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Photoresponsive polymers: An investigation of their photoinduced temperature changes during photoviscosity measurements

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Abstract

Photoresponsive polyelectrolyte of polyacrylic acid with spiropyran in the side chain was synthesized by reacting polyacryloyl chloride with 1′-(2-hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-indoline] and by subsequent hydrolysis of acid chloride. The conformation of this material was photomanipulated and the associated changes in viscosity were studied by using a custom-modified rheometer. It was observed that the specific viscosity of the spiropyran-based polymer solution increased by about 12% upon UV irradiation and decreased due to visible irradiation. The viscosity changes were found to be reversible. The photoinduced heating effects during in situ photoviscosity measurements on two classes of materials, the polyelectrolyte and a series of azobenzene-based polymers, were also measured using a modified rheometer cone. The origin and magnitude of the heating effect were identified, and the associated viscosity changes of the solutions were decoupled to obtain a more accurate view of the photoviscosity behaviour. The magnitude of the photoinduced heating effect was found to be linearly dependent on chromophore molecules joined to the polymer chains. The photoinduced heating effect accounted for varying amounts of the observed change in specific viscosity ranging from as little as 2.5% for a highly photoresponsive solution to all of the observed specific viscosity change measured for non-photoresponsive systems.

Keywords: Azobenzene; Spiropyran; Photoviscosity

1. Introduction

Polymer chains with photochromic materials show appreciable changes in their properties upon exposure to UV light resulting in the formation of *trans* to *cis* isomer for azobenzene [1] and merocyanine for spiropyran [2]. When incorporated into polymer systems, the photo-isomerization can be used to control the conformation of the polymer by irradiation [3]. One of the ways in which this conformational change can be observed is a change in solution viscosity during irradiation [3–6]. To fully understand the changes in photoinduced solution viscosity, various types of azobenzene and spiropyran-based polymers have been synthesized and investigated [7–14]. However, with the exception of synthesizing azobenzene containing polyelectrolytes [15] limited attention has been focused on the synthesis and characterization of polyacrylic acid containing spiropyran in the side chain [16].

In the past, this change in viscosity has been attributed almost entirely to a photoinduced conformational change of the polymer rather than to photoinduced heating of the solution [3–6]. Where an increase in viscosity was observed during irradiation, thermal effects were discounted on the basis that the effect of heating would be opposite to that observed during irradiation [3–6]. This assumption is reasonable, although it is possible that the magnitude of the observed effect is reduced

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by a thermal component. Where the viscosity was observed to decrease during irradiation, possible thermal origins of the effect have been discounted either because the temperature change required to reproduce the effect was considered too great to have occurred [3] or the temperature control system was considered to be sufficient to prohibit any heating [16].

Few temperature measurements have been made during irradiation of solutions in a viscometer. Matejka and Dusek observed photoinduced temperature rise of 0.03 °C in solutions of copolymers of maleic anhydride with styrene containing azo-aromatic groups [P(MAH-STY-AAB)] despite controlling the temperature of the system (±0.05 °C) [5]. The presence of a temperature rise during irradiation, even within a controlled environment may affect the apparent viscosity of the solution and hence complicate the interpretation of the results, in the case of Matejka and Dusek, the temperature rise was sufficiently small to be ignored.

Until recently, the irradiation and viscosity measurements of photoresponsive polymer solutions have been performed sequentially, this method potentially allows the solution to return to its controlled temperature before the viscosity measurement, reducing the significance of any photoinduced heating. Recently the authors reported the design and development of an in situ photoviscosity measurement system, which permitted continuous irradiation during viscosity measurements [1]. The authors demonstrated that a small viscosity decrease occurred during UV irradiation, even in non-photoresponsive samples, which recovered within 5 min of the UV irradiation being ceased. This decrease was attributed to be caused by the absorption of photons by the solution during irradiation. The importance of being able to observe the accurate photoresponsive behaviour of a solution is not only because of scientific research but also for industrial applications and this can be achieved only by decoupling any thermal effects from the purely photoresponsive behaviour.

In this paper, we report on the synthesis, characterization and photoinduced viscosity changes of a polyacrylic acid homopolymer with spiropyran in the side chain and a series of copolymers of 4-methacryloyloxyazobenzene with methyl methacrylate. The origin and nature of the photoinduced heating effect of spiropyran-based polyelectrolyte and azobenzene-based copolymers have been investigated and the photoviscosity effects have been corrected.

2. Experimental

2.1. Techniques

A Bruker DPX-250 MHz NMR machine was used to determine the compositions of each component and also the isomeric form of the azobenzene chromophores. The NMR spectra of the samples were recorded either in deuterated chloroform ($CDCl_3$) or in DMSO-d_6 at 27 °C.

The relative weight-average molecular weight (M_w) and number-average molecular weight (M_n) and molecular weight distribution of the copolymers 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 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.

The photoinduced ring-opening and ring-closing phenomena were studied by taking optical spectra of the polyelectrolyte solutions in DMSO using a spectrometer (Zeiss, MCS 522 UV−VIS) with a xenon flash lamp (Zeiss, BLX 500/4). The sample solutions were tested in a 0.5 mm path length quartz cuvette (Hellma, special order) in a fibre-optic cell holder with integrated collimating optics. The samples were irradiated using a Vinten Superlite UV spotcure ($\lambda = 365 \pm 5$ nm). The spectra were collected in real time.

Viscosity measurements were performed using a custom-modified Bohlin CVOR 150-HR rheometer with a UV cell shown in Fig. 1 [1]. The sample reservoir was a quartz plate surrounded by a water jacket with an aperture in the base to be able to fit a liquid light guide. The viscosity measurements were performed using a stainless steel 40 mm diameter 1° cone plate. The temperature of the sample chamber was controlled by a Julabo KTB30 recirculating water bath (±0.1 °C). A solvent trap was used to prevent solvent loss from the solution under investigation during measurement.

The photoviscosity behaviour of each sample was measured under a controlled stress (0.5 Pa) at 25 °C. The viscosity of the sample was recorded in the dark for 15 min to allow the sample to reach a steady state and to establish an initial viscosity reading before UV irradiation. The sample was then irradiated using a Vinten Superlite UV spotcure ($\lambda = 365 \pm 5$ nm) for 15 min. Following the irradiation, the viscosity of the sample

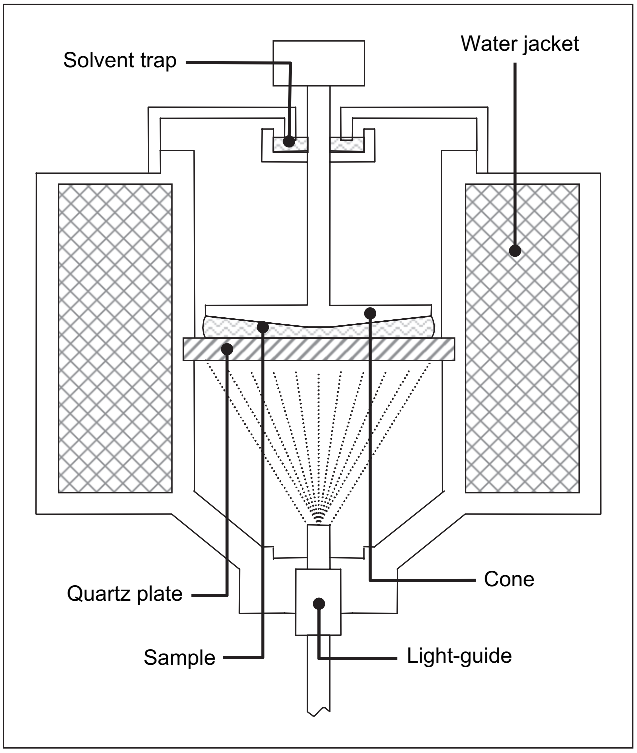


Fig. 1. Schematic of modified rheometer cell [1].

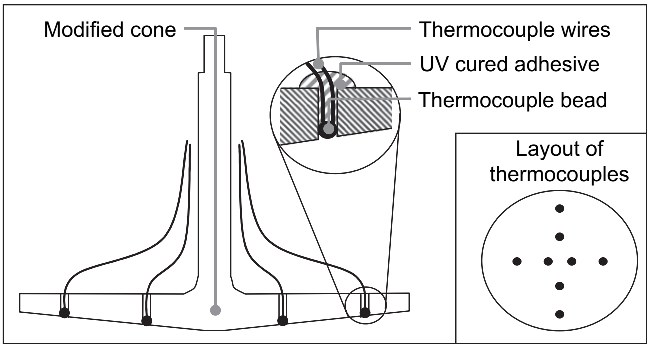


Fig. 2. Schematic of the modified rheometer cone.

was recorded for a further 15 min to observe any short-term recovery.

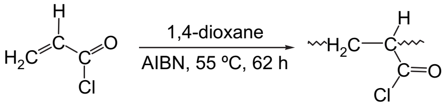
A cone (1°) plate was modified by drilling 8 holes and adding k-type thermocouples through the holes to have access for continuous measurement of localized photoinduced temperature changes caused by irradiation. The thermocouples were positioned such that the thermocouple bead was located flush with the lower surface of the cone as illustrated in Fig. 2. The thermocouples were located at radii of 4, 8, 12 and 16 mm, the arrangement was such that there were two thermocouples at each radius on opposite sides of the cone. Embedding of the thermocouples into the cone did not permit the cone to be rotated, preventing simultaneous measurement of viscosity and the temperature of the sample. Therefore, the cone was used only to carry out photoinduced temperature measurement without the applied shear stress. The temperature was recorded using a thermocouple card (National Instruments, TBX-68T) and a data acquisition card (NI4351). The output from each thermocouple was recorded simultaneously every 2 s using LabVIEW software.

2.2. Materials

2,3,3-Trimethyl-3H-indole (98%), 3-nitrobenzaldehyde (98+%), 2-bromoethanol (98%) and methacryloyl chloride (98+%) were purchased from Sigma–Aldrich and used without further purification. Absolute ethanol, methanol, DMF, DMSO, triethylamine, acetonitrile, ethyl acetate, hexane, petroleum ether purchased either from Sigma–Aldrich or Fluka were all HPLC grade and used as supplied. 1,4-Dioxane and tetrahydrofuran were distilled from CaH_2 prior to use. 2,2′-Azobisisobutyronitrile (96%, Aldrich) was re-crystallized from ethanol prior to use.

2.3. Synthesis of polyacryloyl chloride

Polyacryloyl chloride was synthesized according to the procedure described elsewhere [16]. A typical experimental procedure for homopolymerisation of acryloyl chloride by free radical polymerization is described as follows: acryloyl chloride (8 ml, 984.0 mmol) was degassed under vacuum by freeze–thaw cycles and distilled in the reaction vessel containing dried 1,4-dioxane (20 ml) and 2,2′-azobisisobutyronitrile (40 mg, 0.2 mmol). The reaction mixture was degassed using three freeze–pump–thaw cycles and was then warmed on a thermostated oil bath at 55 °C for 62 h with continuous stirring. After the reaction had completed the solution was concentrated by a rotary evaporator. The product was precipitated from petroleum ether and dried in a vacuum oven at 60 °C for 18 h, which afforded a colourless product with 75% yield. The basic reaction is shown in Scheme 1.



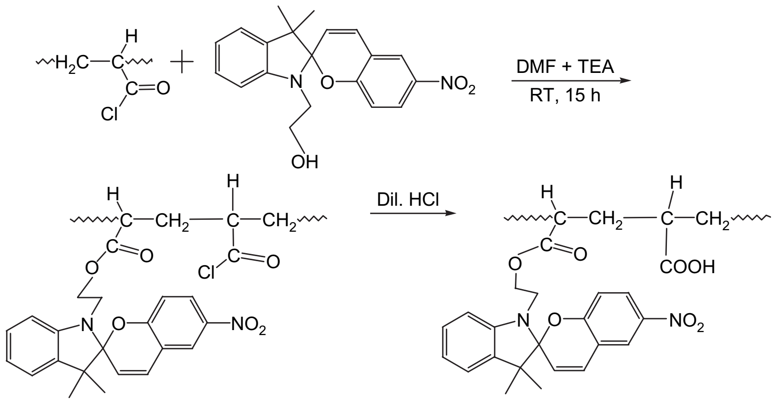
Scheme 1. Synthesis of polyacryloyl chloride.

The product was analysed by IR, GPC and ^1H NMR spectroscopies to afford the following information:

IR (KBr): 2948 (C–H, str), 1782 (C=O, str), 1443 (CH_2, def) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.74 (br d, 2H of CH_2), 3.16 (br t, 1H of CH). GPC (THF): $M_w = 38{,}500\ g\ mol^{-1}$, MWD = 1.52.

2.4. Grafting of spiropyran with polyacryloyl chloride (PAC)

PAC (1 g, 11.0 mmol) was stirred in dry DMF (15 ml) for 30 min under argon atmosphere. In a separate flask 1′-(2-hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-indoline] (0.5 g, 1.3 mmol) was dissolved in DMF (10 ml) and subjected to flash light to bleach the solution. 1′-(2-Hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-indoline] was synthesized using a procedure reported elsewhere [18]. To the solution was added triethylamine (1.5 ml) and the solution was stirred for 20 min. The solution was added to the polyacryloyl chloride solution at ~5 °C with continuous stirring and purging with nitrogen gas. The reaction mixture was stirred for 15 h at room temperature under N_2 protection. Then a suitable amount of water was added into the mixture and stirred for 5 min. The product was precipitated from HCl/water solution (0.01 $mol\ l^{-1}$), collected by filtration, washed several times with water, and dried under vacuum. Hydrochloric acid was used to hydrolyze the unreacted acyl chloride to acrylic acid. The polymer was further purified by dissolving in THF and precipitated from petroleum ether and washed twice with petroleum ether. The final product was dried under vacuum and then in a vacuum oven at 50 °C for 24 h. A pale yellow product was obtained with a yield of 80% and the polymer was assigned by PAA–SP where PAA stands for polyacrylic acid and SP for spiropyran. ^1H NMR (DMSO-d_6): δ 1.15 (br, 6H, 3′, 3′-CH_3), 1.2 (br, 1H of CH from acrylic acid), 2.31 (br, 2H, CH_2 from acrylic acid), 3.62 (br, 2H, N–CH_2), 4.19 (br, 2H, O–CH_2), 6.0 (br, 1H, 3-H), 6.7–7.25 (br, 4H, 5′, 6′, 8′ and 8-H), 8.02 (br, 1H, 7′-H), 8.5 (br, 2H, m, 5,7-H). The coupling reaction of acrylic acid and 1′-(2-hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-indoline] is shown in Scheme 2.



Scheme 2. Synthesis of a linear polyacrylate with spiropyran in the side chain.

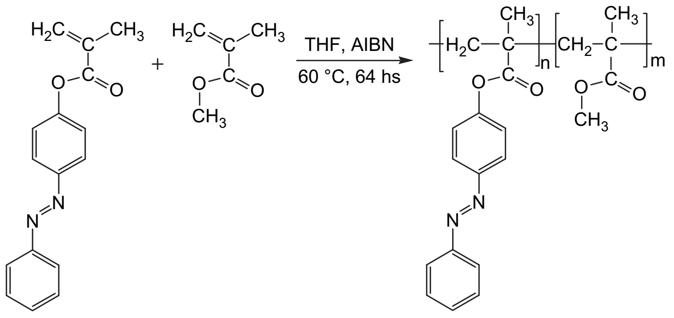
2.5. *Copolymerisation of trans-4-methacryloyloxyazobenzene and methyl methacrylate*

Copolymers of methyl methacrylate and *trans*-4-methacryloyloxyazobenzene were synthesized in tetrahydrofuran using a free radical polymerization route initiated with 2,2′-azobisisobutyronitrile as illustrated in Scheme 3. The detailed synthetic methodology and the reaction schemes have been reported elsewhere [1,17]. All the copolymers have been assigned by M_xC_y, where M denotes the molecular mass and the subscript stands for the weight-average molecular mass and C denotes the chromophore and the subscript stands for the contents in mol%. The molecular weights and molecular weight distribution data were reported elsewhere [1].

3. Results and discussion

3.1. *Synthesis*

The synthetic route of polyacryloyl chloride is shown in Scheme 1. Acryloyl chloride was polymerized in dried 1,4-dioxane. Precautions were taken during the reaction to avoid contact of air and moisture; components that hydrolyze the acid chloride to the corresponding acid. Polymers of polyacrylic acid having spiropyran pendant groups were synthesized by copolymerising methacrylic acid with 1,3,3-trimethylindolino-6′-nitro-8′-[(methacroyloxy)methyl]-spirobenzopyran [6]. In this approach 1′-(2-hydroxyethyl)-3′,3′-dimethyl-6-nitro-spiro[2H-1-benzopyran-2,2′-indoline] was directly attached with polyacryloyl chloride at room temperature as illustrated in Scheme 2. The pure polymer was collected by repeating the dissolution and precipitation of the crude products. The chromophore content was ensured to be 15 mol% by proton NMR spectroscopy. When dissolved in DMSO, polyacrylic acid with spiropyran chromophores in the side chain formed a weak gel. It was reported that polyacrylic acid is a well known polyelectrolyte and one of the characteristic behaviours is that it shows conformational changes in solution [4]. The formation of a weak gel in DMSO was presumably because of the partial folding nature of the hydrophobic backbone at lower degree of dissociation in DMSO and due to inter- or intramolecular aggregation of polymer chains.



Scheme 3. Synthesis of a copolymer of azobenzene and methyl methacrylate.

3.2. *UV–vis spectroscopy of polyelectrolyte*

Polyacrylic acid with spiropyran in the side chain shows reversible photochromism. A solution of polyelectrolyte in DMSO was pale yellow in colour. Upon UV irradiation the solution became purple. Fig. 3 shows the absorption spectra recorded in real time before UV, during UV and visible irradiation. In the dark spectra two absorption peaks at 272 and 351 nm were observed and were assigned to be due to π–π* electronic excitation of the indoline and benzopyran parts of the molecules, respectively, but no detectable

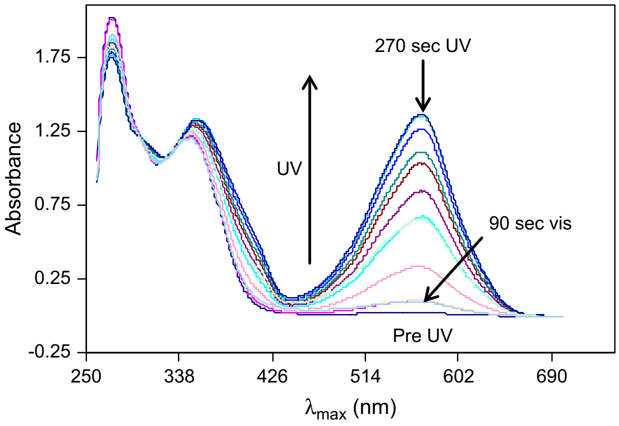


Fig. 3. UV–vis spectra of acrylic acid polyelectrolyte with spiropyran in the side chain. The concentration of the DMSO solution was $1.296 \times 10^{-7}\ g\,l^{-1}$.

absorption peak was observed in the visible region. Upon irradiation with UV light a new absorption peak appeared at 568 nm and the magnitude of the peak intensity increased with irradiation time until a photostationary state was reached within about 4.5 min.

The newly formed absorption peak at 568 nm corresponds to the π–π* electronic excitation of the conjugated merocyanine form of the spiropyran part. Upon irradiation with visible light for 1.5 min the coloured merocyanine reverted to the closed spiropyran structure as was shown by the disappearance of the absorption peak at 568 nm.

3.3. Photoviscosity and photoinduced temperature measurements

The photoregulation of spiropyran when attached to polymer chains produces a change in viscosity; depending on the chain expansion or contraction, the viscosity will increase or decrease. Fig. 4 shows the viscosity changes of polyacrylic acid with spiropyran in the side chain at 25 °C in DMSO. Polyacrylic acid is a well known polyelectrolyte and in solution conformational changes occur as a function of the degree of ionization. At lower degrees of dissociation of carboxylic acid groups the chains remain folded due to hydrophobic backbone and the spiropyran groups. Therefore, in the dark the specific viscosity remains unchanged with time (Fig. 4). Upon irradiation with UV light ($\lambda = 365 \pm 5$ nm) the viscosity showed an uncompensated increase of about 12%. The possibility of this rise being due to the heating effect is readily excluded as the observed effect is the reverse of that expected i.e. a viscosity drops with increasing temperature. This increase in viscosity was thus attributed to be due to molecular interaction. Spiropyrans under ultraviolet irradiation undergo ring-opening reaction resulting in the formation of zwitterionic merocyanine which decreases the hydrophobic interaction and induces a degree of dissociation leading to a more extended random coiled conformation of the polymer chains with the associated increase in the hydrodynamic volume and thus viscosity. Although Irie et al. [4] reported that changes in photoviscosity are caused by intramolecular interaction, the formation of zwitterionic merocyanine may have caused some intermolecular association. Upon irradiation by visible light, the specific viscosity decreased significantly and was attributed to be the combined effect of temperature and chain folding due to the formation of ring closed spiropyran. Upon cutting off the visible irradiation the viscosity increased slowly and stabilized. This recovery was attributed to be due to the stabilization of the solution temperature. It was found that although the measurement was conducted in a temperature controlled system (±0.1 °C) irradiation with visible light caused a temperature rise of ~4 °C.

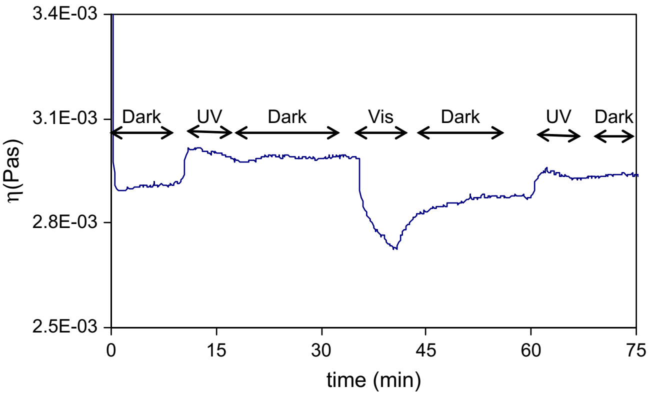


Fig. 4. Reversible specific viscosity changes of polyacrylic acid polyelectrolyte with spiropyran in the side chain.

The second irradiation with UV light again showed an increase of specific viscosity by almost the same order of magnitude (10.5 ± 0.5)%. After irradiation with visible light, the viscosity did not reach the initial value. One possible explanation is that the polymer chains could not rebuild their structures and form gel in DMSO within a smaller time difference (~15 min) between UV and visible irradiation. The photoviscosity effects of spiropyran-based polyelectrolyte are completely opposite to the copolymers of azobenzene with methyl methacrylate [1]. While the specific viscosity of the spiropyran-based polyelectrolyte shows an increase upon UV irradiation the azobenzene-based polymers showed a decrease in the specific viscosity under the same experimental condition [1]. This opposite effect is caused by two very different mechanisms in the two different polymeric systems. Upon ultraviolet irradiation azobenzene undergoes *trans* to *cis* isomerization increasing the dipole moment from 0.5 D to 3.1 D [19] and changing its shape and size. This photoinduced changes in the shape and dipole moment of the azobenzene chromophore exert a dipole–dipole intramolecular interaction causing shrinkage to the polymer chain and thus the solution viscosity decreases.

Using the modified rheometer cone described above, the photoinduced temperature rise was determined for a variety of loading conditions and for a range of spiropyran and azobenzene sample solutions.

A summary of the results from the in situ temperature measurement experiment using the modified rheometer cone with the integrated thermocouples is presented in Table 1. The photoinduced temperature rise was initially measured without any fluid between the modified cone and the quartz plate. Subsequent to this, the temperature rise was measured with distilled water between the cone and plate before the solvent and sample solutions were measured.

Table 1
Summary of photoinduced temperature rises

Chromophore type	Sample, loading condition	ΔT (°C)
No chromophores	No sample	0.56
	Distilled water	0.41
	DMSO	0.42
Polyacrylic acid with spiropyran	2.5 mg/ml	0.47
	5 mg/ml	0.55
	10 mg/ml	0.66
Azobenzene containing copolymer	$M_{39.9}C_{17}$, 20 mg/ml	0.60
	$M_{39.9}C_{17}$, 10 mg/ml	0.44
	$M_{39.9}C_{17}$, 5 mg/ml	0.43
	$M_{19.6}C_{42}$, 5 mg/ml	0.51

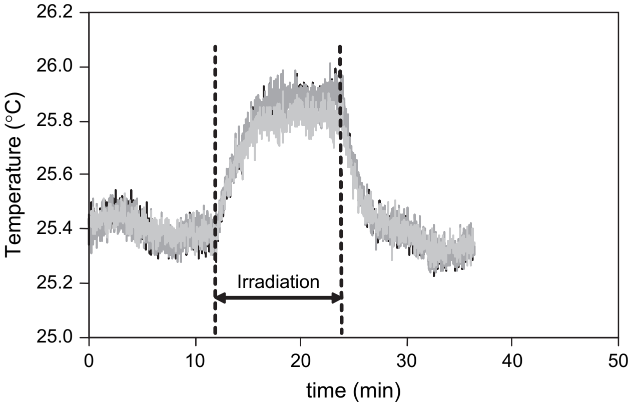


Fig. 5. Temperature response to irradiation measured at each radius with a 5 mg/ml solution of $M_{19.6}C_{42}$.

Fig. 5 shows a typical temperature response observed when a polymer solution was irradiated in the rheometer. The temperature rise due to irradiation was determined by averaging the response of each thermocouple over a period of 5 min before, during and after irradiation.

Due to the geometry of the sample and the intensity distribution of the light source, the temperature rises measured in each of the experiments were dependent on the radial position on the modified cone; the greatest temperature rise was observed towards the center of the cone, as illustrated in Fig. 6. Since the outer 4 mm of the cone contains half of the sample volume and generates half of the torque on the cone, the temperature of the sample reported by the pair of thermocouples located at a radius of 16 mm was assumed to be the average for the solution.

The polyelectrolyte solution in the rheometer showed temperature rises of 0.47, 0.55 and 0.66 °C at solution concentrations of 0.25%, 0.5% and 1% (w/v), respectively. Fig. 7 shows a plot of temperature rise caused by the UV irradiation against the solution concentration. Upon UV irradiation the solution temperature rose linearly with increasing solution concentration. This can be interpreted in terms of the chromophore contents in the solution. As the total number of spiropyran chromophores increases with the increase in solution concentration, more photons are absorbed by the system, and therefore show a higher temperature rise. Other possible effect, such as heating of the thermocouple has not been completely eliminated. When no sample was present, the photoinduced temperature rise in the rheometer was 0.56 °C. This photoinduced temperature rise decreased to 0.41 °C when the test was repeated with distilled water between the cone and plate. Water was chosen as a medium because it has no significant absorption in the wavelength range of the UV light source. The fact that a temperature rise was measured in the stainless steel cone without any sample between the cone and plate indicates that the photoinduced heating of the solutions was not solely due to the absorption of irradiation by the sample.

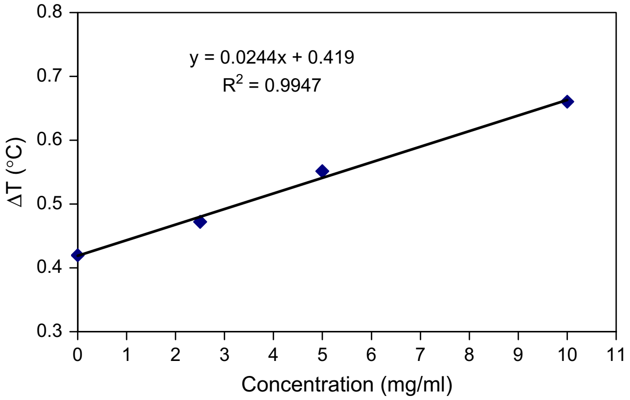


Fig. 7. Observed temperature rise in the polyacrylic acid with spiropyran in the side chain as a function of solution concentration.

The magnitude of the temperature rises was investigated as a function of the concentration of the polymer solutions and azobenzene loading in the polymer chains and compared with the results of spiropyran-based polymer. Fig. 8 shows a plot of photoinduced temperature rise against concentration of azobenzene-based polymer solutions. The results show that the magnitude of the photoinduced temperature rise increases linearly with increasing concentration of the azobenzene-based polymer solution. Maximum increase in temperature was observed in the most concentrated solution (20 mg/ml)

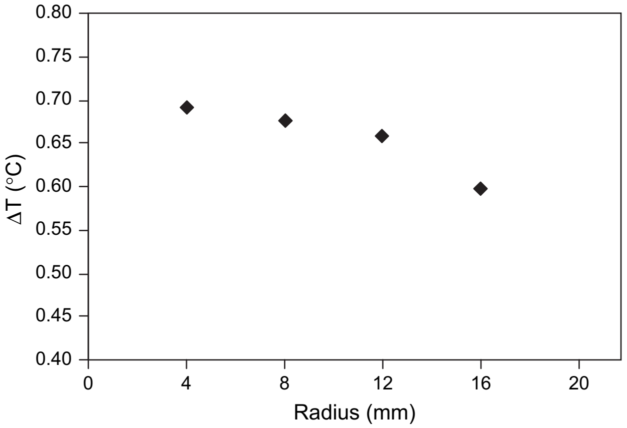


Fig. 6. Radial temperature profile across rheometer cone with a 20 mg/ml solution of $M_{39.9}C_{17}$.

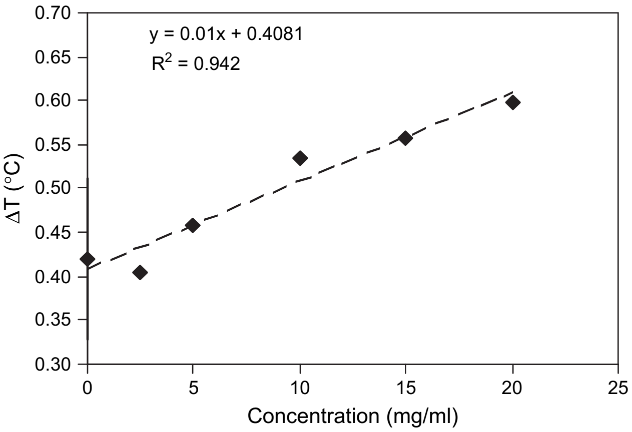


Fig. 8. Temperature rise observed in solutions of $M_{39.9}C_{17}$ as a function of concentration.

implying the fact that temperature rise is dictated by the number of chromophores in solutions. The results suggest that the photoinduced temperature rise is related to the solution concentration and thus the number of chromophores in the solution. The slope obtained from Fig. 7 was 0.0224 while the corresponding value from Fig. 8 is 0.01. This finding suggests that the temperature rise during photoviscosity measurement is not only dependent on the concentration of the chromophores but also on the type of chromophores used in the polymers.

Further experiments were conducted on a range of similar polymers with different percentages of chromophore loadings to justify the above finding. The photoinduced temperature rises are plotted against mol% of chromophore in Fig. 9. The results show that the magnitude of the photoinduced temperature rise is also related linearly to the chromophore loading. This further substantiates the findings that the higher the number of chromophores in a polymer solution greater is the rise in temperature upon irradiation.

The linear relationship observed with concentration and azobenzene loading persists when the results are plotted against azobenzene group content, as does the non-zero intercept of the trend. The observed linear relationship suggests that the photoinduced temperature rise was caused by a combination of the temperature rise of the cone, and the amount of azobenzene groups present and hence the absorption of the solution. The contribution of the absorption of the cone to the photoinduced temperature rise would be expected to decrease with increasing absorption of the solution, as the intensity of the irradiation reaching the cone would be expected to decrease. For the range of concentrations and azobenzene loadings studied here, this effect was not considered to be significant.

In order to determine how significant the photoinduced temperature rises were in terms of viscosity and to attempt to compensate for them, the viscosity behaviour of the polymers was investigated as a function of temperature. A range of sample solutions and DMSO were heated using the water bath in the rheometer and the resulting changes to the solution viscosity were measured. The solvent and sample solutions were subjected to a temperature ramp in the rheometer from 22 to 28 °C at a rate of 0.05 °C/min. After allowing the solution for 25 min, to reach steady shear flow, the rate of change was determined from the slope of the viscosity trace with temperature. The effect of heating on the viscosity of DMSO is shown in Fig. 10.

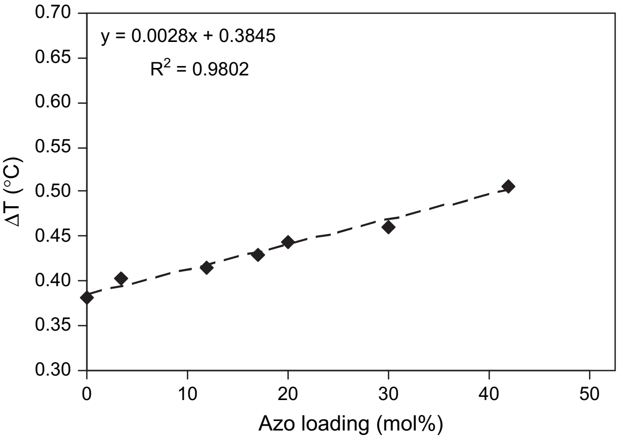


Fig. 9. Temperature rise as a function of azobenzene loading, measured 16 mm from center of the cone. Polymers used in this investigation were $PMMA_{39.6}$, $M_{44.1}C_{3.5}$, $M_{26}C_{12}$, $M_{39.9}C_{17}$, $M_{33.5}C_{20}$, $M_{24.3}C_{30}$, $M_{19.6}C_{42}$. The molecular weight and polydispersity data were reported elsewhere [1].

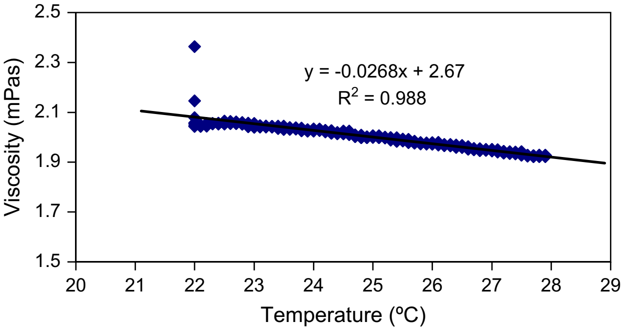


Fig. 10. Effect of deliberate heating on the viscosity of DMSO.

The apparent initial rise in viscosity between 22 and 23 °C was attributed to the sample cooling from room temperature (23 °C) and reaching thermal equilibrium with the quartz plate. To account for this and to allow the sample to reach steady shear flow, the viscosity of the sample below 23 °C was not considered in the calculation of the linear approximation. Over the temperature range studied, the relationship between the sample viscosity and the temperature was considered to be approximately linear. A thermal gradient is expected within the sample due to the low thermal conductivity of the quartz plate. However, the gradient is not expected to be significant at the chosen heating rate. The effect of the thermal gradient would also be diminished by the sample geometry which is such that half of the torque on the cone is generated in the outer 4 mm of the cones radius. The most likely result of any thermal gradient in the sample would be a shift in the temperature axis of the viscosity profile. Under steady heat flow and shear flow conditions, the temperature gradient would not be expected to alter the slope of the temperature–viscosity profile. As the slope of the profile is the only aspect of interest, any temperature gradient in the sample was considered to be insignificant. The slopes of the temperature–viscosity profiles ($d\eta/dT$) for the sample solutions are summarized in Table 2.

Having measured the photoinduced heating of the azobenzene- and spiropyran-based polymer solutions and knowing the temperature dependence of the solvent and its effect on viscosity, it was possible to decouple the photoinduced heating effect and the photoviscosity effect. By calculating the specific

Table 2
Summary of viscosity changes due to temperature

Sample, solution	$d\eta/dT$ (mPa s/°C)
DMSO	−0.0268
$M_{39.9}C_{17}$, 20 mg/ml	−0.0506
$M_{39.9}C_{17}$, 10 mg/ml	−0.0331
$M_{39.9}C_{17}$, 5 mg/ml	−0.0295
$M_{19.6}C_{42}$, 5 mg/ml	−0.0283

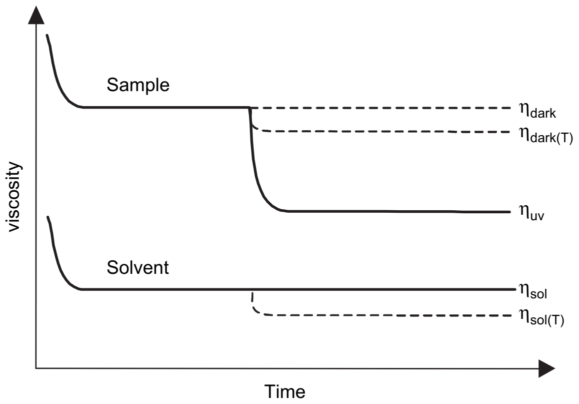


Fig. 11. Idealized viscosity trace of solvent and sample solution.

viscosity of the sample and the solvent at the photoinduced temperature and hence determining the specific viscosity changes at a constant temperature (photoinduced temperature) photoinduced heating effects were decoupled from the photoviscosity effects.

Fig. 11 shows an idealized viscosity trace for a photoresponsive sample solution and the associated solvent, where η_{sol} and η_{dark} represent the viscosities of the unirradiated solvent and solution, respectively, whilst η_{UV} represents the viscosity of the solution during UV irradiation. The viscosity of the solvent and the unirradiated solution after correction for photoinduced heating (i.e. the viscosity at the raised temperature) is represented by $\eta_{\mathrm{sol}(T)}$ and $\eta_{\mathrm{dark}(T)}$, respectively.

The corrected values of the specific viscosity before and during UV irradiation can be found from Eqs. (1) and (2), respectively:

$$\eta_{\mathrm{sp(before)}} = \left(\frac{\eta_{\mathrm{dark}(T)}}{\eta_{\mathrm{sol}(T)}} - 1\right) \tag{1}$$

$$\eta_{\mathrm{sp(during)}} = \left(\frac{\eta_{\mathrm{UV}}}{\eta_{\mathrm{sol}(T)}} - 1\right) \tag{2}$$

and the specific viscosity change can be calculated using Eq. (3) as follows:

$$\frac{\eta_{\mathrm{sp(during)}} - \eta_{\mathrm{sp(before)}}}{\eta_{\mathrm{sp(before)}}} = \frac{\eta_{\mathrm{UV}} - \eta_{\mathrm{dark}(T)}}{\eta_{\mathrm{dark}(T)} - \eta_{\mathrm{sol}(T)}} \tag{3}$$

A summary of the sample viscosity data, photoinduced temperature rise and the results of the temperature compensation calculations is shown in Table 3.

It can be seen from Table 3 that the temperature compensation decreases the apparent change in specific viscosity for each of the samples. The magnitude of the compensation is related to the magnitude of the photoinduced heating effect. The significance of the photoinduced heating effect compared to the photoviscosity effect is related to the magnitude of the photoviscosity effect. For solutions with a large photoviscosity effect such as 5 mg/ml to $M_{39.9}C_{17}$, the photoinduced heating accounts for as little as 2.5% of the observed specific viscosity change. Whereas for a solution (5%) of 4-hydroxyazobenzene that exhibited no photoviscosity effects, the photoinduced heating was accounted for all of the specific viscosity changes.

Coincidently, the temperature compensated specific viscosity change determined from the viscosity before and during UV irradiation corresponds well with calculations of the specific viscosity change determined using the viscosity before irradiation and the viscosity of the solution in the dark after irradiation. This was to be expected for azobenzene-based polymer systems, as the rate of *cis* to *trans* isomerization in the dark is sufficiently slow [20] that the recovery from *cis* to *trans* form after 15 min in the dark can be considered insignificant, whilst the solution would have sufficient time to recover from any photoinduced heating.

It is anticipated that the temperature compensation method detailed here will be useful in determining the photoviscosity effect in photoresponsive systems which recover rapidly after irradiation, such as those based on spiropyran chromophores or systems which are exposed to alternating irradiation at different wavelengths.

4. Conclusions

Polyelectrolyte of polyacrylic acid with spiropyran in the side chain has been synthesized successfully by reacting 1′-(2-hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-indoline] with polyacryloyl chloride. The photostimulated conformational changes and its associated photoviscosity effects were investigated and it was found that a rise of 12% specific viscosity upon UV irradiation occurred; after the addition of the specific viscosity depression by the photothermal effect the rise in specific viscosity was shown to be ~14%. Upon UV irradiation the optical spectra showed an additional absorption peak at 568 nm, which corresponded to a coloured merocyanine form of the spiropyran moiety. This peak at 568 nm disappeared upon irradiation with visible light and was due the reformation of closed spiropyran rings. The photoinduced ring-opening reaction of spiropyran-based polymer

Table 3
Summary of photoviscosity results

Sample, conc.	η_{dark} (mPa s)	η_{UV} (mPa s)	ΔT (°C)	η_{sol} (mPa s)	$d\eta/dT$ (mPa s/°C)	$\eta_{\mathrm{dark}(T)}$ (mPa s)	$\eta_{\mathrm{sol}(T)}$ (mPa s)	$\Delta\eta_{\mathrm{sp}}$ (%)	$\Delta\eta_{\mathrm{sp}(T)}$ (%)
PAA−SP, 5 mg/ml	2.903	3.005	0.55	2.021	−0.028	2.891	2.007	12	13.7
$M_{19.6}C_{42}$, 5 mg/ml	2.297	2.054	0.51	1.985	−0.028	2.283	1.971	−77.9	−73.4
$M_{39.9}C_{17}$, 5 mg/ml	2.589	2.102	0.43	2.002	−0.030	2.576	1.990	−83.0	−80.9
$M_{39.9}C_{17}$, 10 mg/ml	2.566	2.432	0.44	2.198	−0.033	2.551	2.186	−36.4	−32.6
$M_{39.9}C_{17}$, 20 mg/ml	2.884	2.693	0.60	2.198	−0.051	2.853	2.182	−27.8	−23.8

is associated with a specific viscosity increase, whereas photoinduced *trans* to *cis* isomerization of the azobenzene-based polymers showed reduction of the specific viscosity. Two different polymeric systems showed opposite photoviscosity effects due their different photoisomerisation products and conformational changes in different mechanisms. Ring opening of spiropyrans results in a decrease of the hydrophobic interaction and induces a degree of dissociation leading to a more extended random coiled conformation to the polymer chains, with the associated increase in the hydrodynamic volume and thus specific viscosity. Whereas, the photoinduced changes in the shape and dipole moment of the azobenzene chromophore exert a dipole–dipole intramolecular interaction causing shrinkage of the polymer chain and thus decrease the specific viscosity of the solution.

Photoinduced temperature changes in the polymer solutions were measured in situ by using a modified rheometer cone. The measurement of the photoinduced temperature rises revealed the presence of a photoinduced heating effect which was primarily due to the absorption of irradiation by the sample solution. This effect was found to be linearly dependent on the presence of chromophores in the solution. Photoinduced heating accounted for as little as 2.5% of the specific viscosity change in the photoresponsive solutions, but accounted for a much larger portion of the specific viscosity change dependent on the photoresponsiveness of the system such that it was responsible for all of the effect observed in non-photoresponsive systems.

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