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Negative Photochromic Polymers. Synthesis and Photochemical Properties of Poly(methyl methacrylate) Having Spirobenzoselenazolinobenzopyran Side Groups

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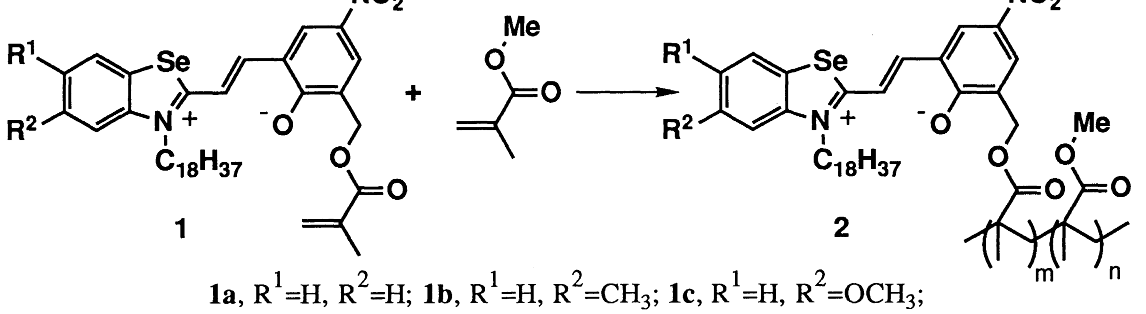
A series of novel negative photochromic poly(methyl methacrylate) having spirobenzoselenazolinobenzopyran side groups was newly synthesized, and their reversible photochemical color changes were studied: their metastable colorless spiro - forms induced by Vis light irradiation was stabilized more than 90 days, although that dispersed in polymer film was thermally unstable turning to the stable merocyanine-form. Kinetic study to investigate their thermocoloration process was performed.

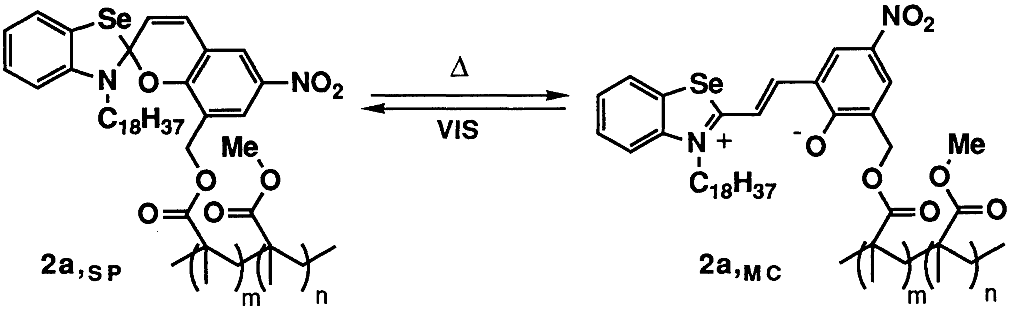
Photochromic organic dyes have featured in recent research interests in photo-functional materials such as optical memories. In particular, spiropyrans being one of the most typical organic photochromic compounds have been currently attracted as photo-receptor in photochromic polymers.1) In addition to drastic color change by UV light irradiation due to the formation of merocyanine dye, the transformation between the colored and colorless forms is potentially capable of affecting the polymer properties such as viscosity2) and turbidity.3) However, a major difficulty for controlling these polymer properties induced by light may be ascribed to the poor stability of the metastable colored-form of the photochromic spiropyrans in polymer matrix. Previously, we reported synthesis and *negative* photochromic properties of novel spirobenzoselenazolinobenzopyrans (SeSP),4) and described their structural characterization in detail.5) In this paper, we report synthesis of a series of novel negative photochromic poly(methyl methacrylate) anchoring spirobenzoselenazolinobenzopyrans as side groups, and discuss their photochemical properties by focusing on fixation of the metastable colorless spiro-form in polymer matrices.



1a, R^1=H, R^2=H; **1b**, R^1=H, R^2=CH_3; **1c**, R^1=H, R^2=OCH_3;
1d, R^1=OCH_3, R^2=OCH_3; **1e**, R^1=H, R^2=H, isotactic

A series of spirobenzoselenazolinobenzopyran monomers **1a-d** prepared by the method reported previously[4,5] were copolymerized with methyl methacrylate either by radical polymerization using AIBN as an initiator, or ionic polymerization using PhMgBr to afford isotactic PMMA having SeSP.[6,7]

These SeSP-MMA copolymer **2** immediately colored to blue purple by dissolving in $CHCl_3$ due to the formation of merocyanine colored-form **2a,$_{MC}$** of zwitterionic 3-methyl-benzoselenazolenium-2-*trans*-(5'-nitrostyryl-2'-oxide) moiety.[5] The resulting colored solution was rapidly bleached by Vis light irradiation (>500 nm) to generate the colorless spiro-form **2a,$_{SP}$**, while the bleached solution was completely recovered to the initial color in the dark at room temperature in a few minutes, as shown in Fig. 1a). Namely, these copolymers **2** repeated photobleaching and thermocoloration cycle due to the *negative* photochromism. Interestingly, a spin coat film of **2a** which was initially colored to blue purple was rapidly bleached by Vis light irradiation, while the resulting colorless films retained without thermal coloration in the dark after initial coloration up to 15% of the original absorbance as illustrated in Fig. 1b). These colorless films readily colored by being heated over 80 °C in the dark.



2a,$_{SP}$ **2a,$_{MC}$**

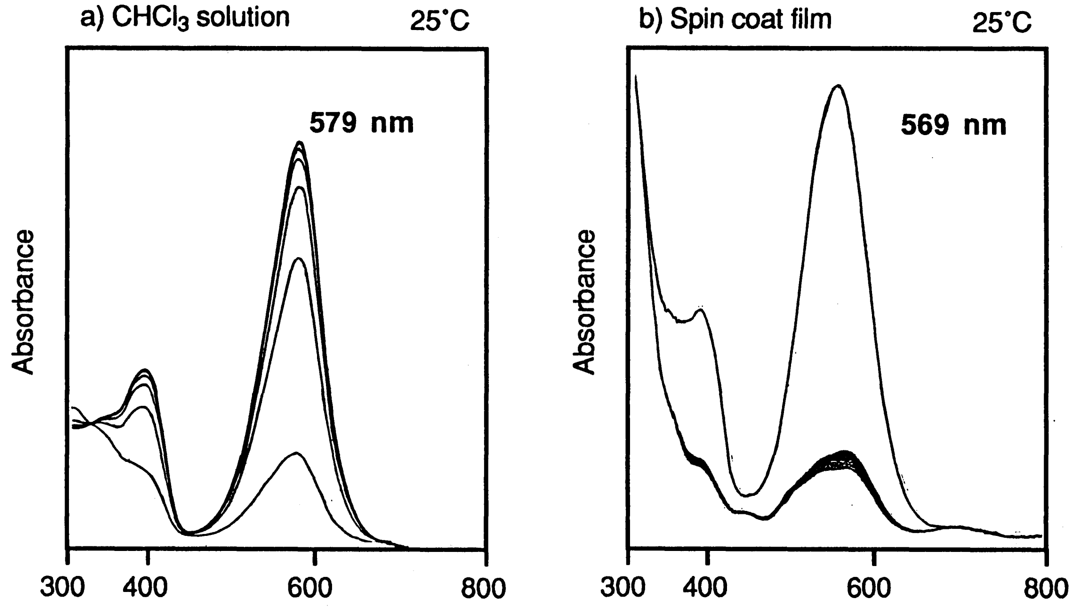


Fig. 1. UV-Vis spectral changes of **2a**; a) in $CHCl_3$, each spectrum was recorded at 1.5 min intervals immediately after irradiating a purple solution of **2a** by Vis light, b) in spin coat film, each spectrum was recorded at 3 min interval.

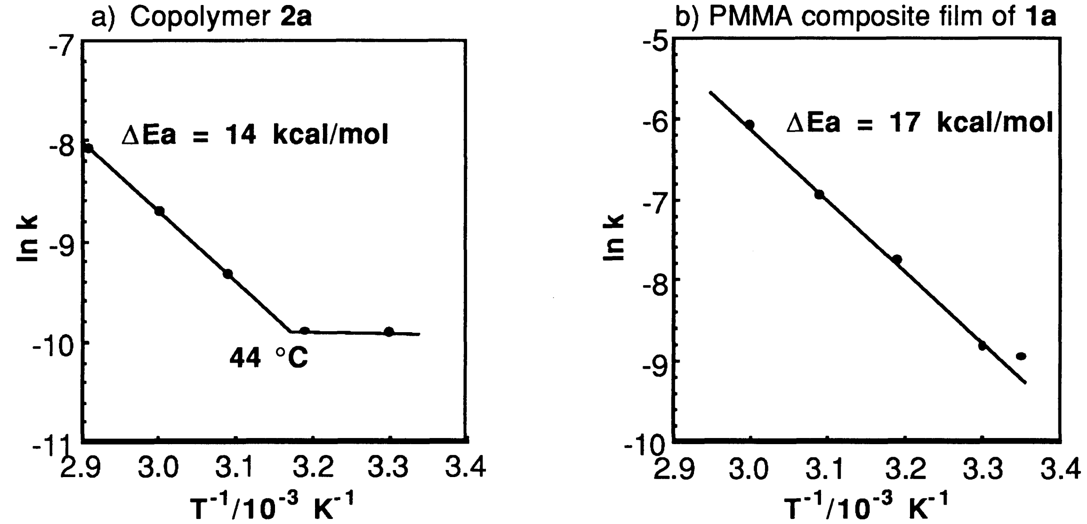
In Table 1, absorption maxima (λ_{max}), half lives of the metastable colorless form ($\tau_{1/2}$), and the amount of fixation (%) of the metastable colorless form in spin coat films were tabulated. The substituent group on benzoselenazoline ring gave no significant effect on absorption maxima and life time of the metastable form in $CHCl_3$ solution. The electron-donative group at 5- and 6-positions induced apparent blue-shift with increasing the amount of fixation of the colorless form. Surprisingly, isotactic copolymer **2e** exhibited apparent red shift by 20 nm both in $CHCl_3$ and in film, whereas the amount of fixation of the colorless form largely decreased to 24%. It should be noted that the metastable colorless form of **2a** in copolymer with MMA were stabilized over 90 days after initial slight thermal coloration, whereas **1a** dispersed in the polymers and the chromophore in the isotactic copolymer **2e** were not fixed and colored slowly even at room temperature.

Table 1. Photochromic properties of SeSP-MMA copolymers

Copolymer	SeSP monomer unit / mol%	λ_{max} /nm			
		In $CHCl_3$	($\tau_{1/2}$/min)[a]	Film[b]	(Fixation/%)[c]
2a	0.23	579	(1.3)	569	(85)
2b	0.24	579	(1.1)	561	(83)
2c	0.24	584	(1.3)	561	(84)
2d	0.24	582	(1.0)	540	(92)
2e[d]	0.10	597	(0.7)	580	(24)
composite 1a[e]	0.23			579	(55)

a) Half life of **2**,SP in $CHCl_3$ at 25 °C. b) Films were prepared by spin coat method and film thickness was determined as ≈1.0 μm by SEM. c) The amount of fixation of metastable colorless form **2**,SP were obtained by the following equation: $[(A_{init} - A_{24})/(A_{init}-A_0)] \times 100$, where A_{init} is absorbance at the initial state before Vis light irradiation, while A_0 and A_{24} represent absorbance at t=0 and 24 h at 25 °C after irradiating with Vis light, respectively. d) Tacticity of 92% (mmmm) was determined by ^{1}H-NMR. e) Spin coat film of PMMA composite doped with **1a** in 0.23 mol%.

To better understand reasons why the metastable colorless spiro-forms were thermally stabilized in the copolymer film, we have studied kinetics of their thermocoloration process by comparing the behavior of **1a** dispersed in PMMA.[8] Figure 2 demonstrates that the Arrhenius plot of thermocoloration rate constant k for copolymer **2a** showed the clear break at 44 °C which corresponds to the α' transition of Tα' for PMMA attributing to the local mode relaxation of the polymer main chain,[9] while the composite film of **1a** gave a straight line with no such break point. This may indicate the metastable spiro-form in the copolymer **2** can be thermally stabilized at least below the temperature at Tα'. More detailed studies for physical and optical properties of these photochromic polymers are in progress.


a) Copolymer **2a**

b) PMMA composite film of **1a**

Fig. 2. Arrhenius plots on thermocoloration of copolymer **2a** and PMMA composite film of **1a**.

References

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6) SeSP-methyl methacrylate copolymer **2a** was typically prepared by the reaction of **1a** (20.0 mg) with MMA (800 mg) using AIBN (5.0 mg) in dry DMF (4.0 ml) at 60 °C under N_2 in the dark (67% yield). SeSP content was determined as 0.23 mol% by comparison of absorbance of SeSP **1a** in $CHCl_3$ with that of the copolymer. Mw was obtained as 1.10 x 10^5 and Mn as 4.70 x 10^4 by GPC analysis (polystyrene standard). Mw's of **2b-d** were determined to be 8.6-11 x 10^4 and their SeSP contents were analyzed in the range of 0.10-0.24 mol%. Isotactic PMMA of **2e** was prepared by ionic polymerization using PhMgBr as a catalyst.[7)]
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8) Thermocoloration rate was measured by monitoring absorbance changes at 569 nm for copolymer **2a** and 579 nm for composite film of **1a**. Plot of $\ln\{(A_{init}-A_t)/(A_{init}-A_0)\}$, where A_{init} represents initial absorbance of **2a** and A_t is that at time t, versus time t at certain temperature gave straight lines with slight curvatures in the initial stages, and the resulting thermocolorarion kinetic followed the pseudo first-order process as far as the main portion of the straight lines were concerned.
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