Interaction between dispersed photochromic compound and polymer matrix

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Received 16 October 2002; received in revised form 10 March 2003; accepted 10 March 2003

Abstract

Thin films containing photochromatic spiropyran (SP) was prepared from polymethyl methacrylate (PMMA), polyethyl methacrylate (PEMA), poly(n-butyl methacrylate) (PnBMA), and styrene–butadiene–styrene copolymer (SBS). The thin films were illuminated with the ultraviolet light (365 nm) under various temperatures. The photochromic response was monitored with a multichannel photodetector. The results show that the photocoloring rate of SP was faster in PMMA, while the thermal decoloring rate was faster in SBS. In addition, the decoloring rate was higher in a polymer matrix with lower $T_g$.

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Keywords: Photochromism; PMMA; PEMA; PnBMA; SBS

1. Introduction

In 1956, Hirshberg proposed using photochromic colorants as photochemical memory devices [1–3]. Since then, a great deal of industrial and academic efforts have been invested to realize this idea [4–7]. With the advances of laser and holographic technology, this application seems making a great progress. However, the photochromic memory storage devices are not yet commercialized mainly due to the thermal instability and the fatigue behavior in the performance of these materials.

A photochromic memory must have the following characteristics. It must be colored by illumination. This colored form must be thermally stable at room temperature so that the data can be indefinitely preserved in the dark. It must have low or no chemical fatigue property so that the data can be written or erased repetitively. It must be highly sensitive so that the color form can be converted or reverted at specific wavelengths. It must not have internal filtering to the activation photon. It must have low damage to the resolution of the data. And finally, it must not be degraded during the preparation of the photochromic polymer film.

Many photochromic compounds used for photochemical memory have been proposed [4–7]. Among these photochromic colorants, most of them have spiropyran (SP) structure. Once exposed to light such as ultraviolet, a cleavage would occur at the C–O bonding on SP, resulting an amphoteric ionic structure of merocyanine. When the latter is heated or illuminated by visible light, it would reverse to the SP structure [8–10]. The reaction can be expressed as follows:

\[
\text{UV} \rightarrow \text{Vis, or heat}
\]
Because the coloration of SP is caused by the cleavage of covalent bonding, it has poor thermal stability that leads to degradation. This limits the application of SP as a memory storage material. On the other hand, SP is very sensitive to UV light and its color is vivid, and its application in photochromic microimage is under development [11–14].

Spirooxazine was first reported in 1961 by Fox [15]. He found that the toluene solution of spirooxazine changed from colorless to blue after illuminating with ultraviolet light at 10 °C. The chemical structure of spirooxazine is similar to SP. The only difference is that the C=C in pyran is replaced by C=N in oxazine. After UV illumination, heterolytic bond cleavage occurs at the oxygen adjacent to spirocarbon and forms photomerocyanine with maximum absorbance in its visible spectrum. The coloring mechanism is given in Scheme 1. The intermediate X is produced first after illumination, and then forms four isomers MI–MIV. The solution exhibits strong solvatochromic effect which was studied by Schneider [16,17].

The formation of merocyanine depends on the position of R₁ groups, the viscosity and the polarity of the solvent. In a polar solvent, the maximum absorbance occurs at lower energy, causing a red shift.

In a non-polar solvent as well as aprotic solvent, MI and MII are dominant, whereas in protic solvent, MIII and MIV are dominant. Since the dipole moment of MIII is higher, it is the most stable form in a protic solvent.

The thermal fading of spirooxazine dispersed in cyclic isoprene rubber is not a first order reaction [18]. As reported by Kryszewski, the reaction of dispersed compounds in a glassy medium is controlled by diffusion [19–21].

Photochromic materials are potentially applicable in personal protection, data displays, camouflage, and decoration. Although the requirements for each application

![Scheme 1. The coloring mechanism of SP.](image-url)
may differ, the common requirement is the durability. Among hundreds of photochromic compounds, only spirooxazine has good optical durability [22]. This durability can be enhanced by adding organo-nickel photostablizing agent without reducing its colorizability [23].

Although spirooxazine is similar to SP, it has the characteristics of fast fading, and is stable for long term usage without decaying the color.

The goal of this work is to study the interaction between photochromic materials and the polymer medium. The results of this work throw more light into the understanding of the effect of the polarity and the molecular mobility of the polymer medium on the photochromism, the temperature dependence, the thermal stability, and the comparison of the photochromism of spirooxazine and SP.

2. Experimental

2.1. Materials

Both the SP colorant, 1,3,3-trimethylindoline-6′-nitrobenzopyrylospiran (SP) and the spirooxazine colorant, 1,3,3-trimethylindoline-naphthospirooxazine (SO) were purchased from Tokyo Kasei, Japan. Polymethyl methacrylate (PMMA) was obtained from ICI, UK. Polyethylene methacrylate (PEMA) and poly(n-butyl methacrylate) (Pn-BMA) were purchased from Aldrich, USA. Styrene–butadiene–styrene (SBS) was obtained from Philips, USA.

2.2. Preparation of thin films

To 20 ml of CH2Cl2, 0.4 g of the polymer was added and stirred until completely dissolved. Then a specified amount (1–5 wt.% of the polymer) of SP was added to the polymer solution and stirred well to mix. This solution was poured into a petridish and kept in a dark room. After the complete evaporation of the solvent, the dish was baked in an oven at 60 °C for 20 min. The film was then peeled off from the dish. The thickness of the resulting film was about 30–40 μm. The resulting films were kept in a dark room.

2.3. Photochromic experiment

A monochromator (SN86-154, Panasonic, Japan) was used to disperse the ultraviolet wavelengths, and the wavelengths used to illuminate the film to produce photocoloring were 330, 350, 365, and 380 nm. The intensity of the UV source was controlled by a UV controller (UVL-200, Hexman Corp., Taiwan). A multichannel photodetector (MCPD-110, Otsuka Electronics Co., Japan) was used to monitor the photochromic response of the film. The variation in the maximal absorbance was then plotted against time. The coloring rate constant can be calculated assuming a first order kinetics.

2.4. Thermo-decoloring measurement

Thin films were exposed to 365 nm, and the decoloring was monitored using the MCPD at various temperatures. The variation in the absorbance was then plotted against time, and the decoloring rate constant was calculated assuming a first order kinetics.

2.5. Determination of molecular mobility

The films were subject to a heating rate of 6 °C/min in a rheology dynamic spectroscopy to determine the loss in elastic modulus with respect to temperature.

2.6. Dielectric measurement

The films were scanned using a dielectric measuring system (Microment Instruments Corp.) at different temperatures and frequencies.

2.7. Thermal stability measurement

The thermal degradation of the film was determined using a thermogravimetric analyzer (TGA) (Du Pont 9900, Du Pont, USA) in either N2 or air. The heating rate used was 10 °C/min.

3. Results and discussion

3.1. Matrix effect on the photochromism of SP

Merocyanine, an amphoteric ion, is the coloring form of SP after exposing to ultraviolet light [12,24]. Because of the ionic nature of merocyanine, it is possible to interact with a polar polymer matrix. This point is supported by the spectra in Fig. 1. In non-polar SBS matrix the maximum absorbance of SP occurred at 600 nm, whereas in polar PMMA matrix, the maximum absorbance shifted to 575 nm. The blue shift was apparently caused by the extra interaction between polar PMMA and ionic merocyanine. Further shift of the maximum absorbance occurred at 560 nm in PnBMA. In addition to a polar polymer, PnBMA has a lower Tg than PMMA. This means that PnBMA has higher mobility than PMMA. Thus SP interacts more with PnBMA and hence leads to more blue shift.

Fig. 2 shows the difference in the coloring behavior of SP in SBS and PMMA matrices. The coloring rate in SBS is about half of that in PMMA. On the other hand, for thermal decoloring, the rate constant is higher in SBS.
than in PMMA, as shown in Fig. 3. That means that the thermal decoloring of SP is slower in a more polar matrix such as PMMA. In addition, from the slope of the fitted line in the Arrhenius plot in Fig. 3, the decoloring in PMMA requires higher activation energy (17 ± 1 kcal/mol) than in SBS (14.2 ± 0.5 kcal/mol). This can also be attributed to the extra interaction with polar PMMA.

The interaction can be observed from the temperature scanning of the dielectric property variation. Fig. 4 shows the variation of dielectric loss $\varepsilon''$ of PMMA with respect to temperature. In this figure, the $T_g$ of pure PMMA is at 107 °C, and that of SP-dispersed PMMA is shifted to 115 °C. This shift in $T_g$ can be attributed to the interaction between merocyanine and PMMA. Although this observation is in contrast to the plasticizing effect of photochromic molecules in polystyrene concluded by Lawrie et al. [25], we think this can be attributed to the dipole–dipole interaction between SP and PMMA [26] which restricts the mobility of PMMA molecules. Furthermore, SP also caused lower dielectric loss below $T_g$, as shown in Fig. 4. This is due to the lowering of the polarity of PMMA by the interaction with SP. Fig. 5 illustrates the dipole–dipole interaction between the side chain of PMMA and merocyanine.

The $T_g$ of SBS is not as distinguishable as PMMA; only a small shoulder indicates the location of $T_g$. In addition, the presence of SP only shifted the $T_g$ of SBS from 123 to 125 °C. Apparently this can be attributed to the lower interaction between merocyanine and SBS. When SP was added to SBS, it may plasticize the matrix, but SP also interacts with SBS molecules (to a lesser degree than with PMMA). Thus the $T_g$ of SBS was increased slightly with the adding of SP.

3.2. Effect of molecular mobility of polymer matrix

Three polymers of similar structure but different $T_g$s were employed to study the effect of molecular mobility

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**Fig. 1.** Effect of polymer matrix on the spectra of SP. The absorption peak shift toward lower wavelength in polar matrix.

**Fig. 2.** The coloring at 365 nm of SP in PMMA and SBS at 20 °C.

**Fig. 3.** Arrhenius plot of the thermal decoloring rate constant of SP in polymer matrix.

**Fig. 4.** Temperature effect on dielectric loss $\varepsilon''$ of SP in PMMA.
on the photochromism of SP. These polymers and their $T_g$s are listed in Table 1. Fig. 6 shows that the coloring of SP in PMMA is faster than in both PEMA and PnBMA. Since these polymers are similar in their polarities, the coloring rate is obviously affected by the molecular mobility. During the cleavage of C–O bond, the reaction will be interfered by the molecule of the polymer matrix. With lower $T_g$, PnBMA has higher molecular mobility than PEMA and PMMA. Thus in PnBMA, the coloring process was interfered more frequently than both in PEMA and PMMA, and hence was slower. The interference of the matrix molecule would also destabilize merocyanine. Thus as shown in Fig. 7, the half-life of merocyanine is much shorter in PnBMA than in PEMA and PMMA. The coloring form, merocyanine, was the most stable in PMMA whose $T_g$ is the highest of these three polymers.

### 3.3. Temperature dependence of photochromism

In liquid solutions, the coloring and decoloring of SP are due to first order reaction. On the other hand, in solid solutions, the mechanism is more complicated. The coloring of SP is accompanied with thermal decoloring. When dispersed in PMMA or SBS, the coloring rate decreased with the increase of temperature. At 100 °C, the decoloring and coloring rates are equal causing no further increase in coloring.

Fig. 8 depicts the decoloring of SP in PMMA under various temperatures and shows that the decoloring reaction accelerates with the temperature. The variation in the absorption is not linear. This suggests that the mechanism of the decoloring is not first order, but as Gardlund [12] suggests, is like two parallel first order reactions. In these cases, the rate constants were calculated from the initial slopes of the curve. Tork et al. [27] mentioned that there are two coloring forms, a and b, for SP. In this work, the decoloring temperature was less than 95 °C, which cannot surpass the 30 kcal/mol barrier of the photoisomerization. Thus although photoisomerization may occur during coloring process, the decoloring in this work is predominantly due to the closure of the a form.

Fig. 9 is the Arrhenius plot of the decoloring rate constants and shows a jump at the $T_g$, and above the $T_g$ of the polymer matrix, the decoloring rate increased.

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**Table 1**

The activation energies of the thermal decoloring of BIPS in polymer matrices

<table>
<thead>
<tr>
<th>Polymer matrix</th>
<th>$T_g$ (°C)</th>
<th>$\Delta E$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>107</td>
<td>$T &gt; T_g$ 17.3</td>
</tr>
<tr>
<td>PEMA</td>
<td>66</td>
<td>22.4 $T &lt; T_g$ 16.1</td>
</tr>
<tr>
<td>PnBMA</td>
<td>27</td>
<td>25.4 $T &lt; T_g$ 15.2</td>
</tr>
<tr>
<td>SBS</td>
<td>123</td>
<td>-- $T &gt; T_g$ 14.2</td>
</tr>
</tbody>
</table>

**Fig. 5.** The dipole–dipole interaction between side chains of PMMA and merocyanine.

**Fig. 6.** The coloring of SP in various polymer matrices at 20 °C excited at 365 nm.

**Fig. 7.** The temperature effect on the half-life of SP in various polymer matrices.
abruptly. This is attributed to the increase in the free volume above the $T_g$. From the slope of the fitted lines, the activation energy $\Delta E$ can be calculated and summarized in Table 1. From the entries in Table 1, we can see that in polyalkylmethacrylates, when the length of the side chain increases, $\Delta E$ is decreased, and the difference between the $\Delta E$’s in glassy state and rubbery state is enlarged.

3.4. Coloring and decoloring of spirooxazine in polymer matrices

The coloring mechanism of SO is similar to SP because SO produces metastable merocyanine after UV illumination and absorbs visible light.

The coloring rates of SO in polymer matrices vary with the illuminating wavelength, and the highest rate occurs at 365 nm. This is because most of the photons are absorbed at the surface so that they will not reach inner molecules. This shielding effect for SO is lower at 365 nm than at 310–350 nm. On the other hand, photons at 380 nm have lower energy than photons at 365 nm. Thus the coloring is the highest at 365 nm.

The polarity of the polymer matrix can affect the maximum absorbance. The maximum absorbance in non-polar SBS is at 595 nm, while that in polar PMMA is at 603 nm. This agrees with the results of Schneider [16,17].

The effect of the matrix on the coloring is depicted in Fig. 10. We can see that the coloring rate is faster in PMMA than in SBS. This is because that the polar side groups of PMMA interact with merocyanine. Among these polymer matrices, the highest coloring rate occurs in PMMA, followed by PEMA and PnBMA. This is due
to the accompanying decoloring reaction. Higher interaction causes higher decoloring rate, as shown in Fig. 11. We can see also in Fig. 11 that the decoloring rate in SBS is the lowest. This explains why in Fig. 10 the coloring rate of SO in SBS is lower than in PMMA, but still higher than in PEMA and PnBMA.

In a polar matrix such as PMMA, the thermal decoloring rate increases with the concentration as shown in Fig. 11. Apparently this is due to the higher collision frequency between merocyanine and the polymer molecules.

4. Conclusion

In this work, the effect of polymer matrix on the coloring and decoloring of SP and spirooxazine was studied. In addition, the interaction between the colorant and the polymer was also investigated. Several points are concluded as follows:

Polar PMMA causes a blue shift in the maximum absorbance of SP, while causes a red shift in the maximum absorbance of spirooxazine. Based on the results of dielectric studies, the photochromic form of SP has amphoteric ionic structure and interacts strongly with the polar side chains of polymer matrix. This shifts the $T_g$ of the polymer higher. Because of molecular interaction, photochromic colorant has faster coloring rate and slower decoloring rate in polar polymer matrices. Polymer matrix with lower $T_g$ and higher mobility can provide thermally less stable environment for SP and spirooxazine. This accelerates the decoloring rate.

The coloring mechanism of SP is not of first order. The Arrhenius plot has a jump at the $T_g$. Based on the results of TGA, spirooxazine is thermally more stable than SP and causes a red shift in the maximum absorbance of SP, while causes a blue shift in the maximum absorbance in PEMA and PnBMA.

The results of TGA, spirooxazine is thermally more stable than in PMMA, but still higher than in PEMA and PnBMA.

References


