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Control of Photochromism through Local Environment Effects Using Living Radical Polymerization (ATRP)

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

CSIRO Molecular Science, 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

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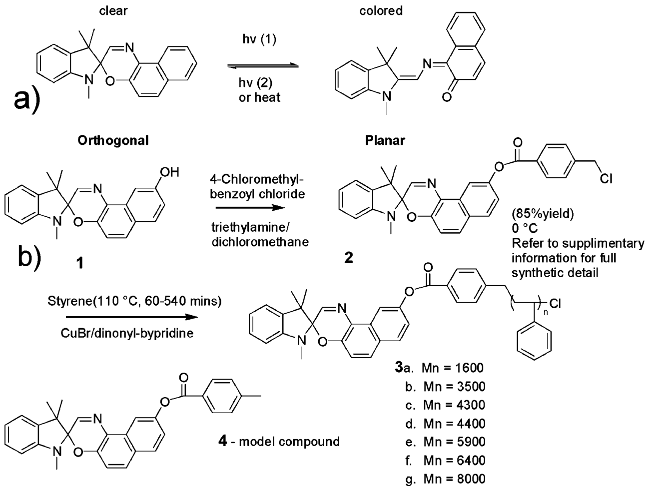
Photochromic materials have been successfully commercialized in the ophthalmic lens industry for application as photosensitive lenses.[1] However, tailoring the design of materials with a specific photochromic response still requires at best a semiempirical research approach. This has hindered the development of more advanced photochromic materials such as data recording, optical switching applications, displays, and nonlinear optical components.[2]

Typically photochromic compounds have been added to a polymer matrix, either by physical dispersion in the polymer matrix[3] or by covalent attachment via the radical copolymerization of a monomer with photochromic functionality.[4] Neither of these approaches permits control over the molecular architecture, molecular weight distribution, or placement of the dye molecule. The aim of our current research is to create a precise molecular environment for photochromic molecules and correlate this to their photophysical responses with the objective of reducing the level of empiricism in this area of material design. Ultimately, the goal is to be able to dial up a designated switching speed without affecting the electronic structure of the dye or the mechanical properties of the host matrix. For example, this ability could be utilized in multidye ophthalmic systems where switching speeds of all dyes must be synchronized to prevent a color shift in the transitions between clear and dark states. Spirooxazines were chosen for this study as they are a key class of photochromic molecules (Scheme 1).[2]

ATRP is one of a handful of living radical polymerization methods that has emerged over the past 10 years.[5−8] Living radical techniques enable the synthesis of polymers with highly defined structure. In this work a spirooxazine-functional halo-initiator capable of initiating an atom transfer radical polymerization (ATRP) was synthesized and used to grow a single polymer chain with controlled molecular weight and polydispersity from a single photochromic molecule. This is the first time the influences of molecular weight of a photochromic−polymer conjugate with precisely known structure on photochromic response have been investigated.

Scheme 1. (a) Photochromic Isomerization of Spirooxazine;[2] (b) Synthesis of Spirooxazine Initiator (2) and Polystyrene−Spirooxazine Conjugates (3)



The hydroxyl spirooxazine **1**[9] was reacted with 4-(chloromethyl)benzoyl chloride to give the photochromic initiator **2** (Scheme 1). Styrene polymer was then grown from the initiator under the following typical procedure: initial reactants were mixed at a 100:1:1:2 ratio of styrene (17.4×10^{-3} mol), spirooxazine initiator (17.4×10^{-5} mol), catalyst (CuBr, 17.4×10^{-5} mol), and ligand (dinonylbipyridine, 34.9×10^{-5} mol). The reactions were degassed using three freeze−thaw cycles on a high-vacuum Schenk line and then polymerized at 110 °C in a constant temperature oil bath. The polymers were purified by precipitation in methanol. Molecular weight and polydispersity of the polymers were obtained using gel permeation chromatography (GPC), calibrated with poly(styrene) standards with tetrahydrofuran as eluent. The polymer conversions were obtained from ^{1}H NMR spectra recorded on a Bruker AC200 spectrometer.

The ATRP behavior of the styrene polymerization initiated from the spirooxazine initiator conformed well to living behavior; molecular weight (M_n) increased linearly with conversion, as shown in Figure 1. The experimental M_n was as predicted although some deviation was observed at long reaction times, which we attribute to some radical loss processes (**3g**). Low polydispersities were obtained. The living nature of the polymerization was confirmed by the chain extension of one of the isolated spirooxazine-initiated polymers. Confirmation of the polymer structure **3** (Scheme 1) was achieved by end-group analysis via NMR spectroscopy with signals of the terminal CH−Cl (4.5 ppm) and the spirooxazine N−CH_3 (2.42 ppm) and geminal CH_3 groups (1.06, 1.23 ppm) clearly observed. Molecular weight calculated using end-group analysis agreed with those obtained by GPC for low molecular weight polymers. The end groups in the higher molecular weight systems were hidden or too broad to allow meaningful molecular weight calculations to be made.

Photochromic analyses were performed on lenses composed of a 1:4 weight ratio of poly(ethylene glycol) 400 dimethacrylate (9G) and 2,2′-bis[4-methacryloxyethoxy]phenyl]propane (Nouryset 110) with 0.4 wt % AIBN. The mol % of the photochromic conjugates was maintained at 1.2×10^{-3} mmol. The photochromic

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[†] CSIRO Molecular Science.

[‡] CRC for Polymers.

[§] The University of New South Wales.

[*] Corresponding authors. E-mail richard.evans@csiro.au and T.Davis@unsw.edu.au.

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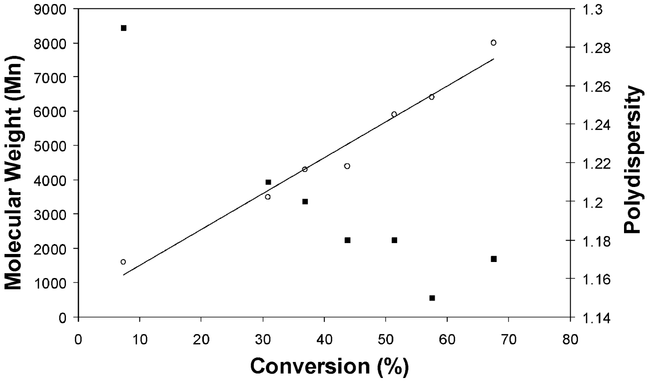

Figure 1. Molecular weight (○) and polydispersity (■) vs time of the atom transfer polymerization of styrene at 110 °C where [styrene]/[CuBr]/[dinonylbipyridine]/[I] = 100:1:2:1. (—) Calculated molecular weight using NMR. Polymerization times were from 60 min (~10% conversion) to 540 min (~70% conversion).

responses (at maximum absorbance ($\lambda_{\max}$) of the colored form, 605 nm) were analyzed on a light table comprised of a Cary 50 spectrophotometer and a 300 W Oriel xenon lamp as the incident light source. The polystyrene–spirooxazine conjugates **3a–g** were dissolved in a standard monomer mix of 9G:Nouryset 110 and cured (80 °C, 8 h) to give clear test lenses. The fact that the lens are clear indicates a good compatibility between the different components.

The photochromic initiator **2** underwent chain transfer reactions yielding covalent bonding within a cross-linked network. This result is consistent with the known propensity of benzyl chlorides to chain transfer. Therefore, **4** was used as the control dye for comparison with the conjugates **3a–g**. Both rates of coloration and decoloration decreased when the molecular weight of the conjugate was increased, as shown in Figure 2. Initiator **2** has the slowest kinetics consistent with its binding to the cross-linked polymer matrix via chain transfer. In contrast, the dye **4** shows the fastest response. It appears that the polystyrene–spirooxazine conjugates are not bonded to the matrix as their kinetics do not approach that of the initiator **2** as the molecular weight decreases, but of the model compound **4**. These results are summarized in Table 1. The decoloration curves were analyzed using the following biexponential equation

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

where $A(t)$ is the optical density at the $\lambda_{\max}$, 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 ∞. This model was used in previous work by Biteau et al.[10] There is a great deal of discussion in photochromic literature on the correct model to fit decoloration;[11] a biexponential has been a commonly used model and appears to fit quite well in this case (R^2 values ~ 0.99). The $t_{1/2}$ value given in Table 1 is a convenient measure of decoloration speed; it refers to the time taken to reach half of the initial absorbance.

The results in Table 1 clearly show control over the decoloration rate has been achieved solely through choice of the length of the polystyrene chain with no modification of dye's electronic structure or to the host polymer needed. Fade speeds ($t_{1/2}$) were tunable from 16 s (**4**) to 49 s (**3g**).

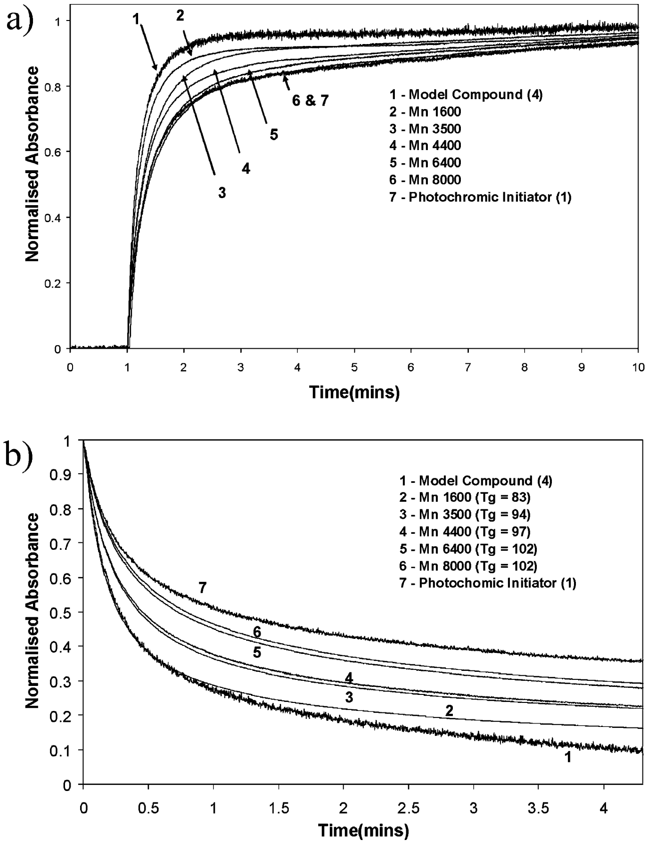

Figure 2. Photophysical investigation of polystyrene–spirooxazine conjugates in 9G:Nouryset 110 lenses where (a) normalized coloration and (b) normalized decoloration. Samples were irradiated for 1000 s (300–400 nm) at 20 °C and monitored at 605 nm.

These experimental results can be interpreted in terms of four factors that govern photochromic response, such as polarity, free volume, rigidity, and direct interactions. In these systems, we assume that altering the chain length of the polystyrene will have a minimal effect on both polarity and free volume (of the bulk polymer). As there is no covalent bonding, we expect any direct interactions to be the same for all of the studied polymers.

We can speculate about the local environment of the photochromic molecule, with the conjugate polymer chain either simply acting as an anchor within the lens matrix or whether it is creating a pseudo-nanoencapsulation of the photochromic, where the local environment is formed by the polymer conjugate excluding the bulk lens matrix. In the former case we would not predict a large molecular weight influence. However, in the latter case the molecular weight can have an effect on chain rigidity (T_g) and thus can have a major influence on the local environment of the photochromic molecule.

More rigid environments are known to retard the photochromic transition.[11] The T_g of the polystyrene–spirooxazine conjugates increase steadily, concomitant with molecular weight as shown in Table 1. This result suggests a link between molecular weight, chain rigidity, and photochromic response for these conjugates, consistent with a pseudo-nanoencapsulation of the photochromic molecules.

We have successfully applied the living radical polymerization technique ATRP to the control of photochromism. ATRP allowed the creation of polystyrene–spirooxazine conjugates consisting of polystyrene of

Table 1. Photophysical Analysis of Polystyrene–Spirooxazine Conjugates in 9G:Nouryset 110 Host Matrix

spirooxazine conjugates	M_n[a]	time[b] (min)	A_0[c]	$t_{1/2}$ (s)	K_1 (min^{-1})	K_2 (min^{-1})	A_1	A_2	A_{th}	T_g (°C)[d]
2			0.83	63	1.13	0.043	0.46	0.26	0.13	
4			0.42	16	5.41	0.57	0.56	0.36	0.07	
3a	1600	60	0.99	16	2.39	0.078	0.63	0.18	0.03	83
3b	3500	180	1.01	26	1.72	0.060	0.59	0.21	0.06	94
3d	4400	300	0.95	28	1.64	0.062	0.57	0.22	0.06	97
3f	6400	420	0.84	44	1.24	0.057	0.53	0.26	0.06	102
3g	8000	540	0.92	49	1.36	0.065	0.51	0.27	0.08	102

[a] Molecular weight determined by GPC using polystyrene standards. [b] Polymerization time of the polystyrene–spirooxazine conjugate. [c] Absorbance of lens sample at maximum coloration time (1000 s). [d] Thermal analyses of polystyrene–spirooxazine conjugates done using a Mettler Toledo DSC821. Samples (10 mg) were heated from 25 to 150 °C at 10 °C/min under nitrogen.

known molecular weight with a single spirooxazine dye attached at the end. Surprisingly, control over the photochromic coloration and fade speeds in a rigid host matrix was achieved solely thorough choice of the size of the polymer conjugate with no modification to the electronic structure of the dye required. As a way of providing a highly localized controlled environment, the new technique we have developed is a generic methodology that should allow control over the switching speeds of other classes of photochromic molecules without affecting the electronic structure or the mechanical properties of the host matrix. In future work we will be investigating low-T_g monomers in an attempt to create rigid bulk systems with fast decoloration. In a broader sense this methodology has the potential to allow control over other nanomechanical molecules in polymers or solutions and this will also be investigated.

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Supporting Information Available: Synthesis and characterization of compounds **2** and **4** and end-group analysis done using NMR spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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