Stimuli-responsive polymers. 11. Highly adaptive poly(urea-amide)s that display solvent, light and heat modulated chiroptical behavior

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ABSTRACT

Commercially available 4,4′-methylene bis(phenyl isocyanate), when copolymerized with the atropisomeric monomer S-(-)-1,1′-binaphthyl-2,2′-diamine, provides convenient access to urea-linked polymers that exhibit exceptional levels of solvent-dependent chiroptical behavior. The use of different solvent media affords a high degree of control over both the sign and magnitude of the optical rotations that are ultimately displayed by these conformationally dynamic systems. The polarity of the solvent environment appears to play a role in shaping polymer responses. A number of related poly(urea-amide) constructs fitted with azobenzene backbone segments are also sensitive to the application of light and heat, ultimately providing for highly adaptive material systems with chiroptical outputs that can be dynamically modulated in real-time by a combination of different input signals.

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1. Introduction

Although many polymers display some degree of environmental sensitivity to their immediate surroundings, materials that can be rapidly switched between discrete chemical, physical, mechanical or biological states by the application of one or more stimuli constitute an important technological development [1–4]. The resultant properties changes generated in this manner can be harnessed directly for a variety of "smart" materials applications, or they can be utilized indirectly to detect and quantify external perturbations that are remotely applied to a "sensing" polymer system.

The modular design and assembly of stimuli-responsive materials from carefully selected, functionalized building-blocks remains a central focus of this laboratory [5–7]. In this regard, the covalent attachment of photo- and thermo-responsive azobenzene stimuliphores to atropisomeric R- or S-binaphthylene units has been particularly fruitful, leading to a variety of polymeric and oligomeric constructs that exhibit stimuli-responsive chiroptical behavior both in dilute solution and in low Tg solid-state environments. As we have discussed in a number of earlier reports, responsive outputs monitored at the sodium D-line can be readily tuned by altering the three dimensional architectures [8–10], molecular compositions [11–14] and conformational features [15] that are engineered into each chiral system.

The inclusion of a second stimuli-responsive element into azobenzene modified materials of this kind provides an opportunity to broaden the range of their response envelopes. In this study, commercially available 4,4′-methylene bis(phenyl isocyanate) was employed as an amine reactive building-block. On reacting with S-(-)-1,1′-binaphthyl-2,2′-diamine, this co-monomer served to introduce solvent-sensitive urea groups directly into the chiral polymer backbone. As will be demonstrated in this article, this approach led to a series of poly(urea-amide)s that were doubly fitted with urea and azobenzene main-chain stimuliphoric segments. These new chiral materials displayed a wide range of optical rotatory power that could be dynamically modified in real time by the application of a series of coordinated solvent, light and heat-based input signals.

2. Experimental

2.1. Materials

S-(-)-1,1′-binaphthyl-2,2′-diamine (99%, Aldrich) was recrystallized from warm methanol and then rigorously dried *in vacuo* before use. 4,4′-Methylene bis(phenyl isocyanate) (98%, Aldrich) was fractionally distilled under reduced pressure. Anhydrous N,N-dimethylacetamide (DMAC) and anhydrous tetrahydrofuran (THF) (Aldrich) were both stored under Ar over 4 Å molecular sieves. All other reagents (>98%) and anhydrous grade solvents were obtained from Aldrich and were used without further purification.

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2.2. Monomer synthesis

2.2.1. trans-Azobenzene-4,4′-dicarbonyl chloride (trans-*1*)

This diacid chloride monomer containing the azobenzene stimuliphore was synthesized in a manner described earlier [16,17]. M.p.: 164.5−165 °C (lit [17] m.p.: 164 °C). ^{1}H NMR (CDCl$_3$, 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).

2.3. Preparation of polymers

2.3.1. Polyurea *2S*

A magnetically stirred solution of S-(-)-1,1′-binaphthyl-2,2′-diamine (1.03 g, 3.62 mmol) and 4,4′-methylene bis(phenyl isocyanate) (0.910 g, 3.63 mmol) in DMAC (50 mL) was stirred at room temperature for 24 h under an argon atmosphere. The resulting solution was poured into water (300 mL) giving an off-white stringy solid. The solid was redissolved in THF (30 mL) and then precipitated from hexanes (300 mL). After two additional dissolution-precipitation steps, the polymer product was collected by filtration and then dried *in vacuo* for 48 h to give polyurea *2S* as a course light tan solid. FTIR (powder) 3400-3200 cm^{-1} (urea N−H stretch, br), 1683 cm^{-1} (urea C=O stretch), M$_n$ = 6900; [α]$_D$ = (−) 87 (c = 0.104 g/dL, THF).

2.3.2. Poly(urea-amide) trans-*3S*

A magnetically stirred solution of S-(-)-1,1′-binaphthyl-2,2′-diamine (1.25 g, 4.40 mmol) and 4,4′-methylene bis(phenyl isocyanate) (0.825 g, 3.30 mmol) in DMAC (50 mL) was stirred at room temperature for 24 h under an argon atmosphere. A second solution containing monomer *trans-1* (0.337 g, 1.10 mmol) in DMAC (20 mL) was next added dropwise over a 10 min period in the absence of light. The resulting solution was stirred in the dark for an additional 24 h and then poured into water (300 mL) giving an orange solid. The solid was redissolved in THF (30 mL) in the dark and then precipitated from hexanes (300 mL). After two additional dissolution-precipitation steps, the polymer product was collected by filtration and then dried *in vacuo* for 48 h to give poly(urea-amide) *trans-3S* as a fibrous orange solid. FTIR (powder) 3350-3200 cm^{-1} (urea + amide N−H stretch), 1680 cm^{-1} (urea + amide C=O stretch, br), M$_n$ = 7100; [α]$_D$ = (−)16 (c = 0.0680 g/dL, THF).

2.3.3. Poly(urea-amide) trans-*4S*

This copolymer was prepared from S-(-)-1,1′-binaphthyl-2,2′-diamine (1.19 g, 4.18 mmol), 4,4′-methylene bis(phenyl isocyanate) (0.53 g, 2.11 mmol) and *trans-1* (0.64 g, 2.08 mmol) using a two-step polymerization sequence as described for polymer analogue *trans-3S* above. Product *trans-4S* was isolated as a fibrous orange solid. FTIR (powder) 3350-3200 cm^{-1} (urea + amide N−H stretch), 1670 cm^{-1} (urea + amide C=O stretch, br), M$_n$ = 6100; [α]$_D$ = (+) 94 (c = 0.0482 g/dL, THF).

2.3.4. Poly(urea-amide) trans-*5S*

This copolymer was prepared from S-(-)-1,1′-binaphthyl-2,2′-diamine (1.53 g, 5.38 mmol), 4,4′-methylene bis(phenyl isocyanate) (0.336 g, 1.34 mmol) and *trans-1* (1.238 g, 4.03 mmol) using a two-step polymerization sequence as described for polymer analogue *trans-3S* above. Product *trans-5S* was isolated as a fibrous orange solid. FTIR (powder) 3350-3200 cm^{-1} (urea + amide N−H stretch, br), 1650 cm^{-1} (urea + amide C=O stretch, br), M$_n$ = 7400; [α]$_D$ = (+)228 (c = 0.0923 g/dL, THF).

2.3.5. Polyamide trans-*6S*

This polymer was prepared from equimolar quantities of S-(-)-1,1′-binaphthyl-2,2′-diamine and *trans-1* as previously described [8,9]. FTIR (thin film) 3300-3200 cm^{-1} (amide N−H stretch, br), 1652 cm^{-1} (amide C=O stretch), 1535 cm^{-1} (amide N−H bend); M$_n$ = 8300; [α]$_D$ = (+)535 (c = 0.0251 g/dL, THF).

2.4. Model compound synthesis

2.4.1. Urea model compound *7S*

A magnetically stirred solution of S-(-)-1,1′-binaphthyl-2,2′-diamine (0.67 g, 2.36 mmol) and phenyl isocyanate (0.62 g, 5.20 mmol) in anhydrous methylene chloride (50 mL) was stirred at room temperature under an argon atmosphere for 24 h. The resulting solution was concentrated *in vacuo* to give a crude off-white solid. The solid was dissolved in CHCl$_3$ (300 mL) and washed with water (3 × 100 mL) and brine (50 mL). The organic phase was dried over anhydrous sodium sulfate and then concentrated *in vacuo* to furnish model compound *7S* (81% yield) as a fluffy white solid: H^1 NMR (DMSO-d$_6$, 500 MHz) δ 9.05 (s, 2H), 8.61 (d, 2H), 8.10 (d, 2H), 7.98 (d, 2H), 7.29−7.45 (m, 8H), 7.16−7.27 (m, 6H), 6.88−6.94 (m, 2H), 6.80−6.85 (m, 2H); FTIR (powder) 3420−3200 (N−H stretch), 1675 (C=O stretch); MS m/e: 523.21 ([M]H$^+$); [α]$_D$ = (−)93 (c = 0.470 g/dL, THF).

2.5. 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 was consistently employed. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired at 500 MHz on a Bruker Avance DRX-500 instrument. Tetramethylsilane was employed as a reference standard. Fourier transform infrared (FTIR) spectra were recorded with a Thermo-Nicolet 6700 FTIR spectrometer that was equipped with a SensIR Durascope diamond attenuated total reflectance accessory. Samples were measured in thin-film or powdered form. High resolution electron impact mass spectra (MS ei) were furnished with a VG 70-250SE double-focusing mass spectrometer. UV−visible (UV−Vis) spectra were obtained with an Agilent Cary 5000 uv/vis/nir spectrophotometer that was fitted with a temperature-regulated multicell holder. Measurements were obtained at 25 °C unless otherwise indicated.

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 utilized for the purposes of GPC calibration.

Specific rotations, reported here as deg dm^{-1} g^{-1} cm^3, were evaluated at the sodium D-line (589 nm) with a Perkin Elmer Model 241 polarimeter. Polymer samples were dissolved in specified solvents at concentrations falling between 0.030 and 0.050 g/dL. Standard 10 cm path length cells were utilized for all measurements. Polarimetry cells were connected to a thermostated circulating bath (VWR model 1166) that was maintained at a constant temperature of 21 or 25 °C unless otherwise indicated. 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 given as deg cm^2 dmol^{-1}. All CD measurements were carried out at room temperature unless otherwise noted.

Low intensity UV irradiations of polymer solutions were performed with a Blak-Ray Long Wavelength UV lamp (San Gabriel,