Rapid Photochromic Switching in a Rigid Polymer Matrix Using Living Radical Polymerization

Georgina K. Such,[†,‡,⊥] Richard A. Evans,*[,‡,§,⊥] and Thomas P. Davis*[,§,⊥]

Department of Chemical and Biomolecular Engineering, University of Melbourne, Parkville 3010 Vic, Australia; CSIRO Molecular and Health Technologies, Bag 10, Clayton 3169 Vic, Australia; CRC for Polymers, 32 Business Park Drive, Notting Hill 3168 Vic, Australia; and Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, 2052 NSW, Australia

Received September 14, 2005; Revised Manuscript Received November 22, 2005

ABSTRACT: Fast switching of a photochromic dye in a rigid host matrix has been achieved without any modification of electronic nature of the photochromic entity. The method utilizes living radical polymerization (atom transfer radical polymerization (ATRP)) to grow a low glass transition temperature (T_g) poly(*n*-butyl acrylate) polymer from a spirooxazine core, creating a low-T_g environment to cushion the photochromic dye while keeping the bulk matrix rigid. In these systems, decoloration speed of the photochromic ($t_{1/2}$) was reduced by 40−75% depending on the molecular weight of the poly(*n*-butyl acrylate) attached. We have demonstrated with this methodology a controlled tuning of photochromic switching. Coarse and fine tuning can be achieved by adjusting first the choice of polymer and second the molecular weight of the polymer.

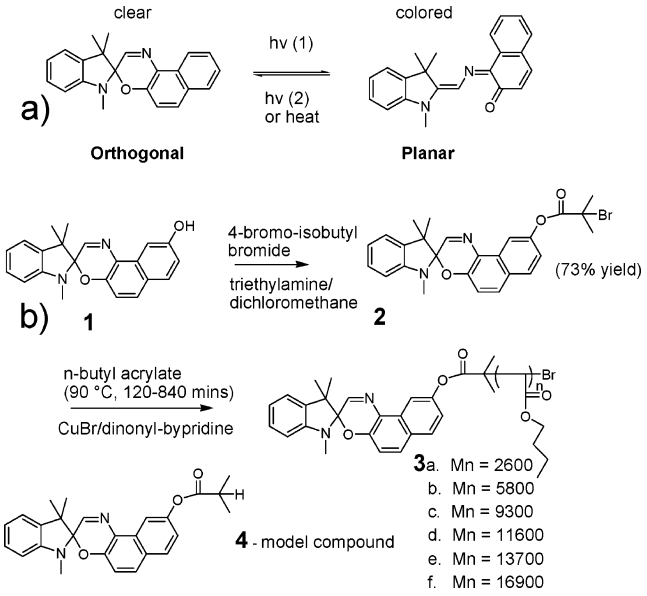
Introduction

Fast switching in a polymer matrix has been an ongoing challenge in the use of photochromic dyes.[1−4] Some control over this property has been observed through changing electronic effects; however, the results are unpredictable, and other properties such as color are also affected.[5,6] Switching rates of a photochromic dye can also be influenced by attributes of the host environment, e.g., rigidity, polarity, and free volume.[7,8] Some control over switching rates has been observed by changing properties of a host polymer; however, this requires bulk modification of the matrix.[2,9−12] Consequently there is little opportunity for control over the location of each photochromic moiety without modifying the entire matrix. There has been little prior research into customizing a uniform environment for the photochromic compound and investigating systematic changes in this environment. The use of living radical polymerization techniques[13−17] such as atom transfer radical polymerization (ATRP)[13,18] offers the potential to design such a customized environment. The goal of this research was to create a uniform local environment which would facilitate controlled changes in the photochromic switching rates.

Spirooxazines are a key family of photochromic compounds that undergo switching between their clear and colored states by photostimuli and/or thermal stimuli (Scheme 1a).[1] They were chosen for this study due to their good fatigue resistance and highly colored secondary state.

In this research, a living radical initiator based on a spirooxazine compound was used to polymerize a polymer chain of well-controlled molecular weight and polydispersity. This technique facilitated the construction of a polymer−spirooxazine conjugate with every photochromic moiety convalently attached to an almost identical polymer chain. The photochromic behavior of these new polymer−spirooxazine conjugates was investigated in a cross-linked polymer matrix with a glass transition temperature (T_g) of ∼120 °C. The glass transition temperature provides an indication of the rigidity of the polymer; a decrease in T_g indicates increased flexibility.

Scheme 1[a]



[a] (a) Typical photochromic transition of a spirooxazine compound; (b) synthetic scheme for photochromic initiator (**2**), model compound (**4**), and *n*-butyl acrylate polymerization (**3a**−**f**).

Earlier work showed that the photochromic behavior demonstrated a direct correlation with the rigidity of the polymer conjugate attached.[19,20] It was postulated that the attached polymer acted as a customized local environment for the photochromic moiety, encapsulating it from the host matrix. Consequently, systematic tailoring of the photochromic switching rates was achieved by changes in the characteristics of the attached polymer. To our knowledge, this is the first technique to control the local environment of a photochromic compound and thus the first example of systematic tuning of photochromic switching rates.

† University of Melbourne.
‡ CSIRO Molecular and Health Technologies.
§ CRC for Polymers.
⊥ The University of New South Wales.
* Corresponding authors. E-mail: richard.evans@csiro.au; T.Davis@UNSW.EDU.AU.

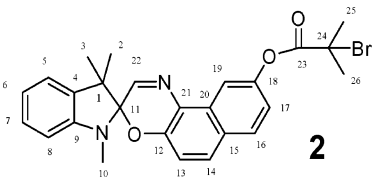
10.1021/ma052002f CCC: $33.50
Published on Web 01/21/2006

The previous research using this technique was performed using high-T_g polymers.[19,20] In this work we have used low-T_g polymers in an attempt to achieve tunable fast switching in a rigid polymer matrix. A low glass transition temperature (T_g) polymer, poly(*n*-butyl acrylate), was used for this work and demonstrated fast and tunable fade rates was possible using this methodology. This is a significant development on our previous work on high-T_g polymers[19,20] and allows the formulation of selection rules in determining appropriate polymer characteristics for a desired switching speed. We have recently reported related work on poly(dimethylsiloxane) oligomers.[4,21]

Experimental Section

General Procedures. *n*-Butyl acrylate (99% purity, Aldrich) was purified by vacuum distillation. All other reagents and solvents unless otherwise stated were obtained from Aldrich at the highest purity and used without further purification.

Synthesis of 9′-(2-Bromo-2-methylethoxycarbonyl)-1,3,3-trimethylspiro[indoline2,3′-[3*H*]naphtha[2,1-*b*][1,4]oxazine] (2). 9′-Hydroxy-1,3,3-trimethylspiro[indoline2,3′-[3*H*]naphtha[2,1-*b*]-[1,4] oxazine] (**1**) was synthesized as described in Kakishita et al.[22] The spirooxazine initiator **2** was synthesized as detailed in Such et al. (refer to Scheme 1b).[20] ^{1}H NMR ($(CD_3)_2CO$) δ: 1.34 (s, 3H, H-2), 1.36 (s, 3H, H-3), 2.16 (s, 6H, H-25 & H-26), 2.78 (s, 3H, H-10), 6.67 (d, J = 7.8 Hz, 1H, 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), 7.24 (d of d, J = 9 Hz, 2.4 Hz, 1H, H-14), 7.85 (d, J = 8.8 Hz, 1H, H-17), 7.85 (s, 1H, H-22), 7.95 (d, J = 8.8 Hz, 1H, H-16), 8.29 ppm (d, J = 2.4 Hz, 1H, H-19). ^{1}H NMR (C_6D_6) δ: 1.05 (s, 3H, H-2), 1.21 (s, 3H, H-3), 1.79 (s, 6H, H-25 and H-26), 2.40 (s, 3H, H-10), 6.33 (d, J = 7.9 Hz, 1H, H-8), 6.73 (d, J = 9.0 Hz, 1H, H-13), 6.82−6.90 (m, 2H, H-5), 7.06−7.22 (m, 3H, H-7,16, 17 or 14), 7.85 (d, J = 8.8 Hz, 1H, H-14 or 17), 7.54 (s, 1H, H-22), 8.91 ppm (d, J = 2.4 Hz, 1H, H-19).^{13}C NMR ($(CD_3)_2CO$) δ: 21.03 (C-2), 25.77 (C-3), 29.85 (C-10), 30.95 (C-25 and C-26), 52.69 (C-1), 57.34 (C-24), 99.95 (C-11), 108.13 (C-8), 113.39 (C-19), 117.69 (C-13), 119.70 (C-14), 120.79 (C-6), 122.39 (C-5), 123.90 (C-21), 128.45 (C-15), 128.88 (C-7), 130.67 (C-16), 131.12 (C-17), 132.64 (C-20), 136.77 (C-4), 145.86 (C-12), 148.65 (C-9), 150.91 (C-18), 152.35 (C-22), 170.93 ppm (C-23). Mass spectrum (EI): *m*/*z* 494 (M^+ + 1, 34%), 159 (100), 412 (35), 494 (35), 158 (34). Mass spectrum (HR, EI): *m*/*z* 492.1043 ($C_{26}H_{25}BrN_2O_3$ requires 492.10). The nonstandard numbering system is given in the following diagram:



Synthesis of 9′-(2-Dimethylethoxycarbonyl)-1,3,3-trimethylspiro[indoline2,3′-[3*H*]naphtha[2,1-*b*][1,4]oxazine] (4). The model compound **4** was synthesized as above using isobutyryl chloride in place of 2-bromo-isobutyl bromide. A pure yellow powder was produced (0.23 g, 20% yield). ^{1}H NMR ($(CD_3)_2CO$) δ: 1.33 (s, 3H, H-2), 1.33 (s, 3-H, H-3), 2.77 (s, 3H, H-10), 2.92 (m, 1H, H-24), 6.65 (d, J = 7.6 Hz, H-8), 6.86 (t of d, J = 7.6, 0.8 Hz, 1 H, H-6), 7.03 (d, J = 8.8 Hz, 1 H, H-13), 7.14 (app d, J = 7.6 Hz, 1H, H-5), 7.18 (m, 2H, H-7 & H-14), 7.81 (d, 9.2 Hz, 1H, H-17), 7.82 (s, 1H, H-22), 7.88 (d, J 9.2 Hz, 1H, H-16), 8.21 ppm (d, J = 2.4 Hz, 1H, H-19). ^{13}C NMR ($(CD_3)_2CO$) δ: 19.31 (C-2), 21.04 (C-3), 25.79 (C-25 & C-26), 29.46 (C-10), 34.88 (C-24), 52.67 (C-1), 99.87 (C-11), 108.13 (C-8), 113.68 (C-19), 117.33 (C-13), 120.59 (C-14), 120.78 (C-6), 122.39 (C-5), 123.85 (C-21), 128.25 (C-15), 128.88 (C-7), 130.34 (C-16), 131.06 (C-17), 132.70 (C-20), 136.81 (C-4), 145.72 (C-12), 148.69 (C-9), 151.21 (C-18), 152.18 (C-22), 176.03 ppm (C-23). The nonstandard numbering system for structure **4** is as for structure **2** above. Mass spectrum (EI): *m*/*z* 414 (M^+, 100%), 159 (100), 399 (80), 158 (64), 329 (62) 415 (52). Mass spectrum (HR, EI): *m*/*z* 414.1920 ($C_{26}H_{26}N_2O_3$ requires 414.19).

General Polymerization Procedure. The ATRP polymerization of poly(*n*-butyl acrylate) using the spirooxazine initiator **2** was performed using the following procedure: initial reactants were mixed at a 100:1:1:2 molar ratio of *n*-butyl acrylate monomer (17.5 × 10^{-3} mol), spirooxazine initiator **2** (17.5 × 10^{-5} mol), catalyst (CuBr (17.5 × 10^{-5} mol)), and ligand (dinonyl-bipyridine (34.9 × 10^{-5} mol)). The reactants were added to an ampule and then degassed by four freeze−pump−thaw cycles using a Schlenk line. The polymerizations were then carried out at 90 °C in a constant temperature oil bath. The polymerization mixtures were purified by precipitation twice into methanol.

Specific Example of the Polymerization Procedure. Synthesis of poly(*n*-butyl acrylate)−spirooxazine conjugate **3a** using the spirooxazine initiator was performed using the following procedure: initial reactants were mixed at a 100:1:1:2 molar ratio of *n*-butyl acrylate (2.328 g, 18.2 × 10^{-3} mol), spirooxazine initiator **2** (0.0861 g, 17.5 × 10^{-5} mol), catalyst (CuBr (0.0254 g, 17.7 × 10^{-5} mol)), and ligand (dinonylbipyridine (0.1427 g, 34.9 × 10^{-5} mol)). The reactants were added to an ampule and then degassed by four freeze−pump−thaw cycles using a Schlenk line. The polymerization was then carried out at 90 °C in a constant temperature oil bath for 2 h. The polymerization mixture was purified by precipitation twice into methanol (0.09 g of clear brown polymer obtained). The polymer **3a** obtained had a molecular weight (M_n) of 2890 (conversion 11.2%). ^{1}H NMR ((C_6D_6) δ: 0.69−0.97 CH_3 (**d**), 1.07 CH_3 (H-2), 1.21 CH_3 (H-3), 1.23−1.38 CH_2 (**c**), 1.46−1.75 CH_2 (**b** and polymer backbone), 1.78−2.00 CH_2 (polymer backbone), 2.18−2.33 CH_2 (polymer backbone), 2.41 CH_3 (H-10), 2.63−2.82 CH (polymer backbone), 3.89−4.22 CH_2 (**a**), 6.31 d (photochromic aromatics), 6.69 d (photochromic aromatics), 6.79−6.94 m (photochromic aromatics), 7.06−7.24 m (photochromic aromatics), 7.31−7.41 m (photochromic aromatics), 7.44−7.51 m (photochromic aromatics), 7.57 s (photochromic aromatics), 8.84 s (photochromic aromatics). The nonstandard numbering of the photochromic peaks for the photochromic initiator **2** is given above and the lettering system for the polymer in Figure 2.

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 × 5 μm Mixed-C and 1 × 3 μm Mixed-E), and Millennium Software. The GPC was calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories EasiCal, MW from 264 to 256 000). Mark−Houwink parameters were used to convert values obtained to poly(*n*-butyl acrylate) equivalents.[23] ^{1}H and ^{13}C NMR spectra were obtained with a Bruker Av400 or a Bruker AC200. Chemical shifts are reported in ppm from external tetramethylsilane. Monomer conversions were obtained from ^{1}H NMR spectra recorded on a Bruker AC200 spectrometer. The resonances integrated to obtain conversions were the vinyl peaks at 5.86, 6.16, and 6.36 ppm (monomer only) and the CH_2 peak at 4.14 ppm (monomer and polymer). High-resolution electron impact (HREI), mass spectra were run on a ThermoQuest MAT95XL. Photochromic analyses were performed on lenses composed of polymer−photochromic conjugates **3a**−**f** (1.2 × 10^{-3} mmol/g) dissolved in a standard industrial lens formulation of 1:4 weight ratio of poly(ethylene glycol) 400 dimethacrylate (PEGDMA) and 2,2′-bis[4-methacryloxyethoxy]phenyl]propane (EBPDMA) with 0.4% azobis(isobutyronitrile) (AIBN) and cured (80 °C, 8 h) to give clear test lens. The photochromic responses of the lens were analyzed on a light table comprised of a Cary 50 spectrophotometer and a 300 W Oriel xenon lamp as an incident light source. A series of two filters (Edmund Optics WG320 and Edmund Optics band-pass 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

Table 1. Polymerization Characteristics of Poly(*n*-butyl acrylate) Conjugates 3a−f (Refer to Scheme 1b) Using Spirooxazine Initiator 2

sample	polymerization time (min)[a]	conv[b] (%)	expt M_n[c]	theor M_n	PDI
3a	120	11.2	2600	1900	1.11
3b	300	25.3	5900	3700	1.09
3c	420	41.0	9300	5700	1.07
3d	540	54.8	11500	7500	1.08
3e	660	64.3	13700	8700	1.08
3f	840	75.2	16900	10100	1.10

[a] Polymerizations where performed neat at 90 °C with butyl acrylate (17.4×10^{-3} mol), spirooxazine initiator 2 (17.4×10^{-5} mol), CuBr (17.4×10^{-5} mol), and dinonylbipyridine (34.9×10^{-5} mol). [b] Determined using ^{1}H NMR spectra recorded on a Bruker AC200 spectrometer. [c] Poly(*n*-butyl acrylate) equivalents using Mark−Houwink parameters on a polystyrene calibration.

maximum absorbance of the colored form (605 nm) for a period of a thousand seconds. Then the decoloration was monitored for a further 6000 s.

Results and Discussion

The polymerizations using spirooxazine initiator **2** was performed under homogeneous ATRP conditions with copper bromide as the catalyst and dinonyl-bipyridine as the ligand (Scheme 1b). ATRP is a radical process, which utilizes a transition metal complex to create a reversible equilibrium between growing radicals formed from a suitable organo-halide initiator and dormant species. By keeping the concentration of active species low throughout the reaction, a living radical polymerization is achieved.[24]

Poly(*n*-butyl acrylate)−spirooxazine conjugates were synthesized successfully using the technique illustrated above (Scheme 1b). The characteristics of the synthesized polymer conjugates correspond to those expected for a living radical polymerization. There are several factors that indicate a successful living polymerization. Polydispersity is a very important property of living systems; it can be calculated by dividing weight molecular weight (M_w) by the number molecular weight (M_n). The polydispersity value is of specific interest in this work as it is a measure of the uniformity of the polymers synthesized. In a living system polydispersity should decrease as conversion increases, reaching values in the range of 1.1. In this work, polydispersities remained consistently low (∼1.10) as expected (Table 1). Surprisingly, low polydispersity was obtained relatively early in the polymerization at only 10% conversion.

The second indication of a living system is linear growth of molecular weight (M_n) with conversion. This was also observed in the polymer−spirooxazine conjugates; however, values were systematically higher than the theoretical values expected (Figure 1). This may be due to inefficient initiation, which means not all initiator is able to participate in the polymerization. Consequently, the ratio of initiator to monomer is greater than expected, which leads to higher molecular weights. The livingness of the poly(*n*-butyl acrylate)−spirooxazine conjugates was also confirmed by regrowth of a polymer chain (Supporting Information). From the above evidence we can conclude that the poly(*n*-butyl acrylate)−spirooxazine conjugates are living systems with well-controlled properties. Further details of the polymer conjugates synthesized are given in Table 1.

The mechanism of ATRP using the spirooxazine initiator **2** should result in the polymer of the structure **3** (Scheme 1b). The successful repolymerization experiment described above implies that halogen terminates the polymers. Further confirmation of the composition of the polymers was achieved by directly

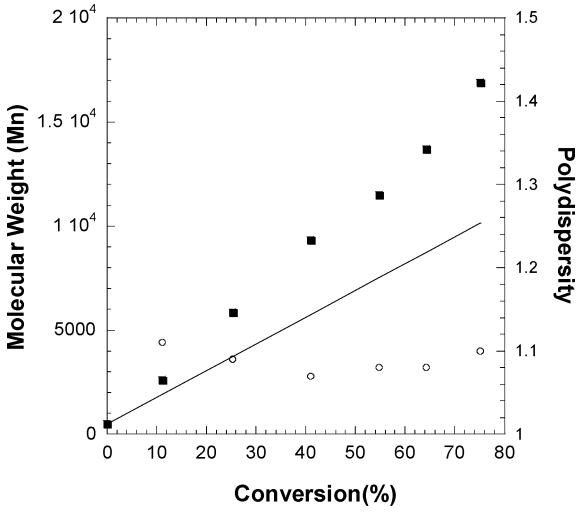


Figure 1. Evolution of molecular weight (■) and polydispersity (○) of the photochromic polymer conjugate **3** (Scheme 1a) during the atom transfer radical polymerization of poly(*n*-butyl acrylate) initiated by spirooxazine **2** at 90 °C where [*n*-butyl acrylate]/[CuBr]/[dinonylbipyridine]/[**2**] = 100:1:2:1. Molecular weight and polydispersity determined by GPC using poly(butyl acrylate) equivalents. (—) Theoretical molecular weight. Monomer conversion and theoretical molecular weight determined by ^{1}H NMR spectroscopy. Polymerization times ranged from 120 min (∼11% conversion) to 840 min (∼75% conversion).

observing both the spirooxazine and halo end groups by NMR spectroscopy.

A comparison of a poly(*n*-butyl acrylate)−spirooxazine conjugate **3a** ^{1}H NMR spectra with the corresponding spirooxazine initiator **2** is given in Figure 2. The photochromic peaks can be clearly seen in the polymer for the methyl groups (1.07 and 1.20 ppm H-2 and H-3; 2.41 ppm H-10), and in the aromatic region the characteristic peaks for the oxazine (7.54 ppm, H-22), naphthyl (6.73 ppm, H-13, 8.91 ppm, H-19), and indole (6.33 ppm, H-8) parts of the spirooxazine are clearly observed (Supporting Information Figure S2). The use of benzene-d_6 causes additional complexity to the aromatic region, and later work on related molecules found that acetone-d_6 is the solvent of choice for the ^{1}H NMR spectroscopic analysis of the aromatic region. The two CH_3 groups of the isobutyryl moiety present on the photochromic initiator are no longer visible in the poly(*n*-butyl acrylate) conjugates. The methyls are now part of the polymer backbone and have been shifted upfield. They are expected to reside under the bulk polymer peaks at 1−2 ppm. Evidence for the nonphotochromic polymer end group can also be observed. The end group of the poly(*n*-butyl acrylate) polymer can be observed upfield of the polymer peak at ∼4.0 ppm. These ^{1}H NMR spectra allow us to confidently identify the polymers synthesized as having the structures depicted in Scheme 1b.

Each poly(*n*-butyl acrylate)−spirooxazine conjugate was added to the PEGDMA:EBPDMA lens formulation and cured to give a test lens. Photochromic properties of these systems were then examined using the model compound **4** as a reference. Two rates are important for photochromic performance: first, the rate of the forward reaction to the secondary state (coloration) and, second, the rate of the reaction back to the initial state (decoloration). Both these rates were examined. $T_{1/2}$ is a measure of decoloration rate; it describes the time taken to reach half the initial absorbance.

The photophysical investigation of the poly(*n*-butyl acrylate)−spirooxazine conjugates **3a**−**f** in PEGDMA:EBPDMA lens showed extremely fast decay characteristics for all conjugates

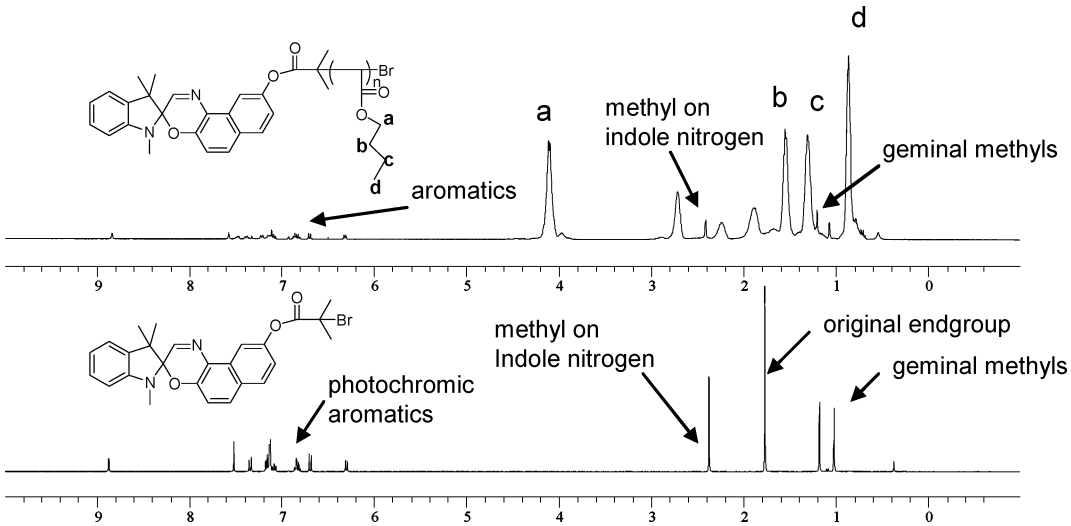


Figure 2. End-group analysis of the poly(*n*-butyl acrylate)−spirooxazine conjugates (upper) by comparison of the polymer NMR with the original initiator **2** (lower). The solvent used was benzene-d_6; however, solvent peaks were removed for easier observation of important peaks in the spectra. "Geminal methyls" refers to the geminal methyl groups on the indole fragment of the spirooxazine.

Table 2. Photophysical Analysis of the Decolorization of Poly(*n*-butyl acrylate)−Spirooxazine Conjugates Relative to a Model Compound 4 in a Poly(ethylene glycol) 400 Dimethacrylate (PEGDMA): 2,2′-Bis[4-methacryloxyethoxy]phenyl]propane (EBPDMA) Test Lens[a]

sample	M_n[b] PD[c]	$t_{1/2}$[d] (s)	$t_{3/4}$[d] (s)	A^0[e]	k_1 (min^{-1})[f]	A_1[f]	k_2 (min^{-1})[f]	A_2[f]	A_{th}[f]
model **4**		21	150	1.15	2.1	0.64	0.06	0.22	0.04
3a	2900 (1.11)	12	38	1.09	3.3	0.74	0.10	0.13	0.02
3b	5600 (1.09)	9	27	1.04	4.1	0.78	0.12	0.11	0.01
3c	9900 (1.07)	10	43	1.03	3.5	0.69	0.10	0.15	0.02
3d	12300 (1.08)	7	22	1.03	5.0	0.78	0.12	0.11	0.01
3e	14400 (1.08)	8	25	0.96	4.6	0.78	0.11	0.12	0.02
3f	17400 (1.10)	5	18	0.97	6.0	0.74	0.12	0.11	0.02

[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 (M_n) in poly(*n*-butyl acrylate) equivalents using Mark−Houwink parameters with polystyrene calibration standards. [c] Polydispersity equal to the weight molecular weight (M_w) divided by the number molecular weight (M_n). [d] The time taken to reach half ($t_{1/2}$) and three-quarters ($t_{3/4}$) of the initial absorbance, respectively. [e] Measured absorbance of each system before normalization. [f] 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.

compared to the model compound **4** (Figure 3a). The rate of the decoloration is much faster than would be expected for the high-T_g host matrix. In fact, the results approach those expected for a flexible matrix or even a solution.[4] In addition, decoloration rates show a general increase with molecular weight; $T_{1/2}$ values vary from 12 to 5 s over the range of conjugates.

The decoloration curves were also analyzed using the following biexponential equation

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

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, and A_{th} is coloration when time approaches infinity. This model was used previously by Biteau et al.[25] A biexponential is one of the many models used to fit photochromic decoloration.[8] It was found to accurately fit the data in this study (R values ∼0.99). The values for the constants for each conjugate in the series are given in Table 2.

The attachment of a poly(*n*-butyl acrylate) chain gave a ca. 300% increase in the fast component of the decoloration k_1 relative to the model compound (model **4**, 2.1; model **3f**, 6.0). In addition, the kinetic profile of the fade also changed, with the fast decoloration component not only faster but a greater proportion of the fade kinetics A_1 (model **4**, 0.64; model **3a**−**f**, ca. 0.75). There was also a general trend of increasing decoloration rate (k_1) with increasing length of the poly(*n*-butyl acrylate) chain attached; however, interestingly the k_2 value remained essentially the same (k_2 ca. 0.11). Decoloration speed as measured by $t_{1/2}$ was reduced by 40−75% depending on the molecular weight of poly(*n*-butyl acrylate) chain attached.

The coloration of the poly(*n*-butyl acrylate)−spiroooxazine conjugates showed a pattern similar to the decoloration results (Figure 3b). Coloration occurred more rapidly in the conjugates than in the model compound, and there was also a general trend of an increase in rate with an increase in molecular weight. A slightly different shape of **3f** is observed when the photochromic dye exhibits particularly fast switching speeds; it is identified as a slight overshoot in coloration. A more pronounced overshoot has been reported in the work on poly(dimethylsiloxane)−spirooxazine conjugates.[4] It is ascribed to the environment being highly mobile such that dye molecules can switch readily before the coloration nearer the UV source provides a type of self-filtering. The absorbance maximum then returns to a steady-state value.

Effect of Polymer T_g on Conjugate Switching Speed. Our new results obtained with poly(*n*-butyl acrylate) spirooxazine conjugates provide valuable data of a fast switching spirooxazine system in a rigid host matrix. Earlier work using poly(methyl methacrylate) and polystyrene demonstrated tuning of photochromic rates was accessible using this novel technique of attaching a polymer conjugate to a spirooxazine dye.[19,20] It was proposed that these polymer conjugates create a de facto or statistical encapsulation around the photochromic dye due to the natural tendency of the polymer conjugate to coil.[4] Thus, the factors important for photochromic response such as rigidity, free volume, polarity, etc., directly around the dye could be

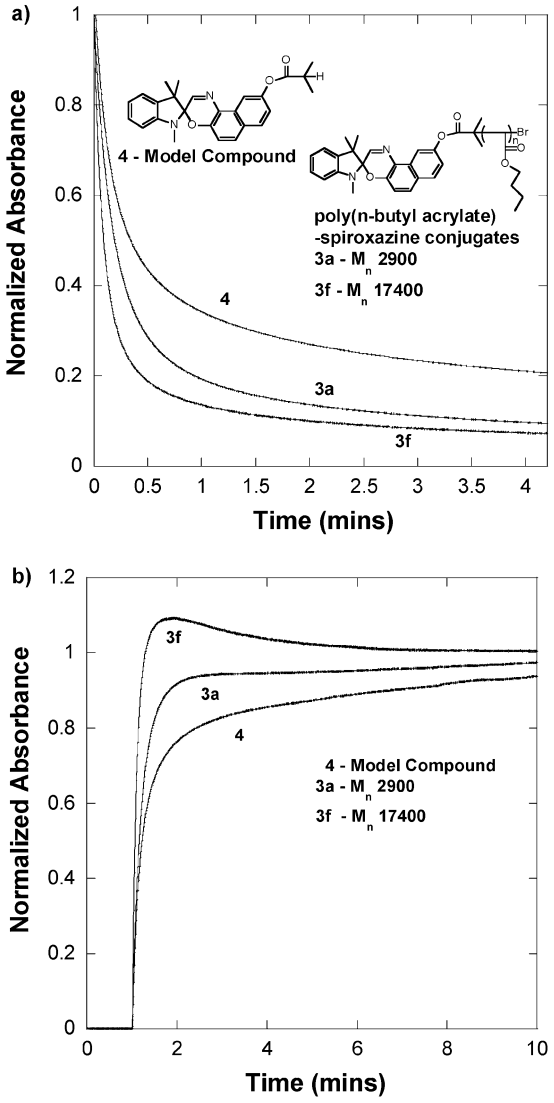


Figure 3. (a) Normalized decoloration of a low and high molecular weight poly(*n*-butyl acrylate)−spirooxazine conjugate relative to a model compound **4** in PEGDMA:EBPDMA lens. (b) Normalized coloration of a low and high molecular weight poly(*n*-butyl acrylate)−spirooxazine conjugate relative to a model compound **4** in PEGDMA:EBPDMA test lens.

controlled by the choice of the attached polymer. In both of these former cases, the attached polymers were high T_g (100 °C). High T_g is known to slow down photochromic response, and that was what was observed experimentally (Figure 4).[20] In this case, the T_g of the poly(butyl acrylate) is low (∼−50 °C), and thus we would expect fast decoloration if consistent with our encapsulation model. This expectation was confirmed experimentally (Figure 3). Our methodology clearly provides a coarse control of photochromic decoloration by choice of the polymer used. Decoloration rates ($t_{1/2}$) can be varied over a very large range from 5 s for low-T_g polymer (i.e., poly(*n*-butyl acrylate) conjugates to 120 s for high-T_g polymer (i.e., poly(methyl methacrylate) conjugates (Figure 4)). An interesting avenue of future work is to determine what attached polymer (and its T_g) is needed in order for it to have a neutral effect (neither speeding nor slowing) on the dye for a given matrix.

Effect of Polymer Length on Conjugate Switching Speed. In the polymer−spiroxazine conjugates with polystyrene and poly(methyl methacrylate), the decoloration kinetics decreased with increasing molecular weight.[19,20] This observation can also be explained using the encapsulation model; the longer the polymer chain, the more efficient the encapsulation of the photochromic dye. In the high-T_g case this should result in slower fades, which is observed experimentally.[19,20,26] However, in the poly(*n*-butyl acrylate) case which is a low-T_g polymer, a more efficient encapsulation would make the local environment around the dye more flexible, and thus faster fades would be expected. As predicted, the $T_{1/2}$ values were observed to decrease from 12 to 5 s as molecular weight of the poly(*n*-butyl acrylate) increased. This fine tuning provides a second level of control over the photochromic behavior. The methodology allows us to create a fast switching photochromic entity in a rigid host matrix by controlling the local environment around the dye. The use of living polymerization allows control over properties such as molecular weight so that finer tuning within a fast decoloration range can be achieved.

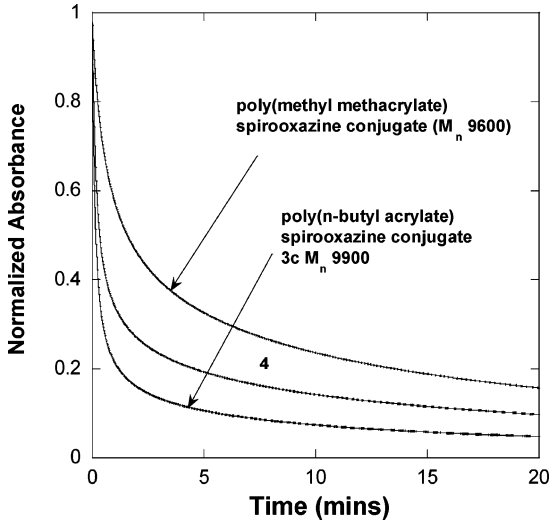


Figure 4. Comparison of decoloration curves for poly(*n*-butyl acrylate) (M_n 9900) and poly(methyl methacrylate) (M_n 9600)[20] spirooxazine conjugates relative to the model compound **4** (in PEGDMA:EBPDMA test lens).

Conclusion

We have shown using a range of polymers that we can tailor photochromic response easily by solely adjusting the characteristics of polymer attached. This methodology allows us to create a fast switching photochromic compound in a rigid host matrix by attaching a low-T_g polymer to the photochromic. Both coarse and fine tuning can be achieved by adjusting first the choice of monomer and second the molecular weight of the polymer. As the controlling oligomers are derived from a common commercial monomers, the modification is relatively cheap. The method has the potential not only for fast fade but also allowing synchronous switching in multidye systems to give a consistent coloration/decoloration without intermediate color shifts. In future work we will examine the technology with other classes of dyes and matrices and also use the living polymerization technique to construct more complex environments around the dye.

Acknowledgment. The authors thank CRC for Polymers for funding this research. T.P.D. is grateful for the award of an Australian Professorial Fellowship from the Australian Research Council.

Supporting Information Available: Details of the regrowth experiment and GPC results. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bouas-Laurent, H.; Durr, H. *Pure Appl. Chem.* **2001**, *73*, 639−665.
(2) Wirnsberger, G.; Scott, B. J.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **2000**, *12*, 1450−1454.
(3) Ribot, F.; Lafuma, A.; Eychenne-Baron, C.; Sanchez, C. *Adv. Mater.* **2002**, *14*, 1496−1499.
(4) Evans, R. A.; Hanley, T. L.; Skidmore, M. A.; Davis, T. P.; Such, G. K.; Yee, L. H.; Ball, G. E.; Lewis, D. A. *Nat. Mater.* **2005**, *4*, 249−253.
(5) Metelitsa, A. V.; Micheau, J. C.; Voloshin, N. A.; Voloshina, E. N.; Minkin, V. I. *J. Phys. Chem. A* **2001**, *105*, 8417−8422.
(6) Metelitsa, A. V.; Lokshin, V.; Micheau, J. C.; Samat, A.; Guglielmetti, R.; Minkin, V. I. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4340−4345.
(7) Krongauz, V. A. In *Photochromism: Molecules and Systems*, 1st ed.; Dürr, H., Bous-Laurent, H., Eds.; Elsevier Science Publishing: Amsterdam, 1990; Vol. 40, pp 793−820.
(8) Such, G. K.; Evans, R. A.; Yee, L. H.; Davis, T. P. *J. Macromol. Sci., Polym. Rev. C* **2003**, *43*, 547−579.
(9) Krongauz, V. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1994**, *246*, 339−346.
(10) Ivanov, A. E.; Eremmev, N. L.; Wahlund, P.-O.; Galaev, I. Y.; Mattissson, B. *Polymer* **2002**, *43*, 3819−3823.
(11) Gonzalez-De Los Santos, E. A.; Lozano-González, M. J.; Johnson, A. F. *J. Photochem. Photobiol. A: Chem.* **1997**, *109*, 259−266.
(12) Schaudel, B.; Guermeur, C.; Sanchez, C.; Nakatani, K.; Delaire, J. A. *J. Mater. Chem.* **1997**, *7*, 61−65.
(13) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(14) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3746.
(15) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379−410.
(16) Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. In *Controlled/Living Radical Polymerisation*; Matyjaszewski, K., Ed.; Oxford University Press: New York, 2000; pp 278−297.
(17) Barner-Kowollik, C.; Davis, T. D.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365−375.
(18) Matyjaszewski, K. *Macromol. Symp.* **2001**, *174*, 51−67.
(19) Such, G.; Evans, R.; Davis, T. *Macromolecules* **2004**, *37*, 9664−9666.
(20) Such, G. K.; Evans, R. A.; Davis, T. P. *Mol. Cryst. Liq. Cryst.* **2005**, *430*, 273−279.
(21) Ichimura, K. *Nat. Mater.* **2005**, *4*, 193−194.
(22) Kakishita, T.; Matsumoto, K.; Kiyotsukuri, T. *J. Heterocycl. Chem.* **1992**, *29*, 1709−1715.
(23) Hutchinson, R. A.; Paquet, D. A., Jr.; McMinn, J. H.; Beuermann, S.; Fuller, R.; Jackson, C. *DECHEMA Monogr.* **1995**, *131*, 467−493.
(24) Shipp, D. A. *J. Macromol. Sci., Polym. Rev.*, in press.
(25) Biteau, J.; Chaput, F.; Boilot, J.-P. *J. Phys. Chem.* **1996**, *100*, 9024−9031.
(26) Evans, R. A.; Such, G. K. *Aust. J. Chem.* **2005**, *58*, 825−830.

MA052002F