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Synthesis of Azobenzene-Based Polymers and the in-Situ Characterization of Their Photoviscosity Effects

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ABSTRACT: A new in-situ technique for the measurement of photoviscosity effects in polymer solutions has been developed using a custom-modified, cone-and-plate rheometer. The new technique permits simultaneous irradiation of the polymer solution and continuous measurement of its viscosity in a temperature-controlled environment. An additional benefit of the technique is the greatly reduced sample volume compared to traditional capillary viscometers. However, adequate measures have to be taken to minimize the evaporation of the sample solution and to maintain the required temperature. Copolymers of methyl methacrylate and azobenzene monomers with a chromophore in the side chain have been synthesized and characterized using the new technique. This polymer exhibits a photoviscosity effect when exposed to UV irradiation ($\lambda = 365$ nm), with the reduced specific viscosity (η_{sp}/c) of the polymer being up to 77% lower than in the dark. However, the magnitude of the photoinduced change in η_{sp}/c was found to increase with the number of azobenzene units in the polymer chain, and the greatest effect was shown by a polymer with 42 mol % azobenzene loading.

Introduction

Azobenzene and its derivatives undergo trans-to-cis isomerization when subjected to UV irradiation.[1] This isomerization effectively reduces the distance between attachment points from 9.0 to 5.5 Å, as illustrated in Figure 1.

When the azobenzene molecule is attached chemically to a polymer chain, photoinduced isomerization can result in conformational change being induced in the polymer chains. This can cause significant changes to physical properties such as the dipole moment, refractive index, and solution viscosity. Many of these changes can be reversed by heat or visible irradiation.

Viscosity changes in polymer solution associated with photoinduced conformational change of the macromolecules were reported by Lovrien in 1966.[2] Lovrien reported that, under the influence of UV light, the solution of a copolymer of methacrylic acid and *N*-(2,2′-dimethoxyazobenzene)acrylamide exhibited an increase (5 mL/g) in the reduced specific viscosity (η_{sp}/c). The same author also investigated the photoviscosity effect of poly(methacrylic acid) and chrysophenine in water, reporting a decrease in η_{sp}/c of 50% due to UV irradiation. Following on from Lovrien's work, many more studies have been conducted into the photoviscosity effect in azobenzene-based polymers. The effects of azobenzene groups in the side chains of a polymer have been studied in a copolymer of maleic anhydride with styrene,[3] where irradiation was found to decrease the η_{sp}/c of the solution by between 24 and 30% in 1,4-dioxane and by between 1 and 8% in tetrahydrofuran (THF). The authors found that the decrease in viscosity was reversible and speculated that it was not attributed to heating of the sample. The magnitude of the effect was found to depend on the concentration of the azobenzene groups in the polymer and on the duration of the irradiation. The rate of conversion was shown to decrease with increasing solution concentration.

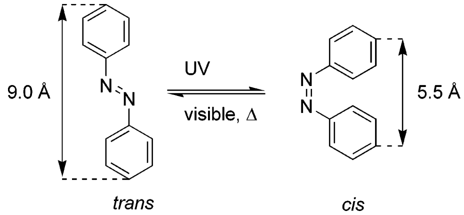

Figure 1. Schematic of the reversible isomerization of azobenzene upon UV/vis irradiation.[1]

Hallensleben and Menzel[4] reported that due to irradiation ($\lambda > 470$ nm) the viscosity of a 1,4-dioxane solution (0.64 g/L) of poly(5-(4-phenylazobenzyl)-L-glutamate) decreased by 9% compared to that of the unirradiated sample. This change was accompanied by a 23% cis isomerization as inferred by UV−vis spectroscopy. Under UV irradiation (360 nm) the viscosity dropped by a further 9% with a corresponding 86% cis isomerization.

The majority of previous publications on photoviscosity of azobenzene have focused on the effect of these functional groups in the polymer backbone. Irie and co-workers[5] synthesized a range of polyamides containing azobenzene groups in the backbone. All of the polyamides exhibited a degree of the photoviscosity effect. They reported a 60% specific viscosity reduction due to irradiation ($410 > \lambda > 350$ nm) of a solution of *N*,*N*′-dimethylacetamide. The initial viscosity was regained after 30 h of being stored in the dark at 20 °C. It was reported that the rate of recovery could be increased with the aid of visible irradiation ($\lambda > 470$ nm), with the recovery time being reduced from 30 h to 10 min. The authors investigated the influence of spacer groups in the polymer backbone and speculated that the magnitude of the photoinduced change in the viscosity decreases with the addition of flexible units such as methylene chains.

Kumar and co-workers investigated a range of polyureas[6] with azobenzene groups in the polymer backbone in DMSO at 35 °C. The intrinsic viscosity was found to be about 30% lower during UV irradiation ($410 > \lambda > 350$ nm) than in the dark. The photoviscosity change

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was attributed to a conformational change of the polymer chain rather than interchain interactions. The original viscosity was recovered in the dark after 8 h at 20 °C. A study of similar polyureas was performed in DMSO at 30 °C,[7] with the intrinsic viscosity reported to be about 40% lower during UV irradiation than in the dark.

Poly(dimethylsiloxane) with azobenzene residues in the main chain was studied in toluene; the intrinsic viscosity after UV ($400 > \lambda > 350$ nm) irradiation was 20% lower than in the dark.[8] After irradiation the viscosity recovered in 30 h at 20 °C; the recovery was accelerated by visible ($\lambda > 450$ nm) irradiation, reducing the recovery time to 5 min.

The following section presents a brief review of the experimental apparatus used by previous authors to study the photoviscosity phenomena. In the 1966 study,[2] Lovrien used a capillary viscometer immersed in a water bath to measure the η_{sp}/c of the test solutions. Similarly, other authors[3,4,6,7] have used an Ubbelohde capillary viscometer to perform their measurements. With the exception of Hallensleben and Menzel,[4] the viscometers were all modified for irradiation. The measurement system used by Hallensleben and Menzel was not adapted for UV irradiation; for example, a quartz glass viscometer was not used. As a consequence, the observed rate of cis isomerization was much slower compared to reverse isomerization with visible light. Throughout their investigations, Irie and co-workers[5,8−12] used an Ubbelohde viscometer, which had been adapted specially for irradiation. However, no details of the adaptation were reported. In each case, the solution viscosity was measured at a range of concentrations. Capillary viscometers are unable to measure solution viscosity continuously as they require the flow to be reversed between measurements. As a result, most of the data represent the difference between the viscosity in the dark and under irradiation after a photostationary state had been reached. For many of the samples,[5,9,10,12] the viscosity was measured at various points during its slow recovery in the dark at 20 °C. Previous investigations have also measured the change of the viscosity during alternate irradiation with UV and visible light.[4,5,8,9,12] Matejka and Dusek[3] were among the earliest to measure the viscosity at various points during irradiation, prior to the photostationary state being reached. However, the measurements were at least 2 min apart, and the solution needed to be stirred during irradiation to distribute the irradiated polymer evenly throughout the solution. Other varieties of capillary flow viscometers such as Cannon-Ubbelohde[13,14] or Desreux-Bishoff[15] dilution viscometers have also been used for photoviscosity measurements, with similar experimental methods.

This paper presents photoviscosity data on a range of polymers, which were synthesized with azobenzene groups in the polymer side chains. The photoviscosity experiments were carried out on a custom-modified rotational rheometer. The lower plate in a standard cone-and-plate geometry was replaced by a quartz window, allowing samples to be irradiated via a liquid light guide. Details of this apparatus are given in the next section.

Experimental Section

Synthesis of *trans*-4-Methacryloyloxyazobenzene. *trans*-4-Methacryloyloxyazobenzene was prepared by the condensation reaction of 4-hydroxyazobenzene and methacryloyl chloride in THF, where triethylamine (TEA) was used to act as a promoter. 4-Hydroxyazobenzene (10 g, 50.50 mmol) was dissolved in 120 mL of THF, to which triethylamine (50.60 mmol) and 5 mg of inhibitor (2,6-di-*tert*-butyl-*p*-cresol) were added. The solution was purged with nitrogen gas and stirred for 30 min at 21 °C. Methacryloyl chloride (15 mL, 150 mmol) was injected gradually to the solution via a glass syringe while the solution temperature was kept below 5 °C with the aid of an ice-cooled water bath. The formation of the triethylammonium salt in the form of a precipitate was observed immediately after the addition of methacryloyl chloride. The reaction mixture was stirred for 48 h at 21 °C. At the end of the reaction, the resulting precipitate was filtered off, and the excess methacryloyl chloride was hydrolyzed to methacrylic acid. The solution was diluted four times by adding a mixture of $CHCl_3$ and water (3:1). The organic layer was washed three times with distilled water to remove the polar materials. Finally, the yellow organic layer was dried on anhydrous Na_2SO_4, and the residual solvent was removed in vacuo. The resulting yellow solid was purified from silica column chromatography [silica gel 60 (70−230 mesh ASTM)] using chloroform as the solvent. The product was crystallized twice from *n*-hexane and dried under high vacuum. A yield of 70% was obtained. The reaction associated with this synthesis is presented in Figure 2.

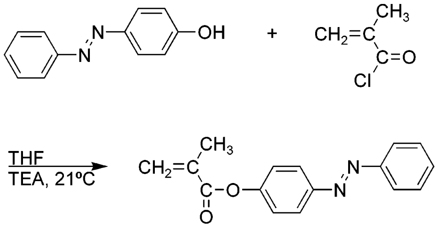

Figure 2. Synthetic route to the production of *trans*-4-methacryloyloxyazobenzene.

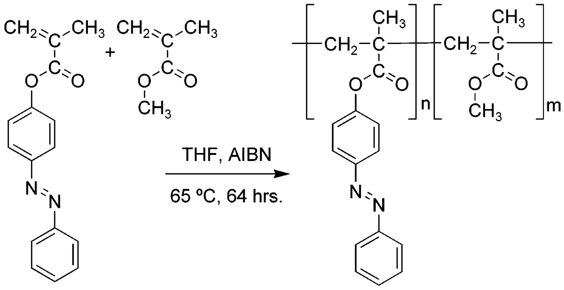

Figure 3. Synthetic route used in the preparation of the copolymer of MOAB and MMA.

Copolymerization of *trans*-4-Methacryloyloxyazobenzene and Methyl Methacrylate. The copolymer of *trans*-4-methacryloyloxyazobenzene (MOAB) and methyl methacrylate (MMA) was prepared by free radical polymerization in THF initiated with 2,2′-azobis(isobutyronitrile) (AIBN). A high-vacuum glass apparatus joined with two Young's taps was used to conduct the synthesis. The basic reaction is presented in Figure 3.

With reference to Figure 3, the synthetic route that was used for copolymerization of MOAB and MMA can be described as follows: *trans*-4-methacryloyloxyazobenzol (0.90 g), methyl methacrylate (1 g = 0.9 mL), and AIBN (60 mg, 3% w/w) were dissolved in THF (20 mL). The reaction mixture was degassed under vacuum by freezing the solution in liquid nitrogen. The freezing and degassing cycles were repeated three times to ensure complete removal of air from the reaction flask. The polymerization reaction was allowed to take place for 64 h at 65 °C. At the end of the polymerization reaction, the product was precipitated from methanol. The pure polymer was isolated by precipitating it from DCM/methanol. Finally, the product was dried under high vacuum and a yield of 80% was obtained.

Table 1. Molecular Weight and Photoviscosity Data of Polymers Investigated[a]

polymer	$M_w \times 10^3$ (mol/g)	polydispersity	AB loading (mol %)	η_{sp}/c change (%)
$M_{44.1}C_{3.5}$	44.1	1.84	3.5	3.3
$M_{26.5}C_{12}$	26.5	1.82	12	36
$M_{39.9}C_{17}$	39.9	1.81	17	60
$M_{33.55}C_{20}$	33.55	1.59	20	61
$M_{38}C_{23}$	38.00	2.13	23	74
$M_{24.3}C_{30}$	24.3	1.70	30	39
$M_{19.2}C_{42}$	19.2	1.75	42	77
PMMA	39.6	1.55	0	0

[a] Photoviscosity was measured using a solution of DMSO (10 mg/mL). All the experimental conditions were identical.

Several more copolymers with varying composition of azobenzene were synthesized and are summarized in Table 1. The polymer designations are of the form M_xC_y, where x and y are the molecular mass (kg mol^{-1}) and chromophore loading (mol %), respectively.

Characterization. The monomer and its copolymer were characterized by ^{1}H NMR spectroscopy. ^{1}H NMR was recorded on Bruker 250 MHz NMR machine at room temperature on 5% (w/v) sample solution of $CDCl_3$. Chemical shifts are in ppm from internal standard tetramethylsilane (TMS).

The weight-average molecular mass (M_w) and number-average molecular mass (M_n) and molecular mass distribution of the copolymer were determined by a size exclusion chromatograph (Waters 2410) equipped with a refractive index detector. The column was packed with PL-gel 5 μm MIXED-C phase. The length and diameter of the column were 300 mm and 7.5 mm, respectively. The calibration curve was obtained using polystyrene standards, and the mobile phase was THF with a flow rate of 1 mL/min.

Photoviscosity Measurements. The photoviscosity measurements were performed using a Bohlin CVOR 150-HR rheometer with a custom-modified UV cell. The UV cell consisted of a quartz lower plate surrounded by a water jacket; the cell had an aperture to permit irradiation via a light guide. All the viscosity measurements were performed using a 40 mm diameter 1° cone geometry. Temperature control was provided by a Julabo KTB30 water bath. A schematic of the modified cell is shown in Figure 4.

Viscosity measurements were performed in the rheometer's controlled stress mode. Sample viscosity was measured in the dark for 15 min to permit the sample to reach steady state and to establish an initial viscosity. The sample was then irradiated for 15−20 min, allowing sufficient time for it to complete any change in viscosity. Following this period of irradiation, the sample was returned to the dark to observe any short-term recovery behavior of the viscosity. The duration of the tests was dictated primarily by the evaporation rate of the solvent used. To reduce the rate of solvent loss during the experiment, the UV cell was fitted with a solvent trap and the chamber was flooded with argon.

Samples were filtered and stored in the dark until required. All tests were performed at 25 °C. Irradiation was performed using a Vinten Superlite UV spotcure ($\lambda = 365 \pm 5$ nm).

The photoviscosity tests were performed on an azobenzene-based monomer and its copolymer with methyl methacrylate at a range of concentrations in DMSO. To confirm that the observed effects were due to the photoisomerization of the azobenzene groups and not due to heating of the sample by irradiation, a series of blank tests were performed using a mixture of hydroxyazobenzene and PMMA in DMSO. Hydroxyazobenzene does not exhibit any photoisomerization in DMSO, so any change in viscosity would have to be produced by a mechanism other than due to conformational changes.

Results

Synthesis and Characterization. Initially, an attempt was made to prepare MOAB from 4-hydroxyazobenzene and methacryloyl chloride. The successive transformation of 4-hydroxyazobenzene into monomer was conducted following the method described by Haitjhema et al.[16] Compared to the reaction times reported for the synthesis of 4-acryloyloxyazobenzene[17] and diacryloyloxyazobenzene,[18] the rate of reaction between 4-hydroxyazobenzene and methacryloyl chloride is slow. This is due to the steric hindrance caused by the methyl group in the methacryloyl chloride; therefore, a longer reaction time was required to obtain optimum yield. Purification of the product by column chromatography and crystallization from n-hexane achieved a purity of >99%.

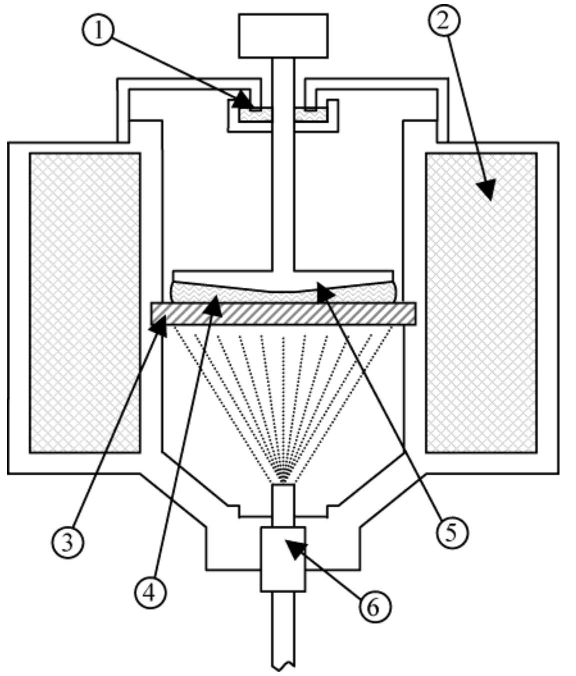

Figure 4. Schematic of modified rheometer cell: 1, solvent trap; 2, water jacket; 3, quartz plate; 4, sample; 5, 40 mm diameter 1° cone; 6, light-guide.

The melting point of the product was determined to be 110 ± 3 °C. The ^{1}H NMR resonance signals obtained were as follows: $\delta = 7.9-7.99$ (m, 4H ortho position to $-N{=}$), $\delta = 7.45-7.55$ ppm (m, 3H, aromatic), and $\delta = 7.25-7.31$ ppm (d, 2H, ortho positions to $-O-CO-$) are associated with trans isomer of the azobenzene, $\delta = 5.8$ and $\delta = 6.4$ ppm correspond to the vinyl protons of $C{=}CH_2$, and $\delta = 2.03$ ppm (s, CH_3) arises from the methyl protons of the methacrylate group. The ratios of integration of aromatic and vinyl signals showed the stoichiometry of azobenzene and vinyl groups to be 1:1.

Copolymerization of MOAB and MMA in THF at 65 °C using 3% w/w AIBN as an initiator achieved 80% yield. Any unreacted azobenzene monomer (if present) and the lower molecular weight polymer were removed by dissolving it in THF or DCM and precipitating with methanol repeatedly. It is worth noting that the azobenzene monomer is soluble in methanol, and therefore, any residual monomer was removed with methanol. ^{1}H NMR of the copolymer was obtained in $CDCl_3$, and the resulting resonance signals were as follows: aromatic $\delta = 7.94$ ppm (4H), $\delta = 7.49$ ppm (3H), and $\delta = 7.26$ ppm (2H) correspond to azobenzene chromophore, and $\delta = 3.59$ ppm (OCH_3) originated from methyl methacrylate. The compositions of azobenzene and methyl methacrylate obtained by integrating the aromatic and aliphatic OCH_3 signals are presented in Table 1.

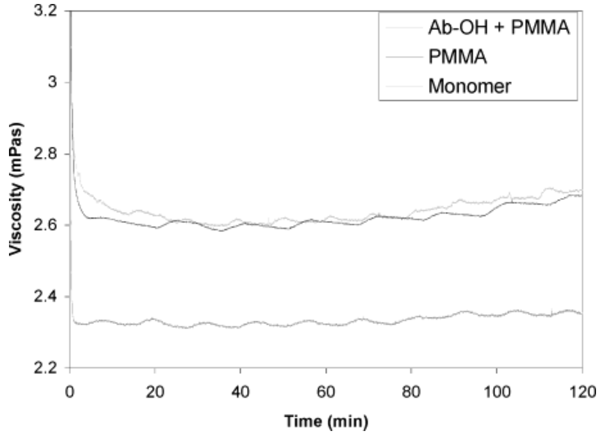

Figure 5. Photoviscosity results for the reference materials, where Ab-OH represents 4-hydroxyazobenzene.

The weight-average molecular mass and the polydispersity of the copolymers are summarized in Table 1.

Measurement System. Previous investigations into photoviscosity effects of polymer solutions have been performed almost exclusively using capillary flow type viscometers requiring relatively large sample volumes. The irradiation periods required for photoisomerization to stable state are generally longer due to this larger volume and the depth of the sample. However, in the modified cone-and-plate rheometer smaller sample volumes (340 μL) are required, giving a maximum solution depth of 350 μm; therefore, photoisomerization needs shorter irradiation time (15−20 min). The irradiation and the viscosity measurements can be performed continuously, without the need to reverse the flow. It is important to note that a cone-and-plate rheometer is limited by the selection of solvent. Since the sample chamber is not sealed, low boiling point solvents cannot be used as evaporation gives misleading results. On the other hand, in a capillary viscometer, any solvent can be used as the sample compartment is completely sealed. While a capillary viscometer is limited to dilute solutions, the cone-and-plate rheometer can produce viscosity data from highly concentrated solutions.

Photoviscosity Effect. The blank experiments were performed on a solution of PMMA in DMSO. When subjected to UV light, the viscosity did not change significantly, indicating that there were no photoviscosity effects in solutions without chromophores. Furthermore, there was no photoinduced heating of the solution; the small observed decrease was attributed to heating of the steel cone due to absorption of UV irradiation. The results from these experiments are shown in Figure 5.

The polymer $M_{40.2}C_{17}$ was tested at a range of concentrations from 1.25 to 5 mg/mL. All the samples showed similar trends, with initial viscosity reaching a minimum after about 5 min and remaining unchanged until exposed to UV. A typical viscosity trace for the polymer solution is shown in Figure 6. The apparent decrease in viscosity at the start of the experiment is due to the inertia of the system prior to reaching steady-state rotation. Immediately after commencing UV irradiation, the viscosity of the solution decreased rapidly, reaching a minimum value within 5−10 min. When the viscosity reached a steady value, the irradiation was terminated. Viscosity data continued to be collected until it reached a steady value again. It was found that in the dark period after irradiation the viscosity showed a slight rise before leveling out after about 10 min. This was attributed to a small temperature rise in the steel cone caused by the absorption of UV irradiation.

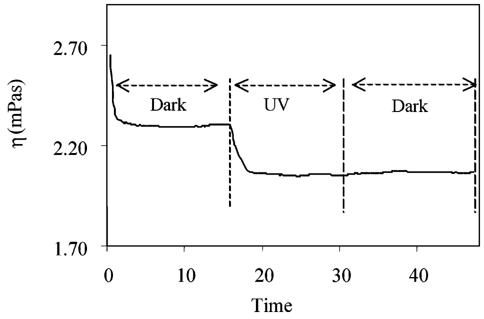

Figure 6. Typical viscosity data for an azobenzene/MMA copolymer in DMSO (5 mg/mL).

One of the most important considerations when looking at photoinduced changes in the material's properties is the distinction between photoviscosity and photoinduced thermal effects. To separate any photoinduced heating effects from the photoviscosity effect, several tests were performed on solutions of 4-hydroxyazobenzene and methacryloyloxyazobenzene (the monomer) mixed with PMMA in DMSO. UV−vis and NMR spectroscopy showed that 4-hydroxyazobenzene did not isomerize in DMSO when exposed to UV irradiation. Having established previously that the PMMA/DMSO solutions do not show any change in viscosity when exposed to UV irradiation, any change in viscosity observed in the hydroxyazobenzene/PMMA solution would have to be due to photoinduced heating of the hydroxyazobenzene. Figure 5 shows that neither the hydroxyazobenzene/PMMA nor the monomer/PMMA solutions showed any decrease in viscosity due to UV irradiation. This suggests that there was no significant photoinduced heating in either solution. As both the hydroxyazobenzene and the monomer have similar UV−vis spectra to that of the polymers, it can be assumed that the azobenzene polymers would also not exhibit any significant photoinduced heating. A detailed investigation is currently underway to measure the temperature of the test liquid contained between the cone-and-plate in the rheometer when exposed to UV radiation. These findings will be published in due course. Despite undergoing trans-to-cis isomerization (73% cis), the monomer/PMMA solution did not show any decrease in viscosity. This suggests that, for the concentration range studied, the chromophores needed to be attached to a polymer chain to produce a photoviscosity effect.

The viscosity data at three concentrations (1.2, 2.5, and 5 mg/mL) of polymer $M_{40.2}C_{17}$ were converted to the η_{sp}/c. A plot of η_{sp}/c against concentration is presented in Figure 7. By extrapolating the η_{sp}/c to zero concentration, it can be shown that the intrinsic viscosity of $M_{40.2}C_{17}$ decreases by 60% when exposed to UV light. After the rheology experiment, the irradiated solution was analyzed by UV−vis spectroscopy, which showed about 80% cis isomerization. Similar photoinduced viscosity changes have been reported in the literature.[2−5]

During the viscosity measurement without using any solvent trap it was found that solution viscosity increased with time, which was assumed to be a combined effect of solvent evaporation and water absorption by DMSO. The use of a solvent trap minimized the evaporation. When a solution of higher concentration was

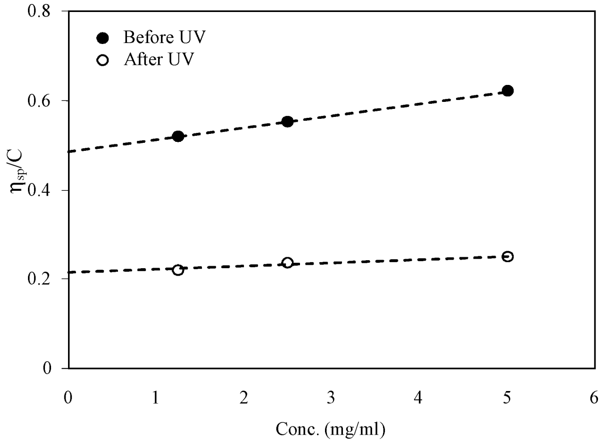

Figure 7. Concentration dependence of the photoviscosity effect of $M_{40.2}C_{17}$ in DMSO.

used, precipitation of the polymer was observed. The resulting precipitate caused intermittent interruption to the rotation of the measuring geometry, making accurate viscosity determination difficult. This precipitation was thought to be due to the absorption of water by the solution. Consequently, the sample chamber was flushed with argon prior to sample loading, which minimized the water absorption by the solution. The effect of this water absorption was more noticeable prior to irradiation, when the majority of the chromophores were in the less soluble trans form. Depending on the volume of water absorbed by a particular batch of sample solution during loading and/or storage, a greater variability of the initial viscosity was observed in repeated runs compared to the viscosity after irradiation. This variation was found to be greater at higher concentrations.

Proposed Mechanisms for the Photoviscosity Phenomenon. The photoviscosity effect of poly(methacrylic acid) with azobenzene side chains in aqueous media was first reported by Lovrien.[2] The increase in the solution viscosity under irradiation was attributed to the reduction of the hydrophobic interaction forces between azobenzene groups along the polymer chain due to isomerization. This was said to permit the polymer chain to expand and increase the viscosity of the solution. In solvents with lower polarity, the behavior of the azobenzene side chains was said to be different. Matejka and Dusek investigated a copolymer of maleic anhydride with styrene in 1,4-dioxane and THF.[3] Here the trans–cis isomerization of the azobenzene groups was reported to induce strong dipoles in the pendant groups, which were said to attract each other in less polar solvents. The net effect of this was claimed to be a contraction of the polymer chain, thereby reducing the viscosity.

Figure 7 shows no effect of concentration on the η_{sp}/c of the polymer solution below a concentration of 0.5%; therefore, the photoinduced decrease of the solution viscosity is believed to be mainly due to intramolecular interaction. It was found that above 0.5% the magnitude of the photoinduced change in the η_{sp}/c decreased significantly with increasing concentration. This could be due to the aggregation of polymer molecules caused by the solvent absorbing moisture; this is likely to be more significant when the concentration of the polymer solution is higher. It is known that DMSO is hygroscospic and can form a dimer, trimer, or even higher complex with water.[19] This aggregation phenomena during photoviscosity measurement at relatively higher concentration (1.9 g/L) was reported previously by Hallensleben and Menzel[4] when they investigated the photoinduced viscosity change of poly[5-(4phenylazobenzyl)-L-glutamate] in 1,4-dioxane.

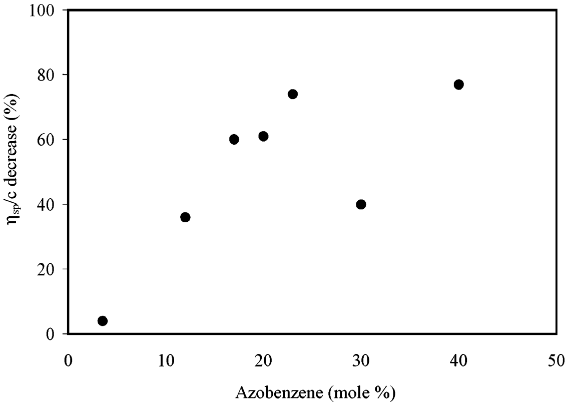

Figure 8. Effect of azobenzene loading on the photoviscosity effect.

The effect of azobenzene loading on the photoviscosity behavior is considered next. Figure 8 shows a plot of the percentage change in η_{sp}/c against azobenzene loading for several of the copolymers of MOAB/MMA, as presented in Table 1. It is quite clear from Figure 8 that the magnitude of the photoinduced η_{sp}/c change increases with the number of azobenzene units in the polymer chain up to 23 mol % chromophore loading. The greatest change in viscosity (77% decrease) was observed at a chromophore content of 42 mol % ($M_{19.2}C_{42}$). In contrast, the polymer with 30 mol % ($M_{24.3}C_{30}$) chromophore loading only showed 39% decrease in η_{sp}/c. Therefore, the photoviscosity effect above 23 mol % azobenzene loading needs further investigation.

A possible interpretation of the results is that the intramolecular dipole–dipole interaction between neighboring azobenzene chromophores plays the most significant role in producing the photoviscosity effect. However, other effects such as any temperature rise upon UV exposure (not reported in this current study), molecular weight distribution of the polymer, and water absorption by DMSO during the progress of the experiment may also have some influence. Under UV irradiation, the azobenzene side chains undergo trans-to-cis isomerization, inducing a dipole across the N=N bond. Neighboring dipoles are believed to orient and attract each other, contracting the polymer backbone and hence decreasing the viscosity. The increase in the magnitude of the photoviscosity effect at higher azobenzene loading is interpreted in terms of the proximity of the side chains to one another. In the low azobenzene content polymer, the distance between two neighboring chromophores is relatively large; therefore, dipole–dipole interaction is minimal. This may account for the smaller photoinduced decrease of η_{sp}/c. As the chromophore content increases, the distance between neighboring chromophores decreases, resulting in more interaction, which could lead to a greater viscosity reduction. It was anticipated that above a critical loading the magnitude of the photoviscosity effect would decrease, as the distance between neighboring chromophores becomes small enough for the steric repulsion between them to balance the dipole–dipole interaction. However, it was not possible to measure the photoviscosity effect in polymers with higher chromophore loading due to their

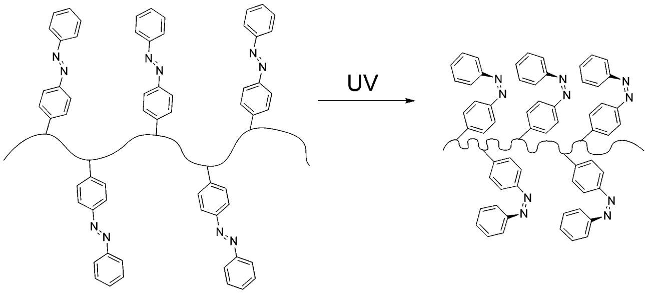

Figure 9. Possible mechanism for photoviscosity effect.

poor solubility in DMSO. Further investigation into the effect of higher azobenzene loadings is in progress in alternative solvents. With reference to the above discussion, a speculative mechanism to account for the lowering of the viscosity upon UV irradiation is presented in Figure 9.

Conclusions

A series of copolymers of *trans*-4-methacryloyloxyazobenzene/methyl methacrylate with azobenzene in the side chains have been synthesized and characterized. These polymers exhibit a photoviscosity effect when exposed to UV irradiation ($\lambda = 365$ nm). This effect is attributed to a conformational contraction of polymer chains due to intramolecular dipole−dipole interaction between neighboring chromophores. The magnitude of the photoinduced decrease in η_{sp}/c increases with the increasing azobenzene chromophores content up to 23 mol %. Above this loading, the results were inconsistent. The critical point of azobenzene loading, where the magnitude of the photoviscosity effect was expected to decrease, could not be explored due to the poor solubility of the polymer with higher azobenzene loading.

A new technique for measuring the photoviscosity effect in polymer solutions has been developed, utilizing a modified cone-and-plate rheometer to permit continuous measurement of viscosity during irradiation. However, adequate measures such as use of a solvent trap and choice of less volatile solvent need to be taken to minimize evaporation. The technique is more efficient for irradiation of the sample, and isomerization is much faster as the test specimen thickness is very small (<350 μm). The apparatus greatly reduces the sample volume required to perform such tests and experimental time as well as simplifying the rate determination.

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