The Use of Block Copolymers to Systematically Modify Photochromic Behavior

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Received July 25, 2006; Revised Manuscript Received October 16, 2006

ABSTRACT: Reversible addition fragmentation chain transfer (RAFT) living radical polymerization has been utilized successfully to allow the systematic tuning of photochromic switching rates in a rigid, ophthalmic quality, polymer matrix. Block copolymers of poly(styrene) and poly(*n*-butyl acrylate) were synthesized using a RAFT functionalized photochromic (spirooxazine) dye. Thus the photochromic dye initiated the polymerizations and allowed the known and precise placement of the dye at the start of the block copolymer chains. The photophysical investigation of these more complex architectures demonstrated that systematic tuning of photochromic rates could be achieved by changing the length and choice of either block. The photochromic rates were significantly more sensitive to the presence of low glass-transition temperature poly(*n*-butyl acrylate) than high glass-transition temperature poly(styrene), even if the poly(*n*-butyl acrylate) was the more distant second block from the spirooxazine.

Introduction

The development of living radical polymerization has facilitated a new avenue for simple macromolecular design of complicated polymer architectures.[1] There are three main techniques referred to a living radical polymerization, atom chain transfer radical polymerization (ATRP),[2,3] reversible addition fragmentation transfer (RAFT),[4,5] and nitroxide-mediated polymerization (NMP).[6,7] A large range of architectures can be accessed easily using these techniques; examples include star, graft, branched, and block copolymers.[8,9] Block copolymers have defined segments of each component monomer that follow sequentially along the main polymer chain (Figure 1).[10] This is distinct from random copolymers that have component monomers randomly distributed along the polymer backbone. The use of block copolymers is one very simple way to get materials with quite different properties by adjusting amounts of opposing monomers such as hard/soft or hydrophobic/hydrophilic to name a few well-researched examples.[11]

Another important benefit of living radical polymerization is that it facilitates the addition of functionality. All living radical polymerization techniques have the ability to incorporate sophisticated functionality on one or both ends of the polymer chain.[12] This functionality is guaranteed to be present on almost all chain ends synthesized during the process. Consequently, living radical polymerization can be utilized to investigate the effects of various polymer systems on a specific functional moiety.[12,13]

The control of photochromism in a rigid, ophthalmic lenslike matrix is one application that could benefit from this technique. Photochromism is referred to as a light-induced reversible transformation of a chemical species between two isomers.[14] It is well documented that the rates of the photochromic transition are influenced by the host environment, e.g., rigidity, polarity, and free volume.[15,16] Spirooxazines are a commonly used type of photochromic compound, which undergoes switching between their clear and colored states by photo and/or thermal stimuli (Scheme 1).[17] It is the large intermolecular rotation needed for switching that causes their rates to be effected by properties such as rigidity and free volume.[17]

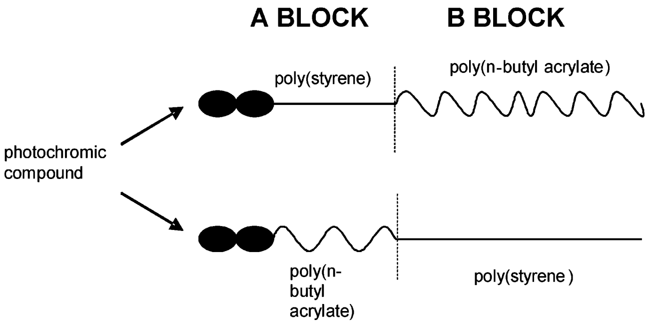

Figure 1. Schematic of this investigation where the A-B block copolymers consist of segments of high and low T_g polymer, which are poly(styrene) and poly(*n*-butyl acrylate), respectively.

There has been limited research into the controlling of photochromic behavior in a host lens matrix. The majority of the research has focused on studies where the host environment was constructed so there was little control or uniformity over the location of the photochromic moiety.[18] Typically the dye is randomly dispersed/dissolved in the medium and control of the photochromic dye can only occur through bulk modification of the matrix. There has been limited investigation using anionic polymerization to construct photochromic dye−polymer conjugates. However, the inconsistent grafting efficiencies (i.e., the reliable attachment of the photochromic dye to the polymer) and the highly rigorous technical demands needed for successful anionic polymerization make the approach relatively unattractive.[19,20] The use of living radical polymerization offers a simpler and more effective method for the synthesis of a customized, uniform environment for the photochromic moiety. In this work,

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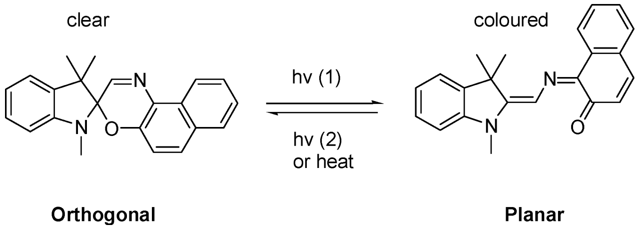
10.1021/ma061674i CCC: \$33.50

Scheme 1. Photochromic Transitions of a Spirooxazine Compound



a radical initiator based on a spirooxazine compound was used to initiate a well-defined polymer chain. This facilitated a conjugate where each photochromic moiety was attached to a single polymer chain that is almost identical in length and characteristics. The properties of this polymer conjugate could be easily varied using living radical polymerization techniques.

These polymer–spirooxazine conjugates were investigated in a rigid polymer lenslike matrix. The photophysical investigation demonstrated that the polymer conjugate acted as a local environment for the photochromic moiety, encapsulating it from the host matrix. Consequently, photochromic switching rates could be tuned based on the characteristics of the attached polymer.

Previous research demonstrated that photochromic properties in a rigid host polymer could be tailored by changing either the T_g or the chain length of the attached polymer.[21,22] That work was performed by using the living radical polymerization technique, ATRP. In this work, block copolymer–spirooxazine conjugates have been synthesized using the RAFT technique in order to investigate the effect of position of high and low T_g segments along the polymer backbone (Figure 1). Poly(styrene) and poly(*n*-butyl acrylate) were used as the high and low T_g polymers, respectively. The photophysical investigation of these systems demonstrated that photochromic behavior could be tailored successfully by changing the length of the secondary block. It was found that the photochromic rates were extremely sensitive to a low T_g component, even when it was separated from the moiety by an intervening high T_g block.

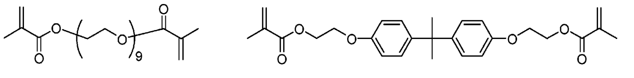
Experimental Section

General Procedures. *n*-Butyl acrylate was purified by vacuum distillation. Styrene was purified by filtration through basic alumina (70–230 mesh) immediately prior to use. The TLC plates used were Merck Silica 60 F_{254}. All chromatography was performed using silica gel 60 (0.40–0.63 mm). Other reagents and solvents unless otherwise stated were obtained from Aldrich at the highest purity and used without further purification.

Experimental Methods. Molecular weights of polymer were characterized by gel permeation chromatography (GPC) performed in tetrahydrofuran (THF, 1.0 mL/min) at 25 °C using a Waters GPC instrument, with a Waters 2414 refractive index detector, a series of four Polymer Laboratories PLGel columns ($3 \times 5\ \mu$m Mixed-C and $1 \times 3\ \mu$m Mixed-E), and Millennium Software. The GPC was calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories EasiCal, MW from 264 to 256 000). For the poly(*n*-butyl acrylate) conjugates, the Mark–Houwink parameters were used to convert values obtained to poly(*n*-butyl acrylate) equivalents.[23] Molecular weight values (M_n) of the block copolymer–spirooxazine conjugates were calculated first using GPC for the initial block and then using NMR to calculate the molecular weight of the second block relative to the first (Figure 2).

Polymer conversions were obtained from ^{1}H NMR spectra recorded on a Bruker Av400 spectrometer. Chemical shifts were reported in ppm from external tetramethylsilane. High-resolution electron impact (EI), chemical ionization (CI), GCMS, and LSIMS (FAB) mass spectra were run on a ThermoQuest MAT95XL. Positive and negative ion APCI mass spectra were acquired with a VG Platform mass spectrometer.

Photochromic analyses were performed on lenses composed of polymer–photochromic conjugates (1.2×10^{-3} mmol/gram) dissolved in a standard industrial lens formulation of 1:4 weight ratio of polyethyleneglycol 400 dimethacrylate (PEGDMA (9G)) and 2,2′-bis[4-methacryloxyethoxy]phenyl]propane (EBPDMA (Nouryset 110)) with 0.4% AIBN and cured (80 °C, 8 h) to give clear test lenses (structures given below).



polyethyleneglycol 400 dimethacrylate (PEGDMA)

2,2'-Bis[4-methacryloxyethoxy]phenyl]propane (EBPDMA)

The photochromic responses of the lenses were analyzed on a light table composed of a Cary 50 spectrophotometer and a 300 W Oriel xenon lamp as an incident light source. A series of two filters (Edmund Optics 320 cutoff and bandpass filter U-340) were used to restrict the output of the lamp to a narrow band (350–400 nm). The samples were monitored at their maximum absorbance of the colored form (610 nm) for a period of 1000 s. Then the decoloration was monitored for a further 6000 s.

Synthesis of 9′-(4-Chloromethylbenzoyloxy)-1,3,3-trimethylspiro[indoline2,3′-[3*H*]naphtha[2,1-b][1,4]oxazine] (1). 9′-Hydroxy-1,3,3-trimethylspiro[indoline2,3′-[3*H*]naphtha[2,1-b][1,4]oxazine] (2.5 g, 72.7×10^{-4} mol) was added to 30 mL of dichloromethane in a 100 mL three-necked round-bottomed flask. Triethylamine (1.10 g, 10.9×10^{-3} mol) was added, and the reaction was stirred for half an hour. 4-(Chloromethyl)benzoyl chloride (1.65 g, 87.2×10^{-4} mol), dissolved in 10 mL of dichloromethane, was added dropwise under argon at 0 °C. The reaction was stirred at ice temperature for 1 h and then at room temperature for a final hour. A TLC in 1:1 diethyl ether/hexane confirmed all starting material was consumed and a single product obtained. The product was washed with 100 mL of 0.5 M NaOH, 100 mL of water, 100 mL of 0.5 M HCl, 100 mL of water, 100 mL of brine, and dried with $MgSO_4$. The final solution was rotary evaporated to produce 3.05 g of material (85% yield). This product was then recrystallized using a combination of methanol and chloroform to give a green powder with a mp 205–208 °C. ^{1}H NMR ($(CD_3)_2CO$) δ: 1.35 (s, 3H, H-2), 1.36 (s 3H, H-3), 2.78 (s, 3H, H-10), 4.87 (s, 2H, H-30), 6.67 (d, $J = 7.8$ Hz, H-8), 6.87 (t of d, $J = 7.4$, 1.0 Hz, 1H, H-6), 7.08 (d, $J = 9$ Hz, 1H, H-13), 7.16 (app d, $J = 7.4$ Hz, 1H, H-5), 7.20 (t of d, $J = 7.8$, 1.2 Hz, 1H, H-7), 7.38 (d of d, $J = 8.8$, 2.4 Hz, 1H, H-14), 7.72 (app d, $J = 8.5$ Hz, 2H, (H-26 and H-28)), 7.84 (s, 1H, H-22), 7.86 (d, $J = 8.5$ Hz, 1H, H-17), 7.96 (d, $J = 8.6$ Hz, 1H, H-16) 8.28 (app d, $J = 8.6$ Hz, 2H, H-25 and H-29)), 8.40 (d, $J = 2.4$ Hz, 1H, H-19). ^{13}C NMR (C_6D_6) δ: 21.10 (C-2), 25.59 (C-3), 29.77 (C-10), 45.50 (C-30), 52.23 (C-1), 99.52 (C-11), 107.89 (C-8), 114.25 (C-19), 117.07 (C-13), 120.41 (C-17), 120.68 (C-6), 122.02 (C-5), 124.1 (C-21), 128.1 (C-15), 129.15 (C-26 and C-28 and C-7), 130.07 (C-16), 130.39 (C-20), 130.70 (C-14), 131.14 (C-25 and C-29), 133.02 (C-24), 136.57 (C-4), 143.36 (C-27), 145.52 (C-12), 148.35 (C-9), 151.17 (C-18), 151.27 (C-22), 165.06 (C-23). The nonstandard numbering system is given on the structure **1** below. Mass spectrum (EI): *m/z* 497 ($M^+ + 1$, 45%), 193 (100), 160(55), 218(40), 457-(35). Mass spectrum (HR, FAB): *m/z* 496.154 ($C_{30}H_{25}ClN_2O_3$ requires 496.16).

Synthesis of RAFT Agent (2). Carbon disulfide (0.59 g, 7.73×10^{-3} mol), butane thiol (0.35 g, 3.87×10^{-3} mol), and triethylamine (0.78 g, 7.73×10^{-3} mol) were added to 15 mL of chloroform in a round-bottomed flask. This mixture was left to stir overnight. Then, compound **1** (1.60 g, 3.22×10^{-3} mol) was added in 10 mL of chloroform and left to stir for another 24 hours. The TLC of the product (3:2 hexane/diethyl ether) showed only small impurities. The product was washed with 100 mL of water and 100 mL of brine and dried with $MgSO_4$. The final solution was rotary evaporated to produce 1.91 g of material (95% yield). The

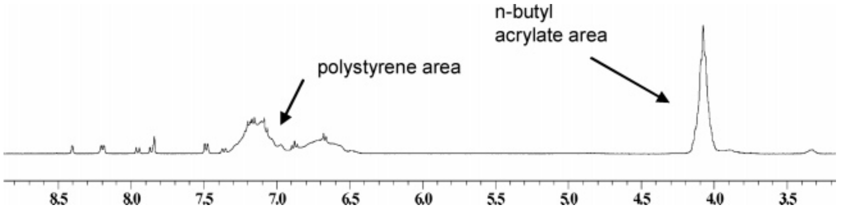
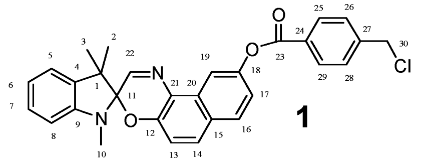


Figure 2. Calculation of molecular weight (M_n) using NMR, where arrows indicate areas used to calculate relative composition. The small peaks in the aromatic region are due to the aromatic hydrogen atoms on the spirooxazine end group.

product was then purified using methanol/chloroform (mp 89−92 °C). ^{1}H NMR ((C_6D_6) δ: 0.69 (t, $J = 7.3$ Hz, 3H, H-35), 1.06 (s 3H, H-3), 1.12 (m, $J = 7.5$ Hz, 2H, H-34), 1.23 (s, 3H, H-2), 1.40 (m, $J = 7.5$ Hz, 2H, H-33), 2.43 (s, 3H, H-10), 3.15 (t, $J = 7.4$ Hz, 2H, H-32), 4.32 (s, 2H, H-30), 6.34 (d, $J = 7.7$ Hz, 1H, H-8), 6.75 (d, $J = 8.8$ Hz, 1H, H-13), 6.87 (m, 2H, H-5 and H-6), 7.03 (d, $J = 8.2$ Hz, 2H, (H-26 and H-28)), 7.12 (t of d, 1H, $J = 7.4$, 1.6 Hz, H-7), 7.22 (d of d, $J = 8.8$, 2.5 Hz, 1H, H-17), 7.24 (d, $J = 9$ Hz, 1H, H-14), 7.43 (d, $J = 8.8$ Hz, 1H, H-16), 7.56 (s, 1H, H-22), 8.07 (d, $J = 8.2$ Hz, 2H, H-25 and H-29), 8.98 (app d, $J = 2.2$ Hz, 1H, H-19). ^{13}C NMR (C_6D_6) δ: 13.94 (C-35), 21.11 (C-3), 22.54 (C-34), 25.59 (C-2), 29.77 (C-10), 30.63 (C-33), 37.38 (C-32), 41.13 (C-30), 52.22 (C-1), 99.51 (C-11), 107.88 (C-8), 114.27 (C-19), 117.00 (C-13), 120.49 (C-17), 120.67 (C-6), 122.02 (C-5), 124.12 (C-21), 128.1 (C-15), 129.86 (C-7), 129.97 (C-25 and C-29), 130.02 (C-16), 130.39 (C-20), 130.69 (C-14), 131.14 (C-26 and C-28), 133.05 (C-15), 136.60 (C-4), 141.88 (C-27), 145.49 (C-12), 148.37 (C-9), 151.21 (C-18), 151.25 (C-22), 165.13 (C-23), 223.68 (C-31). The nonstandard numbering system is given on the structure **2** below. Mass spectrum (EI): *m/z* 497 (M^+, 52%), 159 (100), 158(34), 160(32), 627(22), 144(22). Mass spectrum (HR, EI): *m/z* 626.1739 ($C_{35}H_{34}N_2O_3S_3$ requires 626.17).



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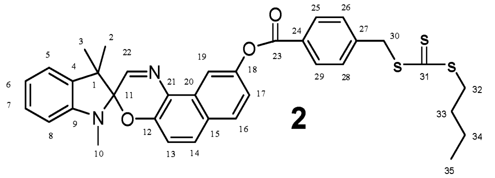
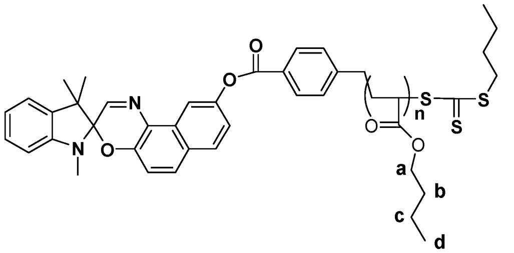


2

Synthesis of Poly(styrene)−Spirooxazine Conjugate Macroagent (3a and 3b). Styrene monomer and RAFT initiator (**2**) were added to an ampule (exact amounts given in table below). The reaction was degassed by four freeze−pump−thaw cycles using a Schlenk line and then flame sealed under vacuum. The polymerizations were then carried out in a constant temperature oil bath at 110 °C for 8 and 29 h, respectively. The polymerization mixtures were purified by precipitation into methanol. Polymer **3a** had a M_n of 2560 (18.6% conversion). ^{1}H NMR ((C_6D_6) δ: 0.61 CH_3 t (H-35), 1.03 s (H-2), 1.19 s (H-3), 1.28 t (H-33), 1.40−1.83 CH_2 (polymer backbone), 1.96−2.34 CH (polymer backbone), 2.39 CH_3 s (H-10), 3.02 CH_2 t (H-32), 5.06−5.36 CH (polymer end group), 6.31 d (photochromic aromatics), 6.38−7.28 (polymer aromatics), 7.32 s (photochromic aromatics), 7.39 t (photochromic aromatics), 7.51−7.53 m (photochromic aromatics), 8.12−8.21 m (photochromic aromatics), 8.98 d (photochromic aromatics). Polymer **3b** had a M_n of 12600 (52.3% conversion). ^{1}H NMR ((C_6D_6) δ: 0.58−0.65 CH_3 (H-35), 1.04 CH_3 s (H-2), 1.20 CH_3 s (H-3), 1.42−1.78 CH_2 (polymer backbone), 1.95−2.33 CH (polymer backbone), 2.40 CH_3 s (H-10), 2.99−3.07 CH_2 (H-32), 6.31 d (photochromic aromatics), 6.40−7.17 polymer aromatics. The nonstandard numbering is given on the labeled initiator **2** above.

synthesis of	mass of styrene	mass of RAFT initiator **2**
3a	5.46 g	0.32 g
3b	8.00 g	0.24 g

Synthesis of Poly(*n*-butyl acrylate)−Spirooxazine Conjugate Macroinitiators (4a and 4b). The *n*-butyl acrylate monomer (7.28 g, 5.67×10^{-2} mol) and RAFT agent (**2**) (0.437 g, 6.98×10^{-4} mol) were added to an ampule, and 5 mol % AIBN was also added relative to the RAFT initiator. The reaction was degassed by four freeze−pump−thaw cycles using a Schlenk line and then flame sealed under vacuum. The polymerizations were then carried out in a constant temperature oil bath at 60 °C for 3 and 7 h, respectively. The polymerization mixtures were purified by precipitation into methanol. Polymer **4a** had a M_n of 5100 (26.0% conversion). ^{1}H NMR ((C_6D_6) δ: 0.63 CH_3 t (H-35), 0.74 m (H-34), 0.78−0.98 CH_3 (**d**), 1.04 s (H-2), 1.20 s (H-3), 1.22−1.42 CH_2 (**c**), 1.43−1.78 CH_3 (**b**) and CH (polymer backbone), 1.79−2.04 CH_2 (polymer backbone), 2.15−2.35 CH_2 (polymer backbone), 2.40 s (H-10), 2.47−2.98 CH (polymer backbone), 3.02 t (H-32), 3.89−4.31 CH_2 (**a**), 5.28−5.38 CH (polymer end group), 6.31 d (photochromic aromatics), 6.71 d (photochromic aromatics), 6.78−6.88 muliplet (photochromic aromatics), 6.93 s (photochromic aromatics), 6.98−7.17 m (photochromic aromatics), 7.22 t (photochromic aromatics), 7.32 s (photochromic aromatics), 7.40 d (photochromic aromatics), 7.52 s (photochromic aromatics), 8.22 d (photochromic aromatics), 8.96 s (photochromic aromatics). Polymer **4b** had a M_n of 13 000 (82.3% conversion). ^{1}H NMR ((C_6D_6) δ: 0.64 CH_3 t (H-35), 0.73 m (H-34), 0.79−0.97 CH_3 (**d**), 1.04 CH_3 s (H-2), 1.20 CH_3 s (H-3), 1.23−1.41 CH_2 (**c**), 1.46−1.62 CH_2 (**b**), 1.62−1.73 CH_2 (polymer backbone), 1.79−2.00 CH_2 (polymer backbone), 2.16−2.33 CH_2 (polymer backbone), 2.40 CH_3 s (H-10), 2.63−2.80 CH (polymer backbone), 3.03 CH_2 t (H-32), 4.00−4.21 CH_2 (**a**), 5.28−5.37 CH (polymer end group), 6.13 s (photochromic aromatics), 6.31 d (photochromic aromatics), 6.71 d (photochromic aromatics), 6.81−6.87 m (photochromic aromatics), 6.92 s (photochromic aromatics), 6.98−7.17 m (photochromic aromatics), 7.23 t (photochromic aromatics), 7.32 s (photochromic aromatics), 7.41 d (photochromic aromatics), 7.53 s (photochromic aromatics), 8.20 d (photochromic aromatics), 8.96 s (photochromic aromatics). The numbers in the assignment refer to the nonstandard numbering system on the RAFT initiator **2** above and the letters to the poly(*n*-butyl acrylate) assigned above.



Synthesis of Block Copolymer−Spirooxazine Conjugates (5a−c). A stock solution was produced containing *n*-butyl acrylate monomer (3.356 g, 2.62×10^{-2} mol), macroinitiator **3a** (0.670 g, 2.62×10^{-4} mol), AIBN (0.0021 g, 1.28×10^{-5} mol), and 3 mL of benzene. This stock solution was then divided into three

Scheme 2. Synthesis of Macroinitiators and Block Copolymers−Spirooxazine Conjugates (3−8) by Free Radical Polymerization Utilizing the RAFT Group Functionalized Spirooxazine (2)

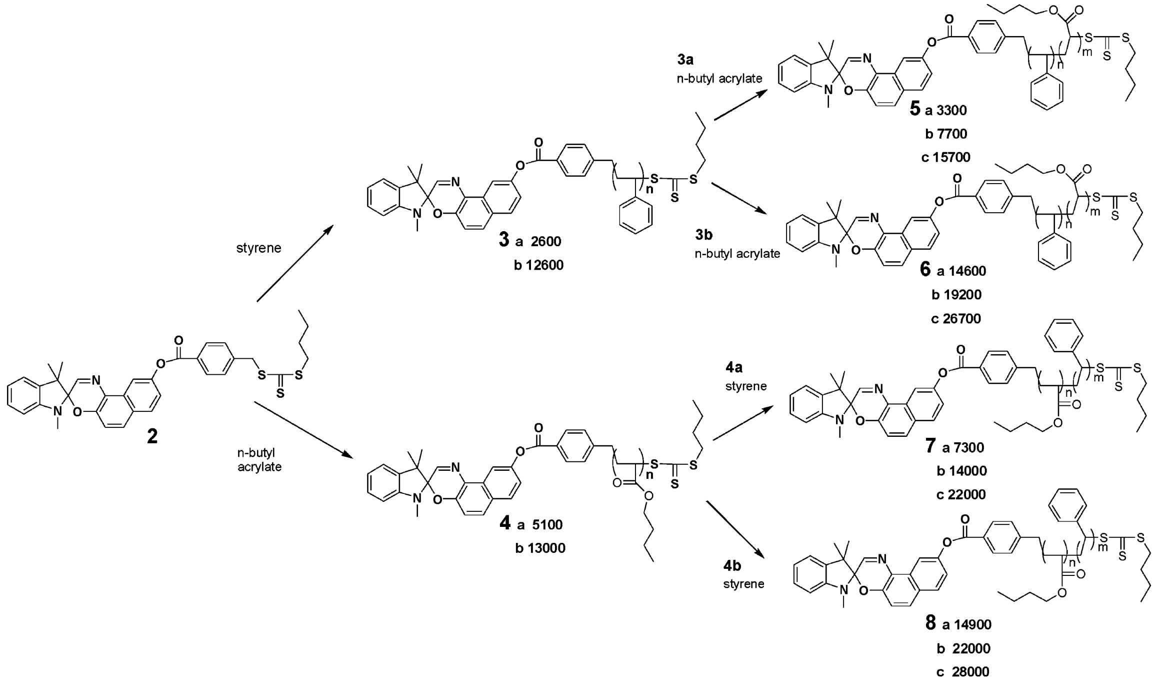


Table 1. Polymer Characteristics of the Block Copolymer−Spirooxazine Conjugates[a]

conjugate		M_n of styrene component[b]	M_n of BA component[b]	total M_n[c]	polydispersity[d]
polystyrene initial block	**3a**	2600		2600	1.13
	5a	2600	800	3300	1.13
	5b	2600	5100	7700	1.08
	5c	2600	13 200	15 700	1.07
	3b	12 600		12 600	1.13
	6a	12 600	2000	14 600	1.15
	6b	12 600	6600	19 200	1.13
	6c	12 600	14 200	26 800	1.18
poly(*n*-butyl acrylate) initial block	**4a**		5100	5100	1.11
	7a	2200	5100	7300	1.09
	7b	8600	5100	13 700	1.09
	7c	16 500	5100	21 600	1.08
	4b		13 000	13 000	1.07
	8a	1900	13 000	14 900	1.06
	8b	9000	13 000	21 900	1.08
	8c	14 900	13 000	27 900	1.11

[a] All M_n values have been rounded to the nearest hundred. [b] Molecular weight values (M_n) of the block-copolymer−spirooxazine conjugates were calculated first using GPC for the initial block and then using NMR to calculate the molecular weight of the second block relative to the first. [c] Sum of both M_n values [d] Polydispersity was calculated using GPC.

ampoules. Each reaction was degassed by four freeze−pump−thaw cycles using a Schlenk line and then flame sealed under vacuum. The polymerizations were then carried out in a constant temperature oil bath at 60 °C for 4, 8, and 16 h, respectively. All polymerizations were precipitated into methanol and then purified by column chromatography with dichloromethane/diethyl ether. Polymer **5a** had a M_n of 3340 (1.67% conversion). ^{1}H NMR ($(CD_3)_2CO$) δ: 0.85−1.01 CH_3 (**d**), 1.36 CH_3 s (H-2 and H-3), 1.23−2.59 (general polymer peaks), 3.32−3.47 CH_2 (H-32), 4.19−3.79 CH_2 (**a**), 4.83−4.94 CH (polymer end group), 6.40−7.40 (polystyrene aromatics), 7.81−7.89 m (photochromic aromatics), 7.94 d (photochromic aromatics), 8.06−8.18 m (photochromic aromatics), 8.42 d (photochromic aromatics). The numbers in the assignment refer to the nonstandard numbering system on the RAFT initiator **2** above and the letters to the poly(*n*-butyl acrylate) polymer assigned above.

Synthesis of Block Copolymer−Spirooxazine Conjugates (6a−c). A stock solution was produced containing *n*-butyl acrylate monomer (2.786 g, 3.73×10^{-2} mol), macroinitiator **3b** (2.501 g, 1.87×10^{-4} mol), AIBN (1.6×10^{-3}g, 9.74×10^{-6} mol), and 2 mL of benzene. This stock solution was then divided into three ampoules. Each reaction was then degassed by four freeze−pump−thaw cycles using a Schlenk line and then flame sealed under vacuum. The polymerizations were then carried out in a constant temperature oil bath at 60 °C for 2, 8, and 48 h, respectively. The ampule removed at 2 h had no polymer, so a further ampule was produced with *n*-butyl acrylate (0.0957, 7.47×10^{-4} mol), macroinitiator **3b** (0.100 g, 7.46×10^{-6} mol), AIBN (6.0×10^{-5}g, 3.65×10^{-7} mol), and 0.25 mL of benzene. This reaction was degassed and sealed as above and then heated in a constant temperature oil bath for 8 h. All polymerizations were precipitated into methanol and then purified by column chromatography with dichloromethane/diethyl ether. Polymer **6a** had a M_n of 14570 (18.7% conversion). ^{1}H NMR ($(CD_3)_2CO$) δ: 0.84−1.02 CH_3 (**d**), 1.34 CH_3 s (H-2 and H-3), 1.26−2.57 (general polymer peaks), 3.39−3.46 CH_2 (H-32), 3.83−4.18 CH_2 (**a**), 4.83−4.93 CH (polymer end group), 6.37−7.39 (polystyrene aromatics), 7.79−8.48 m (photochromic aromatics). The numbers in the assignment refer to the nonstandard numbering system on the RAFT initiator **2** above and the letters to the poly(*n*-butyl acrylate) polymer assigned above.

Synthesis of Block Copolymer−Spirooxazine Conjugates (7a−c). A stock solution was produced containing styrene monomer (3.599 g, 3.46×10^{-2} mol), macroinitiator **4a** (1.651 g, 3.46×10^{-4} mol), AIBN (2.9×10^{-3}g, 1.77×10^{-5} mol), and 2 mL of benzene. This stock solution was then divided into three ampoules, and a further 1.199 g of styrene monomer was added to ampule 3. Each reaction was then degassed by four freeze−pump−thaw cycles using a Schlenk line and then flame sealed under vacuum. The polymerizations were then carried out in a constant temperature oil bath at 60 °C for 16, 46, and 48 h, respectively. All polymerizations were precipitated into methanol and then purified by column chromatography with dichoromethane/diethyl ether. Polymer **7a** had a M_n of 7260 (16.4% conversion). ^{1}H NMR (($(CD_3)_2CO$) δ: 0.86−1.05 CH_3 (**d**), 2.12−1.24 (general polymer peaks), 2.23−2.51 CH (poly(*n*-butyl acrylate) backbone), 3.28−3.38 CH_2 (H-32), 3.81−4.18 CH_2 (**a**), 6.44−7.34 (polystyrene aromatics), 7.36 d (photochromic aromatics), 7.47 d (photochromic aromatics), 7.82−7.89 m (photochromic aromatics), 7.95 d (photochromic aromatics), 8.20 d (photochromic aromatics), 8.40 s (photochromic aromatics). The numbers in the assignment refer to the nonstandard numbering system on the RAFT initiator **2** above and the letters to the poly(*n*-butyl acrylate) assigned above.

Synthesis of Block Copolymer−Spirooxazine Conjugates (8a−c). A stock solution was produced containing styrene monomer (2.332 g, 2.24×10^{-2} mol), macroinitiator **4b** (3.00 g, 2.24×10^{-4} mol), and 2 mL of benzene. This stock solution was then divided into three ampoules. Each reaction was degassed by four freeze−pump−thaw cycles using a Schlenk line and then flame sealed under vacuum. The polymerizations were then carried out in a constant temperature oil bath at 110 °C for 16, 96, and 120 h, respectively. All polymerizations were precipitated into methanol and then purified by column chromatography with dichoromethane/diethyl ether. Polymer **8a** had a M_n of 14900 (7.0% conversion). ^{1}H NMR (($(CD_3)_2CO$) δ: 0.85−1.05 CH_3 (**d**), 1.32−1.78 (general polymer peaks), 1.87−2.00 CH_2 (poly(*n*-butyl acrylate) backbone), 2.27−2.50 CH (poly(*n*-butyl acrylate) backbone), 2.79 CH_3 s (H-10), 3.29−3.38 CH_2 (H-32), 3.96−4.18 CH_2 (**a**), 6.41−7.33 (polystyrene aromatics), 7.36 d (photochromic aromatics), 7.48 d (photochromic aromatics), 7.83−7.88 m (photochromic aromatics), 7.95 d (photochromic aromatics), 8.19 d (photochromic aromatics), 8.40 s (photochromic aromatics). The numbers in the assignment refer to the nonstandard numbering system on the RAFT initiator **2** above and the letters to the poly(*n*-butyl acrylate) assigned above.

Results and Discussion

Polymer Chemistry. The RAFT polymerization using compound **2** as the initiator was performed using either AIBN or the thermal initiation of styrene monomer as a radical source. Propagating chains add to the carbon sulfur double bond reversibly, forming an equilibrium of mostly dormant chains allowing a living radical polymerization to occur. A detailed mechanism of the RAFT process has been reported and discussed previously by others.[24] In our case, the design of the RAFT spirooxazine conjugate is such that the spirooxazine initiates the polymerization and the RAFT group terminates the polymer chain.

The use of two different monomers sequentially allowed block copolymers to be synthesized with structures identified in Scheme 2. The two monomers used were styrene and *n*-butyl acrylate due to the significant differences in the T_g of their homopolymers. Four initial blocks were synthesized corresponding to a high and low M_n example of each type of polymer. Each initial polymer was then used to polymerize a low, medium and high M_n secondary block of the opposing polymer.

The block copolymer−spirooxazine conjugates synthesized (Table 1) also had polydispersity values in the range 1.1−1.2, which is consistent with a living radical polymerization. Further evidence that these block copolymer−spirooxazine conjugates behave as living systems is given in Figure 3.

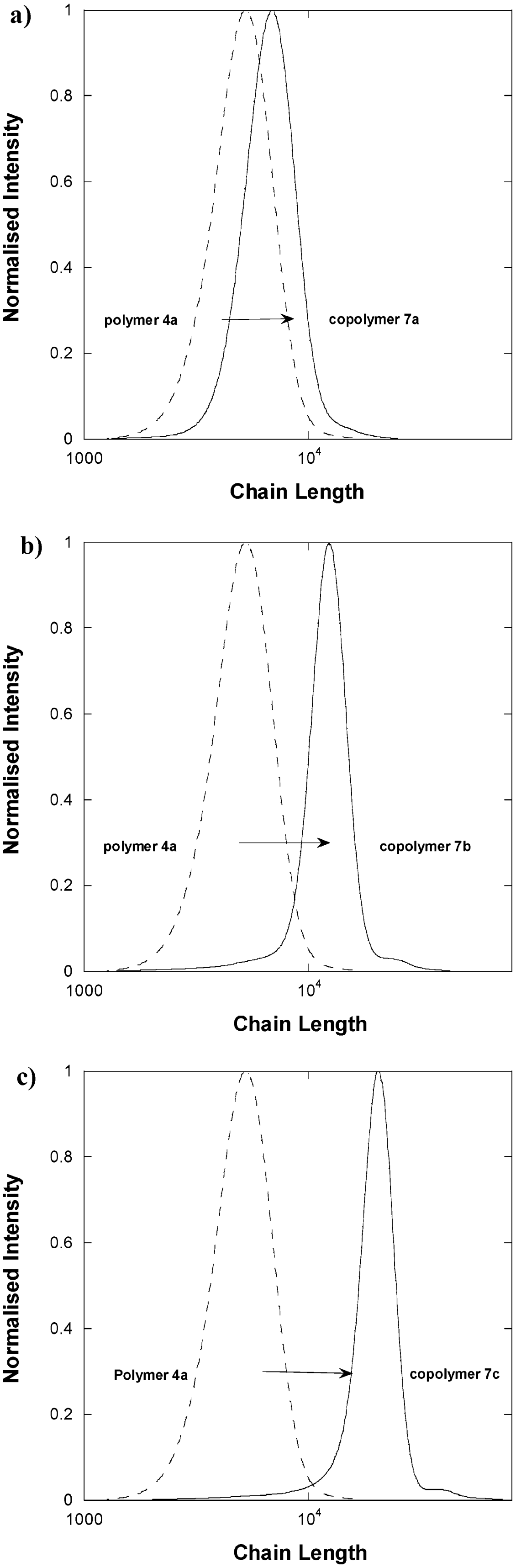


Figure 3. GPC traces of a range of block copolymer−spirooxazine conjugates with increasing polystyrene component (**7a**−**c**) relative to the starting poly(*n*-butyl acrylate)−spirooxazine macroinitiator (**4a**). (a) Block copolymer−spirooxazine conjugate: low M_n polystyrene second block. (b) Block copolymer−spirooxazine conjugate: medium M_n polystyrene second block. (c) Block copolymer−spirooxazine conjugate: high M_n polystyrene second block.

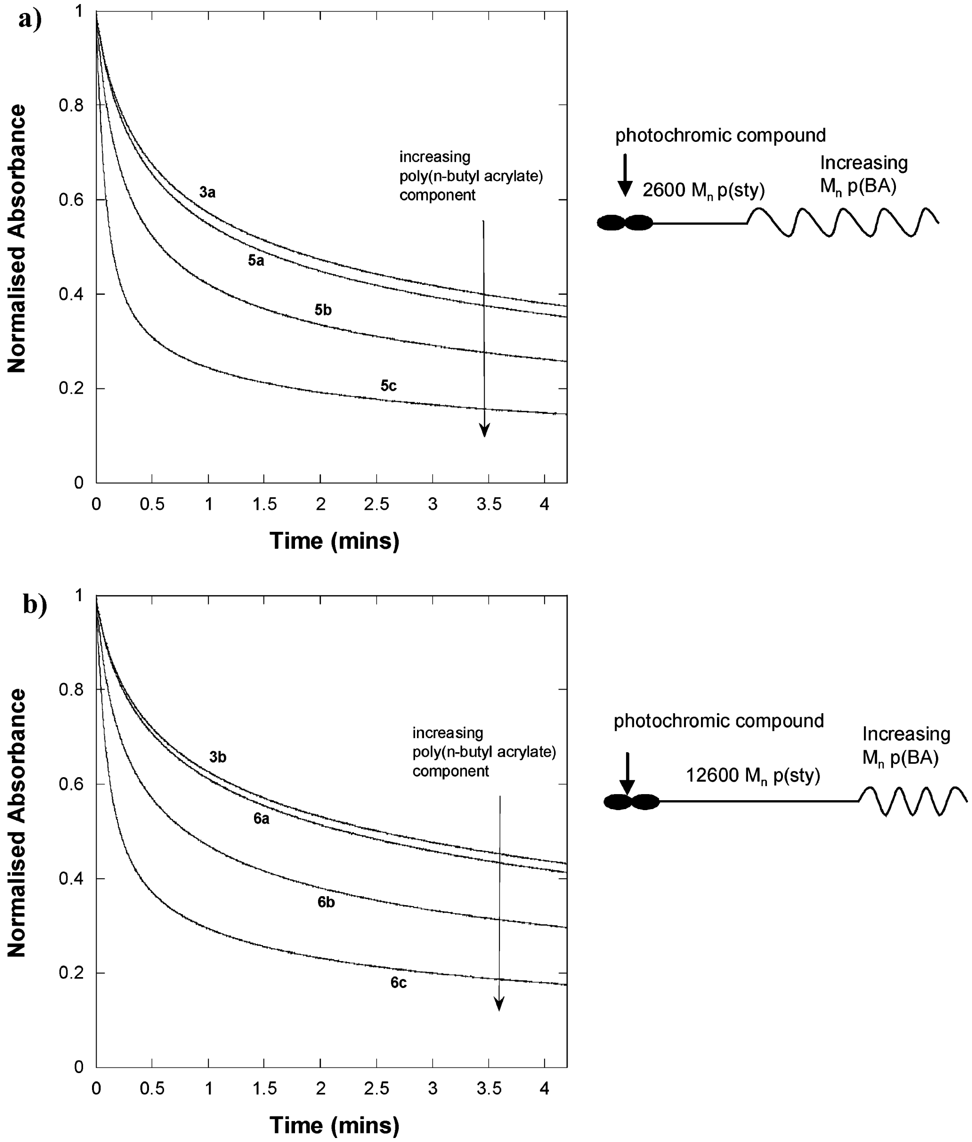


Figure 4. Photochromic thermal decoloration rates of a range of block copolymer−spirooxazine conjugates with polystyrene as the A-block where (a) the polystyrene block (**5a**−**c**) is short (M_n 2600) and (b) the polystyrene block (**6a**−**c**) is long (M_n 12 600) and the amount of poly(*n*-butyl acrylate) B-block is increasing. Spirooxazine−polymer conjugates **3a**−**b** are the corresponding A-block only controls. (a) Decoloration of block copolymers−spirooxazine conjugates with small styrene A-block. (b) Decoloration of block copolymers−spirooxazine conjugates with large styrene A-block.

Regrowth experiments have been utilized in previous ATRP work using spirooxazine initiators to provide further confirmation of living behavior.[25] As with these previous ATRP systems, the RAFT−spirooxazine conjugate mediated polymerizations demonstrated good living behavior (Figure 3). However, unlike the previous research, in this regrowth experiment, the second monomer used is different from the first. This facilitates the construction of block copolymers−spirooxazine conjugates. The length of the second polymer has been adjusted to provide a range of copolymers to investigate (Figure 3).

Photophysics. All of the block copolymer−spirooxazine conjugates were added to the PEGDMA/EBPDMA lens formulation and cured to give optically clear test lenses. Although block copolymers can give rise to phase separation, this is undesirable in this work, as the resulting haze makes the lens unsuitable for ophthalmic applications. Thus, our systems are designed not to phase separate. The macroinitiators used to form the blocks and the original initiator were also made into lenses and used as reference materials. Two rates are important for the photochromic performance: first, the rate of the forward reaction to the secondary state (coloration) and, second, the rate of reaction back to the initial state (decoloration). Both of these rates were examined. $T_{1/2}$ is a measure of decoloration rate, and it is used to describe the time taken to reach half the initial absorbance.

The first set of results investigated was the sets of block copolymer−spirooxazine conjugates with a poly(styrene) A-block component (**5a**−**c**, **6a**−**c**). In both of these sets, the decoloration rates increased steadily when the B-block of poly(*n*-butyl acrylate) was increased. Interestingly, the size of the styrene component did not seem to make a difference in the magnitude of this change (Figure 4). The initial $T_{1/2}$ values were slower for the set of conjugates with the longer polystyrene A-block. However, the $T_{1/2}$ values when a medium and large length poly(*n*-butyl acrylate) component were added were similar in both series even though the initial A-block **3b** was four times as long as **3a** (Table 2).

A similar trend was observed with the coloration rates of the block copolymer−spirooxazine conjugates. A significant increase in the coloration rate occurred with an increase in the B-block poly(*n*-butyl acrylate) component (Figure 5).

All photochromic decoloration rates have also been investigated by mathematical modeling. A biexponential equation has

Table 2. Photophysical Results of Block Copolymer−Spirooxazine Conjugates with a Styrene A-Block (5a−c, 6a−c) in a Polyethyleneglycol 400 Dimethacrylate (PEGDMA)/2,2′-bis[4-methacryloxyethoxy]phenyl]propane (EBPDMA) Test Lens[a]

sample	M_n[b]	$T_{1/2}$[c] (s)	$T_{3/4}$[c] (s)	A^{0}[d]	k_1[e] (min^{-1})	k_2[e] (min^{-1})	A_1[e]	A_2[e]	A_{th}[e]
3a	2600	99	680	0.71	0.80	0.055	0.45	0.33	0.08
5a	3300	84	579	0.84	0.87	0.057	0.47	0.32	0.07
5b	7700	35	270	0.81	1.39	0.067	0.52	0.26	0.06
5c	15 700	9	55	0.85	3.60	0.084	0.59	0.17	0.03
3b	12 600	151	1017	0.41	0.66	0.049	0.41	0.35	0.10
6a	14 600	134	891	0.40	0.68	0.050	0.42	0.35	0.09
6b	19 200	48	395	0.67	1.17	0.063	0.48	0.28	0.07
6c	26 800	8	96	0.73	2.55	0.078	0.56	0.20	0.04

[a] Decolorization monitored at λ_{max} of the colored form of the dye (605 nm) at 20 °C after irradiation at 350−400 nm. [b] Molecular weight calculated using GPC for initial block and then NMR for final block. Measured absorbance of each system before normalization. [c] The time taken to reach half ($t_{1/2}$) and three-quarters ($t_{3/4}$) of the initial absorbance, respectively. [d] Measured absorbance of each system before normalization. [e] Kinetic parameters of biexponential decoloration expression where k_1 and k_2 are the fast and slow rate constants, A_1 and A_2 are the contributions to the initial absorbance, and A_{th} is the absorbance when time approaches infinity.

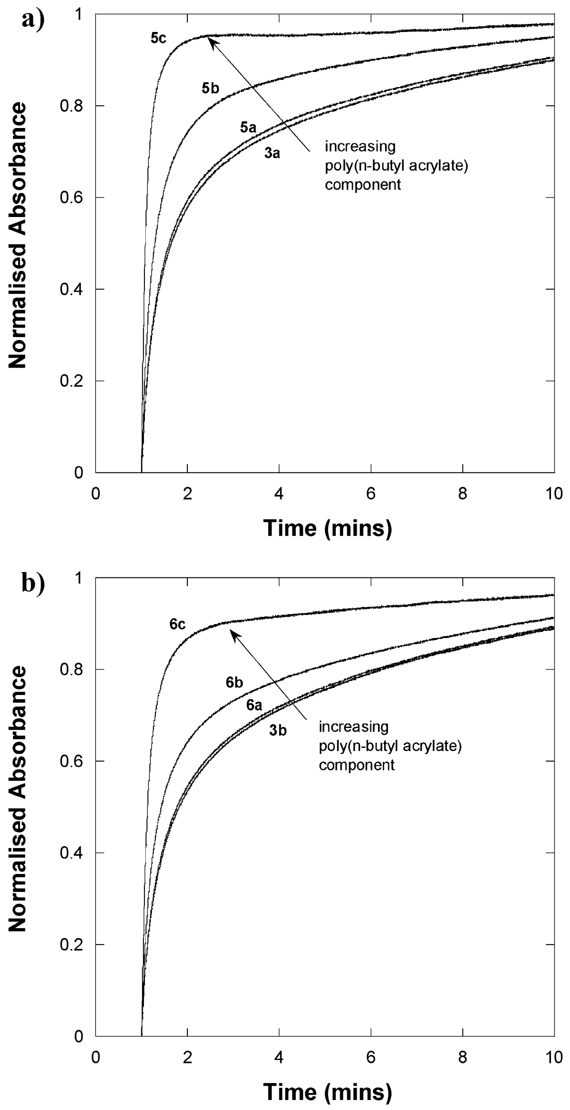


Figure 5. Photochromic coloration rates of a range of block copolymer−spirooxazine conjugates with polystyrene as the A-block where (a) the polystyrene block (**5a**−**c**) is short (M_n 2600) and (b) the polystyrene block (**6a**−**c**) is long (M_n 12 600) and the amount of poly(*n*-butyl acrylate) B-block is increasing. Spirooxazine−polymer conjugates **3a**−**b** are the corresponding A-block only controls. (a) Coloration of block copolymers−spirooxazine conjugates with short styrene A-block. (b) Coloration of block copolymers−spirooxazine conjugates with long styrene A-block.

been used to fit the decoloration kinetics of the block copolymer−spirooxazine conjugates:

$$A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_{th}$$

where $A(t)$ is the optical density at the λ_{max}, A_1 and A_2 are contributions to the initial optical density A_0, k_1 and k_2 are the rates of the fast and slow components, respectively, and A_{th} is coloration when time approaches ∞. This model was used in a previous work by Biteau et al.[26] A biexponential is one of the many models used to fit photochromic decoloration.[16,26] It was found to accurately fit the data in this study. The values for the constants for each conjugate in the series are given in Table 2.

The addition of poly(*n*-butyl acrylate) to the block copolymer−spirooxazine conjugates gave a ca. 400% increase in the fast component k_1 of the decoloration relative to the model compound (**3a** 0.80, **5c** 3.60, **3b** 0.66, **6c** 2.55). In both series, there was a general increase in k_1 as a longer poly(*n*-butyl-acrylate) B-block was added. The percentage of the k_1 component showed a corresponding increase. A smaller increase in k_2 was also observed across the range of copolymer−spirooxazine conjugates.

In the second set of results with the *n*-butyl acrylate as the initial block, a less significant change in the photochromic rates was observed (**7a**−**c**, **8a**−**c**) (Figure 6). A small increase in the $T_{1/2}$ was observed as a greater component of styrene was added to the block copolymer−spirooxazine conjugate. When the initial poly(*n*-butyl acrylate) was large, this increase in $T_{1/2}$ was only seen when the styrene component added was of a comparable size (Table 3).

These results were also investigated with the biexponential model discussed above, and the constants of that model are given in Table 3. The addition of polystyrene to the block copolymer−spirooxazine conjugate gave a ca. 20-30% decrease in the fast component k_1 of the decoloration relative to the model compound (**4a** 1.89, **7c** 1.34, **4b** 4.10, **8c** 3.30). In both series, there was a decrease in k_1 as more polystyrene component was added to the copolymer. The slower decoloration rate k_2 also showed a small decrease with an increase in the polystyrene component.

In previous research, a detailed model for these polymer−spirooxazine conjugates has been discussed. It is postulated that the behavior of the polymer−spirooxazine conjugates is due to statistical or probabilistic encapsulation of the photochromic dye by the polymer chain.[21,22,27] This encapsulation leads to the polymer providing an averaged customized local environment for the photochromic compound. Thus, for a given host matrix, photochromic response is dependent on the characteristics of the attached polymer, and systematic changes in photochromic switching speed are achieved by adjusting the properties of polymer. The effects observed would be dependent on a number of factors like the geometry of the attached polymer and the

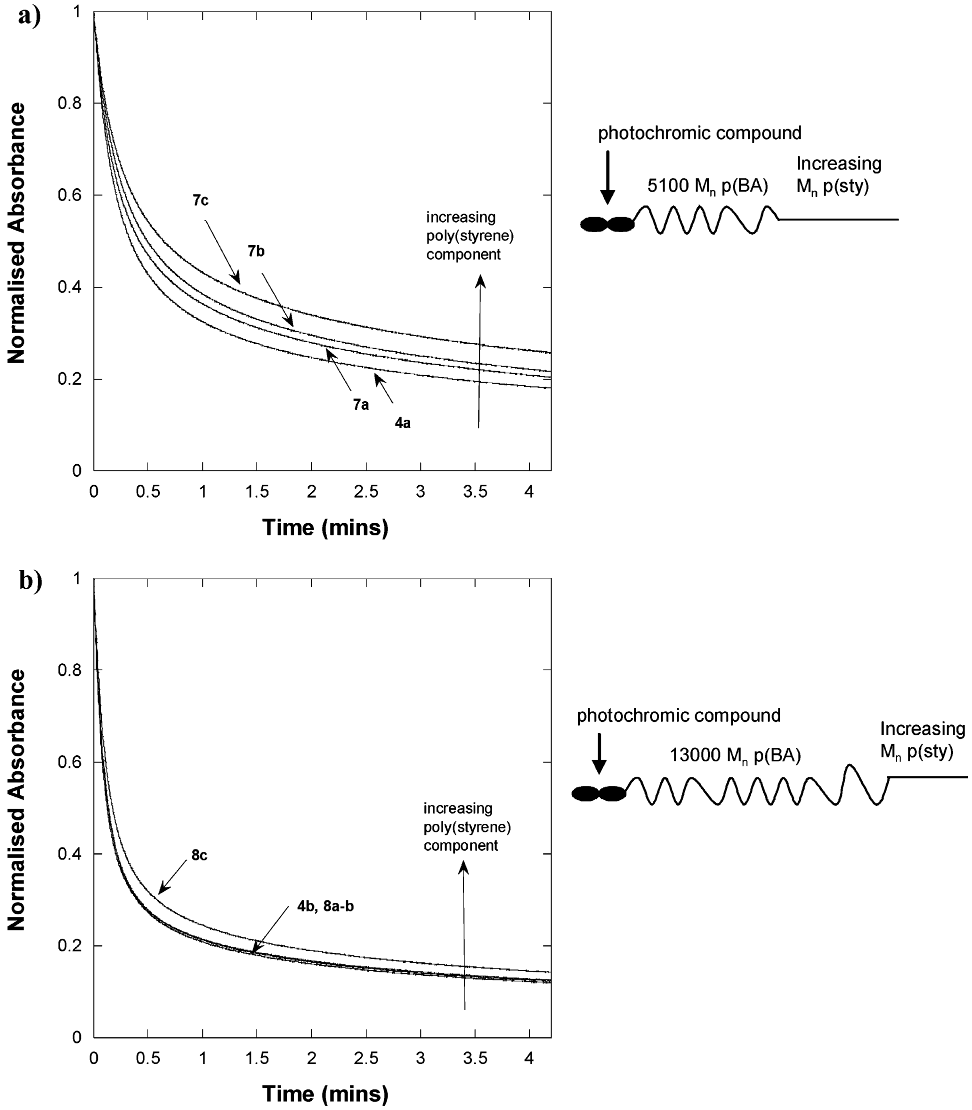


Figure 6. Photochromic thermal decoloration rates of a range of block copolymer−spirooxazine conjugates with poly(*n*-butyl acrylate) as the A-block where (a) poly(*n*-butyl acrylate) A-block (**7a**−**c**) is short (M_n 5100) and (b) poly(*n*-butyl acrylate) A-block (**8a**−**c**) is long (M_n 13 000). Spirooxazine−polymer conjugates **4a**−**b** are the corresponding A-block only controls. (a) Decoloration of block copolymer−spirooxazine conjugates with a small poly(*n*-butyl acrylate) A-block. (b) Decoloration of block copolymers−spirooxazine conjugates with a large poly(*n*-butyl acrylate) A-block.

Table 3. Photophysical Results of Block Copolymer−Spirooxazine Conjugates with a Poly(*n*-butyl acrylate) A-block (7a-c, 8a-c) in a Polyethyleneglycol 400 Dimethacrylate (PEGDMA)/2,2′-bis[4-Methacryloxyethoxy]phenyl]propane (EBPDMA) Test Lens[a]

sample	M_n[b]	$T_{1/2}$[c] (s)	$T_{3/4}$[c] (s)	A^0[d]	k_1[e] (min^{-1})	k_2[e] (min^{-1})	A_1[e]	A_2[e]	A_{th}[e]
4a	5100	20	116	0.71	1.89	0.079	0.61	0.21	0.04
7a	7300	25	157	0.69	1.61	0.077	0.57	0.24	0.04
7b	13 700	30	181	0.75	1.54	0.076	0.57	0.24	0.04
7c	21 600	39	269	0.84	1.31	0.068	0.54	0.25	0.06
4b	13 000	8	37	0.80	4.10	0.094	0.65	0.15	0.03
8a	14 900	7	39	0.76	4.41	0.094	0.69	0.15	0.03
8b	21 900	8	39	0.81	4.46	0.094	0.69	0.15	0.03
8c	27 900	10	57	0.92	3.30	0.083	0.63	0.17	0.03

[a] Decolorization monitored at λ_{max} of the colored form of the dye (605 nm) at 20 °C after irradiation at 350−400 nm. [b] Molecular weight calculated using GPC for initial block and then NMR for final block. Measured absorbance of each system before normalization. [c] The time taken to reach half ($t_{1/2}$) and three-quarters ($t_{3/4}$) of the initial absorbance, respectively. [d] Measured absorbance of each system before normalization. [e] Kinetic parameters of biexponential decoloration expression where k_1 and k_2 are the fast and slow rate constants, A_1 and A_2 are the contributions to the initial absorbance, and A_{th} is the absorbance when time approaches infinity.

polarity/T_g of the host matrix and attached polymer as well as compatibility between them. In this work, as many of those factors as possible are kept constant.

Previous work demonstrated photochromic rates could be tuned using either rigidity or chain length of the polymer attached. In this work, block copolymer−conjugates were investigated to explore whether rates could be affected or tuned using the second or "B-" block, which is insulated from the photochromic moiety by an intervening A-block. Blocks of high and low T_g were used for this investigation.

Experimental results demonstrated that changes in a second block could be successfully used to adjust photochromic response. In the series with polystyrene as the first (A-) block, $T_{1/2}$ of the spirooxazine decreased significantly as increasingly larger poly(*n*-butyl-acrylate) B-blocks were added. This indicates an increase in switching speed. This is what would be expected theoretically, as poly(*n*-butyl acrylate) is a low T_g polymer. A larger amount of the lower T_g polymer will make the local environment less rigid, and thus switching will occur more rapidly. What is particularly interesting is that the effect of the low T_g polymer was significant even if it was separated from the photochromic moiety by the block of high T_g polystyrene. $T_{1/2}$ values of the conjugates appeared to be independent of the M_n of the A-block when a significant poly(*n*-butyl acrylate) B-block was added. This observation can be explained using the proposed model. Because of the dynamic coiling of the polymer, the photochromic compound would still have interaction with the low T_g component of the block copolymer, even if it is at the end of a long chain

The results for the second set of data with poly(*n*-butyl acrylate) as the A-block also confirms theoretical expectations. In this case, $T_{1/2}$ increases when a larger polystyrene B-block is added. A larger polystyrene component equates to a more rigid environment, and therefore, slower $T_{1/2}$ is expected. It is interesting to note that the changes in photochromic rates are significantly reduced when the blocks are in this order. This indicates that the photochromic response is more sensitive to the presence of a low T_g environment. When it is close to the photochromic compound such as in the second set of data, it has a very strong effect on kinetics and it is difficult to override its effect with a high T_g B-block unless the initial poly(*n*-butyl acrylate) block is relatively small. However, even as the second block, the low T_g poly(*n*-butyl acrylate) displays a strong influence over photochromic rates and provides strong tuning potential.

Conclusion

Block copolymer−spiroxazine conjugates of poly(styrene) and poly(*n*-butyl acrylate) have been synthesized that demonstrate strong systematic tailoring of photochromic switching rates in a rigid lens host matrix. A particularly wide range of switching speeds were observed when poly(*n*-butyl acrylate) was the second block. Results showed photochromic rates are very sensitive to the addition of a low T_g component even if it is separated from the photochromic moiety by an intervening high T_g component.

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MA061674I