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Photoresponsive Behavior of Methyl Methacrylate/*trans*-4-Stilbene Methacrylate Statistical Copolymers in Solution and the Solid State

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ABSTRACT: Photoresponsive copolymers of methyl methacrylate (MMA) with *trans*-4-stilbene methacrylate (TSMA) of different compositions were synthesized by free-radical copolymerization. Upon irradiation with light of 313-nm wavelength, the trans-to-cis isomerization of the stilbenyl pendant groups in the copolymer can be induced. Both fluorescence and UV absorption spectroscopy show that the reversible photocontrolled isomerization of the copolymer system is limited due to the irreversible side reaction from the *cis*-stilbenyl pendant groups to the phenanthrenyl pendant moieties. Photoinduced changes in physical properties including solubility, relative viscosity, and glass transition temperature were studied. Upon irradiation with light of 313-nm wavelength, a 5 °C increase in demixing temperature was observed for a 36.5 mol % TSMA copolymer in toluene solution whereas an increase in demixing temperature greater than 20 °C was observed for a TSMA homopolymer. Similarly, photoinduced changes in relative viscosity become increasingly negative with increasing TSMA content in the copolymer, with the pure TSMA homopolymer exhibiting a 4.5% decrease in relative viscosity after photoirradiation. The photoinduced change in glass transition temperature from 423 down to 414 K was also observed for a 36.5 mol % TSMA copolymer upon irradiation. The effects of both concentration and environment on the extent of isomerization in solution and the solid state were also examined.

Introduction

The photoresponsive or photosensitive behavior of organic chromophores incorporated in polymeric materials has been a topic of considerable scientific interest with numerous technological applications.[1,2] From a fundamental scientific viewpoint, this interest has been evident in studies of polymer chain mobility in both solution and the solid state.[3-7] From a technological viewpoint, these photoresponsive polymers have been employed or proposed for various applications including guided wave optics, photoresists, and optical data storage devices.[8] Recently, research has been focused extensively on polymers incorporating azobenzene, stilbene, and spirobenzopyran residues as the photoresponsive chromophores. While azobenzene and stilbene residues undergo photoinduced trans-to-cis isomerization, the spirobenzopyran undergoes a photoinduced ring opening isomerization to a merocyanine. Unlike *cis*-azobenzene and merocyanine, *cis*-stilbene possesses excellent thermal stability. However, in addition to isomerization upon exposure to light of appropriate wavelength, *cis*-stilbene undergoes an irreversible cyclization reaction to a phenanthrene.[9-11] This side product is thermally and photochemically stable and thus limits the reversibility of the trans-to-cis isomerization of the stilbene chromophore.

The possibility that photoisomerization of an organic chromophore could alter the equilibrium conformation and hence the dimensions of the surrounding polymer was originally recognized by Lovrien in 1967.[12] Since then, a variety of physical and mechanical properties of photoresponsive polymers[13-33] have been reported to be altered upon irradiation with light of the appropriate wavelength. These properties include dilute solution viscosity,[13-17] pH,[13] conductivity,[13] solubility,[17-20] membrane potential,[21] volume,[14,22-24] shape,[22-25] sol-gel temperature,[26] binding ability,[27-29] wettability,[29,30] miscibility,[31] alignment modes of liquid crystal,[32] and tensile stress relaxation behavior.[33] In addition, the kinetics of conformational changes of polymers with photochromic moieties have also been increasingly studied.[34-38]

In the case of photoresponsive polymers containing stilbene, only a few of the previous studies[14,15,24] have dealt with photoinduced changes in mechanical properties. In several such studies stilbene and its derivatives were incorporated into polymers in the main chain or simply as additives. Stille and Zimmermann[14] investigated polyquinolines containing stilbene units in the backbone. These polymers were found to exhibit both a photoinduced change in viscosity in dilute solution and a photoinduced contraction in solid film upon irradiation. Other results[15,24] have been reported showing modest volume contractions for a polyamide film containing a *trans*-stilbene in the backbone and a nylon film doped with a nonbound cyanostilbene. Recently, Irie and Iga[31] studied photocontrolled miscibility in blends of poly(methyl vinyl ether) with polystyrene having pendant stilbene groups. They reported that the cloud point temperature of the blend decreases upon trans-to-cis conversion of the stilbenyl groups. It should be noted that among these studies,[14,15,24,31] little attention has been paid to the limited reversibility of trans-to-cis isomerization of the stilbene unit.

In this present study, a novel photoresponsive polymer is developed by copolymerizing methyl methacrylate (MMA) with *trans*-4-stilbene methacrylate (TSMA), thus producing a polymer related to poly(methyl methacrylate) but with *trans*-stilbene incorporated as pendant groups. This copolymer will be referred to as poly(MMA-*co*-TSMA). It should be noted that extensive studies by Altomare and co-workers[39-41] and others[42] have dealt with comonomer units similar to

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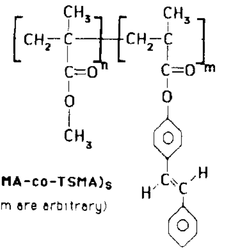

POLY(MMA-co-TSMA)s
(n and m are arbitrary)

TSMA, including a *trans*-4-hydroxystilbene acrylate.[39-41] However, studies on the copolymers made from *trans*-4-hydroxystilbene acrylate and menthyl acrylate concerned only the effects of isomerization on chiroptical or photophysical properties. Photoinduced changes in physical properties were not studied for these systems. This is the first study of *trans*-4-stilbene methacrylate incorporated in a copolymer.[43] It is anticipated that the isomerization will result in a conformational change in the polymer system. Besides studying and commenting on the reversibility of the trans-to-cis isomerization, this paper aims to investigate further the photoresponsive behavior of the resulting copolymers. This study includes the photoinduced changes in the physical properties of solubility, relative viscosity, and glass transition temperature. In addition, the effects of both concentration and the environment on the extent of isomerization are examined.

Experimental Section

A. Photoresponsive Polymer Preparation and Characterization. Monomer Synthesis and Preparation. *trans*-4-Stilbene methacrylate (TSMA) was prepared by using the method reported by Altomare et al.[39] for preparation of the corresponding acrylate. Reaction of 15.7 g (0.08 mol) of *trans*-4-hydroxystilbene (Aldrich) with 12.5 g (0.12 mol) of methacryloyl chloride (Aldrich) and 15.2 g (0.15 mol) of triethylamine in 0.2 L of anhydrous diethyl ether afforded 19.1 g (90%) of a white solid. Recrystallization from hexane yielded pure TSMA. Analysis by GC using a DB-1 column indicated the presence of a single isomer. ^1H NMR (90 M Hz, $CDCl_3$) δ 2.02 (m, 3 H), 5.67 (m, 1 H), 6.31 (m, 1 H), 7.03 (s, 2 H), 7.1–7.6 (m, 9 H).

Methyl methacrylate (MMA) purchased from Aldrich was distilled at a reduced pressure (13 mmHg) and temperature of 53.5 °C before using for copolymerization.

Copolymerization. Copolymers of different feed mole ratios (1/0, 1/3, 1/1, 3/1, 0/1) of methyl methacrylate and *trans*-4-stilbene methacrylate were synthesized by free-radical polymerization. The free-radical copolymerization experiments were performed in benzene at 60 °C in an inert nitrogen atmosphere, using AIBN as initiator. All polymers were precipitated by coagulation in methanol, filtered by using a fritted glass filter, and dried at room temperature for 5 days.

Characterization. ^1H NMR spectroscopy was used for quantitative analysis of the copolymer composition using a Varian EM-390 NMR spectrometer system. $CDCl_3$ was used as the solvent with TMS as the internal standard. Molar extinction coefficients of the copolymer samples with different ratios of MMA and TSMA in chloroform were determined by UV absorption analysis.

Photoisomerization. UV light absorption and fluorescence were used to monitor changes in the concentration of the *trans*-4-stilbene and phenanthrene units in the copolymer samples. All UV absorbance measurements were made on an IBM Instruments 9410 UV/visible spectrophotometer. Fluorescence measurements were made on a SPEX DM1B fluorescence spectrophotometer using a front face geometry.

The light source to irradiate solutions and films consists of a Photon Technology International (PTI) arc lamp housing and a 200-W power supply, attached to a variable width slit monochromator. The monochromator contained a diffraction grating blazed at 300 nm to isolate the wavelength of irradiation. The bandwidth used in this study was 20 nm. The PTI arc lamp housing collects and focuses light from a water-cooled, 100-W mercury xenon compact (high-pressure) arc lamp.

In the case of solution studies, a compartment with a magnetic stirrer was used as the cell holder to provide effective mixing during irradiation. Solutions were prepared in foil-wrapped volumetric flasks and stored in a closed cabinet. Both nitrogen bubbling and freeze–pump–thaw techniques were used for removing dissolved oxygen in cases where a deaerated sample was desired. Films were prepared by pouring copolymer solution onto the center of clean 5 × 5 cm Corning clear glass UV filters transparent to wavelengths of 300 nm and higher. Films were allowed to dry slowly in a covered Petri dish in the dark at room temperature. After the films hardened sufficiently (2–24 hours), the glass plates with the hardened films were then placed in Petri dishes wrapped in aluminum foil. The covered dishes were then placed in a vacuum oven at 60 °C for at least 4 days.

B. Photoinduced Changes in Physical Properties. In order to avoid any possibility of photoirradiation by environmental light sources, samples were stored in the dark and during handling were wrapped in aluminum foil.

Solubility. The solubility measurements with and without photoirradiation were carried out by the optical density method in the UV/visible spectrophotometer. Measurements were made by loading the sample in a water-jacketed cell into the UV sample holder. For the solution appearing transparent at room temperature, optical density was then monitored while the sample cell was subsequently cooled until a sharp increase in optical density was observed. In contrast, for the solution appearing turbid at room temperature, optical density was monitored while the sample cell was continuously heated until a sharp decrease in optical density was observed or until the maximum temperature of the water bath (100 °C) was reached. An optical wavelength of 750 nm was used for monitoring optical density as there was no evidence of absorption from the polymer solutions at that wavelength. Toluene was used as the solvent.

Relative Viscosity and Glass Transition Temperatures. The relative viscosity and glass transition temperature measurements were made by a Cannon-Ubbelohde viscometer (American Scientific Product No. 25) and a Perkin-Elmer (DSC-2) differential scanning calorimeter, respectively. Photoirradiation was performed in a cylindrical quartz glass container with a magnetic stirring bar at room temperature. A good solvent, chloroform, was chosen for dissolving the copolymer and homopolymer. In the relative viscosity measurements, all solutions were prepared by filtering with 0.45-μm membrane filters (Gelman Sciences Inc.) in order to remove dust particles. Relative viscosity measurements were carried out in a water bath maintained at 28.0 ± 0.1 °C. For the glass transition temperature measurements of photoirradiated polymers, the sample preparation was as follows. After irradiation for 30 min at 313 nm, an irradiated solution was allowed to dry slowly in a conventional hood until the resulting film appeared dry, and then the film was placed in a vacuum oven maintained at 60 °C for over 24 h before DSC measurements. A heating rate of 10 °C/min was used for the DSC measurements.

Results and Discussion

Copolymer Characterization. The copolymer composition was estimated on the basis of ^1H NMR analysis by comparing the area of the signals due to the protons of stilbene moieties with that due to the protons on the saturated methoxy group. The copolymerization diagram (Figure 1) shows that all the copolymer samples have a higher mole fraction of TSMA than the corresponding feed monomer mole fraction.

The reactivity ratios were calculated with methods discussed by Pearce et al.[44] The values obtained ($r_{TSMA} = 2.3_7$, $r_{MMA} = 0.8_6$) indicate that the TSMA radical greatly favors its own monomer rather than MMA. The product of the reactivity ratios is a little larger than unity ($r_{TSMA}r_{MMA} = 2.0$). The results obtained for this system are consistent with the previous study by Altomare et al.[39] for a similar copolymer system of menthyl acry-

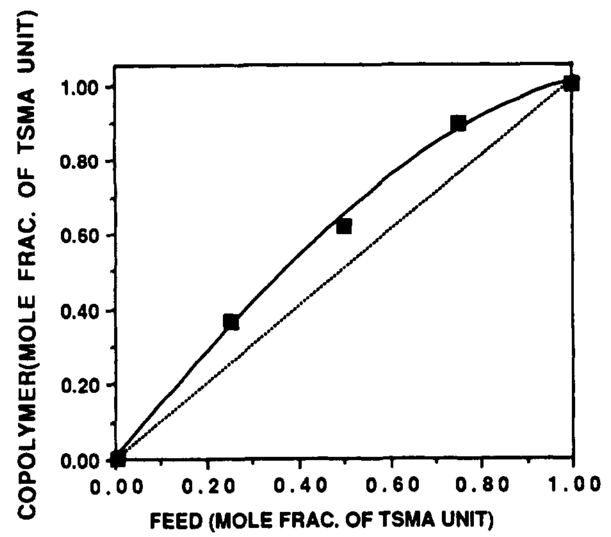

Figure 1. Copolymerization diagram of the system methyl methacrylate (MMA)/*trans*-4-stilbene methacrylate (TSMA).

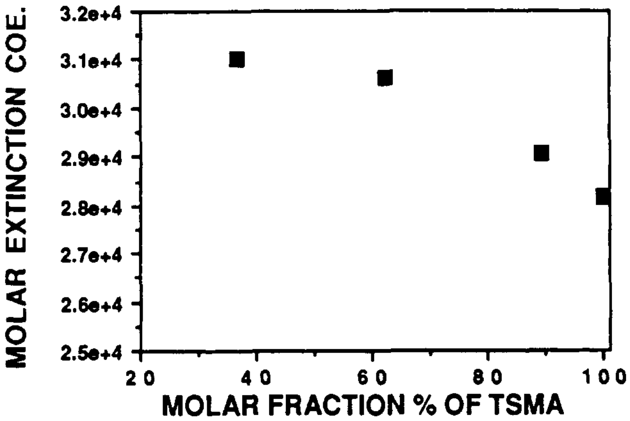

Figure 2. Molar extinction coefficient, expressed in mol^{-1} cm^{-1} and based on TSMA units, at 300 nm of poly(MMA-*co*-TSMA)s versus molar fraction % of TSMA.

late with *trans*-4-hydroxystilbene acrylate. We should note that the conversion of the copolymer synthesized is higher than 10%, and thus the TSMA mole fraction in copolymer given in Figure 1 does not represent exactly an instantaneous TSMA composition of the copolymer. However, according to the previous results of Altomare et al.,[39] it is likely that the TSMA mole fraction in copolymer should not be strongly sensitive to the copolymer conversion. Therefore, we believe the reactivity ratios calculated according to the copolymerization diagram in Figure 1 are not greatly different from those which would be obtained under low conversion conditions.

The absorption spectrum of poly(MMA-*co*-TSMA) in chloroform exhibits a structured absorption band with maxima at around 300 and 313 nm, which corresponds to the electronic transition of the *trans*-stilbene chromophore. The molar extinction coefficient was obtained by measuring the absorbance of copolymer samples of various concentrations in chloroform. Figure 2 shows the molar extinction coefficient at 300 nm of poly(MMA-*co*-TSMA) as a function of TSMA mole fraction. It clearly indicates that the molar extinction coefficient decreases with the increasing molar ratio of TSMA ranging from 36.5 to 100 mol %. This phenomenon is known as hypochromism. It has been reported in some vinyl polymers with large pendant π-electron systems[39,45,46] and has been attributed to electronic interactions between neighboring chromophores in the polymer. The decrease in the molar extinction coefficient with increasing photochromic monomer fraction in copolymer (due to the hypochromism effect) was also reported by Altomare et al.[39] in a similar system, poly(methyl acrylate–*trans*-4-hydroxystilbene acrylate).

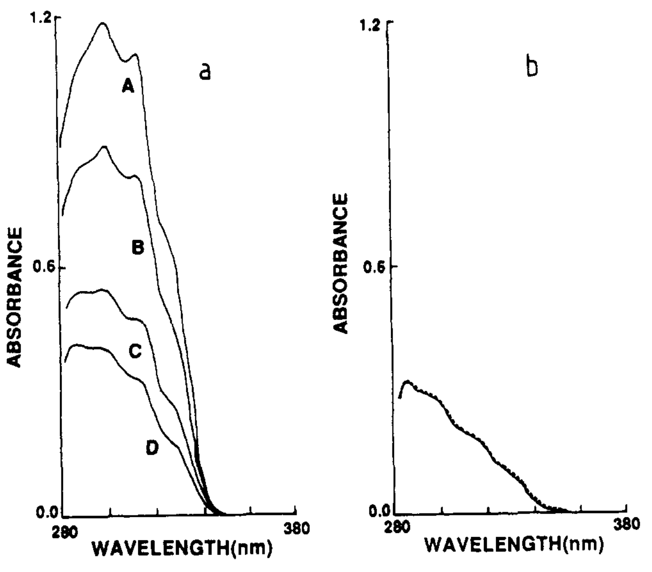

Figure 3. (a) UV absorption spectra for a 36.5 mol % TSMA copolymer sample in toluene before and after photoirradiation at 313 nm for several time periods: A, before irradiation; B, 1 min after irradiation; C, 5 min after irradiation; D, 10 min after irradiation. (b) Spectrum (—) taken immediately after 30 min irradiation. Spectrum (- - -) taken 4 days later.

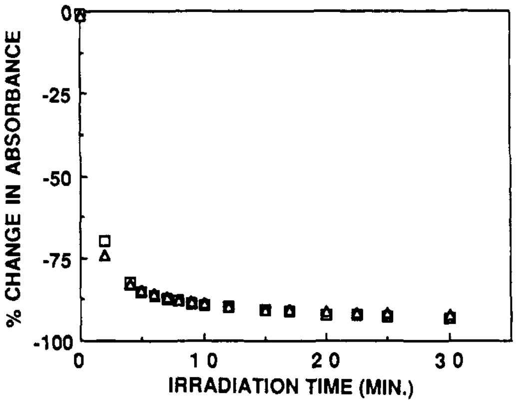

Figure 4. Percentage changes in absorbance at 300 nm as a function of time of irradiation at 313 nm for a 36.5 mol % TSMA copolymer in chloroform: (□) aerated sample; (△) sample by nitrogen bubbling for 10 min.

Photoisomerization. Stilbene is known to be isomerized from the trans to cis form by irradiation with ultraviolet light. Figure 3a shows UV absorption spectra of the 36.5 mol % TSMA copolymer sample in toluene before and immediately following irradiation at 313 nm for several time periods. Figure 3b indicates that little difference was observed between spectra taken immediately after irradiation and that taken 4 days later. This result indicates that this system is thermally stable at 25 °C and that the thermal back reaction can be neglected over the course of the experiment, which is consistent with the known behavior of stilbene. A similar result was also reported in a previous study for a polystyrene having stilbenyl pendant groups in a polymer blend system.[31]

Figure 4 shows the change in absorbance at 300 nm as a function of irradiation time for a 36.5 mol % TSMA sample in chloroform in both aerated and nitrogen-saturated conditions. This result indicates that the system reached equilibrium in about 20–25 min using the irradiation conditions described in the Experimental Sec-

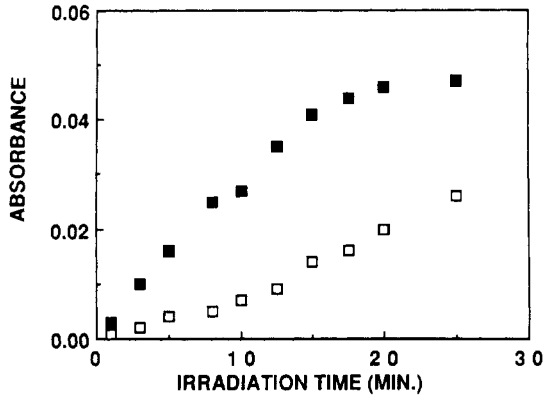

Figure 5. Variations in absorbance at 353 nm as a function of time of irradiation at 313 nm for a 0.036 g/L, 36.5 mol % TSMA copolymer in chloroform: (□) deaerated sample prepared by freeze–pump–thaw technique; (■) aerated sample.

tion. Furthermore, the time required for achieving equilibrium in this system is not affected significantly by dissolved oxygen.

Irie et al.[9] studied the photochemical conversion of poly(2,3-diphenylbutadiene) (stilbene-like units are incorporated in the polymer backbone) to poly(9,10-dimethylenephenanthrene). They found that, in addition to cis-to-trans isomerization, stilbene-like molecules undergo a reversible cyclization reaction to dihydrophenanthrene upon UV irradiation. Owing to the rigidity of the polymer backbone, cyclization dominates over cis-to-trans isomerization for their system. Furthermore, according to their flash photolysis experiments, phenanthrene groups are formed irreversibly in the polymer by two processes, a fast spontaneous dehydrogenation and a slower oxidation. Similar conclusions have been reached by Torkelson[47] in a related study.

In the case of the poly(MMA-*co*-TSMA) system studied here, stilbene-like units are incorporated as pendant groups. Therefore, these materials are not expected to possess a rigidity as great as that of the system in which stilbene-like units are incorporated in the backbone chain.[9] Phenanthrene formation was studied by measuring the absorbance of a characteristic peak attributed to phenanthrene at 353 nm as a function of irradiation time for both the aerated sample and deaerated samples. The samples were 0.036 g/L, 36.5 mol % TSMA copolymer in chloroform. The irradiation wavelength was 313 nm. The deaerated samples were prepared by either nitrogen bubbling for 10 min or freeze–pump–thaw cycles at 10^{-6} Torr. Figure 5 shows changes in absorbance at 353 nm as a function of irradiation time for both the aerated sample and deaerated sample prepared by the freeze–pump–thaw technique. The rate of phenanthrene formation is considerably smaller in the deaerated than in the aerated sample. However, in the run of the sample prepared by nitrogen bubbling, little difference in absorbance at 353 nm was observed in comparison with the result for the aerated sample. This observation suggests that even traces of oxygen are able to facilitate the formation of phenanthrene. In the absence of oxygen, phenanthrene evidently can be formed through a dehydrogenation process.[9]

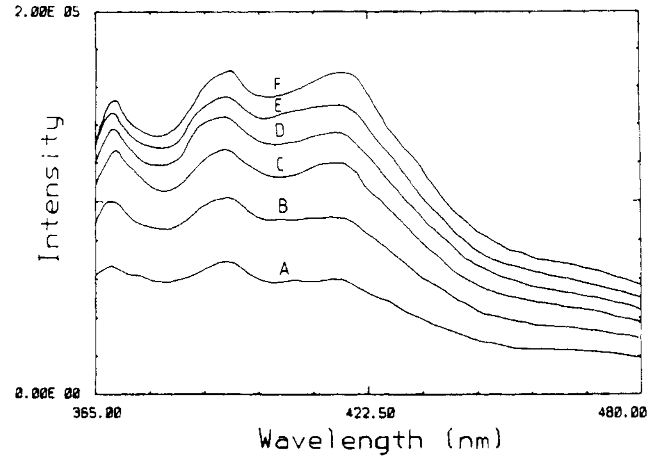

Figure 6. Fluorescence spectra (excitation wavelength is 353 nm) for a 36.5 mol % TSMA copolymer sample in chloroform after irradiation at 313 nm for (A) 5 min, (B) 10 min, (C) 15 min, (D) 20 min, (E) 25 min, and (F) 30 min.

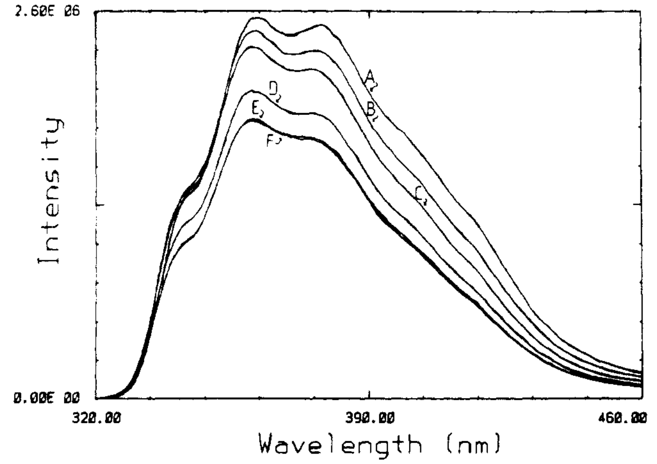

Figure 7. Fluorescence spectra for a 36.5 mol % TSMA copolymer in chloroform(excitation wavelength is 300 nm): (A) before irradiation, (B) after irradiation at 313 nm for 20 min, (C) after irradiation at 313 nm for 30 min, (D) after irradiation at 224 nm for 10 min, (E) after irradiation at 224 nm for 20 min, and (F) after irradiation at 224 nm for 30 min.

Phenanthrene formation was also investigated by using a more sensitive technique, fluorescence spectroscopy. Figure 6 shows the fluorescence intensity ranging from 365 to 480 nm as a function of irradiation time for an aerated sample. An excitation wavelength of 353 nm, near the long-wavelength absorbance maximum of phenanthrene, was chosen for this investigation, and the fluorescence maxima in Figure 6 correspond to those of phenanthrene above 365 nm.[48] Experimental results indicate that the intensity of the fluorescence attributed to phenanthrene increases with the irradiation time. In the case of the freeze–pump–thaw deaerated sample, a similar but smaller increasing trend in fluorescence intensity was observed.

An attempt was made to study the reversibility of photoisomerization by irradiating photoequilibrated samples at 224 nm, the wavelength at which the cis/trans absorbance ratio reaches a maximum. A photoequilibrated sample system was prepared by irradiating a 0.02 g/L 36.5 mol % TSMA sample at 313 nm in chloroform solution for 30 min. This sample was exposed to 224 nm wavelength light, and fluorescence spectra (λ_{ex} = 300 nm) were then taken immediately after each 10-min irradiation period. As shown in Figure 7 the fluorescence intensity attributed to *trans*-stilbene actually decreases significantly during the first 20 min of irradiation and more slowly with continued irradiation. These results suggest that cis-to-trans photoisomerization does not occur to an appreciable extent upon irradiation at 224 nm. A similar result was observed in the case of irradiation at 254 nm. The formation of the thermally and photochemically stable phenanthrene moiety upon irradiation of *cis*-

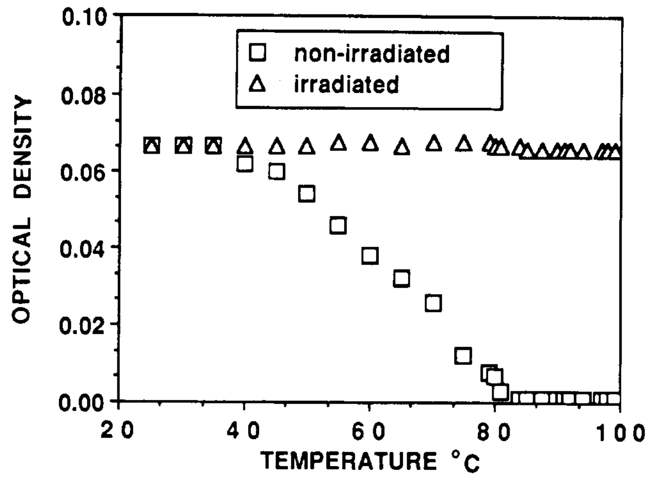

Figure 8. Variations of optical density as temperature is increased from room temperature to 100 °C for a 0.02 g/L TSMA homopolymer in toluene: (□) before irradiation; (Δ) after irradiation at 313 nm for 30 min.

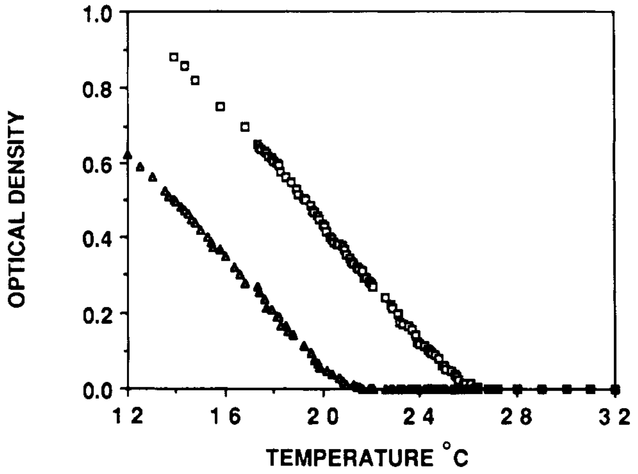

Figure 9. Variations of optical density as temperature is swept from 32 to 12 °C for a 0.032 g/L 36.5 mol % TSMA copolymer in toluene: (Δ) before irradiation; (□) after irradiation at 313 nm for 30 min.

stilbene provides the most likely explanation for these observations.

It should be noted that these results are seemingly contradictory to the previous result by Irie and Iga,[31] who reported on a reversible photocontrol of the cloud-point temperature of poly(methyl vinyl ether) blends with polystyrene containing stilbenyl pendant groups. Their result showed a conversion-dependent decrease in the cloud-point temperature upon trans-to-cis isomerization. They also stated that upon irradiation at 254 nm, part of the *cis*-stilbenyl groups returned to the trans form and thus the cloud-point temperature increased. It is likely that the observation of partial reversibility in their system is due to the low conversions of *trans-* to *cis*-stilbene in their samples. Irreversible conversion to phenanthrene is more likely to occur at the higher conversions[49] of *trans*-stilbene chromophores employed in our investigation. The extent of the irreversible photoreaction versus trans to cis reversible photoisomerization (cis to phenanthrene versus cis to trans) will be investigated in the future.

Solubility Measurements. Photoinduced changes in solubility for both TSMA homopolymer and 36.5 mol % TSMA copolymer solutions were measured by using an optical density method. When a homogeneous solution is cooled, a sharp increase in optical density can be observed as the demixing temperature is approached from above due to the fact that the incident light is scattered by the formation of polymer aggregates. (A complete description of the use and illustration of the sensitivity of optical density methods in determining demixing temperature of liquid polymer systems is given in a previous study[50] by Tsai and Torkelson.) Similarly, when a heterogeneous solution is heated, a sharp decrease in optical density may be observed as the sample goes back to its homogeneous state.

Figure 8 shows a plot of optical density versus temperature for a 0.02 g/L TSMA homopolymer sample heated from room temperature to 100 °C both before and after exposure to 313-nm light for 30 min. The solution of nonirradiated 0.02 g/L TSMA homopolymer in toluene is turbid at room temperature, and its optical density decreases gradually with increasing temperature. At about 80 °C the optical density has decreased to the point that the solution becomes transparent. In contrast, the optical density of the irradiated sample remains approximately constant with increasing temperature over the entire temperature range studied. This result suggests that solubility changes significantly upon irradiation resulting in an increase of over 20 °C in the demixing temperature.

Figure 9 shows an optical density versus temperature plot obtained upon cooling a 0.032 g/L solution of 36.5 mol % TSMA copolymer in toluene before and after irradiation at 313 nm for 30 min. The cooling rate is about 0.29 °C/min. The solution of 0.032 g/L TSMA copolymer in toluene is homogeneous at room temperature. For the nonirradiated solution, the optical density of this solution started to increase sharply at around 21 °C as temperature was varied from 32 to 14 °C. In contrast, in the case of irradiated solution, the optical density starts to increase sharply at around 26.2 °C. This 5 °C increase in demixing temperature indicates that the copolymer changes its conformation upon irradiation.

The results of heating the TSMA homopolymer and cooling the 36.5 mol % TSMA copolymer indicate that polymer solubility decreases upon irradiation. In addition, comparison of the demixing temperature differences for 36.5 mol % TSMA copolymer and TSMA homopolymer samples before and after irradiation suggests that the photoinduced change in solubility of the TSMA homopolymer is more significant. This decrease in solubility presumably results from the decrease in the ability of toluene to solvate the pendant *cis*-stilbene and phenanthrene groups versus the *trans*-stilbene groups of the nonirradiated polymer. A decrease in solvation ability of the pendant groups might result in an overall conformational contraction of the polymer. No attempt was made to distinguish the degrees to which the *cis*-stilbene and the phenanthrene moieties are responsible for this conformational contraction. In addition, the extent of conformational contraction of the polymers can be also measured by other techniques such as GPC and light scattering.[51] The photoinduced decrease in solubility was also reported by Irie and Schnabel[35] for a polystyrene containing small percentages of azobenzene pendant groups (less than 6.5 mol %) in cyclohexane.

Relative Viscosity Measurements. Relative viscosity as a function of TSMA composition in the copolymer was measured before and after irradiation at 313 nm for 30 min. A high polarity solvent, chloroform, was used for this study. All the solution concentrations were adjusted to 2 g/L before the measurement.

Figure 10 shows effects of TSMA molar percentage in the copolymer on the photoinduced change in relative

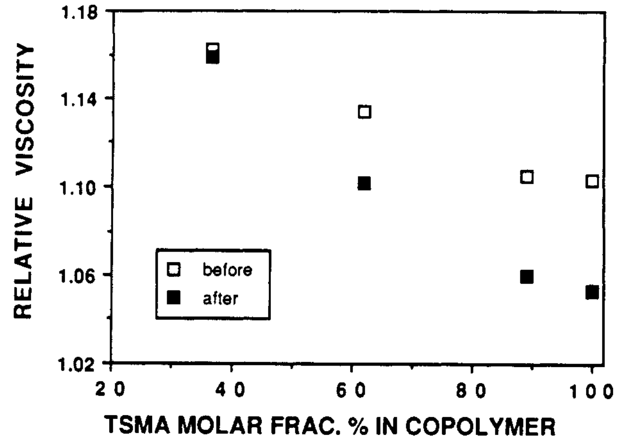

Figure 10. Variations of relative viscosity in chloroform solution as a function of TSMA composition measured both before (□) and after (■) irradiation at 313 nm for 30 min. (All the solution concentrations are adjusted to 2 g/L.)

viscosity. Experimental results indicate that photoinduced changes in relative viscosity become increasingly negative with increasing TSMA copolymer content in the copolymer, with the TSMA homopolymer exhibiting a 4.5% decrease in relative viscosity after photoirradiation. These results imply that the formation of *cis*-stilbene and phenanthrene moieties causes a contraction of the overall conformation in the copolymers and homopolymer in chloroform. In addition, the TSMA content plays a very important role in determining the extent of the contraction in overall polymer conformation.

These results are consistent with the results obtained in the solubility measurements with regard to the contraction in overall polymer conformation upon irradiation. The less significant photodecrease in relative viscosity than in solubility for the 36.5 mol % TSMA copolymer is presumably due to the fact that chloroform has higher polarity than toluene. That is, the solvent–polymer interaction is much stronger in chloroform than in toluene and thus lessens the contraction effect due to isomerization.

Glass Transition Temperature Measurements. Glass transition temperature measurements were made for a 36.5 mol % TSMA copolymer before and after irradiation at 313 nm for 30 min. The 36.5 mol % TSMA copolymer in chloroform was irradiated in a cylindrical quartz grade glass vessel with stirring. Before the glass transition temperature measurement, residual solvent was removed by placing the sample in a vacuum oven at 60 °C for over 24 h. A decrease from 423 to 414 K in glass transition temperature was observed upon irradiation. This result suggests that the *cis*-stilbene and phenanthrene units require less energy for chain segmental motion than the *trans*-stilbene unit.

Concentration and Environmental Effects on the Extent of Isomerization. The effect of PMMA concentration in chloroform solution on the extent of isomerization was studied. To simplify comparison, all samples independent of polymer concentration were prepared with the same extinction coefficient at 313 nm, the irradiation wavelength. This was done by preparing 36.5 mol % TSMA copolymer samples of 0.017 g/L in monodisperse (M_w/M_n = 1.10) 27 000 MW PMMA/chloroform solutions with concentrations of 0.16, 1.4, and 10 g/L. Absorbances at 300 nm were then monitored for each solution after a certain period of time.

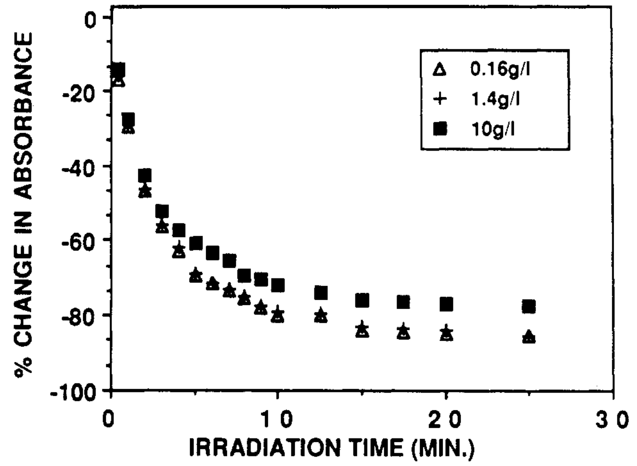

Figure 11. Percentage changes in absorbance as a function of time of irradiation at 313 nm for 36.5 mol % TSMA copolymer samples (C = 0.017 g/L) in 27 000 MW PMMA/chloroform solutions with concentrations of (△) 0.16 g/L, (+) 1.4 g/L, and (■) 10 g/L.

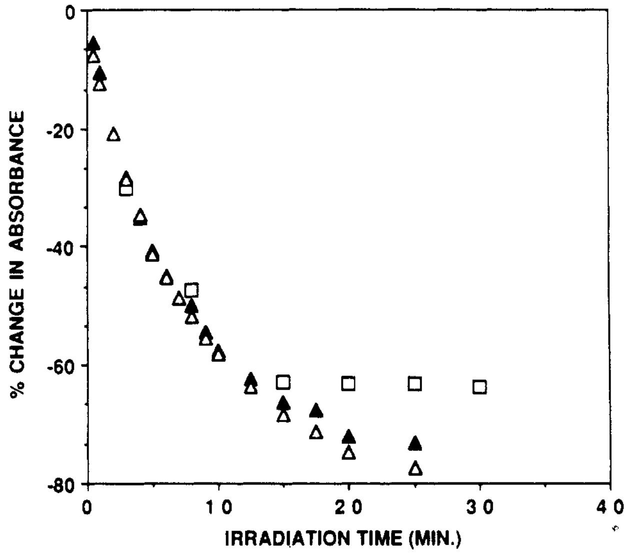

Figure 12. Percentage changes in absorbance as a function of time of irradiation at 313 nm for 36.5 mol % TSMA copolymer samples in (□) the form of a cast film, (▲) methyl isobutyrate, and (△) chloroform. (The original absorbance readouts for all three cases are 0.59.)

Figure 11 shows that there is little difference in the extent of isomerization for PMMA concentration of 0.16 and 1.4 g/L; however the extent of isomerization is lower when the concentration of PMMA is increased to 10 g/L. This experimental result suggests that the conformational hindrance for torsion about the stilbene double bond is only significant when the concentration of PMMA is above a critical value.

The extent of isomerization of copolymer in the form of cast film and in two different solvents, chloroform and methyl isobutyrate, with the same initial absorbance were also investigated. The film was prepared by solvent casting. After the film hardened sufficiently, it was placed in a vacuum oven at 60 °C for more than 4 days. Figure 12 shows the percentage change in absorbance at 300 nm as a function of irradiation time. It is clearly seen that the isomerization extent is most restricted in the case of solid film. This phenomenon is consistent with the result for isomerization of free stilbene probe in solvent and solid film.[52,53] Furthermore, it is believed that the major factor responsible for this reduced isomerization in solid film[52,53] as compared to solution is associated with local free volume restriction in the glassy polymer. Moreover, the experimental result suggests that isomerization is a function of solvent environment as evidenced by the differing levels of isomerization in chloroform and methyl isobutyrate.

Summary

Photoresponsive copolymers of methyl methacrylate (MMA) with *trans*-4-stilbene methacrylate (TSMA) of various compositions have been prepared in an attempt to construct photoresponsive polymer systems. Both fluorescence and UV absorption spectroscopy show the photoinduced reversibility of the trans-to-cis isomerization is limited due to the irreversible side reaction from the *cis*-stilbenyl pendant groups to the phenanthrene moieties. This side reaction can be facilitated in the presence of a trace of oxygen. Photoinduced changes in physical properties which occur upon trans-to-cis isomerization were studied. Upon photoirradiation with 313-nm light, the decrease in both solubility and relative viscosity in solution was found to become increasingly significant with increasing TSMA composition in the copolymers. This result is presumably due to the photoinduced configurational changes of the *trans*-stilbenyl units, thus causing an overall conformational contraction in the polymers. Experimental results show the effects of both concentration and environment play important roles in determining the extent of isomerization in solution and the solid states. In terms of reversible photocontrol in physical properties, the current study provides an understanding of the limits in using stilbene as a photoresponsive chromophore. These copolymers can potentially be applied in devices that are desired to have one way or irreversible photoregulation.

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Registry No. TSMA, 82829-45-6; MMA, 80-62-6; (MMA)(TSMA) (copolymer), 124755-62-0.