

Stimuli-responsive polymers. 4. Photo- and thermo-regulated chiroptical behavior in azobenzene-modified polymers fitted with main chain spirobiindane turns and chiral binaphthyl bends

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Abstract

A series of azobenzene-modified polyamides fitted with main chain spirobiindane turns and chiral binaphthyl bends was prepared from the solution polycondensation of *trans*-azobenzene-4,4'-dicarbonyl chloride with appropriate diamine monomers. When evaluated in their all *trans*-azobenzene configurations, these materials exhibited a good mix of physical properties suitable for high performance applications. Photoinduced *trans* → *cis* isomerization reactions were effected by irradiating polymer solutions with near UV light. Reverse *cis* → *trans* isomerization of the backbone azobenzene segments was triggered by either photochemical or thermal means and was monitored by optical absorbance spectroscopy. Thermally induced *cis* → *trans* reorganization within each polymer followed the first-order rate law. Activation energies calculated for this process in DMAC all fell near 21–23 kcal mol⁻¹ and were not strongly correlated to backbone content. Polymers containing axially asymmetric *S*-(-)- or *R*-(+)-2,2'-binaphthyl main chain linkages exhibited thermo- and photo-responsive chiroptical behavior when evaluated in dilute THF solutions. Specifically, the *trans*-azobenzene-modified materials were all characterized by CD spectra showing intense molar ellipticities within the 300–400 nm spectral window. Specific rotation magnitudes determined for the *trans*-polymers at the sodium D-line ranged into the hundreds of degrees and were dependent on the extent of binaphthyl loading along the polyamide backbone. The irradiation of the polymer samples to drive the *trans* → *cis* isomerization reaction resulted in an immediate chiroptical response, with CD band intensities and optical rotations significantly diminished. These effects were fully reversible and were attributed to the presence of putative one-handed helical conformations in the *trans*-azobenzene-modified polymers that were severely disrupted following the *trans* → *cis* isomerization reaction. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Stimuli-responsive conformational changes in azobenzene-modified polymers have been widely documented and continue to serve as an impetus for the study of these materials [1–3]. Local *trans* ↔ *cis* isomerization reactions in macromolecules endowed with conformationally restricted main chain geometries can often lead to dramatic alterations in global polymer dimensions as evidenced by measured changes in hydrodynamic volumes and solution viscosities. More specific conformational perturbations can also be triggered by the *trans* ↔ *cis* isomerization process. These include helix-to-opposite helix and helix-to-random coil transitions in selected polypeptides [4] and

polyisocyanates [5] fitted with main chain or pendent side chain azobenzene groups.

Central to our efforts to develop high performance materials with stimuli-responsive molecular architectures [6,7] has been the preparation of a new series of azobenzene-modified polymers that contain chiral 2,2'-binaphthyl linkages [8,9]. In recent years, the binaphthyl structural unit has been successfully exploited to impart unusual solubility, architectural and chiroptical features to a wide variety of polymeric materials [10–12]. Polyamides constructed from 1,1'-binaphthyl-2,2'-diamine possess kinked main chain geometries and tend to exhibit enhanced organosolubilities relative to their more linear counterparts [9]. When positioned at regular intervals along a conformationally restricted polymer backbone containing linear *trans*-azobenzene moieties, the axially asymmetric *R*-(+) or *S*-(-) binaphthyl link can also give rise to longer range

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helical order that is itself chiral. As we [9,13] and others [14,15] have shown recently, light induced *trans* → *cis* isomerization reactions in polymers of this kind effectively disrupt the one handed helical conformations present in these systems, allowing for the photo-regulation of chiroptical behavior on a macromolecular level. Such materials are of considerable interest for use as recording media and may also find added utility in various sensor and communications technologies.

In an effort to further extend our studies in this area, we have now prepared a new family of azobenzene-modified polymers that are fitted both with chiral binaphthyl linkages and with bent or curved spirobiindane segments which provide for more complex backbone architectures. The synthesis, physical characteristics and photophysical behavior of these new materials are described herein along with a preliminary investigation of their stimuli-responsive chiroptical behavior in dilute solution.

2. Experimental

2.1. Materials

Anhydrous *N,N*-dimethylacetamide (DMAC) (Aldrich) was stored under Ar over 4A molecular sieves. (*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. All other reagents and solvents (>97%) were obtained from Aldrich and were used without further purification.

2.2. Monomer syntheses

trans-Azobenzene-4,4'-dicarbonyl chloride (**1**) was synthesized as described earlier: [6,16] m.p.: 164.5–165°C (lit [16] m.p.: 164°C); ¹H NMR: (CDCl₃, 300 MHz) δ 8.33 (d, 4H), 8.06 (d, 4H); MS(e.i.): m/e (rel. int.) 307.9921 (37, M⁺), 305.9953 (49, M⁺), 271.0234 (78), 166.9972 (72), 138.9982 (100).

Bis-1,4-(3-Aminophenoxy-4'-benzoyl)benzene (**2**) was prepared as previously reported: [6] m.p.: 162–163°C; ¹H NMR: (TFD, 300 MHz) δ 8.00–8.06 (m, 8H), 7.63–7.71 (t, 2H), 7.35–7.44 (m, 6H), 7.18–7.27 (d, 4H); MS(fab): m/e 501.26 ([M]H⁺).

3,3,3',3'-Tetramethyl-1,1'-spirobiindane (**3**) was synthesized according to the method of Roberts and Abdel-Baset: [17] m.p.: 135–136°C (lit [17] m.p.: 133–134°C); ¹H NMR: (CCl₄, 300 MHz) δ 6.88–7.25 (m, 8H), 2.30 (s, 4H), 1.33–1.48 (m, 12H).

Dinitro-3,3,3',3'-tetramethyl-1,1'-spirobiindane-mixed 5,5', 5,6' and 6,6'-isomers (**4**). To a magnetically stirred solution of **3** (21.0 g, 75.8 mmol) in methylene chloride (50 ml) and acetic anhydride (20 ml) chilled to 5°C was added dropwise a solution of glacial acetic acid (8.8 ml), acetic anhydride (8.5 ml) and fuming nitric acid (9.6 ml). The reaction mixture was maintained between 5–10°C for

2 h and then slowly allowed to warm to room temperature over 24 h. The mixture was poured over ice and the resulting solution was extracted with chloroform (3 × 50 ml). The chloroform extracts were combined, washed with water (3 × 50 ml) and brine (2 × 50 ml) and then concentrated in vacuo to give a crude solid. The solid was recrystallized from methylene chloride to give **4** (78%) as a tan solid: m.p.: 175–186°C (broad); ¹H NMR: (CDCl₃, 300 MHz) δ 6.80–8.10 (m, 6H), 2.20–2.55 (m, 4H), 1.41 (d, 12H).

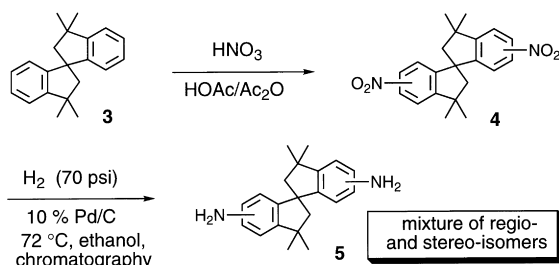
Diamino-3,3,3',3'-tetramethyl-1,1'-spirobiindane — mixed 5,5', 5,6' and 6,6'-isomers (**5**). A solution of **4** (8.9 g, 24.3 mmol) in ethanol (25 ml) containing 10% Pd on activated carbon (1.5 g) was placed into a pressure reactor and then heated to 72°C under 70 psi of hydrogen. After 8 h, the reaction was terminated and the warmed reaction mixture was twice filtered through a pad of Celite. The filtered solution was concentrated in vacuo to give a crude tan solid. The solid was purified by flash chromatography (silica gel/80% ethyl ether–20% tetrahydrofuran as the mobile phase) to give **5** (81%) as a light yellow crystalline solid: m.p. 191–193.5°C; ¹H NMR: (DMSO-d₆, 500 MHz) δ 6.80–6.88 (m, 1H), 6.35–6.44 (m, 4H), 5.92–6.05 (m, 1H), 4.77 (s, 4H), 2.00–2.24 (m, 4H), 1.20–1.35 (m, 12H); Anal. Calcd. for C₂₁H₂₆N₂: C, 82.31; H, 8.55; N, 9.14. Found: C, 82.11; H, 8.69; N, 9.00.

2.3. Preparation of polymers

In a typical polymerization reaction, a mechanically stirred solution of diacid chloride **1** (1.55 mmol) and diamine (or mixture of diamines) (1.50 mmol) in DMAC (30 ml) was warmed to 45°C for 2–3 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 × 150 ml), MeOH (2 × 150 ml) and acetone (1 × 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 **6–12** were polymerized in the dark to minimize the isomerization of the *trans*-azobenzene backbone linkages. The polymer structures reported herein were consistent with ¹H NMR and IR spectroscopic data.

2.4. Polymer film formation

Polymers **6–12** (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 ± 2°C for 24 h during which time the DMAC slowly evaporated away. The resulting film was carefully peeled from its 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 10–20 μm thick.



Scheme 1.

2.5. Model compound synthesis

Bis-amide from S(-)-1,1'-binaphthyl-2,2'-diamine and benzoyl chloride (13(S)). To a magnetically stirred solution of *S(-)-1,1'-binaphthyl-2,2'-diamine* (0.50 g, 1.76 mmol) and triethyl amine (0.40 g, 3.95 mmol) in DMAC (20 ml) was slowly added benzoyl chloride (0.51 g, 3.63 mmol). After the addition was complete, the reaction mixture was warmed to 35–40°C for 2 h and then cooled to room temperature. The resulting solution was poured into water (200 ml) giving a tan precipitate. The solid was collected by filtration and then dissolved into ethyl ether (75 ml) and extracted with water (3 × 50 ml) and brine (1 × 50 ml). The organic phase was concentrated in vacuo, giving **13(S)** (87%) as a light tan crystalline solid: m.p.: 187–189°C; ¹H NMR: (DMSO-d₆, 500 MHz) δ 9.91 (s, 2H), 8.10–8.15 (m, 2H), 7.99–8.04 (m, 2H), 7.84–7.90 (m, 2H), 7.41–7.55 (m, 8H), 7.29–7.38 (m, 6H), 7.02–7.08 (m, 2H); MS(K⁺IDS): m/e 531 ([M]⁺K⁺); [α]_D^{RT} = (-)56.9 (c = 0.021 g dl⁻¹, THF).

Bis-amide from R(+)-1,1'-binaphthyl-2,2'-diamine and benzoyl chloride (13(R)). This model compound was prepared in 89% yield from *R(+)-binaphthyl-2,2'-diamine* and benzoyl chloride using the same procedure described above for derivative **13(S)**: m.p.: 188–191°C (lit. [18] m.p.: 190°C); ¹H NMR: (DMSO-d₆, 500 MHz) δ 9.91 (s, 2H), 8.11–8.16 (m, 2H), 7.99–8.03 (m, 2H), 7.84–7.91 (m, 2H), 7.42–7.56 (m, 8H), 7.29–7.39 (m, 6H), 7.03–7.09 (m, 2H); MS(K⁺IDS): m/e 531 ([M]⁺K⁺); [α]_D^{RT} = (+)55.8 (c = 0.016 g dl⁻¹, THF).

2.6. Analytical methods

Melting points were determined in open capillary tubes with a Laboratory Devices (Holliston, MA) Mel-Temp unit and are uncorrected. A heating rate of 2°C min⁻¹ was consistently employed. Routine 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 generally 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. High-resolution electron impact mass spectra (MS ei) were provided by a VG 70-250SE double-focusing mass spectrometer. Fast atom bombardment mass spectra (MS fab) were furnished by a VG ZAB-E double-focusing mass spectrometer equipped with a xenon-ionization gun. Potassium ionization of desorbed species mass spectroscopy [19](MS K⁺IDS) was performed on a Finnigan 4615B quadrupole GC/MS system. Elemental analyses were provided by Galbraith Laboratories (Knoxville, TN).

Inherent viscosity measurements were obtained in sulfuric acid at 25°C with polymer concentrations at 0.5 wt.%. 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 10°C min⁻¹ under N₂ unless otherwise noted.

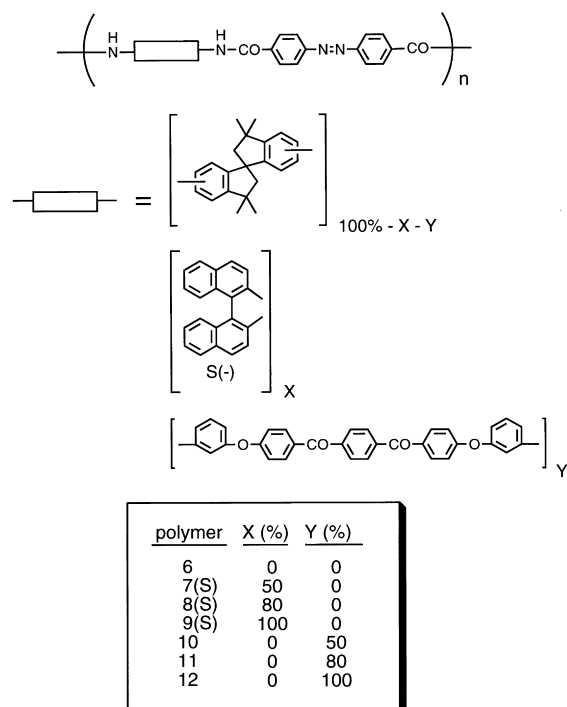
Specific rotations, given as deg dm⁻¹ g⁻¹ cm³, were evaluated at the sodium D-line (589 nm) with a Perkin–Elmer model 341 polarimeter. Samples were dissolved in THF and a standard 10 cm pathlength cell was utilized for all measurements. Circular dichroism (CD) spectra were obtained with a Jasco J600 spectropolarimeter fitted with a 450 W xenon arc lamp as a light source. Sample concentrations were typically on the order of 5 × 10⁻⁵ M and data are reported as deg cm² dmol⁻¹. All measurements were carried out in THF at room temperature 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) with a maximum intensity centered near 360 nm. Higher intensity UV irradiations were effected with a 450 W medium-pressure quartz mercury arc (Ace-Hanovia, Vineland, NJ; model 7883-14) equipped with a model 7830-60 power source. The lamp was fitted with an aluminum reflector having a reflectivity of 85%. Lamp-to-sample pathlength was typically 10 cm. When desired, a combination of optical cut-on and band-pass filters (Oriel Co., Stratford, CT) were employed to furnish radiation within a desired spectral window.

3. Results and discussion

3.1. Synthesis of monomers and polymers

trans-Azobenzene-modified polymers **6–12** were prepared in the absence of room light by the solution polycondensation of *trans*-azobenzene-4,4'-dicarbonyl chloride (**1**) with the appropriate diamine monomers. These included the spirobiindane diamine **5** and either the chiral 1,1'-binaphthyl-2,2'-diamine or the more linear bis-1,4-(3-aminophenoxy-4'-benzoyl)benzene monomer. In all



Scheme 2.

cases, anhydrous DMAC was utilized as a solvent to effect the polymerization step. Monomers **1** and **2** were synthesized as described previously [6,16] while diamine **5** was furnished in several steps as outlined in Scheme 1. 3,3,3',3'-Tetramethyl-1,1'-spirobiindane (**3**), prepared according to a low-yield route devised by Roberts and Abdel-Baset, [17] was first treated with nitric acid and a solution of acetic acid and acetic anhydride to give the dinitro derivative **4** as a complex mixture of 5,5'-5,6'- and 6,6'-isomers. The hydrogenation of this mixture in the presence of a carbon supported palladium catalyst then provided the corresponding diamine as a broad melting (183–195°C) crystalline solid. The fractionation of this product mixture by column (silica) chromatography using an ethyl ether-THF mixture (80:20) as the mobile phase ultimately furnished a sample of diamine **5** where the 5,6'-disubstituted derivative was the predominant (>85%) species as evidenced by ¹H NMR spectroscopy. The melting point for this purified sample

was observed to narrow considerably, falling between 191–193.5°C. Although the spirobiindane ring system in **5** is chiral, no attempt was made to resolve the diamine monomer into its individual, optically active components for the purposes of this study.

Following the polycondensation reactions, *trans*-polymers **6–12** (Scheme 2) were isolated by precipitating their DMAC solutions into water. Multiple extractions of the polymers with water and methanol served to remove traces of the DMAC solvent from these materials. All of the *trans*-azobenzene-modified polymers exhibited coarse, fibrous textures and deep orange colors. Analysis of polymer films by IR spectroscopy showed clearly the presence of amide I (carbonyl stretching) and amide II (NH bending) bands near 1650 and 1530 cm⁻¹, respectively. A third signal centered near 3320 cm⁻¹ was also apparent for these materials. The breadth and position of this third band suggested a considerable degree of hydrogen bonding within the polymer samples as would be expected for IR data gathered in the solid state. Well defined absorptions specific to nitrogen bond stretching frequencies for the *trans*-azobenzene chromophore between 1450–1380 cm⁻¹ were not directly observable due to the presence of overlapping signals from other functional groups residing in these polymers [20,21]. Similar observations have been made for other azobenzene-modified polyamides [6].

Theoretical polymer backbone compositions for **6–12**, confirmed by ¹H NMR spectroscopy, are provided in Table 1 along with inherent viscosity data obtained in H₂SO₄. As expected, solution viscosity behavior was strongly tied to the amount of spirobiindane or *S*(-)-binaphthyl monomer incorporated into the polymer backbones of these materials. When compared to the polymer *trans*-**12** fitted with linear aryl ether ketone linkages, *trans*-polymers **6–11** all had substantially reduced inherent viscosity values, with those measured for **6** and **9**(S) showing the greatest reductions in magnitude. Although differences in the degrees of polymerization for these polymers could account for some of this behavior, these trends are also consistent with a disruption of extended chain or rigid-rod backbone conformations that are present in polymers like **12**. CPK (Corey–Pauling–Koltun) molecular modeling has shown that both the binaphthyl

Table 1
Polymer composition and inherent viscosity data

Polymer (<i>trans</i> -)	Spirobiindane (wt.%)	<i>S</i> (-)-Binaphthyl (wt.%)	Azobenzene (wt.%)	η_{inh} (dl g ⁻¹) ^a
6	50.8	0	33.3	0.36
7 (S)	26.0	23.9	34.2	0.61
8 (S)	10.5	38.7	34.6	0.65
9 (S)	0	48.8	34.8	0.35
10	21.5	0	28.3	0.76
11	7.9	0	25.9	0.72
12	0	0	24.5	1.77

^a Measured in H₂SO₄ (0.5 wt.%) at 25.0°C.

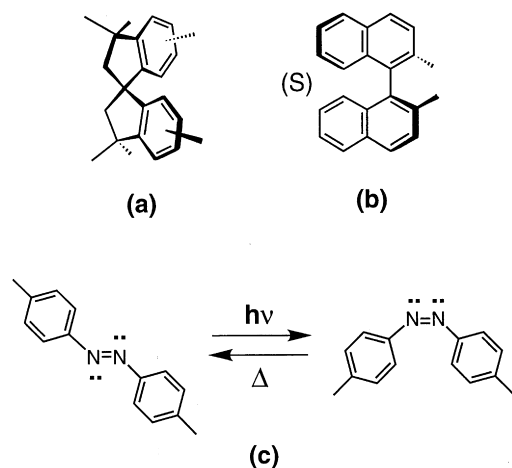


Fig. 1. (a) Spirobiindane (only one stereoisomer shown); (b) (*S*)-binaphthyl; and (c) reversible *trans* ↔ *cis*-azobenzene backbone kinking elements.

and the spirobiindane residues impart a considerable degree of curvature to the polymer backbone, effectively kinking or bending the chain from an extended linear orientation. As will be discussed in greater detail below, the placement of axially asymmetric *S*(-)- or *R*(+)-binaphthyl linkages at regular intervals along the conformationally restricted polymer backbone can actually lead to longer range helical geometries that are stable in solution. Along the same lines, spirobiindane monomers like **5** have been extensively utilized for the preparation of low molecular weight cyclic oligomers where the existence of highly curved chain conformations is clearly required [22,23]. It is interesting to note that for *trans*-azobenzene-modified polymers **6–11** described here, even more highly contorted main chain geometries are to be expected following the *trans* → *cis* isomerization process (Fig. 1).

3.2. Polymer solubilities

As we have discussed in several earlier reports, [6,9] most polyamides constructed from *trans*-azobenzene-4,4'-dicarbonyl chloride (**1**) possess limited solubilities in DMAC, methyl sulfoxide (DMSO) and other aggressive organic solvent media. This behavior is especially apparent

for derivatives that adopt rigid rod or extended geometries in solution. Not surprisingly, the introduction of main chain spirobiindane bends or binaphthyl kinks into these materials had a dramatic effect on their solubility behaviors. As qualitatively illustrated in Table 2, *trans*-polymers **6–9(S)** were highly soluble in DMAC, DMSO and were also readily dissolved into less aggressive polar solvents like tetrahydrofuran (THF) and acetone at room temperature. To a first approximation, the spirobiindane and binaphthyl moieties appeared to be equally effective at promoting organo-solubility behavior when incorporated into the polymer backbone at similar weight-percent loadings. Interestingly, as linear aryl ether ketone segments were substituted for these “bent” monomer linkages in polymers **10–12**, THF and acetone solubilities were noted to fall off markedly. Indeed polymer **12**, comprised entirely of *trans*-azobenzene and aryl ether ketone backbone segments, was completely insoluble in these less aggressive solvent systems.

3.3. Thermal properties

The thermal characteristics of *trans*-polymers **6–12** were evaluated under nitrogen by tandem TGA and DSC procedures. Each of these materials showed good resistance to thermal decomposition at temperatures under 400°C. Temperatures for the onset of 5 and 50% weight loss determined by TGA are provided in Table 3. Polymer residues recovered after heating these samples to 600°C were highly discolored and were insoluble in all of the organic solvent media listed in Table 2. As for other highly kinked *trans*-azobenzene-modified polymers prepared in our laboratory, [8,9] well-defined melting transitions were absent from the DSC scans obtained for *trans*-**6–12**. However, all of the samples exhibited a strong exothermic transition (T_{azo}) falling within the 407–418°C temperature window (Table 3). As we [6,9] and others [24–26] have demonstrated previously, this exotherm corresponds to the extrusion of molecular nitrogen from the azobenzene backbone segments present in these materials. It is interesting to note that the loss of molecular nitrogen and the onset of weight loss along the polymer backbone tend to occur over the same temperature range for each of the samples evaluated (Table 3). That these two thermal events are

Table 2
Polymer solubilities at 25°C (+++, very soluble; ++, soluble; +, slightly soluble; –, insoluble)

Polymer (<i>trans</i> -)	Solvent medium					
	H ₂ SO ₄	DMAC	DMSO	(CF ₃) ₂ CHOH	THF	Acetone
6	+++	+++	+++	++	+++	+
7(S)	+++	+++	+++	++	+++	+
8(S)	+++	+++	+++	++	+++	+
9(S)	+++	+++	+++	++	+++	+
10	+++	+++	+++	++	++	–
11	+++	+++	+++	++	+	–
12	+++	+++	+++	++	–	–

Table 3
Polymer thermal properties

Polymer (<i>trans</i> -)	Onset of weight loss (°C) ^a		T_{azo} (°C) ^b
	5%	50%	
6	436	> 600	418
7(S)	432	> 600	413
8(S)	431	591	418
9(S)	418	> 600	411
10	428	> 600	410
11	438	> 600	415
12	439	> 600	407

^a TGA; 10°C min⁻¹, under nitrogen.

^b DSC; 10°C min⁻¹, under nitrogen.

inter-related is highly plausible and has been the subject of earlier discussion [6].

3.4. Photophysical behavior in dilute solution

Reversible *trans* ↔ *cis* isomerization reactions within these polymers were conveniently monitored by optical absorption spectroscopy. Samples were dissolved in DMAC or THF at concentrations near 10⁻⁵ M. A spectrum for *trans*-**8(S)** in THF is provided in Fig. 2. Absorbance bands near 338 and 440 nm are clearly apparent and correspond to the π–π* and forbidden n–π* transitions for the backbone *trans*-azobenzene chromophores residing in this polymer. The higher energy side of this spectrum is also dominated by other poorly resolved transitions specific to the binaphthyl and spirobiindane ring systems. The irradiation of the polymer solution with filtered (370 < λ < 400 nm) UV light to drive the *trans* → *cis* isomerization reaction produced an immediate change in the absorbance profile for **8(S)**. Specifically, the absorbance intensity centered near 338 nm stemming from the π–π* band for the *trans*-azobenzene link was reduced substantially with the transition for the newly formed *cis*-azobenzene chromophore displaced to the higher energy side of the spectrum

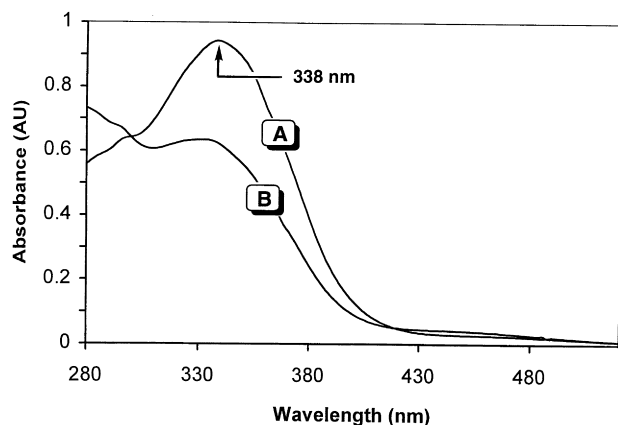


Fig. 2. Optical absorbance spectra in THF. Spectrum A: *trans*-**8(S)**. Spectrum B: **8(S)** after irradiation.

Table 4

Activation parameters for thermally induced *cis* → *trans* isomerization in azobenzene-modified polymers measured in DMAC

Polymer	E_{act} (kcal mol ⁻¹) ^a	ΔG^\ddagger (kcal mol ⁻¹) ^b
6	22.4	25.0
7(S)	21.8	25.0
8(S)	22.5	24.9
9(S)	22.7	24.9
10	23.3	25.1
11	23.4	25.0
12	21.6	24.9

^a Values typically ±1%.

^b Values for ΔG^\ddagger were calculated for the 30°C isotherm.

(Fig. 2). Small perturbations were also noted for the weak n–π* band located near 440 nm, with that for the *cis*-azobenzene moiety being somewhat more intense than for the *trans*-azobenzene isomer. The other azobenzene-modified polymers described in this study exhibited similar behavior when evaluated in THF or DMAC environments. Interestingly, the photo-stationary states achieved under these conditions were generally independent of polymer backbone structures, with approximately 70% of the azobenzene segments in these materials ultimately adopting the higher energy, “kinked” *cis*-configuration in response to ultraviolet light exposure.

For each of the polymers examined, *cis* → *trans* or “reverse” isomerization of the stimuli-responsive azobenzene main chain segments was effectively triggered by either photochemical or thermal means. Illumination of the polymer solutions with visible light above 420 nm rapidly restored the population of *trans*-azobenzene linkages in these materials within a matter of minutes as evidenced by optical absorbance spectroscopy. Thermal *cis* → *trans* recovery rates in DMAC or THF were evaluated at the 30, 45 and 60°C isotherms and were found to be strongly temperature dependent. When dissolved in DMAC, polymer **8(S)** exhibited a *cis*-azobenzene half-life near 26 h at 30°C versus only 54 min when heated to 60°C. The other azobenzene-modified polymers described in this study behaved similarly. As expected, *cis* → *trans* reorganization along each polymer backbone was completely reversible and followed the first-order rate law, regardless of the solvent used. Activation parameters measured in DMAC for the thermal or “dark” isomerization process in polymers **6–12** are tabulated in Table 4 for comparison.

The kinetic data provided in Table 4 suggest that the course of the *cis* → *trans* isomerization process within these materials was not significantly influenced by the overall composition or conformational flexibility of the polymer backbone. Activation energies determined in DMAC for **6–12** fell between 21.6 and 23.4 kcal mol⁻¹ while ΔG^\ddagger values calculated for this isomerization process were all centered near 25 kcal mol⁻¹. This non-variance in the kinetic data is consistent with earlier work undertaken in our laboratory for other azobenzene-modified polymers having

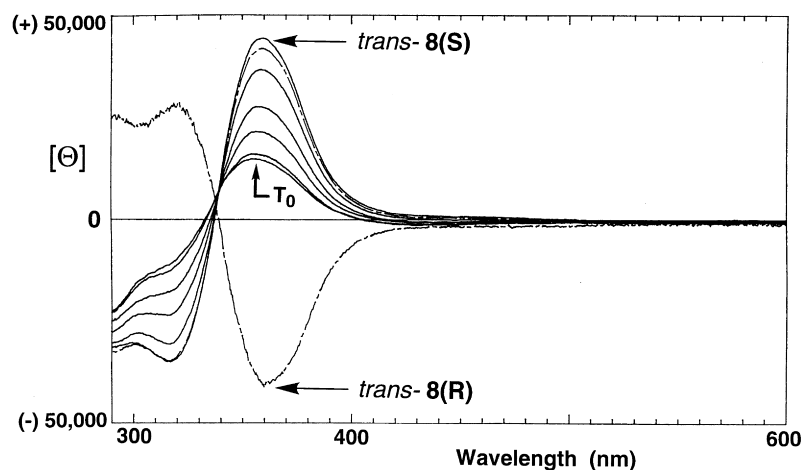


Fig. 3. CD spectra for *trans*-**8(S)** and *trans*-**8(R)** obtained in THF. Time-resolved CD plots for **8(S)** acquired 0.5 (T_0), 4, 20, 44, 92 and 164 h after irradiation at room temperature.

conformationally restricted, main chain geometries [7–9]. In solution, conformational adjustments within each macromolecule apparently occur with sufficient velocity so as not to impede the series of “local” *cis* → *trans* isomerization reactions that take place along the polymer backbone. Interestingly, ΔS^\ddagger values determined for **6–12** were all strongly negative with that for polymer **8(S)** falling near $(-)$ 10 cal deg⁻¹ mol⁻¹. Clearly, whether proceeding through an inversional [27–29] or, less likely, a rotational pathway, [30] thermally driven *cis* → *trans* return in these materials is characterized by transition state geometries that are more highly organized and less random than that associated with the *cis*-isomeric state of the polymer backbone. Similar findings have been communicated for other azobenzene-modified species evaluated in dilute solution environments [6,9,31].

3.5. Thermo- and photo-regulated chiroptical behavior

The primary motivation for our efforts in this area has been centered around the development of new high performance materials that exhibit stimuli-responsive chiroptical properties in dilute solution. Under certain conditions, the incorporation of axially asymmetric binaphthyl or biphenyl linkages at regular intervals along a conformationally restricted polymer backbone can lead to longer range helical order that is itself chiral. For polymer *trans*-**9(S)**, the binaphthyl groups present in polymer’s main chain are directly coupled via amide bonds to linear *trans*-azobenzene moieties. As we discussed earlier in a brief report, [13] the chiral binaphthyl linkages in this system can be viewed as “helicogenic” or helix-directing segments, effectively transferring or projecting their asymmetry over the larger polyamide backbone. Preliminary molecular modeling (CPK) studies carried out to date have suggested that *trans*-**9(S)** is capable of occupying distorted helical geometries where three *trans*-azobenzene residues occupy

one turn in the helical coil. On exposing a solution of *trans*-**9(S)** to near UV light, a series of *trans* → *cis* isomerization reactions triggered within the polymer’s backbone can be expected to severely disrupt this helical order. An added level of structural complexity in these materials was gained by randomly incorporating curved or bent spirobiindane segments into the polymer chain which further served to disrupt the putative helical geometries predicted for *trans*-**9(S)**. Computer-aided modeling efforts now underway are expected to provide for additional refinements in the three-dimensional conformational structures currently proposed for these polymer systems.

trans-Azobenzene-modified polymers **7(S)**, **8(S)** and **9(S)** depicted in Scheme 2 were evaluated for thermo- and photo-mediated changes in their chiroptical behavior. A CD spectrum for polymer *trans*-**8(S)** obtained in THF is provided in Fig. 3. As is immediately evident, the dichroic band stemming from the *trans*-azobenzene π – π^* transition is split into two distinct regions having both positive (lower energy side) and negative (higher energy side) molar ellipticity values. The zero point at 338 nm in Fig. 3 corresponds to the wavelength where the *trans*-azobenzene chromophore exhibits a maximum in its optical absorbance spectrum (see Fig. 2). A separate CD plot was also obtained for another polymer, *trans*-**8(R)**, that was constructed from the mirror image *R*-(+)-1,1'-binaphthyl-2,2'-diamine monomer. As expected, this plot was inverted, with molar ellipticities trending from negative to positive as the higher energy side of the spectrum was reached. It is interesting to note that “split” or bisignated dichroic spectra similar to those shown in Fig. 3 have been observed for other azobenzene-modified polymers that adopt one-handed helical symmetries in solution [14,32–34]. In a number of reports, [32–34] this behavior has been attributed to exciton splitting that arises in response to chiral superstructures that position two or more azobenzene groups in close proximity such that dipole–dipole interactions between chromophores

Table 5
Specific rotation values before ($-h\nu$) and after ($+h\nu$) near UV light exposure measured in THF

Polymer	Binaphthyl content (mol.%) ^a	$[\alpha]_D^{RT}$ (deg dm ⁻¹ g ⁻¹ cm ³)	
		$-h\nu$	$+h\nu^b$
6	0	0	0
7(S)	26	(+)246	(+)30
8(S)	42	(+)406	(+)20
8(R)	39	(-)362	(-)21
9(S)	50	(+)511	(+)35

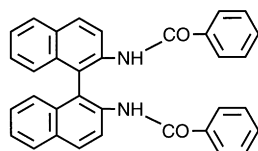
^a Polymer backbone content determined by ¹H NMR spectroscopy.

^b Rotation values measured within 30 min of light exposure.

become possible. In our study, CD line-shapes qualitatively similar to those depicted in Fig. 3 were observed for polymers *trans*-**7(S)** and *trans*-**9(S)**. However, as expected, the absolute magnitude of the molar ellipticity values measured for *trans*-**7(S)** was significantly diminished when compared to variants *trans*-**8(S)** and *trans*-**9(S)** which possessed higher binaphthyl monomer loading along their main chains.

The illumination of polymer *trans*-**8(S)** dissolved in THF with filtered ($370 < \lambda < 400$ nm) UV light to drive the *trans* → *cis* isomerization reaction afforded an immediate change in its CD spectrum (plot T_0 in Fig. 3). Notably, the intensity of the dichroic band falling between 300–400 nm was greatly diminished. This dramatic effect was completely reversible. Time resolved spectra acquired at various intervals following the irradiation procedure are provided in Fig. 3 for a polymer solution that was stored in the dark at room temperature. Importantly, a CD plot obtained for **8(S)** after standing in the absence of light for 220 h (not shown) was identical to that measured for the pre-irradiated polymer *trans*-**8(S)**. The other chiral polymers described herein behaved similarly.

The origins of the reversible chiroptical response depicted in Fig. 3 merit some discussion. As indicated in Scheme 2, most of the main chain azobenzene groups in polymer *trans*-**8(S)** are positioned adjacent to chiral binaphthyl residues and thus reside locally in an asymmetric environment. From our CPK molecular modeling efforts, it



$[\alpha]_D^{RT}$ in THF (deg dm⁻¹ g⁻¹ cm³)

13(S): (-) 57

13(R): (+) 56

Scheme 3.

is equally apparent that this environment will be further influenced by the presence of longer-range helical backbone segments that are also chiral. The light driven *trans* → *cis* isomerization process will significantly diminish the population of *trans*-azobenzene linkages that give rise to the π - π^* band centered at 338 nm in the CD spectrum. At the same time, the isomerization reaction will also perturb the global helical orientations adopted by the polymer. It is quite likely, therefore, that the chiroptical response shown in Fig. 3 actually stems from some combination of these twin effects. Thermally induced *cis* → *trans* relaxation along the polymer backbone will simultaneously restore both the number of *trans*-azobenzene groups and the helical geometries that they induce, reversing the trends in the chiroptical response shown in Fig. 3. That the CD plot in Fig. 3 was fully restored to its “original”, i.e. pre-irradiated, state after 220 h is consistent with a *cis*-azobenzene half-life near 40 h determined in THF for this polymer system under ambient conditions.

Additional insight into the nature of the asymmetry present in these materials was gained by carrying out optical rotation studies in THF. When gathered at the sodium D-line (589 nm), these measurements were well removed from the strong π - π^* and forbidden n - π^* transitions belonging to the azobenzene backbone chromophores. Consistent with expectations derived from earlier studies, [13–15] polymer *trans*-**8(S)** exhibited a significantly enhanced rotation magnitude, with a D-line specific rotation near (+)406 deg dm⁻¹ g⁻¹ cm³. This value was reduced by more than a factor of 20 when the polymer solution was briefly illuminated with near UV light (Table 5). That polymers with single-handed helical backbone conformations can display large rotation magnitudes in solution and in the solid state is now widely acknowledged [35,36]. D-line specific rotations ranging into the hundreds or even thousands of degrees have been reported for a variety of synthetic polymers, including polychloral, [37,38] various poly(tritylmethacrylate)s [39,40] and several poly(isocyanide)s [41,42] that possess chirality solely at the macromolecular or helical level.

Specific rotation values (sodium D-line) for polymers **6**, **7(S)**, **8(S)**, **8(R)** and **9(S)** measured in THF before and after UV light exposure are provided in Table 5 for comparison. The data presented here are interesting in several respects. Firstly, in their non-irradiated, all-*trans* states, all of the polymers modified with axially asymmetric binaphthyl links exhibited large specific rotations, with the absolute magnitude of the rotation values clearly scaling with binaphthyl backbone contents. Secondly, although the isomeric ratio of *cis*-*trans*-azobenzene backbone segments present in each of the illuminated samples was not fixed to a constant value at the time of measurement, the optical rotation magnitudes observed for these systems were all significantly reduced following the irradiation procedure, generally falling between 20–35 deg dm⁻¹ g⁻¹ cm³ when evaluated within 30 min following light exposure. Thirdly,

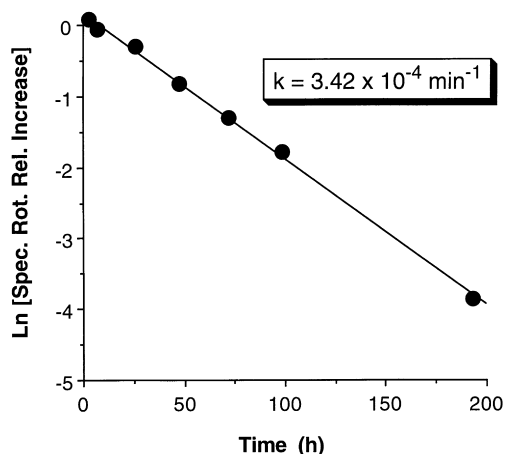


Fig. 4. First-order plot for recovery of $[\alpha]_D$ for polymer **8(S)**. Determined at 24°C in THF.

the rotation data gathered for polymers **8(S)** and **8(R)** was again characterized by “mirror image” behavior, with the two materials showing opposite signs of optical rotation at the sodium D-line in the absence or presence of UV light. Finally, as expected, no chiroptical behavior was observed for polymer **6** fitted with only azobenzene and spirobiindane main chain groups.

The rotation data tabulated in Table 5 can also be compared to the specific rotation values measured for model compounds **13(S)** and **13(R)** shown in Scheme 3. To a first approximation, these species served to mimic a portion of the polymer backbone structure that immediately surrounds the axially asymmetric binaphthyl linkages incorporated into these systems. With a specific rotation near $(-)$ 57 deg dm⁻¹ g⁻¹ cm³, derivative **13(S)** constructed from *S*-(-)-1,1'-binaphthyl-2,2'-diamine exhibited an opposite sign of optical rotation as compared to the strong dextrorotatory behavior recorded for polymers **7(S)**, **8(S)** and **9(S)** that contained the same binaphthyl monomer unit. Moreover, the magnitude of the rotation value for **13(S)** more closely approximated the rotations corresponding to the irradiated polymer systems that were predicted to be devoid of significant helical structure based on CPK molecular modeling studies.

Finally, the specific rotation values for **8(S)** dissolved in THF were also tracked as a function of time following the irradiation process. After nearly 200 h in the dark at 24°C, the specific rotation for **8(S)** was essentially restored to its original (i.e. pre-irradiated) value. As indicated by the linear plot provided in Fig. 4, the recovery of the polymer's rotation magnitude as a function of time obeyed the first-order rate law. A rate constant calculated for this process fell near $3.42 \times 10^{-4} \text{ min}^{-1}$. Within the limits of experimental error, this value was identical to that determined for *cis* → *trans* recovery in polymer **8(S)** measured independently by absorbance spectroscopy. The isomerization process predicted to restore helical backbone structure and the optical rotary power exhibited by the polymer sample thus

appear to be correlated. This finding is fully consistent with the explanation proposed above for the origins of chiroptical behavior in these stimuli-responsive materials.

4. Conclusions

A new series of azobenzene-modified polyamides fitted with main chain spirobiindane turns and chiral binaphthyl bends was prepared via the solution polycondensation of *trans*-azobenzene-4,4'-dicarbonyl chloride with appropriate diamine monomers. When evaluated in their all *trans*-azobenzene configurations, these materials exhibited a good mix of physical properties suitable for high performance applications. The orange film forming polymers were amorphous, highly soluble in non-aggressive organic solvents like THF and displayed good thermal stabilities at temperatures up to 400°C. Photoinduced *trans* → *cis* isomerization reactions were effected by irradiating polymer solutions with filtered UV light. Photostationary state compositions achieved under these conditions (typically 70% *cis*–30% *trans*) were not highly dependent on polymer structure. Reverse *cis* → *trans* isomerization of the backbone azobenzene segments was triggered by photochemical or thermal means and was monitored by optical absorbance spectroscopy. Thermally induced *cis* → *trans* reorganization within each polymer followed the first-order rate law. Activation energies calculated for this process in DMAC all fell near 21–23 kcal mol⁻¹ and were not strongly correlated to backbone content.

Polymers containing axially asymmetric *S*-(-)- or *R*-(+)-2,2'-binaphthyl main chain linkages exhibited thermo- and photo-responsive chiroptical behavior when evaluated in dilute THF solutions. Specifically, the *trans*-azobenzene-modified materials were all characterized by CD spectra showing intense molar ellipticities within the 300–400 nm spectral window. Specific rotation magnitudes determined for the *trans*-polymers at the sodium D-line ranged into the hundreds of degrees and were dependent on the extent of binaphthyl loading along the polyamide backbone. The irradiation of the polymer samples to drive the *trans* → *cis* isomerization reaction resulted in an immediate chiroptical response, with CD band intensities and optical rotations significantly diminished. These effects were fully reversible and were attributed to the presence of putative one-handed helical conformations in the *trans*-azobenzene-modified polymers that were severely disrupted following the *trans* → *cis* isomerization reaction.

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