

The Use of ^1H NMR and UV–vis Measurements for Quantitative Determination of *trans/cis* Isomerization of a Photo-Responsive Monomer and Its Copolymer

M. Moniruzzaman, J. D. R. Talbot, C. J. Sabey, G. F. Fernando

Engineering Systems Department, Royal Military College of Science, Cranfield University, Swindon, Wiltshire, SN6 8LA, United Kingdom

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ABSTRACT: Photo-induced *trans*–*cis* isomerization of *trans*-4-methacryloyloxyazobenzene and its copolymer with methylmethacrylate, synthesized in this work, were investigated in a polar protic (CDCl_3) and a polar aprotic ($\text{DMSO}-d_6$) solvent, using ^1H -NMR. The results were cross-correlated with *trans*–*cis* isomerization calculated from UV–visible spectra. The kinetics of the photoisomerization reaction of the monomer species under UV light irradiation is described by a simple first order exchange between the *trans* and *cis* forms of the monomer. The behavior was found to be similar for both solvents. The *cis*-to-*trans* reversion in the absence of irradiation is about 3% of the back reaction under irradiation. For the polymer in solution, the behavior was

more complicated and is described by the sum of two equilibria, each of first order exchange kinetics of the *trans* form with two different types of *cis* isomer in the polymer; a first type of isomerization similar in behavior to that of the monomer and the second type much faster in *cis/trans* exchange rate. This bi-kinetic behavior is in agreement with that of the azobenzene moiety in PMMA as a solid phase mixture. The relative proportion of the two rates comprising the bi-kinetic effect is solvent-dependent. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1103–1112, 2006

Key words: UV–visible; NMR; azobenzene; photo-isomerization; copolymer

INTRODUCTION

The azobenzene chromophore continues to attract considerable interest as it offers the potential for creating photoresponsive materials.^{1–3} The properties of such materials may be altered reversibly by irradiation at selected wavelengths and/or by temperature. As shown in Figure 1, the azobenzene chromophore exists as a rigid structure about the central $-\text{N}=\text{N}-$ double bond and this gives rise to two isomers, a more stable *trans* form and as a result of steric repulsion between the two aromatic rings, a higher energy, *cis* form. In the dark, the *trans* conformation is the sole thermodynamically stable form but on irradiation by ultraviolet light, the ground state can become excited with subsequent formation of the *cis* isomer. The reaction is reversible since re-isomerization can occur either thermally or under irradiation at a specified wavelength corresponding to the absorption band of the *cis* isomer.^{4,5}

The *trans*–*cis* isomerization phenomena is attractive because of its potential use in devices based on optically-reversible phase transformations such as optical switches, optical memory storage systems, or artificial muscles. Several authors have reported on the synthesis of polymers incorporating the azobenzene group. However, previous studies on the photo-induced *trans*–*cis* isomerization have been primarily concerned with the relative change in isomerization with irradiation time. Quantitative estimation of the exact ratio of the *cis* to *trans* isomer in such a transformation has received limited attention. Principal previous work includes that of Beattie and coworkers⁶ who reported the reversible *trans*–*cis* isomerization of azobenzene modified poly(aryl ether ketone amides) using ^1H -NMR spectroscopy but not of the isomerization correlation with UV absorbance. Wachtveitl et al.⁷ measured ^1H -NMR of *p*-aminophenylazobenzoic acid before and after 30 min irradiation and found only a 10% *cis* content. Thus far, comparatively little has been published on the quantitative correlation between *trans/cis* content as measured by UV–visible absorbance spectroscopy and ^1H -NMR spectroscopy versus time of irradiation.

This paper reports on, the derivatization of 4-hydroxyazobenzene to a monomer (*trans*-4-methacryloyloxyazobenzene) and its copolymerization with methylmethacrylate by a free radical polymerization

Correspondence to: M. Moniruzzaman (m.moniruzzaman@cranfield.ac.uk).

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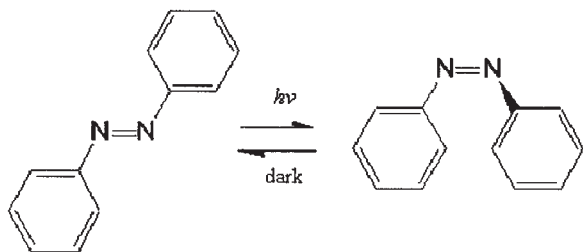


Figure 1 Photo-induced trans to cis isomerization.

route. The quantitative determination of the trans/cis isomers for both the monomer and the copolymer against irradiation time, using $^1\text{H-NMR}$ and UV-visible spectroscopy are described. The kinetics of trans-cis isomerization and the cross-correlation of the results obtained by $^1\text{H-NMR}$ and UV-visible spectroscopy are discussed.

EXPERIMENTAL

Methods

The following reagents were supplied from Sigma-Aldrich and used without further purification; 4-hydroxyazobenzene (98%), triethylamine (99.9%), chloroform (99.9%), 2-6-di-*tert*-butyl-*p*-cresol, dimethylsulfoxide (99.9%), and methanol (99%). Methacryloyl chloride (98+%) from Sigma-Aldrich was purified by distilling under dry nitrogen in presence of 2-6-di-*tert*-butyl-*p*-cresol prior to use. 2, 2'-Azobisisobutyronitrile (AIBN, 98%) from Fisher Chemicals was purified by recrystallization from ethanol and dried under vacuum prior to use for polymerization.

Synthesis of trans-4-methacryloyloxyazobenzene

trans-4-Methacryloyloxyazobenzene was prepared following a method described previously.⁸ 4-Hydroxyazobenzene (4 g, 20.1 mmol), inhibitor (10 mg, 2-6-di-*tert*-butyl-*p*-cresol), and triethylamine (20.2 mmol) were dissolved in tetrahydrofuran (100 mL). The mixture was stirred at room temperature while being purged with dry nitrogen gas. The flask was sealed with a subaTM seal. The solution was cooled to about -10°C and methacryloyl chloride (22.2 mmol) was added in a dropwise manner. The reaction mixture was stirred at room temperature (21°C) for 38 h under a nitrogen atmosphere. The content of the flask was filtered to remove the triethylammonium chloride salt. It was then diluted to four times of its original volume with a mixture of chloroform and distilled water (3 : 1). The organic layer was washed with dilute HCl and then with distilled water to remove any polar contaminants. Finally, the organic layer was dried using anhydrous sodium sulfate and the solvent was

evaporated under reduced pressure. The crude product was air-dried and its purity ascertained by thin layer chromatography (TLC). The residue was purified by column chromatography on silica gel 60 (70–230 mesh ASTM) with chloroform and recrystallization from petroleum ether ($40-60^\circ\text{C}$). Finally, the crystalline product was dried under vacuum and a yield of 75% was obtained.

Synthesis of polymer

The copolymer of trans-4-methacryloyloxyazobenzene and methylmethacrylate was prepared by free radical polymerization in tetrahydrofuran. Azobisisobutyronitrile (AIBN) was used as the initiator. A high-vacuum apparatus joined with two Young's taps was used as the reaction vessel. The synthetic process used for polymerization was as follows: trans-4-methacryloyloxyazobenzene (0.45 g), methylmethacrylate (1.412 g, 1.0 mL) and AIBN (5% w/w) were dissolved in THF (20 mL). The reaction mixture was degassed using a freeze-thaw procedure involving the use of liquid nitrogen. Polymerization reaction was conducted under vacuum at 65°C for 64 h. The polymer was precipitated from methanol and purified by repeated precipitation from THF/methanol. Finally, the product was dried under vacuum and a yield of 80% was obtained.

Measurements

Nuclear magnetic resonance

A Bruker DPX250 NMR instrument was used to confirm the structures of the parent material, monomer, and polymers. The $^1\text{H-NMR}$ spectra were recorded using a 1.5% w/v sample solution in deuterated chloroform (CDCl_3) and deuterated dimethylsulphoxide ($\text{DMSO-}d_6$) with tetramethylsilane (TMS) as an internal standard.

The conversion of trans isomer to the cis form was investigated by conventional $^1\text{H-NMR}$ using the same spectrometer as mentioned above. The sample was contained in a standard NMR tube. The sample was then irradiated using a Vinten Superlite UV spotcure ($\lambda = 365 \pm 5 \text{ nm}$). The intensity of the light source was $30-40 \text{ mW/cm}^2$ with the internal 365 nm filter.

The bulk monomer (15 mg) was dissolved in 1 mL and of CDCl_3 and about 0.7 mL of this solution was transferred to the NMR tube and the $^1\text{H-NMR}$ spectrum was recorded. The solution was irradiated with the spotcure unit for exposure times of 5, 20, 55, 100, 140, and 175 min. A similar experimental procedure was used on the monomer in $\text{DMSO-}d_6$. The composition of the trans and the cis isomers were calculated from the integration of the resonance of the aromatic and vinyl protons.

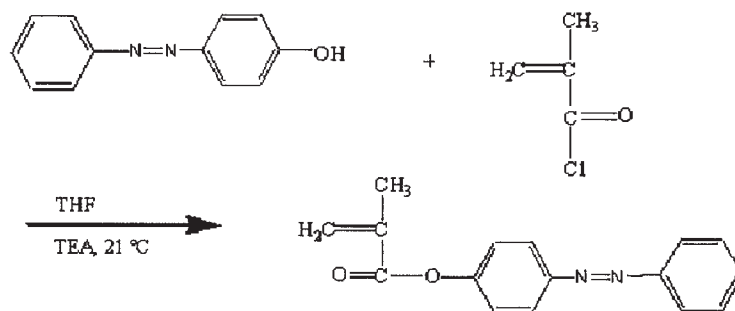


Figure 2 Reaction scheme for the synthesis of *trans*-4-methacryloyloxyazobenzene.

Photo-induced *trans*–*cis* isomerization of the polymer in $CDCl_3$ was monitored at 5, 45, 132, 162, and 175 min. The analysis of a fresh sample of the same polymer was done in $DMSO-d_6$ after 5, 45, 132, 165, and 207 min of irradiation. The reverse reaction, i.e., the *cis*–*trans* isomerization of the azobenzene monomer and the pendant azobenzene side groups in the polymer was investigated by storing the irradiated solutions in dark and monitoring the rate of reverse isomerization against storage time by 1H -NMR.

Gel permeation chromatography

The weight-average molecular mass (M_w), number-average molecular mass (M_n) and molecular mass distribution of the copolymer were determined by size exclusion chromatography (SEC) on a Waters 2410 instrument with a refractive index detector. The column was packed with PLgel 5 μ m 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 with THF as the mobile phase with a flow rate of 1 mL min^{-1} .

Differential scanning calorimetry

The thermal properties were measured on a TA instruments DSC Q1000. An isothermal heating scan rate of 10°C min^{-1} was used and a cooling rate of 0.1°C min^{-1} or 10°C min^{-1} was used. The glass transition temperature and the crystalline melting temperature were calculated using DSC Q1000 standard software.

UV–visible spectra

UV–visible spectra were recorded using a Cary 4G UV–visible spectrometer. Samples were contained in 10-mm path-length quartz cuvettes and spectra were collected in single beam mode over a wavelength range of 260 nm to 600 nm. A 1.5% $DMSO-d_6$ solution of monomer was irradiated in an NMR tube, from which samples were collected after 0, 5, 20, 45, 90, 135, and 180 min of irradiation. An identical UV–visible

analysis was also conducted on a 1.5% DMSO solution of the polymer.

RESULTS AND DISCUSSION

Synthesis and characterization of monomer and copolymer

Monomer

The basic reaction scheme for the monomer synthesis is shown in Figure 2. As described above, the azobenzene monomer was prepared with a yield of 75%. To ensure complete reaction of 4-hydroxyazobenzene, an excess of methacryloyl chloride (20% mol) was used. The unreacted methacryloyl chloride was subsequently hydrolyzed to its corresponding acid with dilute HCl at the end of the reaction and removed by extracting with distilled water. Thin layer chromatography analysis was used to verify the formation of the product. The final product was thus isolated using silica column chromatography and crystallization. The melting point of the product was determined to be $(110 \pm 2)^\circ C$.

The structure and purity of the monomer was ensured with the help of 1H -NMR (in $CDCl_3$) spectroscopy. Figure 6 (a) shows the chemical shifts of protons at different electronic environments. The signals at δ 7.90–7.99 (m, *ortho*-position to $-N=N-$), δ 7.44–7.54 (m, *meta* and *para* to $-N=N-$) and δ 7.16–7.30 (m, *ortho*-positions to $-O-CO-$) correspond to four, three and two aromatic protons respectively. Two additional signals of identical intensity at δ 5.79 and δ 6.84 correspond to the vinyl protons of $C=CH_2$. The signal at δ 2.08 (s, CH_3) arises from the methyl protons of the methacrylate group. The ratios of integration of aromatic and vinyl protons proved the two components are in a stoichiometric ratio of 1 : 1.

Polymer

The copolymerization reaction of *trans*-4-methacryloyloxyazobenzene and methylmethacrylate is shown in Figure 3. Synthesis of the polymer also achieved a

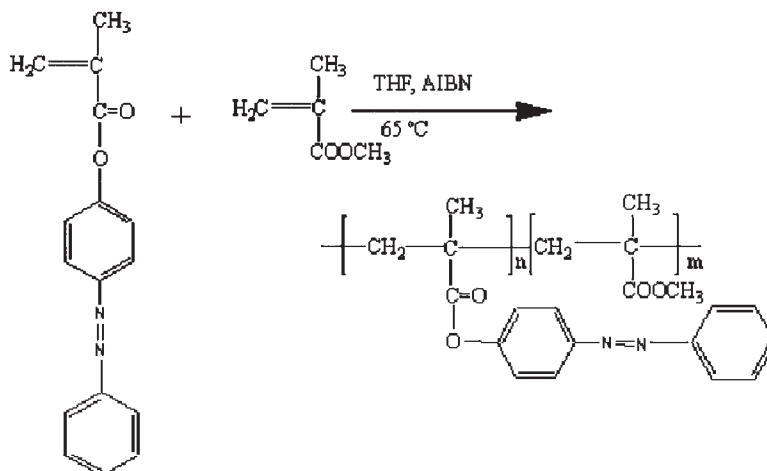


Figure 3 Reaction scheme for the synthesis of the copolymer of *trans*-4-methacryloyloxyazobenzene and methyl methacrylate

very good yield (80%). The relative composition of the copolymer was obtained by $^1\text{H-NMR}$ ($\text{DMSO-}d_6$), comparing the integration of the broad aromatic signals (Fig. 7) at δ 7.87–7.97 (4H), δ 7.56 (3H), and δ 7.31 (2H) with that at δ 3.53 (3H, OCH_3 of methyl methacrylate). The result indicated a presence of 13 mol % of pendant azobenzene groups in the polymer and 87 mol % methylmethacrylate.

The M_w and the M_n of the copolymer were determined against the polystyrene conversion molecular mass to be $26,400 \text{ g mol}^{-1}$ and $14,500 \text{ g mol}^{-1}$ respectively. The molecular weight distribution (M_w/M_n) was 1.8. $M_n = 14,500 \text{ g mol}^{-1}$, corresponding to around 120 monomer units of which about 15–16 on an average will have pendant azobenzene units.

The heating scan showed two broad endotherms, the first one at about 95°C and the second one at 101°C . The lower temperature endotherm at 95°C is probably due to the melting of poorly defined crystallites, while the higher temperature endotherm at 101°C corresponds to the melting of more regular structure. In addition to the melting temperature, the heating scan showed a transition at about 127°C and was assigned to be the glass transition temperature (T_g) of the polymer.

Determination of *trans/cis* concentrations by UV–visible spectroscopy

Monomer

As outlined previously, the reversible photo-induced *trans*–*cis* isomerization of *trans*-4-methacryloyloxyazobenzene (monomer) in DMSO was investigated by UV–visible spectroscopy. Figure 4 shows the UV–vis spectra of monomer against irradiation time. The unirradiated sample solution showed two absorption bands, an intense one at 328 nm attributed to the π – π^*

electronic transition of *trans*-azobenzene moiety and a weak band at 444 nm due to the forbidden n – π^* electronic transition. As expected, the intensity of the absorption band at 328 nm attributed to the *trans*-azobenzene chromophore decreases with increasing irradiation time. With reference to Figure 4, a photostationary state was reached after 3 h and two isobestic points were observed implying the presence of only *trans* and *cis* isomers.

The photo-induced *cis/trans* content in the monomer was calculated with the aid of $^1\text{H-NMR}$ in DMSO using the relationship shown in eq. (1):

$$\chi_{\text{trans}} = \frac{A_I}{A_0} \quad (1)$$

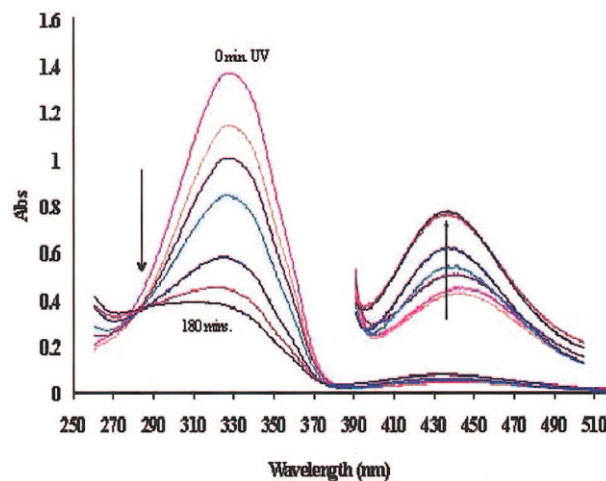


Figure 4 Absorption spectra of *trans*-4-methacryloyloxyazobenzene, 15 mg/mL DMSO solution was irradiated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

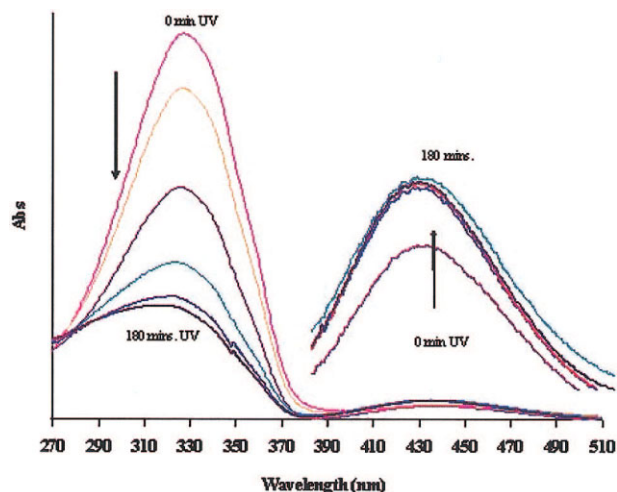


Figure 5 Absorption spectra of 15 mg/mL solution of polymer in DMSO, after a range of irradiation time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

where χ_{trans} is the relative content of trans isomer, A_I = absorbance of the irradiated sample (328 nm), and A_0 is the absorbance of unirradiated sample (328 nm). As mentioned above, the isomerization process under the conditions employed was completed within 3 h. $^1\text{H-NMR}$ analysis confirmed the trans-azobenzene content to be >99% when in the unirradiated state. The photostationary state comprised of 73% of the cis form.

Polymer

UV-visible spectra were recorded after specified irradiation times and are presented in Figure 5. The unirradiated polymer solution showed an intense absorption at 327 nm, due to the $\pi\text{-}\pi^*$ electronic transition and a less intense absorption at 442 nm due to the forbidden $n\text{-}\pi^*$ transition of azobenzene. As expected, upon irradiation, the intensity of the absorption band at 327 nm decreases, while that at 442 nm increases, this is the usual trend observed for trans-cis isomerization. Similar to the monomer, a photostationary state was reached after approximately 3 h of irradiation, where 73% of the polymer was converted to the cis conformation.

Kinetics of trans/cis isomerization determined by $^1\text{H-NMR}$ spectroscopy

Monomer

Figure 6 shows the photo-induced trans-cis isomerization as a function of irradiation time. $^1\text{H-NMR}$ spectra (in $\text{DMSO-}d_6$) of the unirradiated sample showed three types of aromatic signals at chemical shifts of δ 7.89–7.99 (m, 4H), δ 7.58–7.62 (m, 3H), and

δ 7.41–7.45 (m, 2H), and these have been assigned to the trans-azobenzene chromophores of the monomer. Two signals at δ 5.95 (s, 1H) and δ 6.33 (s, 1H) were due to the vinyl protons from methacrylate. The signal showed at δ 2.03 was due to the resonance of the CH_3 protons of the methacrylate. Upon UV irradiation, new sets of aromatic signals appeared in addition to the trans signals at δ 6.84–6.93 (m, 4H), δ 7.10–7.19 (m, 3H), and δ 7.30–7.36 (m, 2H) due to the formation of the cis isomer. Two additional signals were also observed at δ 5.88 and δ 6.24 correspond to vinyl signals from the cis conformation. The appearance of a signal at δ 1.99 was assigned to the cis- CH_3 group of the monomer. Because the size of each peak in the NMR spectrum is proportional to the number of protons present, the analysis does not require a molecule-specific coefficient of absorption to be derived. The concentration of each isomer was ascertained unambiguously with irradiation time.

The $^1\text{H-NMR}$ results for the cis proportion of the monomer in deuterated chloroform and deuterated dimethylsulphoxide as a function of irradiation time are given in Table I. Here, x is the mole fraction of cis isomer as a proportion of total azobenzene concentration (i.e., cis + trans). The experimental measurements are plotted and compared to a best-fit theoretical equilibration curve using the simple kinetic model in Figures 7 and 8. The model assumed that, for constant irradiation, the isomer of each conformer is first order with respect to concentration i.e.

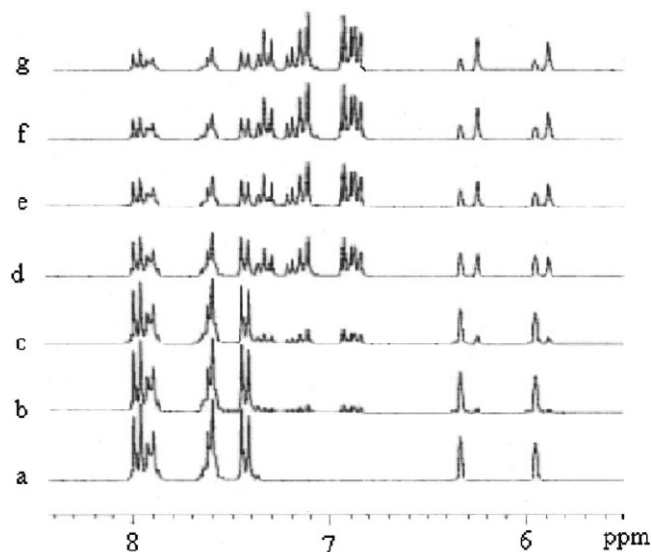


Figure 6 $^1\text{H-NMR}$ spectra of monomer in $\text{DMSO-}d_6$ against irradiation time. (a) Before UV-irradiation, b, c, d, e, f, and g correspond to 5, 15, 55, 100, 146, and 175 min respectively.

TABLE I
Mole Fraction of Monomer Cis Isomer, x_{cis} , as a Function of Irradiation Time

Time (s)	Monomer in CDCl_3	Monomer in $\text{DMSO-}d_6$
0	0.04	0.01
300	0.15	0.09
900	—	0.18
1200	0.26	—
3300	0.48	0.48
6000	0.68	0.60
8400	0.77	—
8800	—	0.69
10500	0.83	0.73

where k_f and k_b are the rate constants for the forward and back reaction respectively, under illumination. The forward and back reactions are:

$$d[\text{Cis}]/dt = k_f[\text{Trans}]\Phi \text{ and } d[\text{Trans}]/dt = k_b[\text{Cis}]\Phi \quad (3)$$

where Φ is a function of the incident intensity of the radiation (simplified, from Rau, 2002).⁹ For steady irradiation and low initial cis content, Φ is constant and was assumed so in this work. The form of the equation at any time for initial conditions of $x_{\text{cis}} = 0$ at time $t = 0$ is:

$$1 - x_{\text{cis}} = [k_b + k_f \exp\{-(k_f + k_b)t\}]/(k_f + k_b) \quad (4)$$

Best fitted results for k_f and k_b for the monomer in both solvents are given in Table II. It can be seen from Figures 7 and 8 that the monomers both follow the kinetics expected from first order kinetics appropriate to simple first order trans–cis interconversion and the shape of the curves are similar for each solvent. The initial portion of each curve is dominated by the value of k_f and for the two solvents are within 7% of a mean of $2.15 \times 10^{-4} \text{ s}^{-1}$. The implication is that photoisomerization of the trans conformer for the monomer is almost independent of whether a protic or aprotic solvent is used. The values for k_b show greater divergence although they are still within 25% of a mean of $0.325 \times 10^{-4} \text{ s}^{-1}$ for both solvents. The photostationary state is given by the ratio of k_f/k_b . This is $x_{\text{cis}} = 0.90$ in chloroform and $x_{\text{cis}} = 0.83$ in DMSO.

Polymer

The extent of isomerization against irradiation time is shown in Figure 9. The resonance signals at about δ 7.87–7.97 (4H), δ 7.56 (3H), and δ 7.31 (2H) are attributed to the trans isomer of the pendant azobenzene side group. Signals within δ 6.84–7.17 are due to the cis isomer of the azobenzene chromophore. Results are given in Table III. As shown in Figures 10 and 11 the initial isomerization is somewhat faster than that of the simple monomer and is not predicted via simple first order exchange kinetics. The final photostationary state however, was of a similar magnitude to that for the monomer. The main difference between the two

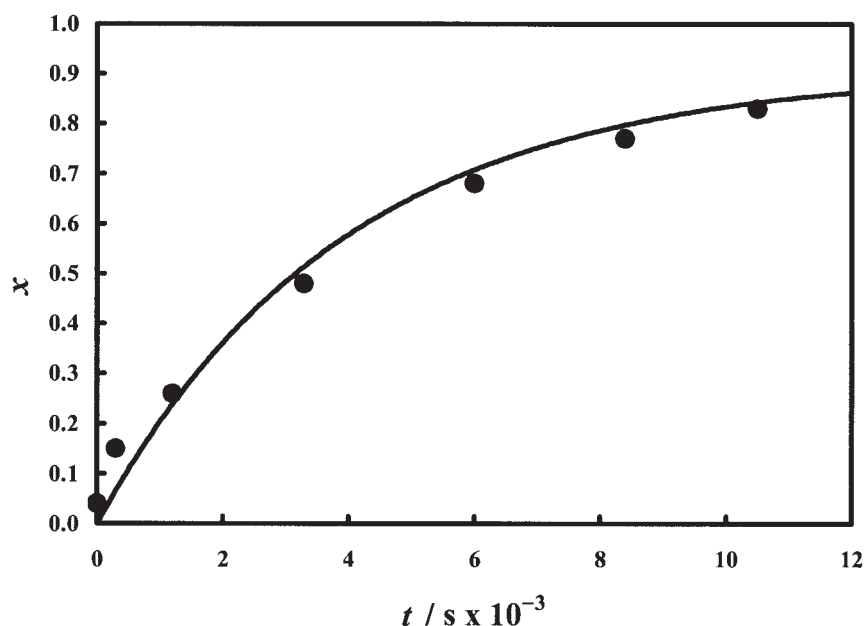


Figure 7 Extent of trans to cis conversion of azobenzene monomer dissolved in deuterated chloroform (15 g dm^{-3}) as a function of UV radiation time, t , showing theoretical curve fitted to experimental values. x is the mole fraction of the cis isomer.

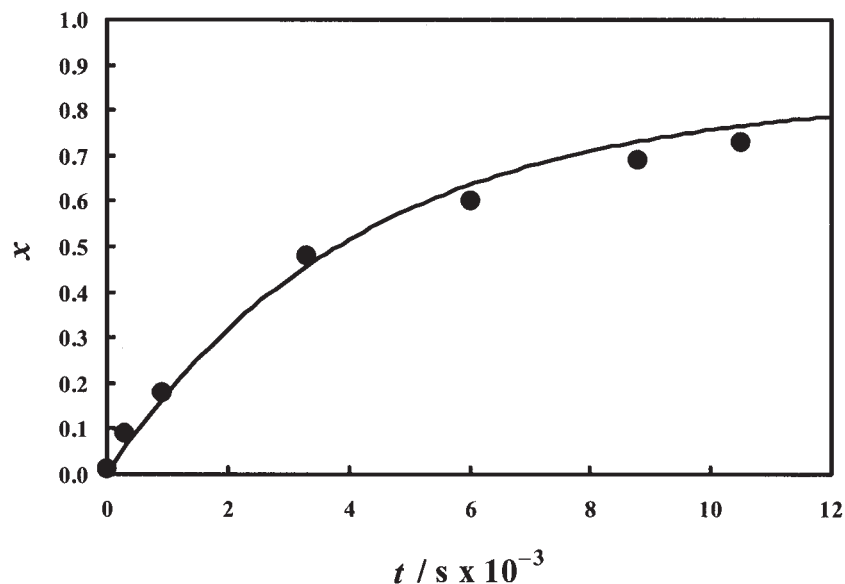
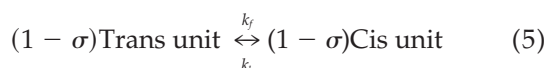
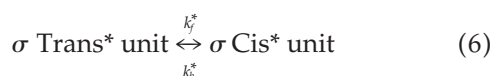


Figure 8 Extent of trans to cis conversion of azobenzene monomer dissolved in deuterated DMSO (15 g dm^{-3}) as a function of UV radiation time, t , showing theoretical curve fitted to experimental values. x is the mole fraction of the cis isomer.

solvents is that the proportion of isomerization by this faster kinetic route (as given by σ below) is however different for each solvent and this exerts the most pronounced effect on the shape of the curves in Figures 10 and 11. The initial fast kinetics of the polymer in each solvent is adequately modeled by considering a bikinetic approach, i.e., that a proportion of the polymer behaves in the same way as the monomer in the same solvent but that the remainder exhibits the same first order kinetics but at a faster rate i.e., if σ is the proportion of the faster site.



and



To minimize the number of fitting parameters, the ratio k_f^*/k_b^* was fixed at 2.0. This was found that the value that conformed best to both solvents was neces-

sitated because the scanning time of the technique employed ($^1\text{H-NMR}$) limited the amount of collectable data. Values of k_f , k_b , k_f^* , k_b^* , and σ are given in Table II and the theoretical curves shown in Figures 10 and 11. It can be seen that the fits are generally of a good order, equal to those obtained with the monomers. The bikinetic effect has been previously observed in the solid polymers (azobenzene mixtures in PMMA)¹⁰ and also in the decay kinetics of ultrafast dynamics in the laser-excited states of 1-phenylazo-2-hydroxynaphthalene.¹¹ The latter study also reported that for ultrafast decay of the species in question, the time decay constant of the faster of the two first order rates [eq. (6)] was dependent on the viscosity of the solvent to the power, $\eta^{2/3}$ and was correlated to a model by Förster and Hoffman.¹² It is interesting to note, that the values of σ in this work are remarkably different for each solvent. However for the two solvents used, chloroform and DMSO, the value of σ obeys the simple relation:

$$\sigma = (1 - 0.445/\eta^{2/3}) \quad (7)$$

TABLE II
Rate Constants for Forward and Back Reactions for Trans–Cis Isomerization Under UV Irradiation

Sample	$k_f \times 10^{-4}$ (s^{-1})	$k_b \times 10^{-4}$ (s^{-1})	$k_f^* \times 10^{-4}$ (s^{-1})	$k_b^* \times 10^{-4}$ (s^{-1})	σ
Monomer in CDCl_3	2.3	0.25	—	—	—
Monomer in $\text{DMSO-}d_6$	2.0	0.40	—	—	—
Polymer in CDCl_3	2.3	0.25	16	8	0.66
Polymer in $\text{DMSO-}d_6$	2.0	0.40	30	15	0.27

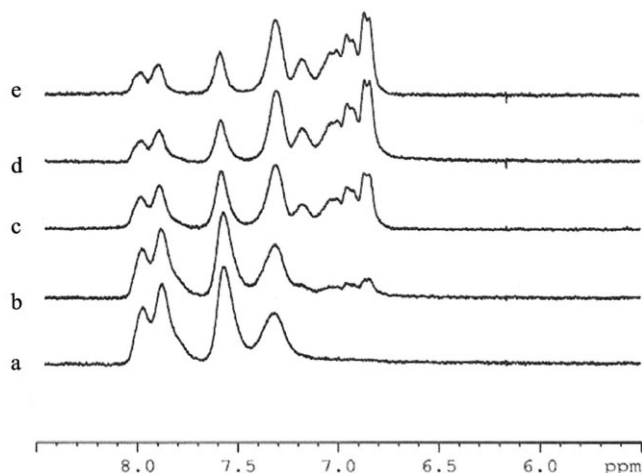


Figure 9 $^1\text{H-NMR}$ spectra of polymer in $\text{DMSO-}d_6$ against irradiation time. (a) Before UV-irradiation, b, c, d, and e correspond to 5, 45, 165, and 207 min UV irradiation respectively.

This implies that a similar type of mechanism, i.e., a viscosity-dependent fast inversion and a competing solvent independent slow inversion, is involved in the trans–cis interconversion of the polymer in solution, whereas in the monomer solution only the solvent independent inversion is present.

To simplify the system in understanding the solute–solvent interactions—and because of the limited amount of monomer and polymer available—it was decided to restrict the solvents used to “ideal” model solvents consisting of semi-spherical solvents e.g., with no carbonyl groups (as this tends to produce a “flat” molecule, cf. acetone or DMF) and which do not exhibit significant secondary solute salvation. For this work, it was decided to limit studies to two solvents which conform to these criteria: a protic solvent (chloroform) and an aprotic one (DMSO). The viscosity effect outlined above lends evidence for the ideal behavior for these materials in such solvents but for other solvents the situation may be more difficult to interpret. It is thus planned to investigate these phenomena in greater depth in an in-depth future study.

The reversion reaction for the monomer and polymer in CDCl_3 and $\text{DMSO-}d_6$ in the dark are shown in Figure 12. Three facts are illustrated:

1. The decay is very slow and the typical rate of decay is around 3% of the back reaction under illumination.
2. The rate order appears to be apparently zero order, i.e., it does not depend on the cis concentration. The rate for each species, monomer and—in the zero order part of the graph—the polymer, is more or less independent of solvent.
3. For the polymer, the curves are in two parts; firstly a steep drop, followed later by slow zero

order kinetics similar to the monomer, though at a slower rate as previously mentioned. If the zero-order line is extrapolated to the y-axis and compared to the starting cis mole fraction (0.73 for the polymer in each solvent) the proportion of the polymer that undergoes the initial faster decay is the same as that given by σ in Table II.

From observations 1 and 2 it can be seen that the mechanism of the reversion, cis to trans in the dark, is different from the same transformation under irradiation as given by the term k_b and is ascribed to the thermal reversion of the higher energy cis form to the stable trans form. This is consistent with literature values for thermal reversion kinetics of the azobenzene moiety, which is of the order of 2 to 3 days.¹³

The correlation of the two-part behavior of the polymer reversion reaction with the σ values in Table II is significant and suggests that the solvent-dependent mechanism previously mentioned concerning establishment of the photostationary state in the polymer [eqs. (5) and (6)] is also involved in the decay kinetics of the polymer in the absence of irradiation.

Comparison of $^1\text{H-NMR}$ and UV–vis measurements

The kinetic behavior as of cis–trans inversion as measured by both $^1\text{H-NMR}$ and UV–visible spectrometry was compared (Figs. 4, 5, 6, and 9). The relative proportion of cis and trans conformers obtained by UV–visible spectra was consistent ($\pm 3\%$, allowing for any uncertainties in baseline positions for the UV–spectra) with that determined via $^1\text{H-NMR}$ spectra and showed that, for the polymer but not the monomer, the bi-kinetic behavior was also observed. The relative molar absorption coefficient of each conformer appeared to be completely independent of any changing external environment (e.g., concerning the polymer component or solvent effects) during cis–trans conversion. However though correlation of conformer concentrations obtained from UV–vis spectra with $^1\text{H-}$

TABLE III
Mole Fraction of Polymer Cis Isomer, x_{cis} , as a Function of Irradiation Time

Time (s)	Polymer in CDCl_3	Polymer in DMSO_4
0	0.09	0.03
300	0.24	0.21
2700	0.59	0.52
7920	0.69	0.71
9720	0.73	—
9900	—	0.73
10500	0.73	—
12420	—	0.73

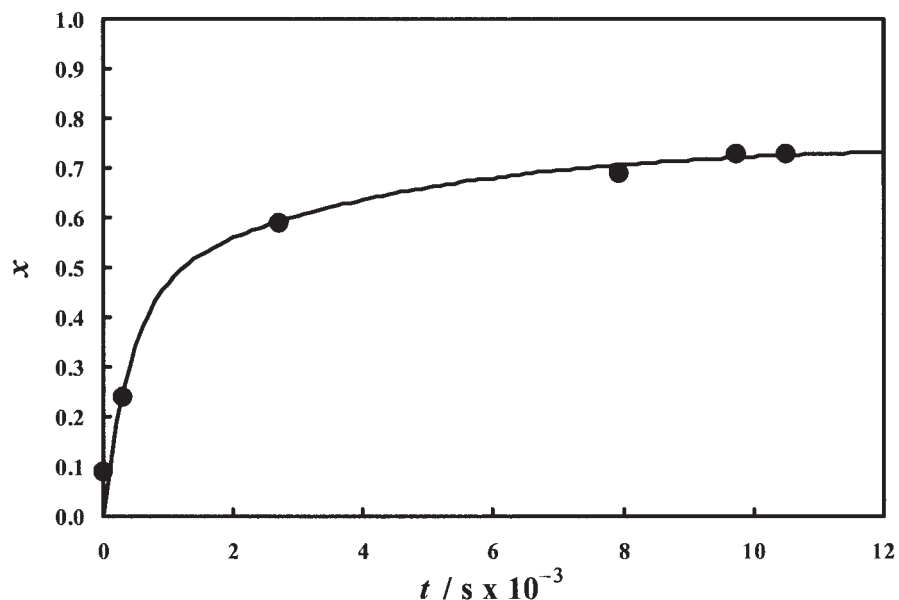


Figure 10 Extent of trans to cis conversion of azobenzene polymer dissolved in deuterated chloroform (15 g dm^{-3}) as a function of UV radiation time, t , showing theoretical curve fitted to experimental values. x is the mole fraction of the cis isomer.

NMR spectra was good, the NMR spectral data were preferred for calculations in this paper for two reasons; (a) since the ratio of the proton signals of the two conformers is directly dependant on their relative mole fraction it gives an absolute measurement of this parameter, and (b) the cis form is never obtained in the pure state (its maximum concentration when the photostationary state is achieved also contains significant trans form), so absolute quantification of the concen-

tration of this conformer from UV-vis spectra contains will always contain some error.

CONCLUSIONS

This work has investigated the nature of the photo-induced isomerization of trans-4-methacryloyloxyazobenzene and its copolymer with methyl methacrylate. The stoichiometric ratio of trans/cis interconversion

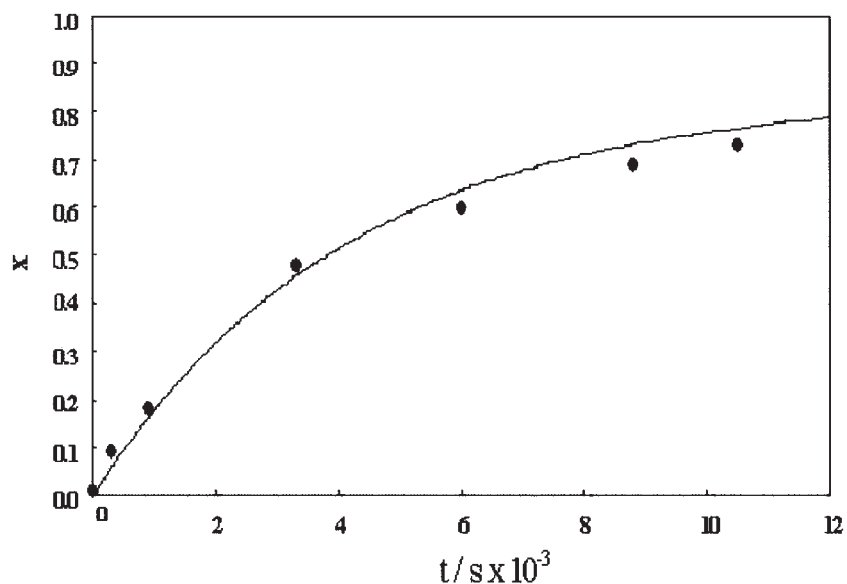


Figure 11 Extent of trans to cis conversion of azobenzene polymer dissolved in deuterated DMSO (15 g dm^{-3}) as a function of UV radiation time, t , showing theoretical curve fitted to experimental values. x is the mole fraction of the cis isomer.

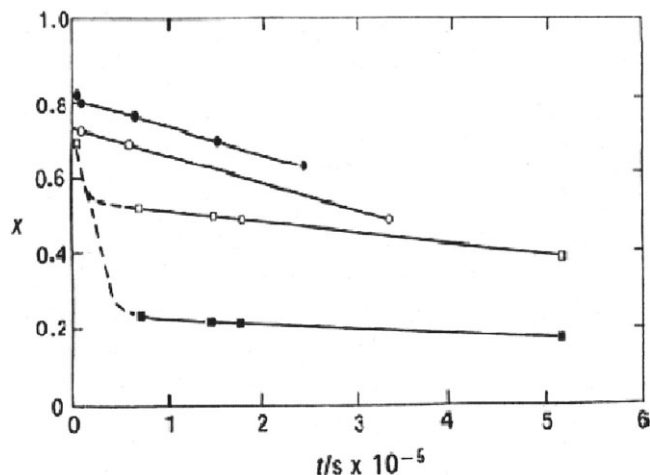


Figure 12 Reversion reactions of irradiated solutions stored in the dark. All Solutions 15 g dm^{-3} . x is the mole fraction of the cis isomer. (●) Monomer in CDCl_3 ; ○ Monomer in $\text{DMSO-}d_6$; ■ Polymer in CDCl_3 ; □ Polymer in $\text{DMSO-}d_6$

has been established and interpreted in terms of $^1\text{H-NMR}$ and UV-spectroscopy. The cross-correlation of NMR and UV-visible spectra indicated that NMR spectroscopy is the better tool for the quantitative measurement of trans/cis isomerization in azobenzene based photoresponsive material. The kinetics of this transformation have been evaluated and expressed in terms of the simple first order model. The findings

have been interpreted in terms of some simple solvent-solute interactions.

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