# Tuning the color switching of naphthopyrans *via* the control of polymeric architectures<sup>†</sup>‡

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A range of polymerisable photochromic naphthopyrans were prepared *via* the synthesis of an acrylate moiety on either the naphthalene ring (R) and/or the di-aryl (Ar) rings on the 3-position of the naphthopyran. The monomers obtained (NA) were copolymerised with methyl methacrylate (MMA) and methyl acrylate (MA) by the RAFT (reversible addition fragmentation chain transfer) process in order to control the structure of the polymeric chains and accurately control the number of photochromic molecules per chain. Films were prepared with the synthesized photochromic polymers and their photochromic properties were assessed. We found that the fading rate of the photochromic dye was slower in a matrix of PMMA (higher  $T_g$ ) than in a matrix of PMA (lower  $T_g$ ). By producing block copolymers of PMMA-*b*-poly(MA-*co*-NA), the fading rate was increased, and the production of PS-*b*-poly(MA-*co*-NA) block and the PS block. This study presents an example of tuning the photochromic properties of a dye *via* variation of the architecture of its polymeric support.

#### Introduction

Photochromism is a reversible transformation of a chemical system which is induced at least in one direction by electromagnetic radiation.<sup>1</sup> When irradiated with ultraviolet (UV) light, photochromic compounds undergo a reversible change between two molecular structures resulting in a change from colourless to coloured. Photochromism can be divided into two areas depending on how the dye reverts to the colourless form. Dyes which revert by light are defined as P types whereas those which revert by thermal radiation are T types.<sup>1</sup> There are many organic molecular families exhibiting photochromism, including spiropyrans, spirooxazines, naphthopyrans (chromenes), fulgides, diarylethenes and azo compounds. In all these main classes of organic photochromic compounds, naphthopyran is one of current great interest because of the breadth of colour generated, absence of background colour, fine control over fading kinetics, good thermal reversibility and good resistance to photochemical fatigue. The photochromism of naphthopyrans was first reported by Becker and Michl in 1966.<sup>2</sup> The photochromic reaction of the naphthopyrans involves initial heterolytic cleavage of C-O bonds on irradiation with UV light generating two coloured ring-opened structures, a trans-cis (TC) and a trans-trans (TT) merocyanine isomer (Scheme 1). The TC isomer is thermally cyclised at low temperatures over time while the TT species is more stable and its ring-closing only occurs on irradiation with visible light.<sup>3–5</sup>

Photochromic materials have great potential in various applications such as ophthalmic lenses,<sup>6</sup> erasable optical storage,<sup>7-9</sup> optical switching<sup>7,9,10</sup> and nonlinear devices.<sup>11</sup> For practical applications of these materials, the photochromic compounds are required to be incorporated into a polymer media to form film, sheets, or bead. To date, photochromophores are uniformly incorporated into, or applied to, a polymer matrix by several methods, including the dissolution of photochrome in the monomer before free radical polymerisation, dissolution/dispersion within the host polymer, or insertion as a separate layer between adjacent layers of the polymer matrix.<sup>12</sup> The use of photochromic monomers that can covalently bond to a polymer chain by copolymerisation is an alternative approach that offers a number of advantages such as prevention of the leaching of the photochrome, thus reducing risks of toxicity, and prevention of phase separation between the polymer matrix and the photochrome. This approach has been widely studied for a range of spirooxazine, spirobenzopyran, and diarylethene derivatives, which have been copolymerised with monomers such as styrene, methyl methacrylate (MMA), methacrylonitrile, and 2-vinylnaphthalene.<sup>13–17</sup> Naphthopyran monomers have however not received a great deal of attention, in spite of their significant



Scheme 1 Generic photochromic process for naphthopyran derivatives.

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advantages over other photochromic classes. To the best of our knowledge, there exists only patent data describing the synthesis and use of polyalkoxylated naphthopyrans as monomers.<sup>18</sup> An additional advantage of incorporating a photochromic species into a polymer by covalent bonds is the opportunity to finely tune the kinetics of the switching by modifying the polymer structure. Indeed, Evans et al. were among the first researchers to report the local modification of a photochromic moiety environment by attaching the dye to a polymer support in order to tune its switching properties.<sup>16,19,20</sup> In recent work, they showed that attaching a photochrome to an oligomer chosen for its physical properties would enhance the kinetics of colour switching. Their approach covers the incorporation of oligomers onto photochromic dyes via chemical modification, or living radical polymerisation initiated by spirooxazine.16,19-22

In the past decade, living radical polymerisations (LRP)<sup>23-25</sup> have been very promising for high scale applications in polymer chemistry because of the combination of undemanding reaction conditions and the industrial friendly nature of radical polymerisation with the control of molecular weight, polydispersities and architectures of the living processes. To date, the most important techniques of LRP are nitroxide-mediated polymerisation (NMP),<sup>26</sup> atom transfer radical polymerisation (ATRP),<sup>27,28</sup> reversible addition fragmentation chain transfer (RAFT)<sup>29</sup> polymerisation, and macromolecular architecture design by interchange of xanthates (MADIX)<sup>30</sup> polymerisation. RAFT and MADIX have the same mechanism process and are based on the reversible reaction of a chain transfer agent (CTA), usually a thiocarbonyl thio derivative, with the propagating species. The tolerance to a wide range of polymerisable monomers and solvent under a wide range of reaction conditions (i.e. bulk, solution, suspension, and emulsion) make RAFT and MADIX two of the most versatile living polymerisation processes. In addition, the RAFT technique can also produce multiblock copolymers with controlled molecular weight and low PDIs as well as a variety of polymeric architectures such as star. networks (co)polymers, hyperbranched, and comb/brush copolymers.<sup>31,32</sup> Since the reaction proceeds with retention of the thiocarbonyl thio end group, an AB di-block copolymer can be synthesized by the simple addition of a second monomer.

This work investigates the use of the RAFT process to control the number of naphthopyran moieties incorporated in a polymer and design polymeric architecture to control the photochromic properties.

#### Experimental

#### General data, materials

All solvents, monomers, and other reagents were purchased from Aldrich at the highest purity available. Methyl methacrylate (MMA, 99%), styrene (Sty, 99%) and methyl acrylate (MA, 99%) were filtered before utilization through a basic alumina (Brockmann I) column, to remove the radical inhibitor. Azobis(isobutyronitrile) (AIBN, 99%) was recrystallised twice from ethanol. 2-(2-Cyanopropyl)dithiobenzoate (CPDB) was synthesized following a published procedure.<sup>29</sup> A typical synthesis of a naphthopyran acrylate derivative is described below.<sup>33</sup> Air-and moisture sensitive compounds were manipulated using standard Schlenk techniques under a nitrogen atmosphere.

#### Differential scanning calorimetry (DSC)

The thermal properties of the photochromic block copolymers were studied by differential scanning calorimetry (DSC) using a TA Instrument DSC 2010 thermal analyzer under a nitrogen atmosphere (200 cm<sup>3</sup> min<sup>-1</sup>). For measurement of the glass transition temperature ( $T_g$ ), about 5–10 mg samples in an aluminium holder were heated from 20 to 150 °C, then cooled to -10 °C and reheated to 250 °C. The heating and cooling rate was set to 10 °C min<sup>-1</sup>. An empty aluminium pan was used as reference. The  $T_g$  value was determined from the onset, end and inflection of a step transition using the TA Instruments Thermal Advantage Universal Analysis software.

#### Size exclusion chromatography (SEC)

The number-average molecular weight  $(M_n)$  and polydispersity index  $(M_w/M_n)$ ) were determined using SEC equipped with a LC 1120 HPLC pump ((Polymer Laboratories, UK), a MIDAS (type 830) auto sampler (Spark Holland, Netherlands), a differential refractive index (DRI) detector (Shodex, RI-101), a 5.0 µm bead-size guard column (50 × 7.5 mm) and two PLgel 5.0 µm MIXED-C columns (300 × 7.5 mm) in series (Polymer Laboratories, UK). THF was used as the eluent at a flow rate of 1 mL min<sup>-1</sup> at ambient temperature and toluene was used as a flow rate marker. The SEC system was calibrated with polystyrene standards (Polymer Laboratories, UK) with molecular weights ranging from 580 to 7 500 000 g mol<sup>-1</sup>.

#### UV/vis spectrophotometry

The photochromic properties of the polymeric films and solution were analyzed by using a SPECORD S100 UV/vis spectrophotometer. Samples were placed in the spectrophotometer and their absorbance was measured from 400 nm to 700 nm. The samples were then irradiated to a constant intensity with UV light (365 nm) at room temperature for 1 minute to ensure the sample has reached steady state coloration. The absorbance decay was then measured in the dark in the same wavelength range every second, for 5 minutes. The wavelength of the maximum absorption  $(\lambda_{max})$  of the ringopened naphthopyran derivative (coloured) form was obtained by plotting the UV spectrum of the sample. Moreover, the time taken for the intensity of the photogenerated colour to decrease to half of its original value (half-life,  $t_{1/2}$ ) was determined by recording successive spectra and plotting the  $\lambda_{\rm max}$  as a function of time. The background spectrum of the slides was automatically subtracted from the samples.

#### <sup>1</sup>H NMR spectroscopy

<sup>1</sup>H NMR (400 MHz) spectra were recorded on a Bruker 400 UltraShield spectrometer at 25 °C and d-chloroform was used as solvent.

#### Typical synthesis of naphthopyran acrylate derivatives synthesis of 9-acryloyloxy-[3,3-bis(4-methoxyphenyl)]-3*H*naphtho[2,1-*b*]pyran (1)

3,3-Bis(4-methoxyphenyl)-9-hydroxy-3H-naphtho[2,1-b]pyran. A mixture of 2,7-dihydroxynaphthalene (6.0 g, 37.5 mmol) and 1,1-di(4-methoxyphenyl)prop-2-yn-1-ol (10.0 g, 37.3 mmol) in toluene (600 mL) was heated at reflux for 45 minutes. Then alumina (20.0 g) was added and the mixture was heated at reflux for 4 hours. The mixture was filtered hot and the residue washed with EtOAc. The filtrate was evaporated and the residue suspended in hexane and 10 drops of EtOAc. The suspension was filtered. Further hexane and EtOAc were added to the solid under heating (100 °C), but the solid did not dissolved entirely. The mixture was heated in order to concentrate it and then allowed to cool at room temperature. Then the mixture was filtered to give a pale brown solid, (3.33 g, 14%). The filtrate was concentrated and the residue suspended in hexane and 10 drops of EtOAc. The suspension was filtered to give the title compound as a red-brown solid with a yield of 35% (5.38 g).  $R_{f}$ : 0.14 (EtOAc-hexane 1 : 1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz, 300 K)  $\delta$ : 7.60 (d, 1H,  $J_{ortho}$  = 8.8 Hz), 7.56 (d, 1H,  $J_{ortho}$  = 8.8 Hz), 7.37 (m, 4H), 7.25 (d, 1H,  $J_{meta}$  = 2.4 Hz), 7.14 (d, 1H,  ${}^{3}J$  = 10.0 Hz), 7.01 (d, 1H,  $J_{ortho}$  = 8.8 Hz), 6.90  $(dd, 1H, J_{ortho} = 8.8 Hz, J_{meta} = 2.4 Hz), 6.83 (m, 4H), 6.17 (d, 1H)$  ${}^{3}J = 10.0 \text{ Hz}$ , 4.99 (s, OH), 3.77 (s, 3H)

9-Acryloyloxy-[3,3-bis(4-methoxyphenyl)]-3H-naphtho[2,1-b] pyran (1). To a suspension of 3,3-bis(4-methoxyphenyl)-9hydroxy-3H-naphtho[2,1-b]pyran (5.0 g, 23.34 mmol) in MeCN (230 mL) cooled to ca. -10 °C, DBU (7.7 mL, 51.54 mmol) was added in a single portion. The solution was stirred for 20 minutes and then acryloyl chloride (5.2 mL, 63.99 mmol) dissolved in MeCN (25 mL) was added dropwise to the mixture. The mixture was stirred until room temperature for 28 hours. MeCN was removed and then water and DCM were added. The aqueous layer was extracted with DCM. The organic layers were washed with a solution of HCl 2 M, combined, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The yellow solid obtained was chromatographed (SiO<sub>2</sub>: EtOAc-hexane 3:7) to yield the title compound (yield: 98%) as an orange solid.  $R_{\rm f}$ : 0.24 (EtOAc-hexane 3 : 7). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz, 300 K) δ: 7.73 (d, 1H, J<sub>ortho</sub> = 8.8 Hz), 7.68 (d, 1H,  $J_{meta} = 2.0$  Hz), 7.36 (m, 4H), 7.17 (d, 1H,  ${}^{3}J =$ 10.0 Hz), 7.14 (d, 1H,  $J_{ortho}$  = 8.8 Hz), 7.09 (dd, 1H,  $J_{ortho}$  = 8.8 Hz,  $J_{meta} = 2.0$  Hz), 6.84 (m, 4H), 6.65 (dd, 1H,  ${}^{3}J_{trans} = 17.2$  Hz,  ${}^{2}J_{gem} = 1.2$  Hz), 6.37 (dd, 1H,  ${}^{3}J_{trans} =$ 17.2 Hz,  ${}^{3}J_{cis} = 10.4$  Hz), 6.19 (d,  ${}^{3}J = 10.0$  Hz), 6.05 (dd,  ${}^{3}J_{cis} =$ 10.4 Hz,  ${}^{2}J_{gem} = 1.2$  Hz), 3.77 (s, 6H)

### Typical homopolymerisation procedure: polymerisation of styrene (St) by the RAFT process

CPDB (1 eq), St (from which inhibitor was previously removed by filtration through activated basic alumina) (500 eq) and toluene (50 wt%) were mixed and put in a series of sample tubes. The oxygen was removed from the reaction mixtures by pumping nitrogen gas into the mixture for 5 minutes, whilst allowing the oxygen to be released through an escape needle. The sealed tubes were then heated to 110  $^{\circ}$ C, and removed at different times. Reactions were quenched in ice and the PS final product was isolated by precipitation in cold hexane. Conversions were calculated *via* <sup>1</sup>H NMR and molecular weight distributions were analysed *via* SEC.

## Typical copolymerisation procedure: copolymerisation of MMA with 9-acryloyloxy-[3,3-bis(4-methoxyphenyl)]-3*H*-naphtho[2,1-*b*]pyran (1) in toluene

MMA (2.1510 g, 21.5 mmol), **1** (0.0992 g, 0.214 mmol), CPDB (0.0471 g, 0.215 mmol), AIBN (0.0175 g, 0.107 mmol) and toluene (1.9789 g) were mixed in a Schlenk tube. Prior to sealing, the mixture was carefully degassed by five freeze–pump–thaw cycles under high vacuum. The reaction was then heated at 60 °C and samples were taken at various times and quenched in ice. Conversions were calculated *via* <sup>1</sup>H NMR and molecular weight distributions were analysed *via* SEC.

#### Typical block copolymerisation procedure: block copolymerisation of PS, MA and 9-acryloyloxy-[3,3-bis(4methoxyphenyl)]-3*H*-naphtho[2,1-*b*]pyran (1)

Polystyrene (PS) homopolymer (6 500 g mol<sup>-1</sup>, PDI = 1.11) was used as macro chain transfer agent for the random copolymerisation of MA with 1 (135 MA : 1 1 : 1 PS : 0.5 AIBN; 50 vol% toluene at 60 °C for 24 h) following a similar experimental setup as that described above. After precipitation, poly(St-*b*-poly(1-*co*-MA)) was analysed by <sup>1</sup>H NMR and GPC to characterise the composition and molecular weight distribution. The dithiobenzoate end group was removed from the polymer by the addition of a large excess of AIBN (20 eq) to a toluene solution of the polymer, followed by heating at 80 °C for 2.5 hours. The polymer was recovered by precipitation in cold hexane and isolated as a pale yellow solid. The pale yellow colour is thought to be due to naphthopyran units remaining in their open-ring form after polymerisation.

#### **Film formation**

Polymers were dissolved in THF or dichloromethane to produce a viscous solution which was spread with a K-bar number 8 or with a spin coater Sheen Spinner (I.C.I Patter N) on microscope glass slides. The films were left to dry at room temperature.

#### **Results and discussion**

#### Naphthopyran acrylate derivatives synthesis

The naphthopyran derivatives were synthesised as described in supporting information. In order to test the steric effect of the polymeric chain on the ring opening kinetics of the naphthopyran, a linker was introduced between the photochromic dye and the backbone (Scheme 2, 2 and 4 vs. 1 and 3). In addition, the attachment point between the naphthopyran moiety and the polymeric backbone was varied from the naphthalene ring (Scheme 2, 1 and 2) and the di-aryl rings on the 3-position of the naphthopyran (Scheme 2, 3 and 4).

#### Statistical copolymerisation

The naphthopyran acrylate (NA) derivatives were copolymerised with MMA and MA as illustrated in Scheme 3, using



Scheme 2 Naphthopyran acrylate (NA) derivatives used in this study.

CPDB as chain transfer agent to mediate the polymerisations. CPDB is a well known chain transfer agent for RAFT polymerisation, and has been shown to control very well both acrylate and methacrylate polymerisations.<sup>31,32</sup> We chose to use RAFT polymerisation rather than a conventional free radical polymerisation process, as RAFT not only allows the control of the polymer molecular weight, but it also permits control of the amount of naphthopyran moieties introduced in each polymeric chain. The incorporation of the photochrome into the polymer backbone was estimated by <sup>1</sup>H NMR, by comparing the characteristic signals of the naphthopyran derivative (*e.g.* H<sub>d</sub>, Fig. 1) with those of the (meth)acrylate polymer (Table 1).

Both compounds 1 and 2 were copolymerised with MMA and MA. Table 1 summarises the reaction conditions and the details of the final product. Each polymerisation was followed kinetically and the molecular weight evolution was plotted *versus* conversion. Fig. 2 shows the linear evolutions of  $\ln(1/(1 - C))$  with time, thus implying a pseudo-first order polymerisation kinetic, characteristic of living radical

polymerisations. It is also noteworthy that MMA polymerisation proceeds faster than MA polymerisation, as previously observed in RAFT. The molecular weights increase linearly with conversion (Fig. 3), although the values are slightly higher than anticipated. Fig. 3 shows a rapid increase in molecular weight early in the reaction, suggesting a loss of control. However, the polymerisation becomes rapidly controlled, as illustrated by the linear evolution of molecular weight with conversion. This loss of control early in the reaction can be explained by the slow reaction of the CTA with the propagating radicals.<sup>34</sup> Nevertheless, the molecular weight remains reasonably close to that expected, within the calibration error of the GPC system, with polydispersities below 1.2 at all time during polymerisation, thus implying reasonably good control over the polymeric chain growth. The final polymers had similar molecular weights ( $\sim 11\ 000\ g\ mol^{-1}$  for methacrylate derivatives and 7 000-8 500 g mol<sup>-1</sup> for acrylate derivatives), and all polymers had a content of  $\sim 1 \text{ mol}\%$ naphthopyran in their final structure. In the case of the acrylate copolymerisation, we noticed that the naphthopyran acrylate was incorporated early in the reaction, as 1 mol% content was reached when polymerisations were stopped as early as 71% monomer conversion. It is also noteworthy that the presence of a complex molecule such as the naphthopyran moiety does not affect either the rate, or the control, of the polymerisation, illustrating the robustness of the RAFT process towards functional groups. Finally, our kinetic and molecular weight data show that, within experimental error, there is no difference between the copolymerisation of naphthopyran acrylate derivatives with and without a linker.

In order to test the influence on the photochromic properties of the attachment point between the naphthopyran and the polymeric backbone, monomers **3** and **4** were also copolymerised with MA by RAFT (Scheme 4). The polymerisation kinetics were similar to those of **1** and **2** (data not shown), and Table 1 summarises the reaction conditions and the final molecular weight and polydispersities of the copolymers of MA with **1**, **2**, **3** and **4**. A similar degree of photochrome incorporation in the final copolymer as that observed with **1** and **2** was achieved, whilst keeping a very good control over the molecular weight and polydispersity of the copolymer.



Scheme 3 Copolymerisation of 1 and 2 with MMA and MA mediated by RAFT.



Fig. 1 <sup>1</sup>H NMR spectrum of 9-[3-(acryloyloxy)propoxy]-3,3-bis(4-methoxyphenyl)-3H-naphtho[2,1-b]pyran copolymerised (2) with methyl acrylate.

Table 1 Final conversion, molecular weight and polydispersity data for the copolymerisation of MMA or MA with compounds 1, 2, 3 and 4

Sample	Naphthopyran acrylate (NA)	Comonomer	Time <sup>a</sup> /min	Conversion <sup>b</sup> (%)	$M_{\rm n}{}^c/{\rm g}~{\rm mol}^{-1}$	PDI <sup>c</sup>	Ratio of naphthopyran incorporated $(\%)^b$
A	1	MMA	1200	99	11 900	1.10	1.1
В	2	MMA	1220	98	10 800	1.08	1.2
С	1	MA	2665	77	7 500	1.16	1.0
D	2	MA	2600	83	8 200	1.10	1.1
Е	3	MA	3535	88	8 500	1.34	0.9
F	4	MA	2130	71	7 000	1.12	0.9

<sup>*a*</sup> Time of the polymerisation carried out with the ratio comonomer (MMA or MA) : NA : CPDB : AIBN = 100 : 1 : 1 : 0.5 in 50 vol% of toluene, under nitrogen, at 60 °C. <sup>*b*</sup> Determined by <sup>1</sup>H NMR (using CDCl<sub>3</sub> as solvent) peak intensity ratio. <sup>*c*</sup> Estimated by SEC using THF as eluent and PMMA standards. <sup>*d*</sup> Determined by integrating the characteristic H of the acrylate moiety (acr) of the photochrome and the H characteristic of the naphthopyran (char) (d at  $\delta = 6.19$  ppm) and the following equation: ( $I_{char}/(I_{acr} + I_{char})$ ).



**Fig. 2** Pseudo-first-order rate plot for the copolymerisaton of MMA with  $1 (\bullet)$  and  $2 (\bullet)$ , and MA with  $1 (\lor)$  and  $2 (\blacktriangle)$ , mediated by CPDB in toluene at 60 °C.

#### Thermal analyses

The  $T_g$  of all polymers were determined by differential scanning calorimetry (DSC). A similar  $T_g$  (98 °C) was obtained for both samples **A** and **B**, which is below the expected value for PMMA homopolymers (105–120 °C).<sup>35</sup> This can be explained by the presence of the bulky naphthopyran moiety in the PMMA chains, which disturbs the order of the chains, and therefore increases their mobility, independently of the presence of a linker. On the other hand, polymers **C**, **D**, **E** and **F**, exhibited a similar  $T_g$  ( $T_g = 7$  °C), which is close to that expected from a poly(methyl acrylate). It is noteworthy that the presence of a linker did not seem to affect the overall  $T_g$  of the polymer.

#### **Photophysics**

In a polymeric structure, factors such as the formation of naphthopyran mesomers, the aggregation of naphthopyrans due to the intermolecular interactions, and the intramolecular



**Fig. 3** Molecular weight and PDI evolution with monomer conversion for the copolymerisation in toluene of MMA with  $1 (\bullet)$  and  $2 (\bullet)$ , MA with  $1 (\lor)$  and  $2 (\bullet)$ , mediated by CPDB. Lines represent the theoretical molecular weight for the polymerisation of MMA (···) and MA (---).

interactions of photochromes with other part of the macromolecule may affect the kinetics and the spectral properties of the system. The samples were irradiated to a constant intensity with UV light at room temperature, prior to measuring their absorbance in the same wavelength range every second, for 5 minutes. The time taken for the intensity of the photogenerated colour to decrease to half of its original value (halflife,  $t_{1/2}$ ) was determined by recording successive spectra and plotting the  $\lambda_{max}$  as a function of time. The data in Table 2 record the wavelength of maximum absorption ( $\lambda_{max}$ ) of the ring-opened species formed when the polymeric films are irradiated to a constant intensity with UV light (365 nm) at 20 °C. Additionally, the time taken for the intensity of the photogenerated colour to decrease to half of its original value (half-life or bleach rate,  $t_{1/2}$ ) is presented (Fig. 4). When comparing samples A and B to C and D, respectively, we observe that the speed of switching is higher for the films based on PMA (10-12 s) than that of the films based on PMMA (over 5 min). The photochromism of polymer A, B, C and D was also tested in a solution of toluene. In all cases, the colourless solutions developed intense colorations under UV light at 365 nm, and regained very rapidly their initial state after ceasing irradiation. This faster fade rate was expected in solution, as the hindrance of the solvent-swollen polymeric chains is greatly diminished.

The photochromic decoloration rates can also be studied by using a mathematical model. We found that a biexponential equation fits best the experimental data:<sup>19</sup>  $A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_{th}$ , where A(t) is the optical density at  $\lambda_{max}$ ,  $A_1$  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, respectively, and  $A_{th}$  is coloration when time approaches infinity. The values for



Scheme 4 Copolymerisation of 3 and 4 with MA mediated by RAFT.

Table 2	Wavelength	of maximum	absorption	and half-life	time of	f the polymers	s prepared in this st	udy
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Sample	Composition	$\lambda_{\rm max}/{\rm nm}$	<i>t</i> <sub>1/2</sub> /s	$k_1/\min^{-1}$	$k_2/\min^{-1}$	$A_1$	$A_2$	$A_{\rm th}$
A	$Poly(MMA_{98,9\%}-co-1_{1,1\%})$	483	>300	0.080	0.007	0.24	0.31	0.53
В	$Poly(MMA_{98,8\%}-co-2_{1,2\%})$	463	>300	0.099	0.008	0.27	0.27	0.56
С	$Poly(MA_{99\%}-co-1_{1\%})$	439	10	0.421	0.013	0.47	0.11	0.32
D	$Poly(MA_{98,9\%}-co-2_{1,1\%})$	437	12	0.444	0.007	0.47	0.07	0.41
Е	$Poly(MA_{99,1\%}-co-3_{0,9\%})$	450	10	0.455	0.013	0.48	0.12	0.35
F	$Poly(MA_{99,1\%}-co-4_{0,9\%})$	480	10	0.568	0.013	0.49	0.16	0.31
G	PMMA- <i>b</i> -poly(MA <sub>99,1%</sub> - $co$ -1 <sub>0,9%</sub> )	428	145	0.181	0.012	0.36	0.40	0.41
Н	PMMA- <i>b</i> -poly(MA <sub>99,2%</sub> - <i>co</i> - <b>2</b> <sub>0,8%</sub> )	443	165	0.161	0.012	0.36	0.40	0.43
I	PS <sub>81%</sub> - <i>b</i> -poly(MA <sub>18%</sub> - <i>co</i> -1 <sub>1%</sub> )	441	100	0.256	0.011	0.45	0.45	0.32



1.0

of copolymers-naphthopyran conjugates. See Table 2 for sample identification

250

300

the constants for each system are given in Table 2. We observed that the incorporation of the naphthopyran derivative into a methyl acrylate matrix gave a larger increase in the fast component  $k_1$  of the decoloration relative to the PMMA system. Higher  $t_{1/2}$  and  $k_1$  for a PMMA matrix can be justified by the high  $T_{\rm g}$  of PMMA when compared to PMA. Indeed, at temperatures below  $T_{g}$ , the movement of the pendant photochrome is restricted, and the ring-closing process is slowed. On the other hand, as the  $T_{g}$  of PMA is far closer to room temperature, the acrylate chains are more mobile and facilitate the switching, resulting in faster kinetics. It is also noteworthy that for both PMMA and PMA copolymers the samples showed a small absorbance in the visible spectrum, due to daylight. This phenomenon is more intense in the case of PMA films, which show a pale yellow colour. Although low  $T_{g}$  of the polymeric support favours rapid photochromic switching, it leads to processing issues in the film making. Indeed, PMA films were difficult to obtain, and were rather unstable by comparison to PMMA-based films. When comparing the films made from samples C and D with E and F, respectively, it appears that the attachment point of the photochrome to the backbone does not affect extensively the kinetics. Finally, comparing sample A with B, C with D and E with F, shows that the presence of a linker does affect the fading rate in the case of the methacrylate copolymers, but does not seem to influence the fading rate of the acrylate copolymers (Fig. 4 and Table 2). The presence of a linker keeps the naphthopyran away from the polymer backbone, and in the cases of steric hindrance, this affects directly the fading rate. In the case of the acrylate polymers, the kinetics of ring closing is too fast to be accurately quantified. Previous studies have shown that the kinetic behaviour of photochromic spiropyran groups covalently bonded to a polymer main chain is very similar to that of spiropyrans incorporated into a polymer matrix.<sup>36,37</sup> In the case of naphthopyrans, however, when comparing A and B with samples in which 1 and 2, respectively, have been mixed in a matrix of PMMA, we

observe that the covalent link of the photochrome to the polymeric backbone seems to slow the fading rate. This effect may be explained by the variation of properties of the polymer on the photochrome that may affect the naphthopyrans more than the spiropyrans.

#### **Block copolymerisation**

As a living radical polymerisation system, RAFT offers the potential to produce block copolymers by sequential addition of monomers. In order to facilitate the switching of the naphthopyran moiety, we aimed to incorporate the photochromic moiety into a block of low  $T_{g}$  (PMA), with a second block made of PMMA, of higher  $T_g$ , which would allow higher rigidity of the overall material, thus facilitating film formation. AB block copolymers poly(MMA)-b-poly(MA-co-NA)), with NA = 1 or 2, were therefore synthesized (Scheme 5). Initially, the homopolymerisation of MMA (70 MMA : 1 CPDB : 0.5 AIBN, 50 vol% toluene, 60 °C) was undertaken as described above, and led to a PMMA of  $M_{\rm p} = 7.700 \text{ g mol}^{-1}$  (PDI = 1.13). After purification by precipitation, the PMMA block was used as macro chain transfer agent for the random copolymerisation of MA with 1 and 2 (30 MA : 1 NA : 1 PMMA : 0.5 AIBN). After precipitation, PMMA-b-P(MA-co-1), G,  $(M_n = 13\ 300\ \text{g mol}^{-1},\ \text{PDI} = 1.18)$ , and PMMA*b*-P(MA-*co*-2), H, ( $M_n = 12\ 000\ g\ mol^{-1}$ , PDI = 1.18) were analysed by NMR and GPC (Table 3), to confirm their compositions and molecular weights. By measuring the fading rates of block copolymers G and H by UV, as described above, we found that both rates were half-way between those of the MMA and MA copolymers (see Fig. 4 and Table 2). However, the processing of the sample (film formation) was close to that of the PMMA copolymers. Therefore, a good compromise was reached between rigidity of the material, provided by the PMMA matrix, and rapid colour switching, favoured by the PMA environment of the naphthopyran.

In order to improve the fading rate whilst keeping good process properties of the final polymer, a block copolymer PSb-poly(MA-co-1) (I) was synthesized. PS-b-PMA block copolymers have been shown to phase separate,<sup>38</sup> and upon phase separation, we expected the photochrome to be embedded in a PMA environment, therefore allowing for rapid colour switching, whilst keeping the rigidity of the PS matrx ( $T_{o}$ (PS)  $\sim 110$  °C). The same procedure as that described above was used, with the initial synthesis of a PS macro chain transfer agent via homopolymerisation of styrene mediated by CPDB ( $M_n = 6500 \text{ g mol}^{-1}$ , PDI = 1.10), followed by block extension with MA and 1. <sup>1</sup>H NMR spectroscopy and GPC analyses demonstrated the successful synthesis of a block copolymer of PS, MA and 1. The molar ratio of styrene, MA and 1 in the block copolymer ( $M_n = 9600$ , PDI = 1.21) were calculated from <sup>1</sup>H NMR, and were similar to those of the PMMA-b-poly(MA-co-NA) copolymers. Moreover, as shown in Fig. 5, successful block copolymerisation was demonstrated by a shift to higher molecular weights of the block copolymer when compared to the macro CTA. The GPC trace of the block copolymer showed a characteristic shoulder on the peak at high molecular weight, indicating the occurrence of chain branching during acrylate polymerisation.<sup>39</sup>



Scheme 5 RAFT polymerisation of MMA followed by chain extension with MA and 1.

Table 3 Final conversion, molecular weight and polydispersity data for the block copolymerisation of PMMA with MA and 1 or 2

Sample	Naphthopyran acrylate	Time/min	Conversion <sup>a</sup> (%)	$M_{\rm n}{}^b/{ m g}~{ m mol}^{-1}$	$PDI^b$	Ratio of naphthopyran incorporated (%) <sup>c</sup>
PMMA	_	1375	98	7 700	1.13	_
G	1	3935	91	13 300	1.18	0.9
Н	2	3920	90	12 000	1.18	0.8
K	1	3920?	91	9 600	1.21	1.0
	1		,			

<sup>*a*</sup> Determined by <sup>1</sup>H NMR (using CDCl<sub>3</sub> as solvent) peak intensity ratio. <sup>*b*</sup> Estimated by SEC using THF as eluent and PMMA standards. <sup>*c*</sup> Determined by integrating one of the H of the acrylate moiety (acr) of the photochrome and the H characteristic of the naphthopyran (char) (d at  $\delta = 6.19$  ppm) and making the calculation: ( $I_{char}/(I_{acr} + I_{char})$ ).



Fig. 5 GPC trace of PS (- - -) and PS-b-poly(MA-co-1) (--).

The phase separation of the block copolymer was demonstrated by DSC analyses, which showed the occurrence of two  $T_{\rm g}$ s, at 5 °C and 119 °C, close to the  $T_{\rm g}$  of PMA (7 °C) and PS (100 °C). The  $t_{1/2}$  of the block copolymer (**K**, Table 2) was measured at 100 seconds, a lower value than that of **G**, confirming that phase separation occurring between the PS and P(MA-*co*-1) blocks allows for the confinement of the naphthopyran moiety in a matrix of low  $T_{\rm g}$  PMA, thus decreasing the fading rate.

#### Conclusion

Naphthopyran acrylate derivatives were synthesised and incorporated into poly(methyl methacrylate) and poly(methyl acrylate) chains *via* radical polymerisation. The use of RAFT polymerisation allowed the control of the number of naphthopyran units introduced in the polymers. Fading rate was shown to be dependent on the matrix surrounding the naphthopyran and the presence of a linker between the photochrome and the polymeric backbone. The use of living radical polymerisation to produce block copolymers that phase separate allowed us to encapsulate the naphthopyran derivative into a low  $T_g$  polymer local environment, therefore enhancing its fading rate, whilst keeping a continuous matrix of high  $T_g$ , to allow easy processing of the polymer into films.

#### References

- 1 H. Bouas-Laurent and H. Durr, Pure Appl. Chem., 2001, 73(4), 639–665.
- 2 R. S. Becker and J. Michl, J. Am. Chem. Soc., 1966, 88(24), 5931-3.
- 3 S. Delbaere, B. Luccioni-Houze, C. Bochu, Y. Teral, M. Campredon and G. Vermeersch, J. Chem. Soc., Perkin Trans. 2, 1998(5), 1153–1157.
- 4 S. Jockusch, N. J. Turro and F. R. Blackburn, J. Phys. Chem. A, 2002, 106(40), 9236–9241.
- 5 X. Sallenave, S. Delbaere, G. Vermeersch, A. Saleh and J.-L. Pozzo, *Tetrahedron Lett.*, 2005, 46(18), 3257–3259.
- 6 S. Higgins, Chasing a Rainbow, Chem. Br., 2003(6), 26-29.
- 7 M. Irie, Chem. Rev., 2000, 100(5), 1685-1716.
- 8 S. Kawata and Y. Kawata, Chem. Rev., 2000, 100(5), 1777–1788.
- 9 Y. Yokoyama, Chem. Rev., 2000, 100(5), 1717–1739.
- 10 G. Berkovic, V. Krongauz and V. Weiss, *Chem. Rev.*, 2000, **100**(5), 1741–1753.
- 11 J. A. Delaire and K. Nakatani, Chem. Rev., 2000, 100(5), 1817–1845.
- 12 C. J. Crano, S. W. Kwak and N. C. Welch, in *Applied photochromic polymer systems*, ed. C. B. McArdle, Blackie, Glasgow and London, 1992, p 255.
- 13 M. Irie, A. Menju and K. Hayashi, *Macromolecules*, 1979, **12**(6), 1176–80.
- 14 M. Irie, A. Menju, K. Hayashi and G. Smets, J. Polym. Sci., Polym. Lett. Ed., 1979, 17(1), 29–31.
- 15 A. Menju, K. Hayashi and M. Irie, *Macromolecules*, 1981, 14(3), 755–8.
- 16 G. K. Such, R. A. Evans and T. P. Davis, *Macromolecules*, 2004, 37(26), 9664–9666; R. A. Evans, G. K. Such, T. P. Davis, N. Malik, D. A. Lewis and J. A. Campbell, *Int. Pat.* PCT/AU2005/001327, 2005.
- 17 P. H. Vandewijer and G. Smets, J. Polym. Sci., Polym. Symp., 1968, 22(Pt. 1), 231–45.
- 18 B. Van Gemert, A. Chopra and A. Kumar, Polymerizable polyalkoxylated naphthopyrans as photochromic agents for

coatings, films and plastics, US Pat. 99-US20663 2000015629, 19990909, 2000.

- 19 R. A. Evans, T. L. Hanley, M. A. Skidmore, T. P. Davis, G. K. Such, L. H. Yee, G. E. Ball and D. A. Lewis, *Nat. Mater.*, 2005, 4(3), 249–253.
- 20 R. A. Evans and G. K. Such, Aust. J. Chem., 2005, 58(12), 825–830.
- 21 G. K. Such, R. A. Evans and T. P. Davis, *Macromolecules*, 2006, 39(4), 1391–1396.
- 22 G. K. Such, R. A. Evans and T. P. Davis, *Mol. Cryst. Liq. Cryst.*, 2005, **430**, 273–279.
- 23 Controlled/Living Radical Polymerization: From Synthesis to Materials, ed. K. Matyjaszewski, ACS Symp. Ser. vol. 944, ACS, Washington DC, 2006.
- 24 Controlled Radical Polymerization, ed. K. Matyjaszewski, ACS Symp. Ser. vol. 685, ACS, Washington DC, 1998, p. 483.
- 25 Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT, ed. K. Matyjaszewski, ACS Symp. Ser. vol. 768, ACS, Washington DC, 2000, p. 484.
- 26 C. J. Hawker, A. W. Bosman and E. Harth, *Chem. Rev.*, 2001, 101(12), 3661–3688.
- 27 M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, Macromolecules, 1995, 28(5), 1721–1723.
- 28 J. S. Wang and K. Matyjaszewski, J. Am. Chem. Soc., 1995, 117(20), 5614–5615.
- 29 J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 1998, 31(16), 5559–5562.
- 30 D. Charmot, P. Corpart, H. Adam, S. Z. Zard, T. Biadatti and G. Bouhadir, *Macromolecular Symposia*, 2000, **150**, 23–32.
- 31 G. Moad, E. Rizzardo and S. H. Thang, Aust. J. Chem., 2005, 58(6), 379–410.
- 32 S. Perrier and P. Takolpuckdee, J. Polym. Sci., Part A: Poly. Chem., 2005, 43(22), 5347–5393.
- 33 See supporting information for all syntheses.
- 34 C. Barner-Kowollik, M. Buback, B. Charleux, M. L. Coote, M. Drache, T. Fukuda, A. Goto, B. Klumperman, A. B. Lowe, J. B. McLeary, G. Moad, M. J. Monteiro, R. D. Sanderson, M. P. Tonge and P. Vana, J. Polym. Sci., Part A: Polym. Chem., 2006, 44(20), 5809–5831.
- 35 E. Penzel, J. Rieger and H. A. Schneider, *Polymer*, 1997, 38(2), 325–337.
- 36 G. Smets, Pure Appl. Chem., 1972, 30(1-2), 1-24.
- 37 A. E. J. Wilson, Phys. Technol., 1984, 15(5), 232-8.
- 38 I. W. Hamley, *The Physics of Block Copolymers*, Oxford University Press, Oxford, 1998.
- 39 A. Postma, T. P. Davis, G. Li, G. Moad and M. S. O'Shea, *Macromolecules*, 2006, **39**(16), 5307–5318.

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