracted with water (2 $\times$ 150 mL) and MeOH (2 $\times$ 150 mL) in a mechanical blender and was then dried *in vacuo* at 60–70°C for 48 h. Unless otherwise noted, azobenzene modified polymers **1(R)** through **6** were polymerized in the dark to minimize the isomerization of their internal *trans*-azobenzene backbone linkages. The polymer structures reported herein were consistent with ¹H NMR and IR spectroscopic data.

Polymer Film Formation

Polymer samples (1.0 g) were dissolved into DMAC (10–15 mL) and then allowed to stand in the dark for a 24 h period. Each solution was poured onto a level, dust-free, non-stick teflon surface, covered with a large inverted funnel and then warmed in the dark to 32 $\pm$ 4°C for 24 h during which time the DMAC slowly evaporated away. The resulting films were carefully removed from the teflon base, loosely taped to a supporting frame and then dried *in vacuo* at 60–80°C for 72 h. Polymer films were employed for infrared spectroscopy measurements and were typically 10 to 20 microns thick.

Analytical Methods

Proton nuclear magnetic resonance (¹H NMR) spectra were obtained at 300 MHz on a General Electric QET spectrometer or at 500 MHz on a Bruker Avance DRX-500 instrument. Tetramethylsilane was employed as a standard. Infrared (IR) spectra were recorded on a Perkin–Elmer 1600 series Fourier transform infrared spectrophotometer. Samples were measured in thin film form. UV-visible (UV-Vis) spectra were obtained with a Hewlett Packard 8453 UV-Vis spectrophotometer.

Gel permeation chromatography (GPC) was carried out with a Waters HPLC 150C equipped with a refractive index detector. Polymer samples were dissolved into DMAC containing trace amounts of Ionol (antioxidant) and toluene sulfonic acid. Measurements were run at 135°C and narrow molecular weight polystyrene standards were employed for the purposes of GPC calibration. Thermal gravimetric analyses (TGA) were obtained with a TA Instruments TGA 2950 Thermogravimetric Analyzer. Differential scanning calorimetry (DSC) was performed with a TA Instruments DSC

2910. Both instruments were interfaced to a TA Instruments Thermal Analyzer 2100. Polymer samples were typically heated at $20^{\circ}\text{C min}^{-1}$ under N_2 unless otherwise noted.

Specific rotations, given as $\text{deg dm}^{-1} \text{g}^{-1} \text{cm}^3$, were evaluated at the sodium D-line (589 nm) with a Perkin–Elmer Model 341 or Model 241 polarimeter. Samples were dissolved in THF or DMAC at concentrations near 0.020 g dL^{-1} and a standard 10 cm pathlength cell was utilized for all measurements. Circular dichroism (CD) spectra were obtained with a Jasco J600 spectropolarimeter fitted with a 450 W xenon arc lamp as a light source. Sample concentrations were typically on the order of $5 \times 10^{-5} \text{ M}$ and data are reported as $\text{deg cm}^2 \text{dmol}^{-1}$. All CD measurements were carried out in THF at 25°C unless otherwise indicated.

Low intensity UV irradiations of polymer solutions were performed with a Black-Ray Long Wavelength UV lamp (San Gabriel, CA; Model B 100 AP). The maximum intensity of light output was centered near 360 nm. Visible light illuminations were carried out with a Scientific Instruments Dyna-Lume Sun-Lite I Illuminator (Skokie, IL; Model 240–190). Solutions were illuminated with near UV or visible light while confined within stoppered polarimetry cells or CD quartz cuvettes. Lamp-to-sample path lengths were typically 6–8 cm. When desired, a combination of optical cut-on and band-pass filters (Oriel Corp., Stratford, CT) were employed to furnish radiation within a desired spectral window.

CPK (Corey–Pauling–Koltun) molecular modeling was performed with models obtained from Harvard Apparatus, Inc (South Natick, MA). All CPK techniques are qualitative in nature and are based on the hard-sphere, excluded volume and freely-rotating bond approximations. Forcefield molecular modeling simulations briefly described in the RESULTS AND DISCUSSION section were carried out as part of an earlier study.⁸

RESULTS AND DISCUSSION

Polymer Syntheses

The *trans*-azobenzene modified polymers described herein were prepared in the absence of room light by the solution polycondensation of *trans*-azobenzene-4,4'-dicarbonyl chloride with the selected aromatic diamines. (*R*)-(+)- and (*S*)-(–)-1,1'-binaphthyl-2,2'-diamine were exploited as helix-directing monomers while 4,4'-(9-fluorenylidene)dianiline served to randomly introduce bulky, achiral diphenylfluorene segments into the polymer backbone. Polymerization reactions were carried out at room temperature in an-

Scheme 1. Azobenzene modified polymers *trans*-1(*R*) through 6.

hydrous DMAC. Polymers *trans*-1(*R*) through *trans*-6 shown in Scheme 1 were isolated by precipitating their viscous DMAC solutions into water followed by multiple extraction steps with water and methanol to remove traces of the DMAC solvent. Polymer structures were fully consistent with ^1H NMR and IR spectroscopic data. When examined as thin films cast from DMAC, all of the polymer variants were characterized by amide I (carbonyl stretching) and amide II (NH bending) bands in their infrared spectra appearing near 1650 and 1540 cm^{-1} , respectively. A third broad absorption centered near 3320 cm^{-1} due to NH stretching was also apparent for each polymer.

Backbone compositions for this *trans*-polymer series were carefully determined by ^1H NMR spectroscopy¹³ by integrating appropriate amide proton signals falling between 10.0 and 10.5 ppm ($\text{DMSO}-d_6$). Compositional data are provided in Scheme 1 (mol%) and in Table I (weight%) for comparison. Azobenzene contents in these materials ranged from about 31 to 35 weight percent while chiral binaphthylene and achiral diphenylfluorene loadings varied far more broadly (Table I). Polymer molecular weights determined by GPC were noted to scale inversely with binaphthylene monomer contents. Molecular weight values recorded for *trans*-1(*R*) and *trans*-1(*S*) were relatively modest when compared to those measured for the other members of this polymer family that were more enriched in the rigid diphenylfluorene backbone unit. These results suggest that chain growth for *trans*-1(*R*) and *trans*-1(*S*) may be sterically hindered to some degree during the polycondensation reaction. Similar observations have been reported Takeishi *et al.*¹⁰ for other polymers con-

Table I. Polymer composition and molecular weight data

Polymer (<i>trans</i> -)	Azobenzene ^a fragment/wt%	Binaphthylene ^a fragment/wt%	Diphenyl fluorene ^a fragment/wt%	M_n^b	M_w/M_n^b
1(R)	34.8	48.7	0	18600	1.52
1(S)	34.8	48.7	0	22500	1.83
2(R)	33.8	35.9	14.2	26600	1.71
3(R)	33.0	26.3	24.9	36800	1.72
4(R)	32.5	19.5	32.5	60200	2.02
5(R)	31.6	8.0	45.4	84700	1.98
6	30.9	0	54.3	64800	1.77

^aDetermined by ¹H NMR. ^bDetermined by GPC in DMAC.**Table II.** Polymer solubilities at 25°C

Polymer (<i>trans</i> -)	Solvent medium					
	H ₂ SO ₄	DMAC	DMSO	THF	(CF ₃) ₂ CHOH	Acetone
1(R)	+++	+++	+++	+++	++	+
2(R)	+++	+++	+++	+++	+	–
3(R)	+++	+++	+++	++	–	–
4(R)	+++	+++	+++	+	–	–
5(R)	+++	+++	+++	+	–	–
6	+++	+++	+++	+	–	–

+++ very soluble; ++ soluble; + slightly soluble; – insoluble.

structed from 2,2'-disubstituted binaphthylenes. That conformational variations between the different polymer species might also have some influence on their hydrodynamic properties and, consequently, on the GPC molecular weight values posted in Table I cannot be ruled out at this time, however.

Polymer Solubilities

As was reported earlier, polymers *trans*-**1(R)** and *trans*-**1(S)** are readily dissolved by a variety of organic solvents, giving homogeneous solutions that are stable in the dark for periods exceeding several months.^{3,4} In these systems, the presence of multiple binaphthylene units within the polymer's main chain provides for highly twisted, helical geometries that are unable to pack efficiently or crystallize in the solid state. As the kinked binaphthylene linkages were systematically replaced by more rigid diphenylfluorene moieties to give variants *trans*-**2(R)** through *trans*-**6** in this study, polymer solubilities evaluated at room temperature were observed to drop in all but the most aggressive solvent media. Copolyaramides fitted with 25 weight percent or more of the 4,4'-diphenylfluorene linkage were insoluble in polar solvents like acetone and hexafluoroisopropanol as indicated in Table II. Polymer solubilities evaluated in THF were also negatively impacted by the presence of the helix-disrupting diphenylfluorene segments.

This trend in solubility behavior is noteworthy since cardo polymers containing sterically demanding 9,9-fluorenylidene side groups^{14–16} generally have excellent organosolubilities owing to reduced solid

state packing efficiencies which serve to disrupt physical bonding interactions between neighboring chains. Apparently, when compared to the conformationally twisted 2,2'-binaphthylene linkage, 4,4'-diphenylfluorene backbone units are less effective at promoting good solubility properties. Indeed, in an unrelated series of studies involving highly conjugated polymer derivatives prepared in our laboratory, we have observed that even at very low levels of incorporation, 2,2'-binaphthylene segments often give rise to dramatic improvements in solubility behavior without significantly compromising other physical attributes of the materials system.¹⁷

Polymer Thermal Properties

TGA and DSC were both employed to examine the thermal characteristics of *trans*-polymers **1(R)** through **6**. When evaluated under nitrogen or air, all of these materials exhibited an onset of weight loss above 400°C. Temperatures for 5% and 50% weight loss under nitrogen are tabulated in Table III for comparison. Polymer residues recovered after heating to 600°C were severely darkened and were insoluble in all of the organic solvent media listed in Table II. As for other *trans*-azobenzene modified polyaramides constructed in this laboratory,^{4,6,12} melting transitions for these materials were notably absent from their DSC scans. However, all of the polymers were characterized by a prominent exotherm (T_{azo}) residing within the 428 to 464°C temperature window (Table III). As we have reported before,^{4,6,12} this transition corresponds to the extrusion of molecular nitrogen from the *trans*-azobenzene mod-

Table III. Polymer thermal properties

Polymer (<i>trans</i> -)	Onset of weight loss/°C ^a		<i>T</i> _{azo} /°C ^b
	5%	50%	
1(R)	418	> 600	428
2(R)	428	> 600	433
3(R)	446	> 600	440
4(R)	455	> 600	446
5(R)	466	> 600	452
6	461	> 600	464

^aTGA; 20°C min⁻¹, under nitrogen. ^bDSC; 20°C min⁻¹, under nitrogen.

ified polymer backbone and serves to ultimately limit the thermal and thermo-oxidative stabilities of these materials beyond 400°C. A comparison of the data provided in Tables I and III reveals that copolyaramides fitted with higher *trans*-azobenzene loadings exhibited slightly reduced weight loss onset temperatures under the standard conditions employed in this study.

Photophysical Behavior

Disubstituted azobenzenes have been widely evaluated for their reversible isomerization behaviors. Interconversion between the *trans*- and higher energy *cis*-isomeric states can be effected both photochemically (*trans* ↔ *cis*) and thermally (*cis* → *trans*) with a high degree of efficiency and an absence of competing side reactions.^{18,19} When incorporated into a properly designed polymer backbone, the azobenzene linkage can serve as a photonically or thermally driven molecular actuator or “stimuliphore”, bringing about controlled alterations in the three dimensional geometries adopted by a macromolecule.

In this investigation, reversible *trans* ↔ *cis* isomerization reactions triggered within **1(R)** through **6** were monitored by optical absorbance spectroscopy. Polymer samples were dissolved in THF or DMAC at 10⁻⁵ M concentrations. The *trans* → *cis* photoresponse was effected by briefly irradiating the polymer solutions with filtered (340 < λ < 400 nm) ultraviolet light. For each polymer system, the illumination step was accompanied by a significant reduction in π, π* band intensity centered at 338 nm for the *trans*-azobenzene chromophore. A concomitant increase in the broad 440 nm n, π* band for the *cis*-azobenzene linkage was also observed. Photostationary state compositions following the irradiation procedure were largely independent of polymer backbone compositions, with about 70–75% of the azobenzene segments in these materials ultimately residing in their more energetic *cis*-configurations.

Cis → *trans* reorganization within **1(R)** through **6** was carried out by either photochemical or thermal means. The exposure of the polymer solutions to vis-

ible (> 420 nm) light rapidly restored the population of main chain *trans*-azobenzene segments in each system. These photo-induced conversions afforded 85 to 90% of the *trans*-isomer and were completed within a matter of minutes as evidenced by optical absorbance spectroscopy. A more gradual and complete return to all-*trans* polymer geometries was provided by the thermal or “dark” *cis* → *trans* isomerization reaction. Activation energies calculated for this first-order process in DMAC fell near 21 to 22 kcal mol⁻¹. Within the limits of experimental error, these values were invariant to differences in polymer backbone compositions. Importantly, *cis*-isomer half-life values determined at room temperature for all of the polymers exceeded 100 h, allowing for the acquisition of chiroptical data over short time periods that were uncomplicated by rapidly shifting *cis*–*trans* isomer populations within the polymer backbones. As observed for other azobenzene modified copolyaramides synthesized in our laboratory,^{4,6,8,13} the interconversion of *trans*- and *cis*-isomeric states within these constructs was completely reversible over numerous isomerization cycles without any apparent hysteresis or photodegradation effects.

Stimuli-Responsive Chiroptical Behavior

Helical macromolecules have been extensively studied with regard to their chiroptical properties. The presence of single-handed helical motifs along a polymer backbone can lead to large optical rotation magnitudes and intense circular dichroic (CD) spectra.^{20–22} Not surprisingly, the chiroptical behavior exhibited by helical macromolecules is necessarily tied to a variety of intrinsic factors that are unique to each system. These include the chemical composition of the polymer backbone as well as the three dimensional geometry, screw direction and conformational stability of the chiral helical coil.

Within polyaramides *trans*-**1(R)** and *trans*-**1(S)**, individual binaphthylene main chain segments are directly coupled through stable amide bonds to linear *trans*-azobenzene residues. Here, the atropisomeric 2,2'-binaphthylene linkages serve as helix-directing groups, collectively projecting their left- or right-handed axial dissymmetries over the larger polyaramide backbones. In these polymers, chirality is present at only the macromolecular or helical level. Local chiral centers are completely absent from these structures. Force field molecular modeling studies carried out earlier suggested that the two polymer constructs are likely to adopt relatively open helical conformations. Here, approximately five binaphthylene and five *trans*-azobenzene units populate one full turn in their chiral helical screws.⁸ In these conformational arrangements,

the twin naphthylene rings in each binaphthylene moiety favor nearly orthogonal orientations ($\pm 87^\circ$). The helical motifs postulated for *trans*-**1(R)** and *trans*-**1(S)** are propagated mainly by the unique directionality of the intermonomer bonding along the polyaramide chain. This geometry is highly favored because alternate rotational isomeric states are not available to this particular sequence of monomer units. Importantly, intramolecular hydrogen bonding interactions do not appear to play a significant role in stabilizing helical structures within these conformationally restricted polymer systems.

Polymers *trans*-**1(R)** and *trans*-**1(S)** exhibit chiroptical behavior that is fully consistent with their proposed chiral architectures. When evaluated in THF or the more polar DMAC solvent medium, these derivatives afford sodium D-line specific rotations near (–) 500 or (+) 500 deg dm^{–1} g^{–1} cm³, respectively. The twin polymers are also characterized by bisignated CD plots with strong Cotton effects appearing over the 300 to 400 nm spectral range. As was discussed earlier,^{6–8} this CD behavior has its origins in exciton coupling between neighboring *trans*-azobenzene chromophores that are positioned along the polymer chains in chiral, helical environments. Importantly, the optical rotations recorded for these *trans*-polymers are preserved even under relatively high temperature conditions. As shown in Figure 1 (lower plot), heating a DMAC solution of *trans*-**1(R)** to 95°C afforded little change in its rotational behavior over a four hour incubation period. The CD spectrum for this polymer was similarly unaffected by this heating step. These results suggest that polyaramides like *trans*-**1(R)** occupy relatively stable conformations and are not prone to thermally driven changes that would serve to radically disrupt helical, main chain geometries in the solution state.

The random placement of achiral 4,4'-diphenylfluorene linkages into *trans*-**1(R)** was undertaken in an effort to explore the influence of helix-disrupting segments in the polymer backbone. As indicated in Scheme 1, a series of polymer constructs was prepared by replacing varying amounts of (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine with the surrogate diphenylfluorene monomer during the polycondensation reaction. Space filling models for the two diamine building blocks are provided in Figure 2. Significant differences in their three dimensional architectures are readily apparent. Unlike the chiral binaphthylene diamine which can occupy a range of closely related conformational states due to restricted rotation about its pivotal 1,1'-bond, the 4,4'-(9-fluorenylidene)dianiline monomer possesses a fixed, almost rigid geometry. In this species, the two reactive amino moieties are firmly localized in space and

Figure 1. Change in specific rotations (sodium D-line) for polymers *trans*-**1(R)** [■] and *trans*-**4(R)** [●] dissolved in DMAC at 95°C under argon as a function of time.

Figure 2. Space filling models for the two diamine monomers (*R*)-1,1'-binaphthyl-2,2'-diamine (top) and 4,4'-(9-fluorenylidene)dianiline (bottom) showing significant differences in their three dimensional geometries.

are separated by a distance that is considerably greater than that found in binaphthylene monomer where the twin naphthylene rings are situated in a nearly orthogonal orientation. When coupled directly into the backbone of *trans*-**1(R)**, a single 4,4'-diphenylfluorene segment will give rise to a localized point-defect within the polymer's chiral helical coil. Based on CPK (Corey–Pauling–Koltun) molecular modeling, this distortion results in a bend or kink along the central axis of the helix. As more of the surrogate diamine monomer is randomly substituted for (*R*)-(+)-1,1'-binaphthyl-2,2'-diamine to give *trans*-variants **2(R)** through **6**, the overall loadings of atropisomeric monomer residues in the

Table IV. Polymer specific rotation values before ($-h\nu$) and after ($+h\nu$) near UV light exposure measured in THF and DMAC

Polymer	Binaphthyl Content ^a by ¹ H NMR /mol%	$[\alpha]_D^{25}/\text{deg dm}^{-1} \text{ g}^{-1} \text{ cm}^3$ ^b			
		$-h\nu$		$+h\nu$ ^c	
		THF	DMAC	THF	DMAC
1(R)	50	(-)530	(-)495	(-)46	(-)115
1(S)	50	(+)511	(+)489	(+)35	(+)123
2(R)	38	(-)335	(-)381	(-)30	(-) 95
3(R)	28.5	(-)231	(-)284	(-)10	(-) 83
4(R)	21.5	—	(-)215	—	(-) 56
5(R)	9	—	(-) 86	—	(-) 30
6	0	—	0	—	0

^aValues typically $\pm 0.5\%$. ^bRotation values typically $\pm 1\%$. ^cRotation data gathered within two minutes of UV light exposure.

polymer backbones are significantly diminished (see Table I). On a more global scale, helical geometries become progressively more scrambled and disordered main chain conformations begin to predominate. CPK modeling efforts predict that polymer *trans*-**5(R)**, fitted with only 9 mol% (8 wt%) of the helicogenic binaphthylene linkage, is likely to occupy randomly oriented backbone conformations that are “punctuated” by occasional placements of the chiral, helix-directing monomer.

Specific rotation values for the *trans*-polymer family are collected in Table IV. These measurements were performed at the sodium D-line (589 nm) and are thus well isolated from the strong π, π^* and much weaker n, π^* azobenzene transitions residing within the polymer backbones. Data are given for both the DMAC and THF solvent media for all cases where the polymers demonstrated sufficient solubility at 25°C. Rotation values for *trans*-**1(R)** and *trans*-**1(S)** are also posted in Table IV for comparison. As expected, the incorporation of helix-disrupting monomer segments into the polyaramide backbones had a significant impact on the optical rotatory powers exhibited by this *trans*-polymer series, with the D-line specific rotation magnitude for *trans*-**5(R)** dropping to about 20% of that observed for *trans*-**1(R)**. Polymer *trans*-**6** was devoid of any optical activity consistent with its achiral structure. Importantly, specific rotation values recorded in DMAC showed a linear dependence on (*R*)-binaphthylene backbone content as demonstrated in Figure 3. A similar trend was noted for three of the more soluble (*R*)-polymer variants when examined in THF (plot not shown). As for the parent *trans*-**1(R)** construct, the optical rotation values exhibited by these materials were invariant to elevated temperatures suggesting that their chiral conformations are not thermally labile. Data for polymer *trans*-**4(R)** dissolved in DMAC and heated to 95°C under an argon atmosphere are graphically displayed in Figure 1 (upper plot).

Figure 3. Specific rotations for polymers **1(R)** through **6** measured in DMAC as a function of (*R*)-binaphthylene backbone content: *trans*-configuration before near UV illumination [●] and after near UV illumination [○].

The exposure of the polymer solutions to filtered ($340 < \lambda < 400$ nm) ultraviolet light to drive the *trans* $\rightarrow$ *cis* photoresponse was accompanied by an immediate change in their rotational behaviors. For each binaphthylene modified polymer, optical rotatory power determined at the sodium D-line was significantly diminished as indicated in Table IV. For the DMAC solvent system where all of the copolyaramide variants could be easily measured, a linear dependence of rotation magnitudes on chiral (*R*)-binaphthylene backbone content was again observed (Figure 3, upper plot). Notably, the extent of the UV light induced chiroptical response was significantly greater when carried out in THF solvent environment (Table IV). This disparity may stem from solvent dependent variations in the final conformational states occupied by the irradiated polymer constructs. That DMAC and THF have different solvating powers and hydrogen bonding potentials that can serve to impact conformational behavior in polymer systems is widely recognized.⁸ *Cis-to-trans* photostationary state backbone compositions immediately following the illumination step were not found to be

Figure 4. First-order plots for the “dark” or thermal mediated recovery of specific rotations for polymer **2(R)**. Data are for the 24 °C and 60 °C isotherms in DMAC.

strongly dependent upon the choice of solvent in this study, however.

The chiroptical perturbations induced by near UV light exposure were fully reversible. Warming the polymer solutions in the dark to promote the thermally mediated *cis* → *trans* isomerization reaction resulted in a gradual restoration of optical rotation magnitudes. As expected, this response was temperature dependent, occurring much more rapidly at elevated temperatures. When carried out at the 60 °C isotherm in DMAC, the recovery of optical rotatory power in copolyaramide **2(R)** was complete within a matter of 8 to 10 h. A similar process monitored at room temperature required several weeks before rotation magnitudes were returned to their original or pre-irradiated values. As suggested by the linear plots provided in Figure 4, the restoration of optical activity in **2(R)** was characterized by first-order behavior. Based on time-resolved polarimetric data, an activation energy for this thermo-regulated process in DMAC was calculated to lie near 21 kcal mol⁻¹. This value is in good agreement with the activation energy for the “dark” *cis* → *trans* isomerization reaction in **2(R)** determined independently by optical absorbance spectroscopy. These results clearly show that the thermal isomerization of azobenzene backbone linkages in polymer **2(R)** and the modulation of optical rotatory power in this stimuli-responsive system are tightly coupled processes. The other azobenzene modified copolyaramide constructs described herein behaved similarly.

The results derived from the present study offer a number of important insights for the design of newer polymers with more advanced stimuli-responsive chiroptical properties. As expected, the specific rotations measured for this family of macromolecular constructs dropped progressively as achiral diphenylflu-

orene linkages were increasingly substituted for (*R*)-binaphthylene helix-directing groups in the polymer backbones. However, for each polymer system, photo- and thermo-regulated changes in rotation magnitudes were qualitatively preserved as indicated in Table IV. At low levels of substitution where distorted helical conformations in the *trans*-azobenzene modified polymers are likely to still predominate, other surrogate diamine monomers could be utilized to randomly position specific functional groups in close proximity to the chiral helical coils. For example, selected monomers fitted with pendant, long-wavelength absorbing chromophores could give rise to a new generation of materials that exhibit stimuli-responsive, induced Cotton effects in their CD spectra. Similarly, helical macromolecules capable of undergoing intermolecular crosslinking reactions to furnish covalently linked “super-helical” aggregates could be prepared from properly designed diamine monomers bearing latent reactive functional groups. Both of these approaches are under active consideration at this time.

That light- and heat-regulated chiroptical behavior were observed for all of the (*R*)-binaphthylene modified copolyaramides described in this report is also noteworthy from a more fundamental point of view. The results posted in Table IV suggest that the presence of long range helical order along the polymer backbone is not a necessary requirement for stimuli-responsive properties of this kind. Although molecular modeling studies have indicated that polymer constructs like *trans*-**1(R)** and *trans*-**1(S)** are likely to favor single handed helical motifs, these larger dissymmetric structures arise in response to the presence of atropisomeric binaphthylene groups that are positioned at regular intervals along the polymer’s main chain. The chiral features of *trans*-**1(R)** and *trans*-**1(S)** can therefore be simultaneously viewed from both global and more local molecular levels. In these systems, the *trans* → *cis* isomerization reaction results in perturbations to chiral helical backbone orientations because configurational and conformational changes occur locally along the polyaramide chain. In contrast, variants like *trans*-**4(R)** and *trans*-**5(R)** probably lack sufficient loadings of the (*R*)-binaphthylene monomer to adopt stable, longer range helical geometries in the solution state. For these constructs, the origins of stimuli-responsive chiroptical behavior are better explained by considering only the local conformational effects of the *trans* → *cis* isomerization process. Of prime importance here are reversible changes in the dihedral angles of the atropisomeric binaphthylene segments that likely occur during the isomerization reaction. For all of the polymer variants described in this study, internal binaphthylene backbone linkages

are flanked on both sides by azobenzene main chain groups. Given their close proximities to the azobenzene stimuliphores, the rotationally flexible binaphthylene segments will be susceptible to steric and/or electronic perturbations that stem from reversible *trans* $\leftrightarrow$ *cis* isomerization processes. That alterations in this dihedral angle can impact the CD and optical rotation behaviors of smaller chiral binaphthylene derivatives has been widely demonstrated in a number of earlier reports.^{23–25} An inspection of the twin plots shown in Figure 3 clearly reveals that the measured rotation magnitudes for polymers **1(R)** through **6** dissolved in DMAC are linearly related to the loading of the (*R*)-binaphthylene groups positioned along the polymer backbone. This trend in the chiroptical data holds both before and after near-UV light exposure. Deviations from linearity that might arise from the added effects of chiral, longer range helical backbone conformations in variants like **1(R)** and **2(R)** that possess significant concentrations of the helicogenic binaphthylene linkage are notably absent from the data presented in Figure 3.

The notion that stimuli-responsive chiroptical behavior in these systems can be attributed to changes in the local chiral environments that reside along the polyaramide chains is further bolstered by considering the unique properties exhibited by derivative *trans*-**7(R)**. Prepared as part of an earlier study,^{7,8} this azobenzene modified construct was designed to mimic a short chiral

fragment of the larger polyaramide backbone present in polymer *trans*-**1(R)**. Comprised of two azobenzene stimuliphores and a central atropisomeric (*R*)-binaphthylene group, this species lacks sufficient size to occupy a coiled helical geometry of the type that might be favored by its larger polymeric analogue. Like polymers *trans*-**1(R)** through *trans*-**5(R)**, however, *trans*-**7(R)** is characterized by a strong Cotton effect between 300 and 400 nm as shown in Figure 5 that corresponds to the *trans*-azobenzene π, π^* transition. In this spectral window, the dichroic bands are split into two distinct portions having both negative and positive amplitudes. That model compound *trans*-**7(R)**

Figure 5. CD spectra for model compound **7(R)** before ($-h\nu$) and after ($+h\nu$) the near UV illumination step. Spectra acquired in THF at room temperature.

exhibits negative exciton chirality in this spectral region is entirely consistent with the chiral geometry imposed by the 2,2'-disubstituted (*R*)-binaphthylene unit. Here, as for larger polyaramide *trans*-**1(R)**, neighboring *trans*-azobenzene π, π^* transition dipole moments are locked into counter-clockwise spatial orientations. Predictably, dichroic band intensities falling within the 300 to 400 nm window were significantly reduced following the UV light induced *trans* $\rightarrow$ *cis* isomerization reaction (Figure 5). When evaluated at the sodium D-line, model *trans*-**7(R)** displays strong levorotatory behavior, with a specific rotation in THF near (–) 205 deg dm^{–1} g^{–1} cm³. Importantly, as for the much larger polymer structures described above, the magnitude of this rotation value was significantly (and reversibly) diminished following the near-UV illumination step as shown in Figure 6. However, in this case, the sign of the rotation recorded for the smaller model compound was also inverted to a positive value as a result of the irradiation process. As has been discussed previously,⁸ this unique behavior likely has its origins in isomerization-driven changes to the dihedral angle within the chiral binaphthylene ring system of **7(R)**. Because the azobenzene “arms” in the smaller model compound are not coupled into sterically restrictive polymer backbones, rotational adjustments within this derivative may occur differently from those triggered within the larger conformationally restricted polymer constructs. Never the less, these results provide additional evidence that longer-range (*i.e.*, polymeric) helical structures are not required for stimuli-responsive chiroptical properties of the type described throughout this report.

CONCLUSIONS

Polyaramides comprised of alternating *trans*-4,4'-azobenzene and helix directing (*R*)-2,2'-binaphthylene

Figure 6. Specific rotations (sodium D-line) for model compound **7(R)** before ($-h\nu$) and after ($+h\nu$) the near UV illumination step. Data acquired in THF at room temperature.

backbone linkages adopt single handed helical conformations in solution. These chiral motifs are reversibly distorted by light and heat regulated *trans* $\leftrightarrow$ *cis* isomerization processes as has been demonstrated previously.^{6–8} In this study, the replacement of (*R*)-binaphthylene backbone groups with helix-disrupting 4,4'-diphenylfluorene segments afforded permanent changes in a number of the properties exhibited by this family of optically active materials. Polymer solubilities in organic solvents like THF and acetone were significantly diminished while thermal stabilities and photophysical behavior remained largely unchanged. Optical rotation magnitudes measured at the sodium D-line dropped in a linear manner with the loss of the atropisomeric binaphthylene linkages. However, all of the polymer variants exhibited stimuli-responsive chiroptical behavior when evaluated in DMAC or THF solution environments. Specific rotation magnitudes were reversibly diminished by the near-UV light induced *trans* $\rightarrow$ *cis* isomerization reaction. Optical rotatory power was restored by reverse *cis* $\rightarrow$ *trans* isomerization processes triggered by heat or by visible light illumination.

That stimuli-responsive chiroptical properties were exhibited by all of the polymer constructs described herein regardless of their monomer compositions indicates that long range or global helical order along the polymer backbone is not necessarily required for this effect. Rather, isomerization induced perturbations to the local dihedral angles residing in the atropisomeric binaphthylene main chain segments likely serve as the genesis for photo- and thermo-regulated behavior. These results suggest that a variety of different molecular constructs containing covalently linked azobenzene stimuliphores and atropisomeric binaphthylene groups could be engineered to exhibit similar

chiroptical effects in response to light and heat stimuli. Interesting avenues for exploration would include the assembly of other low molecular weight analogues similar to model compound **7(R)** and the construction of oligomeric or polymeric systems fitted with pendant side groups containing the optically active, stimuli-responsive component. Materials of this kind are currently undergoing evaluation in this laboratory as they are potentially well suited for chiroptical switching and novel sensory applications.²⁶

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