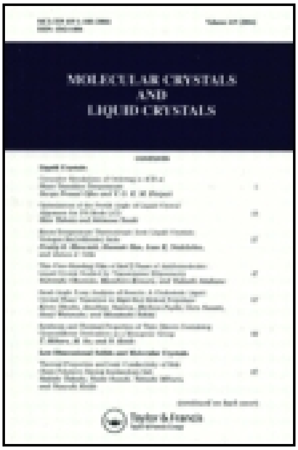

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Tailoring Photochromic Performance of Polymer-Dye Conjugates Using Living Radical Polymerization (ATRP)

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The photochromic performance of polymer-dye conjugates was successfully tailored using the living radical polymerization technique ATRP. ATRP allowed the synthesis of photochromic dye-polymer conjugates consisting of polymer of defined chain length and polydispersity with a single photochromic dye attached at one end. Control over the photochromic switching speed was achieved solely thorough choice of the chain length of the polymer conjugate.

Keywords: ATR; living radical polymerisation; photochromism; spirooxazine

INTRODUCTION

Photochromic materials play a significant role in current ophthalmic technology. Their application in photo-sensitive lenses has created renewed interest in other possibilities for this technology [1]. However tailoring the design of materials with a specific photochromic response still requires

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at best a semi-empirical research approach. This has hindered the development of more advanced photochromic materials such as, data recording, optical switching applications and non-linear optical components [2].

Photochromism can be defined as a reversible transformation of a chemical species between two forms, shifted in one or both directions by absorption of electromagnetic radiation [2]. It is well-documented that the transitions of a photochromic compound are significantly affected by its immediate environment. Factors such as rigidity, polarity and free volume can all play a significant role in adjusting photochromic parameters [3]. In previous studies the effects of local environment have been studied using non-controlled systems, either physical dispersions of photochromic in a polymer matrix [4] or covalent attachment via radical copolymerization of a monomer with photochromic functionality [5]. Neither of these approaches permits control over the molecular architecture, molecular weight distribution or placement of the dye molecule within the polymer environment. 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. Spirooxazines, a key class of photochromic compounds were chosen for this study as they display good fatigue resistance and a highly coloured secondary state [2].

In this work a spirooxazine-functional halo-initiator capable of initiating an atom transfer radical polymerization (ATRP) [6–9] has been synthesized and used to grow a poly(methyl methacrylate) chain with controlled molecular weight and polydispersity from a single photochromic molecule. In other words ATRP will allow the molecular weight of the polymer chain connected to the photochromic to be highly defined and consistently homogenous for each individual photochromic molecule. This will allow a detailed study into the relationship between the photochromic and its local environment. In this investigation methyl methacrylate was used as the monomer. It was found photochromic kinetics could be well controlled by the molecular weight of the polymer-spirooxazine conjugates synthesized.

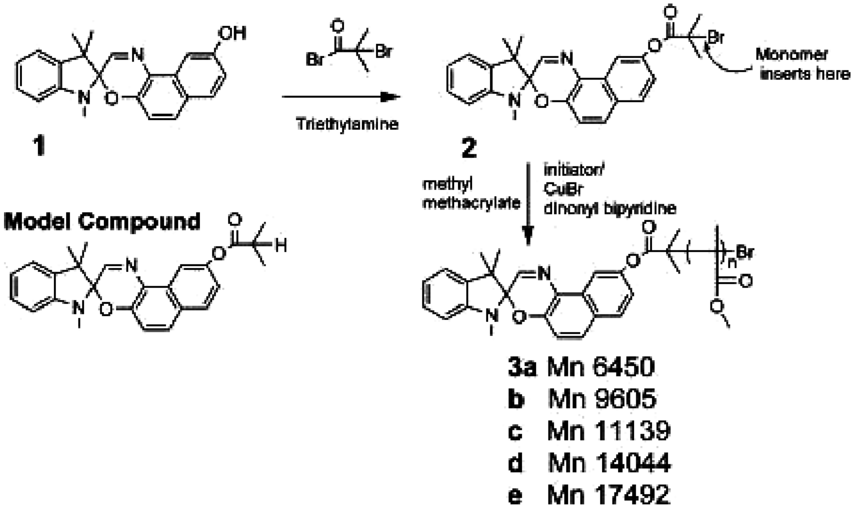
MATERIALS AND METHODS

Synthesis: Spirooxazine Initiator (2)

9′-Hydroxy-1,3,3-trimethylspiro[indoline2,3′-[3H]naphtha[2,1-b][1,4] oxazine] was synthesized as described in Kakishita *et al.* [10]. The starting material (5.0 g, 14.5×10^{-3} mol)was added to 30 mL of dichloromethane in a 100 mL three necked round bottomed flask. Triethylamine (2.20 g, 21.8×10^{-3} mol), was added and the reaction was stirred for half an hour. Then 2-Bromo-isobutylbromide (4.00 g, 17.4×10^{-3} mol), was dissolved in 10 mL dichloromethane and added dropwise to the reaction under argon. The reaction was stirred overnight. TLC (1:1 diethyl ether, hexane) confirmed the product had been obtained. The product was washed with 100 mL 0.5 M NaOH, 100 mL water, 100 mL 0.5 M HCl, 100 mL water, 100 mL brine and dried with $MgSO_4$. The final solution was rotary evaporated to produce 6.08 g of material (85% yield). This product was purified by column chromatography using 1:1 diethyl ether, hexane giving 5.28 g (73% yield) of yellow powder (Scheme 1). ^1H NMR ($(CD_3)_2CO$) δ; 1.34 s, 1.36 s, 2.16 s, 2.78 s, 6.67 d, 6.87 m, 7.08 d, 7.16 d, 7.20 m, 7.24 m, 7.85 d, 7.85 s, 7.95 d, 8.29 d ppm. 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 model compound was synthesized as above however using Isobutyryl chloride in place of 2-Bromo-isobutylbromide.

Polymerization

Poly(methyl methacylate) was grown from the initiator under the following typical procedure: initial reactants were mixed at a



SCHEME 1 Synthesis of initiator and polymer conjugates.

100:1:1:2 ratio of methyl methacrylate (17.4×10^{-3} mol), spirooxazine initiator (17.4×10^{-5} mol), catalyst (CuBr(17.4×10^{-5} mol)) and ligand (dinonyl-bipyridine (34.9×10^{-5} mol)). Benzene (2 mL) was added to each reaction and then they were degassed by repeated freeze-pump-thaw cycles using a schenk line. The polymerization was carried out at 60°C in a constant temperature oil bath. Polymerization mixtures were purified by precipitation into methanol.

EXPERIMENTAL METHODS

Molecular weight and polydispersity of the polymers were obtained using gel permeation chromatography (GPC), calibrated with poly (styrene) standards. Polymer conversions were obtained from ^{1}H NMR spectra recorded on a Bruker AC200 spectrometer. Photochromic analyses were performed on lenses composed of polymer-photochromic conjugates **3a–e** (1.2×10^{-3} mmol/gram) dissolved in a standard monomer mix of 1:4 weight ratio of polyethyleneglycol 400 dimethacrylate (9G) and 2,2′-Bis[4-methacryloxyethoxy] phenyl]propane (Nouryset 110) with 0.4% AIBN and cured (80°C, 8 hrs) to give clear test lenses. Photochromic responses (at $\lambda_{\max}$ 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 (350–400 nm). The samples were irradiated for 1000 seconds at 20°C. Thermal analyses of spirooxazine conjugates (10 mg) were done using a Mettler Toledo DSC821 heating from 25°C to 150°C at 10°C/minute under nitrogen.

RESULTS AND DISCUSSION

A series of methyl methacrylate-spirooxazine conjugates with increasing molecular weight were synthesized. The structure of the conjugates was investigated using NMR and GPC. The polydispersity of the systems was found to be very low (~1.06) as expected for living polymerizations. Consequently the environment for the photochromic was highly controlled and essentially uniform for each photochromic entity.

Figure 1 shows the decolouration of a series of methyl methacrylate-spirooxazine conjugates in a 9G:Nouryset lens. There is a significant decrease in decolouration as molecular weight increases. This can be seen more clearly in Table 1. The $t_{1/2}$ value given in Table 1 is a measure of decolouration speed; it refers to the time taken to reach half of the initial absorbance. The decolouration curves were also analyzed using the following biexponential equation:

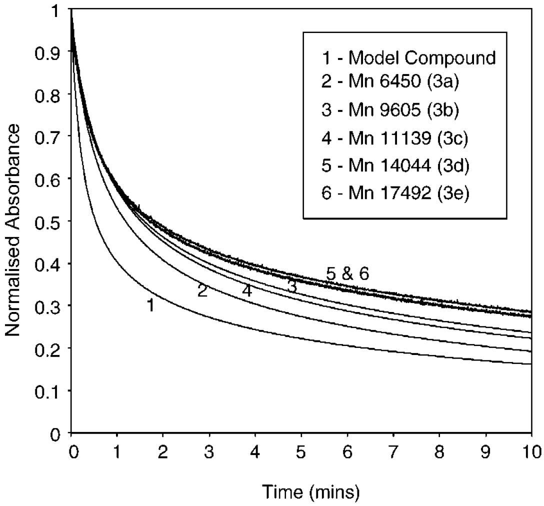


FIGURE 1 Decolouration of methyl methacrylate-spirooxazine conjugates 3a–e in 9G:Nouryset 110 lens.

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

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 ∞- This model was used in previous work by Biteau *et al.* [11] A biexponential is one of the many models used to fit photochromic decolouration [11]. The model was found to fit the data in this study

TABLE 1 Photophysical Constants for Methyl Methacrylate-spirooxazine conjugates

Sample	M_n(PD)[a]	T_g[b]	A_o[c]	$T_{1/2\ (s)}$	K_1(min^{-1})	K_2(min^{-1})	A_1/A_2	A_{th}
model	–	–	1.10	32	1.34	0.060	2.30	0.042
3a	6450 (1.12)	107	1.54	70	0.80	0.057	2.03	0.043
3b	9605 (1.06)	106	1.41	95	0.68	0.048	1.60	0.042
3c	11139 (1.07)	109	1.46	90	0.70	0.051	1.77	0.045
3d	14044 (1.05)	110	1.57	101	0.71	0.044	1.46	0.073
3e	17492 (1.07)	108	1.69	107	0.69	0.041	1.37	0.065

[a] polydispersity of polymer conjugates.

[b] Tg of the polymer conjugates not the 9G:Nouryset 100 lens.

[c] Intensity of absorbance in the coloured form before processing.

3a–e. The values for the constants for each conjugate in the series are given in Table 1.

A previous investigation of styrene-spirooxazine conjugates using living radical polymerization methodology found a similar pattern of decrease in decolouration rate with chain length of polymer conjugate [12]. That investigation showed a strong correlation between decolouration rate, chain length of the polymer and Tg of the polymer-conjugate. This could be explained by an encapsulation model. The tendency of the polymer conjugate to naturally coil was used to create a de facto encapsulation around the photochromic dye. Thus, the factors important for photochromic response such as rigidity, free volume, polarity etc directly around the dye could be controlled by the choice of the attached polymer. Consequently switching speed of the photochromic could be tuned without modification of the host matrix. In the poly(styrene) system, it could be assumed that all properties important to photochromic performance remained constant except for rigidity. The Tg of the polymer conjugate, used as a measure of rigidity, was found to increase with chain length. It was strongly correlated to the decolouration rate of the photochromic. This could only occur as strongly using the model proposed. In other possible models, the polymer conjugate would be arranged randomly through the host matrix, in which case the correlation to conjugate Tg would not occur. The Tg of the conjugate is not the only factor that determines decolouration, using an encapsulation model the chain length of the conjugate would be expected to affect decolouration by increasing the efficiency of encapsulation. As the chain length increases it would be more likely to coil and thus encapsulate. Thus chain length of the polymer also plays a role in controlling the photochromic behaviour.

In the methyl methacrylate conjugates, there was the same correlation observed between switching speed and polymer chain length with longer polymers providing slower colouration and decolouration rates. In this case $T_{1/2}$ could be varied between 32(model compound) and 107(3c) seconds. The Tg of the methyl methacrylate conjugates showed little variation over the molecular weights studied. Although poly(methyl methacrylate) would be expected to have greater compatibility with the host matrix than poly(styrene), encapsulation of the dye must still be occurring as the chain length dependence on fade performance is observed. If the polymer was being completely compatabilized into the host matrix then the decolouration speeds of the polymer-dye conjugates would be expected to be much the same and that is not observed. Thus, the decolouration speed of the spirooxazine decreases as the polymer length increases and so more effectively encapsulates the dye and providing a progressively slower switching environment. The correlation of decolouration rate with chain length is less strong than observed in the styrene case which is linear. This is most probably due to the strong influence of Tg that also contributed in that case.

CONCLUSION

We have successfully applied the living radical polymerization technique ATRP to the control of photochromism using two different monomers. ATRP allowed the synthesis of photochromic dye-polymer conjugates consisting of polymer of known molecular weight with a single spirooxazine dye attached at the end. 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. The use of living polymerization to achieve narrow polydispersities of the dye-polymer Conjugates is central to the success of this method due to the correlation found between switching speed and polymer length.

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