# Synthesis, Characterization, and Photochromic Properties of PMMA Functionalized with 4,4′-Diacryloyloxyazobenzene

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**ABSTRACT:** Attempts to introduce the azo chromophore into poly(methyl methacrylate) (PMMA) molecular chains were made in search for a new approach to obtain functionalized-PMMA (f-PMMA) with high glass transition temperature and an adequate azo content. A novel functionalized monomer, 4,4′-diacryloyloxyazobenzene (DAOAB), was synthesized and used as grafting agent in the polymerization of methyl methacrylate. ^{1}H-NMR spectrum, FTIR spectrum, elemental analysis, and MDSC measurement confirmed that the proposed structure of DAOAB was synthesized successfully. Furthermore, the thermal properties and photochromic behavior of f-PMMA samples were also analyzed by DSC, TGA, and UV–visible spectroscopy. The results have shown that f-PMMA exhibited a better photochromic behavior and considerably improved thermal properties than pure PMMA. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1061–1068, 2002

**Key words:** PMMA; photochromic property; azobenzene; *cis–trans* isomerization

## INTRODUCTION

Recently, increasing attention has been paid to photonic materials for the development of optical data storage device with high-storage capacity and optical switch with ultrafast response.[1–4] Polymers containing substituted azobenzene groups were demonstrated to be good candidates[5–8] for optical data storage, ultrafast optical switch, and other electrooptic devices.

When irradiated at a certain wavelength of light, the azobenzene groups which are not perpendicular to the laser polarization direction will undergo many *trans–cis--trans* isomerization cycles accompanied by reorientation until they fall in one of the directions (in a plane) perpendicular to the laser polarization direction. Thus, a stationary orientation can be obtained when the optical transition moment lies approximately parallel to the long axis of the *trans* azobenzene, and the azo unit is oriented in the plane perpendicular to the polarization direction of the laser beam. The isomerization and anisotropic alignment of azobenzene, which lead to a local modulation of the refractive index in the compounds, give rise to the possibility for them to be used as optical recording materials.

Generally speaking, after the irradiating laser beam is shut off, this alignment could be permanently frozen and permanent information storage is achieved if the glass transition temperature ($T_g$) of the polymer is high. This is because polymers with high $T_g$ showed better long-term stability of the written information than polymers with low $T_g$.[9] Indeed, many amorphous polymers with high $T_g$ were synthesized to increase the
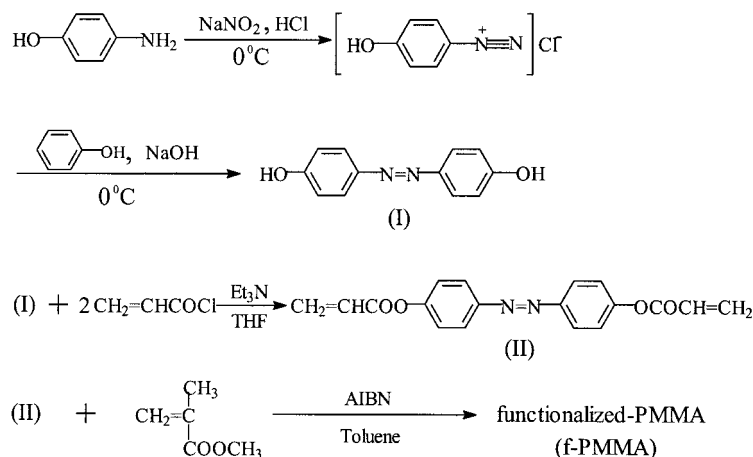
**Figure 1** Synthetic route to the functionalized-PMMA samples.

lifetime of the stored information.[10,11] In addition, it is reported[10,12–19] that polymers with low azo concentrations are particularly useful because of the fact that the writing and erasing efficiency depend on the energy input from the irradiation light during the process. The usefulness of materials for such applications depends on the energy required to induce local variations of optical properties. In principle, lower energies would be required to write and erase information on azo polymers with low azo concentrations. Hence, it is clear that polymers with low azo concentrations and high $T_g$ are particularly useful for the isomerization-induced holographic information storage because these polymers exhibit a very distinct optical anisotropy after irradiation with linearly polarized light and long-term stability of the stored information. To dilute the azo content in polymer materials, two methods were developed. One is by copolymerization.[13–18] The other is the blend of azo polymers with optically inert materials.[15,19]

In this research, a new method was developed and used to prepare functionalized polymer with lower azo contents and higher $T_g$. Our approach to obtain azobenzene-functionalized polymer was quite different from those reported by other literatures. In this study, a novel functionalized monomer, 4,4′-diacryloyloxyazobenzene (DAOAB), was synthesized, which serves not only as chromophores in polymer [functionalized poly(methyl methacrylate) (f-PMMA)] but also as a grafting agent for PMMA to increase the glass temperature of the polymers. The synthesis procedures used for the preparation of photochromic f-PMMA are shown in Figure 1.

## EXPERIMENTAL

### Materials

4-Aminophenol, sodium nitrite, phenol, acryloyl chloride, and hydroquinone were purchased from Aldrich and used without further purification. Methyl methacrylate (MMA) (TCI, Japan) was purified by distillation under vacuum. Azobisisobutyronitrile (AIBN) (TCI, Japan) was recrystallized from acetone and dried under vacuum. THF (Aldrich) was distilled under nitrogen over sodium benzophenone ketyl (Merck, Germany) immediately prior to use.

### Synthesis of 4,4′-Dihydroxyazobenzene (I)

The synthesis procedures utilized can be described as follows: 16.35 g (0.15 mol) of 4-aminophenol was dissolved in a mixture of 41 mL water and 41 mL concentrated hydrochloric acid. This solution was then cooled in an ice-water bath with vigorous stirring. A solution of 11.4 g sodium nitrite in 35 mL water was added to the mixture by a dropping funnel. In the meantime, 13.65 g (0.15 mol) of phenol was dissolved in a solution of 15.0 g NaOH in water and cooled in an ice-water bath. Then, the diazotized solution was slowly added to the cooled phenol mixture. After this, concentrated hydrochloric acid was added to the solution until it became strongly acidic (pH = 1.0). The reaction was allowed to continue for another 2 h under stirring. The precipitate was then filtered and washed with water to remove the acid. The product was recrystallized three times in a mixture of acetone and water.

Mp: 177°C (DSC, 5°C/min).

FTIR (KBr, cm$^{-1}$): 3462 (Ar, OH); 1592, 1506, 1478 (Ar, C=C); 1155 (Ar—N); 836 (Ar, =C—H, 1,4-disubstituted benzene ring)

$^1$H-NMR (acetone-d$_6$, ppm): 7.0 (d, 4H, ArH), 7.80 (d, 4H, ArH), 9.02 (s, 2H, ArOH).

ANAL. calcd for C$_{12}$H$_{10}$N$_2$O$_2$: C, 67.29; H, 4.67; N, 13.08. Found: C, 67.24; H, 4.66; N, 13.04.

### Synthesis of DAOAB (II)

An amount of 0.7194 g (3.4 mmol) of 4,4′-dihydroxyazobenzene (I) was dissolved in a mixture of 1.85 mL Et$_3$N and 10 mL freshly distilled THF. This solution was then cooled in an ice-water bath with vigorous stirring. A solution containing 1.03 mL (12.7 mmol) acryloyl chloride, 7 mL freshly dried THF, and 0.04 g hydroquinone was added to the above mixture by a dropping funnel. After 1 h, the ice-water bath was removed and the reaction was allowed to continue for 5 h at room temperature. The product was washed by ice-cooled methanol under N$_2$ gas atmosphere and recrystallized twice in a mixture of methanol and THF. Mp: 161°C (DSC, 5°C/min).

FTIR (KBr, cm$^{-1}$): 3048 (Ar, =C—H; acrylic, CH$_2$—CH—); 1747 (ester carbonyl C=O); 1637 (acrylic, C=C); 1592, 1507 (Ar, C=C); 1155 (Ar—N); 836 (Ar, =C—H, 1,4-disubstituted benzene ring).

$^1$H-NMR (CDCl$_3$, ppm): 6.09 (d, 2H, vinyl proton), 6.38 (m, 2H, vinyl proton), 6.68 (d, 2H, vinyl proton), 7.33 (d, 4H, ArH), 7.80 (d, 4H, ArH).

ANAL. calcd for C$_{18}$H$_{14}$N$_2$O$_4$: C, 67.08; H, 4.35; N, 8.70. Found: C, 67.05; H, 4.35; N, 8.67.

### Synthesis of f-PMMA

An appropriate amount of MMA, DAOAB (II), AIBN (0.5% w/w), and toluene were added into a round-bottomed flask. Then, it was frozen by liquid nitrogen and thawed repeatedly three times under vacuum. The flask was sealed under a N$_2$ atmosphere and then heated in an oil bath to 65°C. After the solution was magnetically stirred for about 26 h, the reaction mixture was poured slowly into methanol under agitation. The precipitated f-PMMA was redissolved in THF and reprecipitated by methanol repeatedly three times. Then the purified f-PMMA was filtered and dried in a vacuum oven at 50°C.

### Measurements

NMR spectra were recorded on a Bruker 400 NMR spectrometer at 400 MHz in deuterated chloroform with tetramethylsilane (TMS) as an internal standard. The elemental analyses were carried out with a Mitamura riken kogyo microelementary analyzer. DSC analyses were performed at 5°C/min on a TA Instruments 2920 Modulated DSC. Thermal stability measurements were carried out on a Hi-Res TGA 2950 thermogravimetric analyzer under a nitrogen flow at a heating rate of 10°C/min. Molecular weights of samples were measured by gel permeation chromatography (GPC, Waters 410; eluent, THF) calibrated with monodispersed polystyrene standards. UV–Visible spectra were obtained by using a UV–Vis recording spectrophotometer (Shimadzu, Model UV-2501PC). The photochromic experiments were carried out by using an ARC lamp (Oriel, Model 68910, 500 W) as the source. The monochromatic light peaked at 340 nm was isolated by using a glass filter (U-340). The powder f-PMMA samples were dissolved in the appropriate solvents [e. g., CH$_3$Cl and dimethylformamide (DMF)] and then allowed to sit for 24 h in the dark before irradiation. To prepare thin films, the f-PMMA was dissolved in chloroform and the solution was deposited by spin coating onto clean quartz slides.

## RESULTS AND DISCUSSION

### Synthesis of Monomer and f-PMMA Samples

Azobenzene monomer (II) was synthesized from the 4,4′-dihydroxyazobenzene (I) and acryloyl chloride in thoroughly dried THF. To avoid the polymerization of acrylate vinyl function during crystallization, an appropriate amount of hydroquinone was added to the reaction mixture as inhibitor. $^1$H-NMR spectrum (Fig. 2), FTIR spectrum, elemental analysis, and measurement of melting point (one sharp and distinct endothermic peak in DSC) confirmed the proposed structure of (II).

Azocompound f-PMMAs were synthesized by free radical polymerization of monomer MMA and the azobenzene monomer (II). The polymerization reaction was stopped near the gel point by pouring the reaction mixture into methanol in case of the formation of crosslinking polymer. The f-PMMA samples so obtained can be dissolved in common organic solvents (e.g., chloroform, THF, DMF) at room temperature or elevated temperature (50°C in THF). No precipitation was observed after cooling the solution down to room temperature. The compositions and properties of
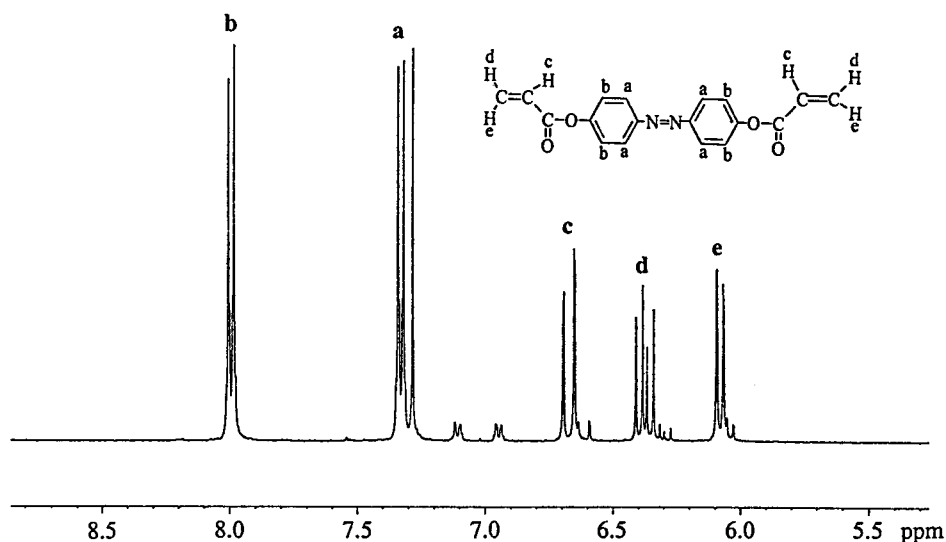
**Figure 2**    $^1$H-NMR spectrum of 4,4′-diacryloyloxyazobenzene (DAOAB) in CDCl$_3$.

the resulting f-PMMA samples along with PMMA homopolymer prepared under similar conditions are listed in Table I. It can be seen that the actual contents of azo function groups in the f-PMMA samples are generally higher than the initial feeds of azo functionalized monomer. This can be attributed to the fact that a certain amount of PMMA homopolymer formed during the polymerization was extracted out by the dissolution/precipitation cycles with THF and methanol. Furthermore, The GPC results in Table I show that the polydispersity of the f-PMMA samples increased with increasing the content of DAOAB because of the increase of grafting degree.

### Thermal Behavior of the f-PMMA Samples

The importance of achieving high $T_g$ in photochromic polymers is well known. Possible applications of such amorphous high $T_g$ photochromic polymers include erasable optical memory disks and tape and erasable holographic storage materials, as well as optical sensors.[20,21] To obtain photochromic polymers with the good stability of the induced birefringence, a grafted-PMMA was designed in which the functionalized azobenzene chromophore units also act as bridges between the PMMA chains to increase the $T_g$ of PMMA. On the other hand, because of being attached between the PMMA chains, the mobility of azobenzene chromophore should be reduced; thus, one could in principle achieve a polymer which exhibits an enhancement in both the photoinduced birefringence level and the stability.

Table I listed the $T_g$ of pure PMMA and f-PMMA samples with different contents of DAOAB (II). The typical DSC thermograms of corresponding samples

**Table I   Compositions and Thermal Properties of f-PMMA Samples**

| Samples | Initial Feed (azo mol %) | Composition[a] (azo mol %) | $M_n$ $(10^{-4})$ | $M_w/M_n$ | $T_g$ (°C) | $T_5$ (°C)[b] | $k_T$ $(\times 10^4 \text{ s}^{-1})$[c] |
|---|---|---|---|---|---|---|---|
| Pure PMMA | 0 | 0 | 4.79 | 2.15 | 113.4 | 279.5 | — |
| f-PMMA1 | 0.16 | 0.94 | 5.12 | 2.63 | 130.8 | 288.7 | 14.5 |
| f-PMMA2 | 0.47 | 1.17 | 4.95 | 2.85 | 132.5 | 307.0 | 12.0 |
| f-PMMA3 | 0.79 | 1.42 | 5.21 | 3.34 | 132.9 | 312.5 | 10.8 |
| f-PMMA4 | 1.12 | 1.72 | 5.37 | 3.67 | 133.2 | 317.0 | 9.34 |

[a] Calculated from UV–Vis spectra.
[b] 5% weight loss.
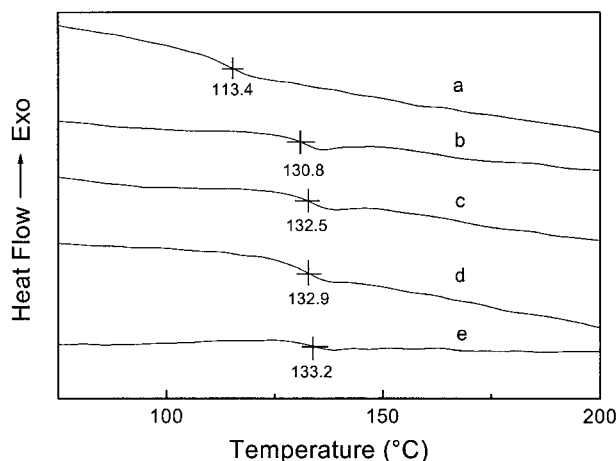[c] Thermal isomerization rate constant.

**Figure 3** DSC thermograms of (a) pure PMMA, (b) f-PMMA1, (c) f-PMMA2, (d) f-PMMA3, (e) f-PMMA4. (The compositions of samples are listed in Table I).



**Figure 5** UV–Vis spectral changes of f-PMMA4 film upon irradiation at 340 nm.

are shown in Figure 3. It can be seen that the $T_g$ of all f-PMMA samples increase about 20°C in comparison to that of the pure PMMA. Therefore, it is reasonable to expect that these functionalized polymers should exhibit better stability because of the decreasing rate of relaxation.

To determine the thermal stability of the samples, TGA of f-PMMA samples and pure PMMA was also carried out under a $N_2$ atmosphere at a scanning rate of 10°C/min; the results are shown in Table I and Figure 4. It is clear that the initial thermal decomposition temperatures of all f-PMMA samples were much higher than that of pure PMMA. It means that the thermal stability of PMMA could be enhanced considerably by
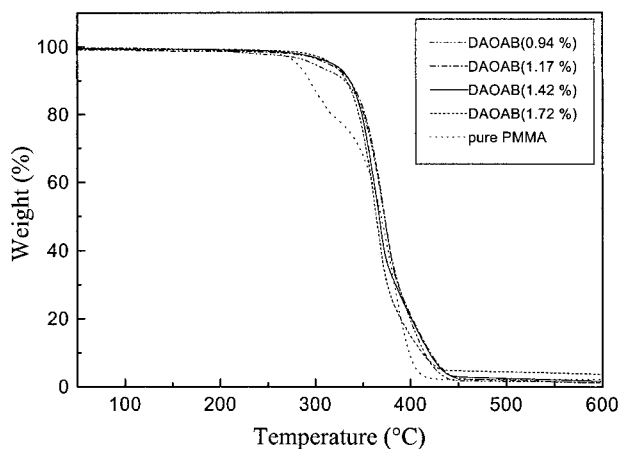


**Figure 4** TGA thermograms of f-PMMA samples and pure PMMA. (The compositions of samples are listed in Table I).
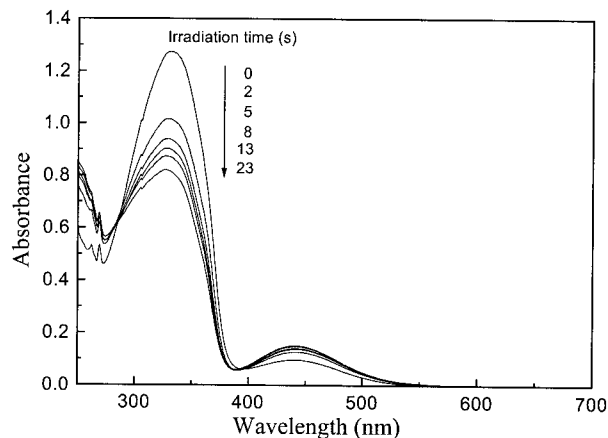
forming functionalized graft polymer. Furthermore, the experimental results also show that the thermal stability (5% weight loss) of f-PMMA increases with increasing the content of DAOAB. This attributed to the fact that the content of DAOAB directly affects the degree of grafting and f-PMMA structure.

## UV Absorption and Photochromic Properties

The UV–Vis absorption spectrum of f-PMMA4 film (Fig. 5) exhibited in the range of 260–600 nm two absorption bands centered around 337 and 450 nm, related, respectively, to the $\pi$-$\pi^*$ and $n$-$\pi^*$ electronic transitions of the azobenzene chromophore. The first band is mainly due to the *trans* isomers ($\epsilon_{trans}/\epsilon_{cis} \approx 20.0$), whereas the second one is mainly derived from the metastable *cis* isomers ($\epsilon_{cis}/\epsilon_{trans} \approx 3.0$). When the film was irradiated by the light of 340 nm, azobenzene chromophore underwent a *trans*-to-*cis* photoisomerization process. The absorption band at 337 nm gradually decreased and the absorption band at 450 nm gradually increased with irradiation time. The presence of three isosbestic points at about 288, 395, and 585 nm confirmed that only two absorbing species, namely *cis*-and *trans*-azobenzene, were present in f-PMMA4 film. Similar observation results were also obtained for other f-PMMA films. In addition, the UV–Vis absorption spectra of f-PMMA in DMF solution irradiated for different duration were also recorded, which showed quite similar photoisomerization behavior.

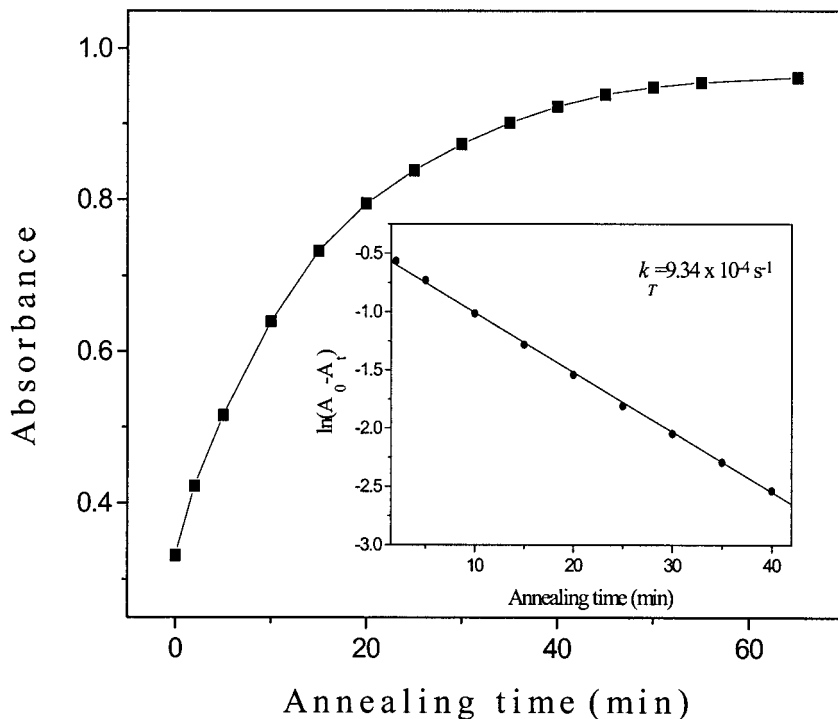On the other hand, when the irradiated samples were thermally annealed at certain temper-

**Figure 6** Plots of absorbance at 337 nm of f-PMMA4 in DMF (0.29 mg/ml) kept in the dark at 70°C after irradiation of light (at about 340 nm for 2 min); inset: first-order rate constant plot of $\ln(A_0 - A_t)$ versus time.

atures, the absorption peak at 337 nm steadily increased up to the starting value before irradiation, thus confirming the reversibility of the photothermal *cis–trans* isomerization process. This clearly indicates homogeneous photochromic behavior for *trans* and *cis* azobenzene chromophores in the f-PMMA sample. Thermal isomerization kinetics were investigated at 70°C in DMF solution. Experiments were performed by heating the irradiated sample solution at 70°C in the dark while monitoring the 377 nm absorbance until a steady state was reached, as shown in Figure 6. The thermal *cis–trans* isomerization of the azobenzene group follows a first-order kinetics, thus suggesting that the above process is not affected by the presence of adjacent azobenzene chromophores along the macromolecular in either the *trans* or the *cis* configuration.[22] The slope of plots of $\ln(A_0 - A_t)$ against time give the thermal isomerization rate constant ($k_T$), where $A_0$ and $A_t$ are absorbances at 337 nm before photoirradiation and after annealing for $t$ min followed by irradiation, respectively.[23] Table I also lists the thermal isomerization rate constant at 70°C of the f-PMMAs. Comparison of rate constant $k_T$ suggests that the thermal isomerization rate con-

stant of f-PMMA samples exhibited a slight decrease with an increase in the content of DAOAB. This reveals that the f-PMMA macromolecular backbone with a higher grafting degree has the tendency to depress the isomerization process, owing to the steric hindrance. However, these effects appear to be rather smaller because of the fact that the amount of DAOAB used in the polymerization of MMA is not enough to produce more grafting points in PMMA molecules to remarkably restrict the isomerization of azobenzene chromophore attached between PMMA chains. This was required for reversible optical data storage.

## Solvatochromic Effect and Optical Switching Characteristics

The UV–Vis spectra of f-PMMA in DMF solution and as a spin-coated film are different (Fig. 7). The maximum absorbance ($\lambda_{max}$) of f-PMMA in DMF solution shows a red shift of about 10 nm in comparison with f-PMMA film (339 nm versus 330 nm in the case of the spin-coated film). The red shift of the absorbance maximum could come not only from the superimposition of bands due to
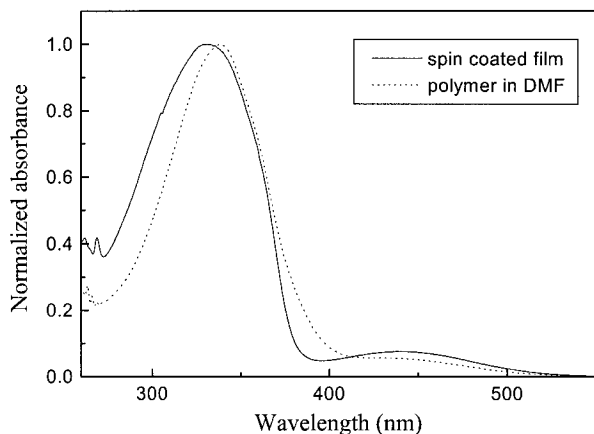
**Figure 7**  UV–Vis absorbance spectra of f-PMMA4 in DMF and a spin-coated film.



**Figure 9**  Comparison of absorbances for f-PMMA4 sample in DMF at 50°C for different periods of time in the dark.

the *trans* and *cis* isomers in various proportions, but also from the disappearance, due to strong dipolar interactions in DMF solution, of antiparallel dimers absorbing at weaker wavelengths.[11] Furthermore, it is very interesting to note that the f-PMMA samples show a systematic shift of the absorbance maxima to longer wavelength as the thermal isomerization temperature (or isomerization time) increases (Figs. 8 and 9). The reason is not very clear at present; it may be due to the changes of the dipolar–dipolar interactions between the azo chromophores under the different isomerization conditions.

The typical switching characteristics of the f-PMMA samples are also investigated, as shown in Figure 10. It can be seen that this kind of material exhibits a better optical switching property
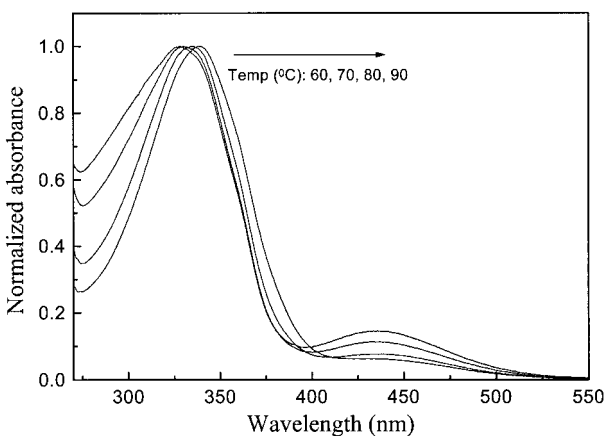
and the switching behavior itself was reversible and highly reproducible. Moreover, f-PMMA4 showed only a very little decay during the photo-induced isomerization and thermal recovery process. Similar results were also obtained for other f-PMMA materials. Further investigations on the effect of the grafting degree on photoinduced birefringence level and its stability are being undertaken in our lab; the results will be published in our next article.

## CONCLUSION

In this article, a new approach for preparing photochromic polymers was introduced, by which a



**Figure 8**  Comparison of absorbances for f-PMMA4 sample in DMF upon heating at different temperatures in the dark (5 min).
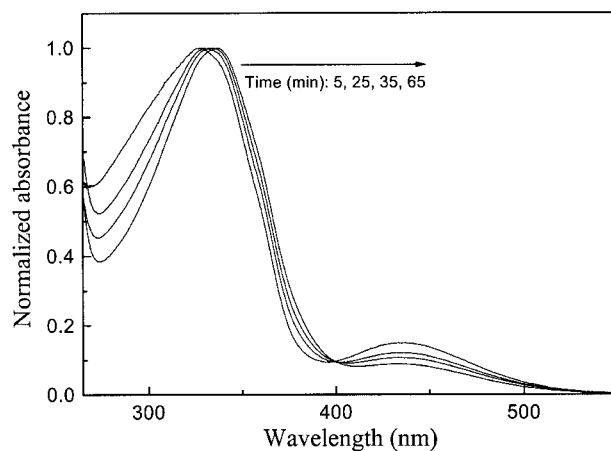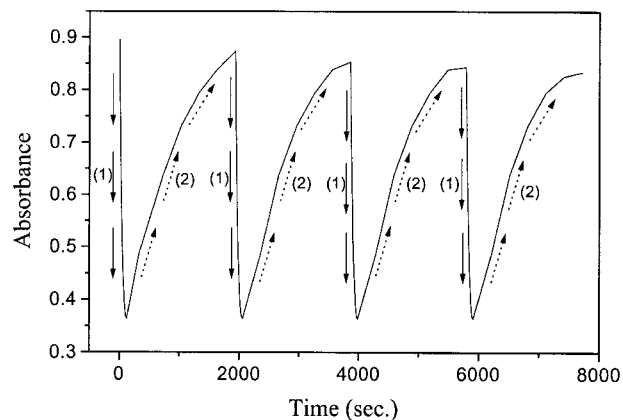


**Figure 10**  Optical switching characteristics of f-PMMA4: (1) photoinduced by the light of 340 nm, (2) thermal isomerization upon heating at 70°C in the dark.

series of f-PMMA samples with a higher $T_g$ and a lower azo content were synthesized. These f-PMMA samples exhibited a better photochromic property and considerably improved thermal behavior. The comparison of the thermal isomerization rate constant ($k_T$) of f-PMMA samples suggests that the f-PMMA macromolecular backbone has the tendency to depress the isomerization process with an increase in the content of DAOAB. Although this kind of material might be unsuitable for the real technological devices at present, it provides a new method to explore the photochromic material with higher $T_g$ and adequate azo contents.

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