

Controlling Molecular Mobility in Polymer Matrices: Synchronizing Switching Speeds of Multiple Photochromic Dyes

Nino Malic,^{†,‡} Jonathan A. Campbell,^{‡,§} Abdelselam S. Ali,^{†,‡} Mark York,^{†,‡} Asha D'Souza,^{†,‡} and Richard A. Evans^{*,†,‡,#}

[†]CSIRO Materials Science and Engineering, Bag 10, Clayton Victoria 3169 Australia, [‡]The Cooperative Research Centre for Polymers, 8 Redwood Drive, Notting Hill Victoria 3168, Australia, [§]School of Chemical Sciences and Engineering, and [#]Centre of Advance Macromolecular Design, School of Chemical Sciences and Engineering, The University of New South Wales, Sydney New South Wales 2052, Australia

Received May 12, 2010; Revised Manuscript Received August 19, 2010

ABSTRACT: We report a method that allows the facile synchronization of multiple photochromic dyes in a rigid polymer lens matrix together with large increases in their switching speeds. This was achieved by simple chromatographic fractionation of dye-poly(dimethylsiloxane) (PDMS) conjugates to provide tunable switching speeds with longer PDMS tails providing faster switching speeds and shorter tails providing slower switching with no effect on the electronic nature of the dyes. This was done for mono end-functional dye-PDMS conjugates (one dye at one end of the PDMS) and new telechelic dye-PDMS conjugates (one dye at each end of a PDMS oligomer) using a wide variety of academic and commercially important spirooxazines and naphthopyrans (chromenes). Telechelic conjugates gave faster fade performance per unit length of PDMS oligomer (greater atom efficiency) while having superior matrix compatibility. Independent photochromic switching of different photochromic dye-PDMS conjugates within the same lens matrix was demonstrated, resulting in the ability to synchronize coloration and decoloration within multidye systems. The utility of the method was shown by the creation of a neutral colored (gray) lens, produced through the combination of three different colored dye-PDMS conjugates having similar independent fade speed kinetics, and showed exceptional fade performance with good hue maintenance compared to the control lens.

Introduction

The mobility of functional molecules in polymer matrices has found application in the remote determination of glass transition temperature¹ or free volume.² This is because the molecular mobility of the functional molecules determines fluorescence or absorption properties. Photochromic dyes, although not generally thought of or used as molecular probes, are also sensitive to their mobility in polymer matrices.

Photochromic dyes are molecules that display a reversible color change upon exposure to UV light.^{3–5} Currently, the largest commercial use of organic photochromic dyes is within the ophthalmic lens industry.⁶ Photochromic sun lenses darken with exposure to solar UV radiation and return to their colorless state through thermal and photochemical (visible light) processes when the wearer returns indoors. The most common type of photochromic dye used in commercial lenses are 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans (Figure 1), where cleavage of the C(sp³)-O bond and an intramolecular rotation to a quasi-planar conformation with extended pi-conjugation results in highly colored open form isomers (merocyanines).

The photochromic lens market is currently worth in excess of US\$1.7 billion annually in trade sales.⁷ Competition and growing demand has pushed research efforts into ever improving generations of photochromic lens products, with focus on properties such as color, clarity and darkness, coloration and decoloration speeds, hot temperature performance, and durability (fatigue resistance). One of the major requirements of a commercial

*To whom correspondence should be addressed. E-mail: richard. evans@csiro.au.

pubs.acs.org/Macromolecules



Figure 1. Mechanics of photochromism of a 1,3,3-trimethylspiro-[indoline-2,3'-[3H] naphtho[2,1-*b*][1,4]oxazine (top) and 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyran (bottom). Change in structure is accompanied by a significant intramolecular rotation.

photochromic lens product is that it has the ability to switch quickly between a state of having high light transmission (clear form) in the absence of ultraviolet light to a state having low transmission (darkening) under solar irradiation, and vice versa. Current commercial lenses can be said to be adequately fast in their coloration performance. However, their inability to quickly fade back to a colorless state remains a major drawback. The performance of a photochromic lens product is a result of both the inherent characteristics of the dyes which it contains as well as the properties of the lens matrix in which they are incorporated. Scheme 1. Synthesis of Telechelic (A) and Mono End-Functional (B) Photochromic Dye-Poly(Dimethylsiloxane) Conjugates^a



^a Control compounds (C).

Despite there being significant ongoing research into the development of inherently fast-fading photochromic dyes the overwhelming influence over fade-speed, however, is matrix rigidity, of which T_{g} (glass transition temperature) is a primary defining measure. The required mechanical properties of a polymeric lens material being, namely, rigidity and hardness for shatter-proofing and scratch resistance, result in an unfavorable host environment for the necessary mechanics of photochromism to occur (Figure 1). A lack of fluidity and free-volume hinders the intramolecular rotation associated with the photochromic dye switching between colorless and colored states, resulting in a significant slowing of switching performance as the T_{g} is increased.⁸

We have previously reported on the enhancement of photochromic performance (coloration/decoloration kinetics) in rigid polymeric matrices through polymer conjugation.¹⁰⁻¹³ Covalent attachment of low T_{g} polymers directly to the dye provides a soft and mobile local environment for relatively unhindered photochromic switching to occur, with the result being significantly increased fade-speeds without compromise of the mechanical properties of the matrix. Of the various polymers we have tested, poly(dimethylsiloxane) (PDMS) was found to be the most effective, the mono end-functionalized dye-PDMS conjugates providing the largest percentage fade-speed enhancement relative to the corresponding nonconjugated photochromic controls. Results also showed that the conjugates achieve a steady state of coloration, and therefore a higher optical density, far sooner than the controls under the test conditions employed. This method of conjugation also has the advantage of being synthetically uncomplicated and uses cheap and readily available PDMS starting materials, therefore presenting with obvious commercial appeal.

Here we report a method to synchronize the switching speeds of different dyes within the same matrix. This goal has been a major scientific and commercial challenge since most current commercial photochromic lenses use mixtures of several dyes in order to obtain neutral tints of gray and brown. Traditionally, large numbers of photochromic dyes are required to be made in order to find a selection for combination that happen to synchronize in terms of their performance characteristics, such as coloration and decoloration speeds, optical densities (intensity of coloration) at their saturation point, and residual baseline coloration. The result of the incorporation of unsynchronized dyes within a lens matrix is an unappealing cascade of different hues during coloration and decoloration. The patent literature indicates ongoing development efforts into the design and synthesis of novel dyes having optimized properties. Our method¹⁴ allows independent alteration of the switching speeds of dyes (without altering their electronic nature) to readily synchronize multidye systems. This can now allow the combination of exceptional but otherwise unsynchronized dyes. In addition, we also report on new advances in the enhancement of photochromic performance in rigid matrices through the development of new atom efficient telechelic dye-PDMS conjugates (see Scheme 1A). These new telechelic conjugates not only address the issue of fast

coloration and decoloration kinetics but also of matrix compatibility, an important consideration where a high degree of optical clarity is required in the event that high loadings of PDMS– conjugated dyes are needed.

Results and Discussion

1. Synthesis and Fractionation of Photochromic Dye– PDMS Conjugates. It must be appreciated that many stateof-the-art photochromic dyes do not appear in the academic literature but remain relatively hidden in patents. This is a measure of the high economic value good dyes have. To illustrate the broad applicability of our technology, we examined a variety of naphthopyrans (chromenes) and spirooxazines that appear in patents of some of the major lens/photochromic dye producers in addition to some conventional literature dyes.

The synthesis of dye-PDMS conjugates is outlined in Scheme 1 and involves the succinate extension of commercially available hydroxyl end-terminated PDMS followed by conversion to the acid chloride and reaction with a hydroxyl (or secondary amine) functionalized (conjugatable) photochromic dye. Alternatively, the succinate functionalized PDMS may be reacted with the photochromic dye in a one-pot procedure using N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide (EDC) hydrochloride and dimethylaminopyridine (DMAP). Yields are high for both procedures with the latter method producing slightly cleaner products. This is not surprising since the process of producing the acid chloride functionalized PDMS involves the use of oxalyl chloride which generates HCl as a byproduct, known to cleave the siloxane backbone.¹⁵ Despite careful control of reaction conditions (maximum of 30 min reaction time at ambient temperature), a small amount of byproduct is inevitable and is detected as nonpolar front-running material during purification by column chromatography. The use of EDC·HCl/DMAP is a less complicated and milder procedure which avoids the in situ formation of deleterious substances and is preferred. The synthesis of control compounds is also depicted in Scheme 1, which are simply the propionyl ester (or amide) derivatives of the starting hydroxyl (or amine) functionalized photochromic dyes.

The PDMS starting materials used here (MCR-C12 and DMS-C15 from Gelest Inc.) are polydisperse mixtures of dimethylsiloxane oligomers, which range in n_{PDMS} (number of dimethylsiloxane repeat units in polymer chain, as defined in the structures in Scheme 1) from 5 to > 20, as determined by electrospray ionization-mass spectrometry (ESI-MS) analysis. As a result, the photochromic products are mixtures containing conjugates with a range of PDMS chain lengths. Therefore, analysis by ¹H NMR determines values for molecular weight and n_{PDMS} which are averages. In addition, conjugates with different chain lengths have different polarities, conjugates with longer PDMS chains being less polar than conjugates with shorter chains. This polarity difference allows simple fractionation using column chromatography. Paradoxically, high molecular weight conjugates of low polarity move faster through a normal phase silica gel column than do conjugates of lower molecular weight. Therefore, the photochromic product generally elutes as a broad band (Figure S1, Supporting Information). The broadness of this band is influenced also by the polarity of the solvent system (mobile phase) which can be adjusted accordingly. The result of this process is that several fractions can be collected which range in average molecular weight (and n_{PDMS}), from high to low, and have narrower polydispersities. The conjugates were fractionated on a silica gel column, generally eluting with a mixture of diethyl ether and hexane.

2. Photochromic Properties. The PDMS conjugates synthesized, their fractions, and corresponding control compounds are outlined in Table 1. These were incorporated within a standard thermoset lens matrix formulation composed of 4 parts (by weight) ethoxylated Bisphenol A dimethacrylate (EBPDMA, EO/phenol = 1.3), 1 part poly(ethylene glycol) 400 dimethacrylate (PEGDMA) and 0.4 wt % AIBN (radical initiator). The mixtures were added to a mold and thermally cured. The test lenses produced had a thickness of approximately 2 mm and were subjected to kinetic testing using a light table comprising a UV-vis spectrophotometer and an external UV light source. The samples were irradiated with filtered UV light (350-400 nm) for a duration of 1000 s (coloration) at which point the light source was turned off and the sample was further monitored in the dark (decoloration). The temperature of the lens was maintained at 20 °C (see Experimental Section for full details of the testing procedure and equipment). When subjected to UV light irradiation the initially colorless test lens samples become colored. Upon cessation of irradiation, the lenses then spontaneously reverted back to their colorless form. The resulting change in absorbance during this coloration/ decoloration cycle was monitored over time at λ_{max} of the colored form of the photochromic.

Decoloration kinetics were analyzed using the following biexponential equation:

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

where A(t) is the optical density at λ_{max} , A_1 , and A_2 are contributions to the initial optical density A_0 (maximum attained absorbance value at 1000 s UV irradiation), k_1 and k_2 are the rates of the fast and slow components, respectively, and A_{th} is the residual coloration when time approaches infinity. Application of biexponential kinetics provided correlation coefficients > 0.99 in all analyses. This is the most common model used for photochromic analysis and allows comparison to other literature reported values.^{10,16–19} Spectrokinetic data for all compounds tested is presented in Table 2. This table also includes values of $t_{1/2}$ and $t_{3/4}$ which are defined as the time taken for the initial absorbance value (A_0) to be reduced by half and three-quarters, respectively, during decoloration. These latter values are of most commercial concern and are commonly used within the patent literature to define fade-speed performance of photochromic dyes within lens matrices.

The results of kinetic testing show that both the telechelic and mono end-functional photochromic dye–PDMS conjugates provide a significant improvement in fade speed over the nonconjugated control compounds (Table 2).

Our previous studies into the conjugation of free-radical derived oligomers to photochromic dyes also demonstrated an ability to tune fade-speed with changing molecular weight.^{11,12,20-23} Low T_g oligomers, namely, poly(*n*-butyl acrylate) and poly(2-ethylhexyl acrylate), provided fade-speed enhancement as molecular weight increased.^{11,12,20} However, large molecular weights, typically between 3000 and 14 000, were required to show an appreciable improvement and a broad distribution of fade-speed performances. Here we demonstrate that poly(dimethylsiloxane) is a far more efficient polymer for this purpose, with large fade-speed improvements gained from relatively low molecular weight oligomers (approximately between 500 and 1800).

As expected, the highest molecular weight conjugates (having longest PDMS chain) for each photochromic dye provide the largest improvement in fade speed performance, with a decrease of $t_{1/2}$ ranging between 71 and 88% and a

Table 1. Photochromic Dye Functionalized PDMS Conjugates, Nonfractionated Parent Conjugate and Subsequent Fractions with Average Molecular Weights (M_n) and Average Siloxane Repeat Units within PDMS Chain (n_{PDMS}) , and the Corresponding Control Compounds

Dye	PDMS Dye	Dye PDMS	
Tele	chelic Conjugate	Mono End-Functional Conjugate	•
Photochromic Dye	Telechelic Conjugate,	Mono End-Functional	Control
	$M_n (n_{PDMS})$	Conjugate, $M_n (n_{PDMS})$	
	1 (nonfrac), 2384 (12.0)	2 (nonfrac), 1677 (11.4)	
	1a (Fr#1), 3220 (23.2)	2a (Fr#1), 1952 (15.1)	
\rightarrow	1b (Fr#2), 2758 (17.0)	2b (Fr#2), 1588 (10.2)	3
_ 0	1c (Fr#3), 2369 (11.8)	2c (Fr#3), 1365 (7.2)	
	1d (Fr#4), 2126 (8.5)		
	4 (nonfrac), 2286 (13.9)	5 (nonfrac), 1634 (12.2)	
	4a (Fr#1), 3164 (25.8)	5a (Fr#1), 1849 (15.3)	6
$\langle \rangle_{N}$	4b (Fr#2), 2144 (12.0)	5b (Fr#2), 1383 (9.0)	-
X	4c (Fr#3), 1772 (7.0)	5c (Fr#3), 1151 (5.9)	
	7 (nonfrac), 2123 (13.6)	8 (nonfrac), 1550 (12.2)	
	7a (Fr#1), 2830 (23.1)	8a (Fr#1), 1784 (15.4)	9
	7b (Fr#2), 1592 (6.4)	8b (Fr#2), 1381 (9.9)	-
	/b (11/2), 10/2 (0.1)	8c (Fr#3), 1106 (6.2)	
-0/ 1/0-	10 (nonfrac), 2592 (14.1)	11 (nonfrac) $1830(13.1)$	
	10a (Fr#1), 3443 (25.6)	11a (Fr#1), 2461 (21.6)	
	10b (Fr#2), 2749 (16.2)	11b ($Fr#2$) 1949 (14.7)	12
A Love	10c (Fr#3), 2447 (12.2)	116 $(Fr#3)$ 1507 (8.7)	
	10d (Fr#4), 2100 (7.5)	He (111/3), 1507 (0.7)	
-0 0-	13 (nonfrac), 2417 (13.4)	14 (nonfrac), 1716 (12.4)	
DØ	13a (Fr#1), 3236 (24.4)	14a (Fr#1), 2256 (19.7)	
×	13b (Fr#2), 2465 (14.0)	14b (Fr#2), 1981 (15.9)	15
CL or	13c (Fr#3), 2269 (11.4)	14c (Fr#3), 1680 (11.9)	10
\bigcirc	13d (Fr#4), 2101 (9.1)	14d (Fr#4), 1438 (8.6)	
	13e (Fr#5), 2048 (8.4)	14e (Fr#5), 1260 (6.2)	
A AN-	16 (nonfrac), 2402 (14.0)	17 (nonfrac), 1672 (12.2)	
	16a (Fr#1), 2908 (20.8)	17a (Fr#1), 2012 (16.8)	10
	16b (Fr#2), 2293 (12.5)	17b (Fr#2), 1699 (12.6)	10
	16c (Fr#3), 1996 (8.5)	17c (Fr#3), 1430 (8.9)	
	19 (nonfrac), 2588 (13.4)	20 (nonfrac), 1849 (13.0)	
QØ	19a (Fr#1), 2924 (17.9)	20a (Fr#1), 2224 (18.1)	
$\langle \langle \rangle$	19b (Fr#2), 2615 (13.7)	20b (Fr#2), 1893 (13.6)	21
Jono.	19c (Fr#3), 2249 (8.8)	20c (Fr#3), 1650 (10.3)	
\triangleleft	19d (Fr#4), 2045 (6.0)	20d (Fr#4), 1416 (7.2)	
	R =	R =	
	-(CH ₂) ₂ O(CH ₂) ₃ (PDMS)(CH ₂) ₃ O(CH ₂);		
QØ	22 (nonfrac), 1960 (12.8)	23 (nonfrac), 1568 (13.2)	$\mathbf{P} = C\mathbf{H}$
, i	22a (Fr#1), 2969 (26.4)	23a (Fr#1), 1965 (18.5)	24
R R	22b (Fr#2), 2034 (13.8)	23b (Fr#2), 1479 (12.0)	
	22c (Fr#3), 1632 (8.3)	23c (Fr#3), 1185 (8.0)	
	22d (Fr#4), 1465 (6.1)	23d (Fr#4), 1085 (6.6)	
	25 (nonfrac), 2571 (14.1)	26 (nonfrac), 1843 (13.4)	
QD	25a (Fr#1), 3179 (22.3)	26a (Fr#1), 2099 (16.9)	27^{a}
	25b (Fr#2), 2405 (11.9)	26b (Fr#2), 1838 (13.3)	21
	25c (Fr#3), 2213 (9.3)	26c (Fr#3), 1574 (9.8)	

Photochromic Dye	Telechelic Conjugate, $M_n (n_{PDMS})$	Mono End-Functional Conjugate, M _n (n _{PDMS})	Control	
	 28 (nonfrac), 2550 (13.7) 28a (Fr#1), 2623 (23.9) 28b (Fr#2), 2196 (18.1) 	 29 (nonfrac), 1791 (12.7) 29a (Fr#1), 2240 (18.7) 29b (Fr#2), 1904 (14.2) 	30	
N C C C C C C C C C C C C C C C C C C C	28c (Fr#3), 1853 (13.5) 28d (Fr#4), 1550 (9.4)	29c (Fr#3), 1555 (9.5) 29d (Fr#4), 1312 (6.2)		
QQ ^k QQ QQ QQ	35a (Fr#1), 3999 (33.6) 35b (Fr#2), 3221 (23.1)	Not synthesized	36	

Table 1. Continued

^a Commercially available (James Robinson Ltd.) 5-methoxycarbonyl derivative used as control.

decrease in $t_{3/4}$ between 80 and 96%, as compared with the control dyes. The lowest molecular weight conjugates (shortest PDMS chain), while being the slowest of all the fractions, also provide a significant fade speed improvement over the control compounds. Here the reduction in $t_{1/2}$ and $t_{3/4}$ values range between 51 and 76% and 61–86%, respectively, across the range of photochromic dyes tested. These results are reflected in the values for k_1 (fast rate constant) which show a steady increase going from fractions of low to high molecular weight. Interestingly, values for A_0 are generally higher for the conjugates compared to the control compounds, achieving a virtual steady state of coloration far before that of the control whose coloration is generally still on the incline at 1000 s UV irradiation. A further feature to note is that the dye-PDMS conjugates tested here have a significantly lower residual coloration (A_{th}) in the last stages of decoloration in the dark than the corresponding nonconjugated control compounds. In addition, lenses containing the conjugates were also observed to have lower baseline coloration in their fully bleached state.

The relationship between fade speed and the length of PDMS chain is depicted in Figure 2 (Figures S2-S9, Supporting Information). This plot shows that fade speed increases with chain length, with extrapolation of the curves indicating an approach to a limit after which longer PDMS chain lengths will not provide further appreciable fade speed enhancements. We also observe that the fade speed of the nonfractionated conjugate product falls on the curve generated by its corresponding derived fractions. This indicates that polydispersity does not influence fade speed, which is only dependent on average molecular weight. Figure 2 shows the plots of $t_{1/2}$ and $t_{3/4}$ versus chain length (n_{PDMS}) of the naphthopyran functionalized PDMS conjugates 10a-d and 11a-c, which indicate a crossover point at n_{PDMS} ca. 15 and 18, respectively, where shorter PDMS chain lengths of telechelic conjugates perform better at enhancing fade speed than the corresponding mono end-functionalized conjugates. Interestingly, this crossover point is also observed for the series of spirooxazine conjugates 1a-d, 2a-c and 4a-c, 5a-c, although here it is shifted to lower n_{PDMS} values (see Supporting Information). This crossover seems to be a relatively common feature of this conjugation system. However, if we were to plot fade speed versus chain length per dye moiety (Figure 2, bottom plot) then all n_{PDMS} values for telechelic conjugates would essentially be halved, putting

their plots considerably to the left of curves corresponding to mono end-functionalized conjugates. Thus, it can be concluded that telechelic conjugates provide a more atom efficient use of PDMS, with less than half the chain length required to provide the same fade speed enhancement.



3. Matrix Compatibility. The atom efficiency of the telechelic approach provided additional flow-on advantages. Reducing the amount of PDMS required for fade speed enhancement also enhances matrix compatibility. Poly-(dimethylsiloxane) itself is an oily substance that is not very compatible with many lens matrix materials, particularly those of commercial significance. Phase separation of PDMS materials within a lens matrix leads to hazing and blooming, a characteristic obviously undesirable in ophthalmic applications. The PDMS materials used herein are of a relatively low molecular weight (average ca. 1200), and therefore the presence of large organic photochromic moieties (molecular weights ca. 400-550) at the PDMS termini dramatically increases the matrix compatibility of the corresponding conjugates. Of course, two photochromes are better than one in this regard and so telechelic conjugates out-perform mono end-functionalized conjugates (see Figure 3). This appears to be a synergistic kind of relationship where the PDMS provides a rapid switching environment and the dye provides matrix compatibility to the PDMS. Matrix compatibility is particularly an issue where high concentrations of photochromics are required, such as in lens coatings. When

 Table 2. Spectrokinetic Data of the Ambient Thermal Decoloration (Colored Form to Uncolored Form) for All Conjugates and Controls within a Test Lens Matrix Comprised of Ethoxylated Bisphenol A Dimethacrylate (EBPDMA): Poly(ethylene glycol) 400 Dimethacrylate (PEGDMA), (4:1)



colored

uncolored

compound	$t_{1/2}$ (s)	$t_{3/4}$ (s)	A_0	A_1	$k_1 (\mathrm{min}^{-1})$	A_2	$k_2 (\min^{-1})$	$A_{\rm th}$	$conc \ (mol/g)$	λ_{\max} (nm)
1	30	77	1.617	0.803	1.611	0.147	0.126	0.012	$0.6 imes 10^{-6}$	630
1 a	21	50	1.279	0.864	2.165	0.106	0.166	0.007		
1b	24	59	1.292	0.834	1.913	0.121	0.141	0.008		
1c	30	76	1.378	0.804	1.571	0.142	0.122	0.013		
1d	33	93	1.334	0.772	1.470	0.170	0.118	0.014		
2	25	67	1.199	0.803	1.849	0.140	0.122	0.014	1.2×10^{-6}	
2a	22	54	1.134	0.838	2.143	0.127	0.161	0.009		
2b	26	69	1.367	0.790	1.831	0.149	0.127	0.014		
2c	37	120	1.351	0.728	1.362	0.196	0.099	0.023	1.2 10 ⁻⁶	
3	80	343	1.169	0.593	0.892	0.296	0.079	0.05/	1.2×10^{-6}	500
4	16	42	0.802	0.816	3.000	0.134	0.151	0.014	0.6×10^{-5}	590
4a 4b	12	27	0.732	0.907	3.793	0.078	0.175	0.008		
40	10	40 56	0.820	0.823	2.601	0.152	0.102	0.015		
-+C -5	14	34	0.799	0.772	3 420	0.102	0.152	0.013	1.2×10^{-6}	
59	12	27	0.611	0.895	3 841	0.084	0.152	0.012	1.2×10	
5h	17	45	0.838	0.801	2 903	0.143	0.142	0.007		
50	21	71	0.839	0.740	2.303	0.143	0.125	0.023		
6	45	213	0.813	0.618	1 396	0.267	0.093	0.025	1.2×10^{-6}	
7	10	28	1.745	0.792	4.289	0.128	0.102	0.020	0.6×10^{-6}	610
7a	7	14	1.440	0.932	6.986	0.062	0.131	0.009	010 / 10	010
7b	15	55	1.855	0.741	3.050	0.166	0.091	0.027		
8	8	21	1.664	0.810	5.129	0.109	0.125	0.014	1.2×10^{-6}	
8a	7	18	1.842	0.850	6.397	0.093	0.123	0.013		
8b	8	21	1.947	0.827	5.287	0.105	0.117	0.014		
8c	11	37	2.161	0.782	3.945	0.135	0.102	0.019		
9	31	234	1.421	0.559	1.699	0.255	0.070	0.053	1.2×10^{-6}	
10	33	127	0.780	0.748	1.572	0.087	0.008	0.117	0.75×10^{-7}	515
10a	29	89	0.843	0.759	1.750	0.106	0.003	0.082		
10b	32	110	0.841	0.748	1.535	0.101	0.003	0.093		
10c	34	125	0.801	0.735	1.448	0.124	0.003	0.074		
10d	40	190	0.825	0.722	1.260	0.052	0.027	0.167	7	
11	35	151	0.922	0.740	1.455	0.060	0.013	0.148	1.5×10^{-7}	
11a	27	84	0.884	0.746	1.835	0.095	0.003	0.094		
11b	33	130	0.948	0.743	1.512	0.083	0.006	0.118		
11c	41	237	0.927	0.702	1.289	0.064	0.029	0.170		
12	92	1482	0.739	0.562	0.976	0.175	0.069	0.217	1.5×10^{-7}	
13	59	183	0.531	0.781	0.869	0.075	0.039	0.108	0.75×10^{-7}	561
13a	52	139	0.943	0.810	0.970	0.070	0.009	0.084		
130	57	16/	0.794	0.782	0.869	0.061	0.040	0.115		
130	38 62	100	0.883	0.776	0.808	0.061	0.040	0.117		
13u 13o	60	109	0.832	0.705	0.820	0.009	0.039	0.116		
13e 14	56	168	0.827	0.705	0.905	0.137	0.113	0.135	1.5×10^{-7}	
14	50 47	120	0.791	0.770	1.021	0.000	0.042	0.059	1.5 × 10	
14h	47 47	120	0.030	0.839	1 009	0.078	0.015	0.039		
140	53	151	0.879	0.788	0.931	0.052	0.039	0.113		
14d	61	198	0.864	0.718	0.998	0.128	0.119	0.130		
14e	71	255	0.757	0.694	0.899	0.151	0.105	0.131		
15	186	978	0.767	0.626	0.335	0.184	0.023	0.119	1.5×10^{-7}	
16	90	594	0.898	0.638	0.812	0.237	0.038	0.091	0.75×10^{-7}	585
16a	81	483	0.935	0.657	0.871	0.243	0.035	0.069		
16b	92	578	0.827	0.638	0.794	0.246	0.038	0.083		
16c	100	617	0.870	0.633	0.740	0.237	0.040	0.096		
17	93	572	0.778	0.629	0.788	0.239	0.043	0.094	1.5×10^{-7}	
17a	82	518	0.910	0.651	0.863	0.234	0.037	0.082		
17b	93	591	0.890	0.638	0.783	0.233	0.038	0.094		
17c	110	777	0.796	0.611	0.720	0.244	0.041	0.110	-	
18	280	2465	0.735	0.529	0.320	0.255	0.023	0.155	1.5×10^{-7}	
19	99	271	0.894	0.743	0.567	0.161	0.094	0.082	0.75×10^{-7}	567
19a	86	211	0.827	0.782	0.618	0.126	0.125	0.074		
19b	94	240	0.860	0.749	0.580	0.144	0.106	0.084		
19c	105	276	0.842	0.745	0.539	0.168	0.092	0.071		
19d	116	332	0.745	0.704	0.529	0.188	0.085	0.087		

compound	$t_{1/2}$ (s)	$t_{3/4}$ (s)	A_0	A_1	$k_1 ({\rm min}^{-1})$	A_2	$k_2 ({\rm min}^{-1})$	$A_{\rm th}$	conc (mol/g)	λ_{\max} (nm)
20	74	220	0.777	0.723	0.776	0.156	0.101	0.091	1.5×10^{-7}	
20a	69	181	0.920	0.756	0.791	0.136	0.145	0.085		
20b	78	219	0.948	0.733	0.725	0.152	0.111	0.087		
20c	78	225	0.841	0.730	0.727	0.156	0.098	0.084		
20d	107	353	0.795	0.670	0.591	0.202	0.077	0.094		
21	237	908	0.620	0.639	0.241	0.207	0.024	0.080	1.5×10^{-7}	
22	37	104	0.622	0.801	1.311	0.083	0.004	0.076	0.75×10^{-7}	463
22a	34	83	0.602	0.842	1.508	0.090	0.002	0.053		
22b	39	109	0.782	0.802	1.252	0.083	0.004	0.076		
22c	42	120	0.697	0.798	1.156	0.081	0.004	0.080		
22d	42	124	0.607	0.792	1.180	0.049	0.016	0.118	-	
23	28	81	0.769	0.780	1.652	0.114	0.003	0.048	1.5×10^{-7}	
23a	27	72	0.688	0.806	1.772	0.117	0.002	0.035		
23b	29	81	0.784	0.789	1.644	0.115	0.003	0.045		
23c	33	108	0.803	0.774	1.459	0.046	0.020	0.133		
23d	36	128	0.737	0.751	1.396	0.056	0.028	0.138	7	
24	100	547	0.690	0.640	0.714	0.157	0.070	0.169	1.5×10^{-7}	
25	27	105	0.972	0.743	2.067	0.093	0.041	0.124	1.5×10^{-7}	592
25a	22	76	1.114	0.759	2.290	0.102	0.016	0.089		
25b	24	101	1.080	0.740	2.221	0.095	0.039	0.123		
25c	27	135	1.103	0.716	2.047	0.106	0.042	0.129	7	
26	28	129	0.715	0.722	2.000	0.098	0.041	0.132	1.5×10^{-7}	
26a	23	88	0.762	0.738	2.099	0.108	0.013	0.088		
26b	27	123	0.756	0.732	2.032	0.095	0.042	0.132		
26c	32	185	0.729	0.704	1.791	0.109	0.048	0.141	7	
27	105	1326	0.613	0.548	0.837	0.217	0.045	0.173	1.5×10^{-7}	
28	9	31	0.624	0.865	5.461	0.170	0.181	0.018	1.5×10^{-7}	623
28a	7	25	0.982	0.771	7.540	0.159	0.121	0.023		
28b	7	28	0.961	0.760	7.307	0.162	0.117	0.027		
28c	8	35	1.011	0.740	6.282	0.168	0.106	0.028		
28d	9	50	0.920	0.709	4.929	0.180	0.094	0.031	_7	
29	9	34	0.572	0.838	5.437	0.176	0.174	0.021	3.0×10^{-7}	
29a	5	11	0.823	0.861	10.852	0.108	0.264	0.011		
29b	6	17	1.074	0.813	7.955	0.123	0.175	0.016		
29c	7	29	1.117	0.752	5.534	0.139	0.119	0.022		
29d	10	47	1.087	0.701	4.146	0.159	0.097	0.030	7	
30	42	303	0.592	0.557	1.624	0.289	0.085	0.067	3.0×10^{-7}	
35a	39	114	0.929	0.772	1.169	0.138	0.044	0.024	0.75×10^{-7}	615
35b	43	115	0.633	0.798	1.083	0.119	0.040	0.028		
36	114	616	0.842	0.584	0.633	0.256	0.047	0.095	1.5×10^{-7}	

Table 2. Continued

the test lenses were loaded with increasing amounts of a mono end-functionalized (11a) and telechelic (10a) PDMSconjugated naphthopyran, it was the mono end-functionalized conjugate that first phase separated (Figure 3). It must be noted that the concentration of PDMS is quite high and it should not be concluded that the mono end-functionalized conjugate has inherently poor compatibility. Rather, telechelic conjugates should be viewed as having superior compatibility.

To analyze the efficacy of telechelic conjugation versus mono end-functionalization in the reduction of phase separation and hazing the naphthopyran conjugates 10a and 11a and spirooxazine conjugates 7a and 8a were incorporated within a test lens matrix (EBPDMA/PEGDMA) at equimolar dye concentrations and with a very high loading. The lenses were then analyzed using a haze-meter, the results of which are given in Table 3. The most striking result here is of the lens containing conjugate **11a** which shows gross phase separation with a severely reduced transmission and large haze reading compared to the lens containing telechelic conjugate 10a, which remains transparent. Such a large difference is not seen between spirooxazine conjugates 7a and 8a, which is an indicator of the influence of the photochromic end group toward overall matrix compatibility. The relatively low transmittance of telechelic conjugate 10a is a result of the high baseline coloration due to the high loading of photochromic.

Thus, compatibility of the PDMS conjugates is influenced by loading, molecular weight, type of photochromic agents, and the geometry of the conjugate. If an issue of phase separation arises, then we have shown that telechelic PDMS conjugates have superior compatibility to the mono-end functional geometry with minimal impact on switching speeds.

4. Independent Switching in Multiple Photochromic Dye Conjugate Systems. The haze associated with the incompatibility of PDMS within matrix materials arises from the phase separation of the polymer, forming aggregates of sufficient size to cause light scattering. As demonstrated in the previous section, sufficient loading of the photochromic dye–PDMS conjugates may result in such phase separation. The question still arises, however, as to whether aggregation still occurs at lower concentrations where no hazing is visible, where aggregates are not sufficiently large to scatter visible light. We postulated that aggregation of different dye–PDMS conjugates having different chain lengths could affect each others kinetic performance, conjugates with long chains may have their kinetic performance slowed on aggregation with shorter chained conjugates, and vice versa.

For PDMS conjugation to be of practical use in the tuning of coloration and decoloration speeds of different dyes, applicable to commercial multidye lens systems with neutral tints, the individual conjugate components must act independently of one another. We devised a test to determine the independence of performance which involved the incorporation of conjugate **13e** within the test lens matrix formulation together with varying amounts of a nonphotochromic model compound **33** (Table 4). This latter compound was synthesized in order to replicate the presence of a second conjugate,



Figure 2. Plots of $t_{1/2}$ and $t_{3/4}$ versus n_{PDMS} (top and middle) for naphthopyran-PDMS conjugates **10**, **10a**–**d** (telechelic conjugates) and **11**, **11a**–**c** (mono end-functionalized conjugates). Plot of $t_{1/2}$ versus n_{PDMS} per dye moiety (bottom), indicating telechelic conjugates to be a far more atom efficient use of PDMS for fade speed enhancement.

both chemically and sterically, but without having an absorption in the visible spectrum. This allowed the accurate analysis of fade speed performance of only the photochromic conjugate by eliminating interference from a second source of variable absorption (a second photochromic). The synthesis of the model compound **33** (Scheme 2) involved the hydrogenation of the pyran double bond of an actual photochromic dye, **31**, producing a colorless and nonphotochromic analogue **32**, which was subsequently conjugated to PDMS and then fractionated. The highest molecular weight fraction ($n_{\text{PDMS}} = 22.3$) was chosen in an attempt to increase the fade speed performance of the low molecular weight photochromic conjugate **13e** ($n_{\text{PDMS}} = 8.4$). The results in Table 4 show no change in decoloration performance between the control test lens containing



Figure 3. Haze test, showing mono end-functional dye–PDMS conjugate **11a** (left) and telechelic conjugate **10a** (right) incorporated within a test lens formulation, ethoxylated bisphenol A dimethacrylate (EBPDMA): poly(ethylene glycol) 400 dimethacrylate (PEGDMA), (4:1), at a high equimolar concentration $(1.975 \times 10^{-5} \text{ mol/g}_{matrix}$ with respect to the photochromic moiety).

Table 3. Haze-Meter Testing of Highly Loaded Lenses Containing Equimolar Quantities (With Respect to Photochromic Moiety) of Telechelic and Mono End-Functionalized Photochromic Dye-PDMS Conjugates

conjugate	concentration (mol/g)	transmittance, %	haze
blank lens	$\begin{array}{c} 0.988 \times 10^{-5} \\ 1.975 \times 10^{-5} \\ 2.0 \times 10^{-5} \\ 1.0 \times 10^{-5} \end{array}$	85.3	2.00
10a		62.9	7.52
11a		33.5	43.5
7a		78.4	4.09
8a		73.0	10.3

Table 4. Decoloration Performance of Photochromic Conjugate 13e $(n_{\rm PDMS} = 8.4)$ in Test Lens Matrix (EBPDMA/PEGDMA) Con-
taining Varying Amounts of Non-Photochromic Model Compound 33 $(n_{\rm PDMS} = 22.3)$

entry	photochromic conjugate, 13e (molar equiv) ^a	non-photochromic conjugate, 33 (molar equiv)	$A_0^{\ b}$	<i>t</i> _{1/2} (s)	t _{3/4} (s)
1	1	0	0.21	74	241
2	1	2	0.21	72	233
3	1	4	0.19	69	222
4	1	8	0.20	72	234
5	1	16	0.19	71	229
			0		

^{*a*}Conjugate conc (1 molar equiv) = 1.88×10^{-8} mol/g (dye conc = 3.75×10^{-8} mol/g). ^{*b*} Absorption at 1000 s UV irradiation.

Scheme 2. Synthesis of the Non-Photochromic Model Telechelic PDMS Conjugate



only the photochromic conjugate (entry 1) and the lenses containing the model conjugate up to 16 mol equiv with respect



Figure 4. Plots of the range of $t_{1/2}$ values of each photochromic dye conjugate system tested in a rigid polymer matrix, indicating (i) fade speed enhancement due to PDMS conjugation to the dye, and (ii) potential for synchronization in multidye systems where overlap is observed.

to 13e (entries 2–5), with $t_{1/2}$ and $t_{3/4}$ values remaining uniform. This indicates that photochromic conjugate 13e is not affected by the presence of a second conjugate, at least at the concentrations tested.

The same experiment was also performed with mono endfunctionalized dye–PDMS conjugate **11c** ($n_{PDMS} = 8.7$), but at two different concentrations (Table S1, Supporting Information). In this case, we also observe that the fade performance of **11c** remains uniform across the whole range of concentrations used, once again indicating independent kinetic performance of the photochromic. Therefore, fade speed matching of different dye–PDMS conjugates via the process of fractionation is indeed feasible.

5. Synchronized Switching in Multiple Photochromic Dye Conjugate Systems. We further tested the system by incorporating two different photochromic conjugates with almost identical kinetic performance within the same lens. The choice of two different and synchronized photochromic conjugates for

this purpose was facilitated by plotting the range of $t_{1/2}$ values obtained for each photochromic dye system (both mono endfunctional and telechelic) as seen in Figure 4. (Note: these ranges are not absolute, as the extremities of each range may be extended by the use of shorter and longer PDMS oligomers than was used herein.) Plots for the ranges of $t_{3/4}$ values are included in the Supporting Information (Figure S10). An overlap in the range of $t_{1/2}$ and $t_{3/4}$ values indicates the potential for synchronization. From analysis of these plots and the kinetic fade data of the various fractions of dyes 14 and 22 it was clear that mono end-functional conjugate 14b ($n_{PDMS} = 15.9$) and telechelic conjugate **22d** ($n_{PDMS} = 6.1$) had similar switching speeds with $t_{1/2}$ values of 47 and 42 s and $t_{3/4}$ values of 122 and 124 s, respectively. Additionally, the λ_{max} values of each dye conjugate (560 and 463 nm, respectively) are sufficiently different so when combined would produce a lens having a broad absorption in the visible spectrum upon UV irradiation. The superimposed normalized kinetic plots of both dye conjugates in separate lenses are shown in Figure 5, which indicates very good synchronicity during coloration and decoloration. A slight deviation is seen after the $t_{3/4}$ point of decoloration and is mainly due to a difference in the residual coloration (A_{th}) of each conjugate. In contrast, when the kinetic plots of the corresponding control compounds, **15** and **24**, are superimposed there is an obvious mismatch (Figure S11, Supporting Information), as is also indicated by their values for $t_{1/2}$ (236 vs. 100 s) and $t_{3/4}$ (908 vs. 547 s), respectively.

Conjugates 14b (purple, $\lambda_{max} = 560 \text{ nm}$) and 22d (orange, $\lambda_{\text{max}} = 463 \text{ nm}$) were then combined in the same lens matrix at a molar ratio of 0.5:1.25, respectively, producing an effective dye ratio of 1:1.25. The lens was analyzed by recording the entire visible spectrum at intervals of 30 s during both coloration and decoloration in the dark (Figure 5, middle plots). Synchronization was then evaluated by plotting the normalized absorption values at the wavelengths of 560 and 463 nm (λ_{max} values of the individual dye components) versus time (Figure 5, bottom plot), which indeed shows an even change in absorption across the visible spectrum with no color shift during coloration and until after the $t_{3/4}$ point of decoloration. This plot is an almost identical replication of the plot of the superimposed kinetic profiles of each individual dye component (Figure 5, top). A photographic illustration of this lens during decoloration under indoor ambient lighting conditions is shown in Figure 6 (left lens) and shows a fast and very uniform color fade to the naked eye.

The decoloration process can be both thermally driven or photoinduced (usually by intense visible light). Decoloration in these experiments was monitored in the dark to allow evaluation of challenging and commercially critical thermal decoloration reactions. The persistence of color of approximately 0.15-0.25 absorbance units (Figures 5, S10, S11, and S12, Supporting Information) is due to the presence of a minor and relatively thermally stable isomer of the open (colored) form of the respective dyes. This is a typical characteristic of these types of 2*H*-naphthopyrans and indeed of other chromene photochromic compounds.^{12,24–28} Therefore, under normal indoor ambient lighting conditions the test samples would and do continue to slowly decolorize.

The two corresponding nonsynchronized control compounds, 15 and 24, were also incorporated together in a test lens matrix as a comparison. As expected, the decoloration process was far slower and an uneven change in absorbance at 463 and 560 nm was observed (Figure S12, Supporting Information). Despite the individual kinetics of these two nonconjugated control compounds being nonsynchronized, as depicted in Figure S11 (Supporting Information), when combined in the same matrix the change in absorption at the corresponding wavelengths of maximum absorption of the individual dyes is not as stark (Figure S12, Supporting Information). This is most probably due to the overlap of the absorbances of each dye in the visible region, which seems to have a "smoothing" effect on the overall decoloration across the broader (combined) absorption profile. The smoothing effect can be explained by the individual orangecolored dye 24 not having an appreciable absorption at 560 nm (the absorption maximum of the purple colored dye 15), whereas both purple dye 15 and orange dye 24 absorb light at 463 nm (the absorption maximum of orange dye 24). So monitoring the change in absorption at 560 nm will essentially be free from the influence of the orange dye and monitoring at 463 nm will produce a kinetic profile that results from the combined influences of both dyes. In effect, since the purple dye is the slower of the two the change in absorbance at 463 nm is thus also slowed when compared to the



Figure 5. Superimposed kinetic profiles of coloration (60-1000 s) and decoloration (1000 s onward) of individual synchronized "speed-matched" photochromic dye–PDMS conjugates **14b** and **22d** (top); visible spectrum at 30 s intervals during coloration and decoloration (middle plots) of lens containing combination of **14b** (purple, $\lambda_{max} = 560 \text{ nm}$) and **22d** (orange, $\lambda_{max} = 463 \text{ nm}$) conjugates with synchronized switching performance, of which the absorbance values at 463 and 560 nm are plotted versus time (bottom plot).



Figure 6. Test lenses at intervals during decoloration. Left lens: combined synchronized "speed-matched" photochromic dye–PDMS conjugates 14b and 22d (fast and synchronized switching). Middle lens: combined nonsynchronized dyes 14b (purple dye–PDMS conjugate) and 24 (orange non-PDMS conjugated control dye). Right lens: nonsynchronized, non-PDMS conjugated control dyes 15 and 24.

individual kinetics of the orange dye. A photographic illustration of this lens during decoloration under indoor ambient lighting conditions is shown in Figure 6 (right lens) and shows a slow but fairly uniform color fade to the naked eye.

To further demonstrate the effects of the combination of nonsynchronized photochromes the control compound **24** (orange, $\lambda_{\text{max}} = 463 \text{ nm}, t_{1/2} = 100 \text{ s}, t_{3/4} = 547 \text{ s}$) was now incorporated with the faster conjugate **14b** (purple, $\lambda_{\text{max}} = 560 \text{ nm}, t_{1/2} = 47 \text{ s},$ $t_{3/4} = 122 \text{ s}$) within the test lens matrix, as an exaggerated example. The visible spectrum was once again recorded at 30 s intervals during coloration and decoloration and the absorbance at 560 and 463 nm plotted over time. Figure 7 (bottom plot) shows the absorbance at 560 nm increasing and decreasing much faster than at 463 nm. (For comparison purposes, the top plot of Figure 7 shows the superimposed kinetic plots of the



Figure 7. Top: Superimposed individual kinetic plots of nonsynchronized dyes 14b (purple dye–PDMS conjugate) and 24 (orange non-PDMS conjugated control dye) within test lens (EBPDMA/PEGDMA, 4:1). Bottom: Monitoring of color development and decoloration in the dark of lens sample containing combined nonsynchronized dyes 14b and 24. Absorbance readings taken at 560 and 463 nm (λ_{max} values of the individual dye components, respectively) from visible spectrum recorded at 30 s intervals.

individual dye components in separate lenses, which mirrors that of the bottom plot corresponding to the lens containing the combined dyes). Physical examination of the lens when exposed to sunlight saw an initial purple color develop due to the faster conjugate **14b**. This was followed by a red-brown as the lens approached its steady state of coloration. Conversely, a yellowing of the lens was observed during decoloration, as the absorbance of the purple colored conjugate, **14b**, decreased at a faster rate than the orange-colored control compound, **24**. The yellowing can clearly be seen in the photographic illustration, Figure 6 (middle lens).

As mentioned previously, several different colored photochromic dyes are usually included in commercial lenses in order to achieve tints of gray or brown, which is acceptable to the consumer. We also have been successful in achieving a neutral gray coloration in our standard test lens formulation by the combination of three dyes (Figure S13, Supporting Information). Conjugation of these three dyes to PDMS, each of different length, allowed us to significantly enhance and synchronize their coloration and decoloration performance compared to that of a control lens containing the same photochromes in their non-PDMS conjugated form. The conjugates 22c, 14b, and 35b were combined in a ratio of 1.25:0.6:1.0 (with respect to the dye moieties), with the blue conjugate **35b** incorporated at a concentration of 0.75×10^{-10} mol/g (effective dye concentration of 1.5×10^{-7} mol/g). The control dyes 24, 25, and 36 were combined in a test lens at the



Figure 8. Decoloration under ambient lighting conditions of fast and synchronized gray colored lens system containing 3 dye–PDMS conjugates (22c, 14b, and 35b, right), versus 3 dye control lens (contains 24, 25, and 36, left).

same ratio. Figure 8 shows the decoloration of both the fast synchronized gray lens (right) and the control lens (left) under ambient lighting conditions.

The two major component dyes in the control lens, **24** (orange) and **36** (blue), coincidentally have very similar fade speed performance, as can be seen from their $t_{1/2}$ and $t_{3/4}$ values (Table 2 and Figure S13, Supporting Information). The resulting gray control lens thus maintains a fairly even neutral hue upon decoloration but is very slow. The very different chain lengths of PDMS required to synchronize the switching performance upon conjugation, orange-colored **22c** has $n_{\text{PDMS}} = 8.3$ versus **35b** having $n_{\text{PDMS}} = 23.1$, demonstrates that every dye is affected differently by conjugation and local environment within the matrix.

The visible spectrum of the gray lens, containing three synchronized dyes, at the point of maximum coloration (1000 s UV irradiation), is included in the Supporting Information (Figure S14, black line). Its gray coloration is

due to the broad and fairly even absorbance across the visible range. The visible absorbance spectra of each individual dye component are also included, with intensities adjusted to approximate each contribution based on concentration (ratio) and optical densities at 1000 s UV irradiation (orange, purple, and blue lines).

Concluding Remarks

This report demonstrated (1) the ability to enhance and tune the coloration and fade speed of photochromic dyes through conjugation to PDMS and fractionation to give a range of conjugate molecular weights (differing average PDMS chain lengths), (2) synchronization of switching speeds of different dyes through the PDMS conjugation and fractionation process, and (3) a more atom efficient method of functionalizing photochromic dyes with PDMS through the use of telechelic PDMS. The fractionation method worked for both telechelic and mono endfunctional PDMS-dye conjugates. As evidenced in Table 2 and Figure 2, fractionation allows the ability to tune the fade speed performance of a photochromic dye within a rigid polymeric matrix, with a clear trend of longer PDMS chain lengths providing faster switching than shorter chain lengths. This process has obvious commercial significance in that many currently available lenses contain mixtures of different colored dyes to produce neutral tints of gray and brown. The individual kinetics of these dyes must be virtually identical to avoid a change in hue during coloration and decoloration. It is not common that a single photochromic dye has all the necessary characteristics required to produce a photochromic lens article with desirable properties, namely, fast coloration/decoloration kinetics in a polymeric matrix, low coloration in the absence of UV light, high coloration during solar irradiation, good fatigue resistance as well as a neutral tint. Therefore, research into the synthesis and discovery of novel photochromic dyes with favorable properties is ongoing. Synchronization between dyes becomes increasingly important as the absolute switching speed increases. A difference of 50 s between two dyes may be acceptable in dyes with $t_{1/2}$ of 250 and 300 s but unacceptable when PDMS conjugation drops the $t_{1/2}$ to only 50 and 100 s. Thus, as products strive toward increasingly faster photochromic transitions in optical lenses the capacity to synchronize dyes becomes essential. It can be seen in this report how PDMS conjugation and fractionation may be employed as a means of both increasing switching speeds and matching two or more dyes that would otherwise not be synchronized, thus opening up further possibilities in advancements over current photochromic lens technology. This methodology would be applicable to other molecules whose functionality depended on their molecular mobility, such as fluorescent or color glass transition (T_g) probes¹ and free volume probes.²

Experimental Section

Materials and Methods. Hydroxy-terminated poly(dimethylsiloxane) starting materials were purchased from Gelest, Inc. All other reagents were purchased from Aldrich and used as supplied, unless stated otherwise. Synthesis procedures for all other conjugatable photochromic dye starting materials can be found in the Supporting Information. Mono end-functional photochromic dye–poly(dimethylsiloxane) conjugates (2, 5, 8, 11, 14, 17, 20, 23, 26, 29) and control compounds (3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 36) were synthesized using identical reaction conditions to those described elsewhere.¹³ The general synthesis procedure for telechelic photochromic dye–PDMS conjugates (two methods) is outlined below using 1 and 4 as examples. Details for all other telechelic and mono end-functional conjugates synthesized can be found in the Supporting Information.

General Experimental Measurements. ¹H (400 MHz/200 MHz) and ¹³C (100 MHz/50 MHz) NMR spectra were obtained

with a Bruker AV400 or a Bruker AC200 spectrometer at 25 °C. Spectra were recorded for samples dissolved in deuterated solvent, and chemical shifts are reported in parts per million from external tetramethylsilane and J values are given in Hz. Positive ion EI mass spectra were run on a ThermoQuest MAT95XL mass spectrometer using ionization energy of 70 eV. Accurate mass measurements were obtained with a high resolution of 5000-10000 using PerFluoroKerosene (PFK) as the reference sample. Positive and negative ion electrospray mass spectra (ESI-MS) were acquired with a VG Platform mass spectrometer using a cone voltage of 50 V with the source maintained at 80 °C. Methanol was used as solvent system with a flow rate of 0.04 mL min⁻¹. Molecular weights of PDMS were obtained from ¹H NMR spectra from integration values of SiCH₂ resonances along the backbone with respect to those of Si(CH₃)₂. Final molecular weights of dye-PDMS conjugates were additionally confirmed from integration of characteristic dye end groups. Photochromic analyses were performed on lenses containing photochromic materials at doping concentrations chosen in order to maintain optical densities in a meaningful detector range during photochromic kinetic tests (refer to Table 2). The fabrication and composition of test lenses are outlined within the main body text. Under continuous irradiation, the photochromic responses of the lenses were analyzed on a light table comprising a Cary 50 UV-vis spectrophotometer to measure absorbance values and a 160 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 maintained at 20 °C and monitored at the maximum absorbance of their colored form for a period of 1000 s. Then the thermal decoloration was monitored in the dark for a further 2400 s (minimum).

General Synthesis of Telechelic Photochromic Dye-PDMS Conjugates.



Carboxylic Acid-Terminated Poly(dimethylsiloxane), n =13.5. Hydroxyethoxypropyl-terminated poly(dimethylsiloxane) (Gelest, DMS-C15, Average MW (¹H NMR): ca. 1246) (20.0 g, 16.05 mmol) was added to dry dichloromethane (80 mL) together with succinic anhydride (3.885 g, 38.52 mmol) and then triethylamine (3.90 g, 38.52 mmol, 5.36 mL). The mixture was stirred at ambient temperature for 4 h and then at reflux for a further 20 min, under nitrogen. Triethyleneglycol monomethyl ether (1.1 mL) was added and the mixture was stirred at ambient temperature for 1 h. The solvent was evaporated and the residue was dissolved in diethyl ether/hexane (1:1), washed with 0.5 M HCl, and dried with MgSO₄. The solution was slowly passed through a short silica gel column, further eluting with diethyl ether. The solvent was evaporated in vacuo to give the pure product as a clear viscous oil (23.2 g, yield: quantitative). ¹H NMR (400 MHz, CDCl₃) δ 4.25 (t, J = 4.8 Hz, 4H, CH₂-5), 3.63 $(t, J = 4.8 \text{ Hz}, 4\text{H}, \text{CH}_2-4), 3.42 (t, J = 7.0 \text{ Hz}, 4\text{H}, \text{CH}_2-3), 2.67$ (m, 8H, CH₂-6,7), 1.61 (m, 4H, CH₂-2), 0.52 (m, 4H, CH₂-1), 0.04-0.08 (m, approximately 85H, SiCH₃). Refer to the graphic above for corresponding numbering system used in NMR assignments.

Acid Chloride-Terminated Poly(dimethylsiloxane). Carboxylic acid-terminated poly(dimethylsiloxane) (1.50 g, 1.04 mmol) was added to anhydrous diethyl ether (10 mL) together with 1 small drop of DMF via syringe. Oxalyl chloride (0.53 g, 4.18 mmol, 0.36 mL) was added in one portion and the mixture was stirred at ambient temperature, under nitrogen, for no longer than 30 min. A slow nitrogen flow was maintained over the reaction mixture by means of a syringe needle through a rubber septum, with a slight positive pressure. The solvent and excess reagent was then evaporated in vacuo. Residual oxalyl chloride and HCl was removed by dissolution in dichloromethane and reevaporation of solvent. The oily product was then used immediately. This material cannot be stored for extended periods as residual HCl degrades the siloxane polymer.



Telechelic Poly(dimethylsiloxane) Conjugated 1.3-Dihydro-1isobutyl-3,3-dimethyl-6'-(4-(N-ethyl, N-(2-hydroxyethyl)amino)phenyl)-spiro[2H-indole-2,2'[2H]naphtha[1,2-b][1,4]oxazine], 1. Method A. Carboxylic acid-terminated poly(dimethylsiloxane) (0.627 g, 0.428 mmol), EDC·HCl (0.214 g, 1.114 mmol), 4-dimethylaminopyridine (0.105 g, 0.856 mmol), and 1,3-dihydro-1-isobutyl-3,3-dimethyl-6'-(4-(N-ethyl, N-(2-hydroxyethyl)amino)phenyl)-spiro[2H-indole-2,2'[2H]naphtha[1,2-b][1,4]oxazine] (0.457 g, 0.856 mmol) were combined in dry CH₂Cl₂ (15 mL) under a nitrogen atmosphere and stirred at room temperature overnight. The solvent was evaporated in vacuo and the residue was purified by column chromatography eluting with 0-20%EtOAc/petroleum ether to give the product as a green oil (0.97 g,95%). This material was then fractionated by column chromatography using the same solvent system. Average molecular weights (M_n) were determined by ¹H NMR analysis. Nonfractionated product, 1: $M_n = 2384$ ($n_{PDMS} = 12.0$). Fraction 1, 1a: $M_n = 3213$ ($n_{PDMS} = 23.2$). Fraction 2, 1b: $M_n = 2710$ ($n_{PDMS} =$ 17.0). Fraction 3, **1c**: $M_n = 2,359 (n_{PDMS} = 11.8)$. Fraction 4, **1d**: $M_n = 1829 (n_{PDMS} = 8.5)$. ¹H NMR (Fraction 3, **1c**; 400 MHz, CDCl₃) & 8.05-7.91 (m, 4H), 7.72 (s, 2H), 7.45 (s, 2H), 7.40-7.33 (m, 8H), 7.21 (dt, J=7.7, 1.2 Hz, 2H), 7.09 (dd, J=7.3, 0.9 Hz, 2H), 6.89 (dt, J = 7.5, 0.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 4H), 6.61 (d, J = 7.8 Hz, 2H), 4.33 (t, J = 6.5 Hz, 4H, CH₂-8), 4.24 (m, 4H, CH₂-5), 3.65-3.61 (m, 8H, CH₂-4,9), 3.48 (q, J = 7.0Hz, 4H, CH₂-10), 3.42 (t, J = 7.1 Hz, 4H, CH₂-3), 2.98 (ddd, J = 23.4, 14.5, 7.6 Hz, 4H, isobutyl-CH₂), 2.71–2.64 (m, 8H, CH₂-6,7), 2.12-2.06 (m, 2H, isobutyl-CH), 1.68-1.58 (m, 4H, CH₂-2), 1.39 (2 \times s, 12H, spirooxazine geminal-CH₃), 1.25 (m, 6H, ethyl-CH₃), 0.98 (d, J = 6.6 Hz, 6H, isobutyl-CH₃), 0.92 $(d, J = 6.7 \text{ Hz}, 6\text{H}, \text{ isobutyl-CH}_3), 0.55-0.49 \text{ (m, 4H, CH}_2-1),$ 0.10-0.04 (m, 76H, SiCH₃) ppm. Refer to graphic above for corresponding numbering system used in NMR assignments.



Telechelic Poly(dimethylsiloxane) Conjugated 6'-Piperazine-1,3,3-trimethylspiro[indoline-2,3'-[3H] naphtho[2,1-b][1,4]-oxazine], 4. Method B. 6'-Piperazine-1,3,3-trimethylspiro[indoline-2,3'-[3H] naphtho[2,1-b][1,4]-oxazine]²⁹ (0.25 g, 0.61 mmol) was dissolved in anhydrous diethyl ether (ca. 20 mL), under nitrogen, with triethylamine (0.25 mL). Acid chloride terminated poly-(dimethylsiloxane) (0.446 g, 0.303 mmol) was then added dropwise and the mixture was stirred at room temperature for 1 h. The whole reaction mixture was passed through a plug of silica gel, eluting with diethyl ether and finally ethyl acetate. The solvent was evaporated to give the pure product as a purple tar (0.60 g). A sample of the material was then fractionated by column chromatography (silica gel, diethyl ether/hexane, 4:1). Average molecular weights (M_n) were determined by ¹H NMR analysis. Nonfractionated product, 4: $M_n = 2286 (n_{PDMS} = 13.9)$. Fraction 1, **4a**: $M_n = 3164 (n_{PDMS} = 25.8)$. Fraction 2, **4b**: $M_n = 2144 (n_{PDMS} = 2144)$ 12.0). Fraction 3, **4c**: $M_{\rm n} = 1772 (n_{\rm PDMS} = 7.0)$. ¹H NMR (nonfractionated material, 4; 400 MHz, acetone- d_6) δ 8.59 (d, J = 8.3 Hz, 2H), 8.15 (d, J = 8.4 Hz, 2H), 7.71 (s, 2H), 7.57 (t, J = 7.3 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 7.7 Hz, 2H), 7.13 (d, J = 7.2Hz, 2H), 6.86 (t, J = 7.4 Hz, 2H), 6.66 (s, 2H), 6.63 (d, J = 7.7 Hz, 2H), 4.16 (t, J = 4.8 Hz, 4H, CH₂-5), 3.80 (s br, 8H, piperazine-H), $3.60 (t, J = 4.8 Hz, 4H, CH_2-4), 3.43 (t, J = 6.7 Hz, 4H, CH_2-3),$ $3.07 (d br, 8H, piperazine-H), 2.74 (s br, 6H, NCH_3), 2.69 (t br, J =$ 6.3 Hz, 4H, CH₂-7), 2.60 (t br, J = 6.3 Hz, 4H, CH₂-6), 1.61 (m, 4H, CH₂-2), 1.34 ($2 \times$ s overlap, 12H, spirooxazine geminal-CH₃), 0.59 (m, 4H, CH₂-1), 0.09-0.13 (m, approximately 88H, SiCH₃) ppm. Refer to graphic above for corresponding numbering system used in NMR assignments.

Acknowledgment. We like to thank the CRC for Polymers, Advanced Polymerik and CSIRO Molecular and Health Technologies for supporting this work.

Supporting Information Available: Synthesis procedures for photochromic dye starting materials and corresponding PDMS conjugates, characterization data, plots of fade speed ($t_{1/2}$ and $t_{3/4}$) versus chain length (n_{PDMS}), kinetic plots (absorbance versus time), absorbance spectra and figures relevant to text. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

- Jager, W. F.; van den Berg, O.; Picken, S. J. Macromol. Symp. 2005, 230, 11–19.
- (2) Jansen, J. C.; Macchione, M.; Tocci, E.; De Lorenzo, L.; Yampolskii, Y. P.; Sanfirova, O.; Shantarovich, V. P.; Heuchel, M.; Hofmann, D.; Drioli, E. *Macromolecules* **2009**, *42*, 7589–7604.
- Photochromism: Molecules and Systems; Bouas-Laurent, H.; Dürr, H., Eds.; Elsevier: Amsterdam, 1990.
- (4) van Gemert, B. In Organic Photochromic and Thermochromic Compounds; Crano, J.; Gugliemetti, R., Eds.; Plenum Press: New York, 1998; Vol. 1, pp 111.
- (5) Lokshin, V.; Samat, A.; Metelitsa, A. V. Russ. Chem. Rev. 2002, 71, 893–916.
- (6) Corns, S. N.; Partington, S. M.; Towns, A. D. Color. Technol. 2009, 125, 249–261.

- (7) Extrapolated from data contained in *Eyeglasses Global Strategic Business Report*; Global Industry Analysts, Inc.: San Jose, CA, March 2008.
- (8) Such, G.; Evans, R.; Yee, L.; Davis, T. J. Macromol. Sci., C: Polym. Rev. 2003, 43, 547–579.
- (9) Krongauz, V. A. Environmental Effects on Organic Photochromic Systems, 1st ed.; Elsevier: Amsterdam, 1990; Vol. 40, pp 793–821.
- (10) 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.
- (11) Such, G. K.; Evans, R. A.; Davis, T. P. *Macromolecules* 2006, 39, 1391–1396.
- (12) Malic, N.; Campbell, J. A.; Evans, R. A. *Macromolecules* 2008, 41, 1206–1214.
- (13) Ercole, F.; Malic, N.; Davis, T. P.; Evans, R. A. J. Mater. Chem. 2009, 19, 5612–5623.
- (14) Evans, R. A.; Malic, N.; Campbell, J. A.; York, M. R.; Ali, A. S. Photochromic polymer and composition comprising photochromic polymer. WO 2009/146509 A1, 10 December 2009.
- (15) Cypryk, M.; Rubinsztajn, S.; Chojnowski, J. J. Organomet. Chem. 1993, 446, 91–97.
- (16) Pardo, R.; Zayat, M.; Levy, D. C. R. Chim. 2010, 13, 212-226.
- (17) Sriprom, W.; Néel, M.; Gabbutt, C. D.; Heron, B. M.; Perrier, S. J. Mater. Chem. 2007, 17, 1885.
- (18) Moorthy, J. N.; Venkatakrishnan, P.; Samanta, S.; Kumar, D. K. Org. Lett. 2007, 9, 919–922.
- (19) Berthet, J.; Coelho, P. J.; Carvalho, L. M.; Vermeersch, G.; Delbaere, S. J. Photochem. Photobiol. A: Chem. 2009, 208, 180–185.
- (20) Ercole, F.; Davis, T. P.; Evans, R. A. Macromolecules 2009, 42, 1500–1511.
- (21) Such, G. K.; Evans, R. A.; Davis, T. P. Macromolecules 2004, 37, 9664–9666.
- (22) Such, G.; Evans, R.; Davis, T. Mol. Cryst. Liq. Cryst. 2005, 430, 273–279.
- (23) Ercole, F.; Malic, N.; Harrisson, S.; Davis, T. P.; Evans, R. A. *Macromolecules* 2010, 43, 249–261.
- (24) Oliveira, M. M.; Salvador, M. A.; Delbaere, S.; Berthet, J.; Vermeersch, G.; Micheau, J.; Coelho, P. J.; Carvalho, L. M. J. Photochem. Photobiol. A: Chem. 2008, 198, 242–249.
- (25) Coelho, P. J.; Carvalho, L. M.; Vermeersch, G.; Delbaere, S. *Tetrahedron* 2009, 65, 5369–5376.
- (26) di Nunzio, M. R.; Gentili, P. L.; Romani, A.; Favaro, G. Chem-PhysChem 2008, 9, 768–775.
- (27) Coelho, P.; Salvador, M.; Heron, B.; Carvalho, L. *Tetrahedron* 2005, 61, 11730–11743.
- (28) Jockusch, S.; Turro, N. J.; Blackburn, F. R. J. Phys. Chem. A 2002, 106, 9236–9241.
- (29) Yuan, W.; Sun, L.; Tang, H.; Wen, Y.; Jiang, G.; Huang, W.; Jiang, L.; Song, Y.; Tian, H.; Zhu, D. Adv. Mater. 2005, 17, 156–160.