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Azobenzene modified poly(aryl ether ketone amide)s. 2. Photo- and thermo-responsive behaviour in dilute solution[‡]

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A number of azobenzene modified poly(aryl ether ketone amide)s with differing backbone geometries were evaluated for their photo- and thermo-regulated behaviour in dilute solution. Photoinduced *trans* → *cis* isomerization reactions were carried out by irradiating the polymer samples with ultraviolet light at wavelengths between 370 and 400 nm. Photostationary state compositions achieved under these conditions typically consisted of about 70% of the higher energy *cis* isomer distributed along the polymer main chain. Reverse *cis* → *trans* isomerization of the backbone azobenzene moieties was triggered by either photochemical or thermal means and was monitored by optical absorbance and ^{1}H n.m.r. spectroscopies. Thermally induced *cis* → *trans* return in each of the polymers obeyed the first-order rate law. Activation energies calculated for the 'dark' isomerization reaction fell near 21 kcal mol^{-1} for each of the polymer samples evaluated. These values were not dependent on the overall structure or molecular weight of the polymer backbone and were nearly identical to those determined for several lower molecular weight model compounds. Calculated half-lives for the isomerization of *cis*-azobenzene linkages buried in the polymer backbone ranged from 1 day near room temperature to about 1 h at the 60°C isotherm. Data gleaned from SEC experiments suggested that polymers endowed with conformationally restricted geometries underwent a two-fold reduction in hydrodynamic radius in response to ultraviolet light exposure. Photo-contractions in more flexible polymer samples appeared to be less dramatic, consistent with molecular modelling and dilute solution viscosity measurements. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: stimuli-responsive polymers; *trans–cis* isomerization; photoinduced volume contraction)

INTRODUCTION

The *trans–cis* isomerization of azobenzene and its related congeners has been widely studied over the past 40 years[1–4]. Interconversion between *trans* and higher energy *cis* isomeric states can be effected both photochemically (*trans* ↔ *cis*) and thermally (*cis* → *trans*) with a high degree of efficiency and an absence of competing side reactions[5,6]. That one configurational isomer is furnished photochemically while the other is favoured thermally makes it possible to effectively drive or 'switch' azobenzene modified species into a desired geometry and polarity. Polymers containing azobenzene moieties often display remarkable photo- and thermo-regulated behaviour when subjected to changes in incident light or heat[6–8]. Materials of this kind are of considerable theoretical and experimental interest and are well suited for a variety of 'smart' applications.

Central to our efforts to develop high performance polymers with stimuli-responsive molecular architectures has been the preparation of a new series of poly(aryl ether ketone amide)s containing main-chain azobenzene linkages (*Scheme 1*). As detailed in the previous report[9], these amorphous polymers are characterized by moderately high glass transition temperatures and are thermally stable in air and nitrogen up to 400°C. In contrast to many azobenzene modified polyaramides, our materials possess enhanced levels of solubility and tractability owing to the presence of conformationally restricted aryl ether ketone segments in their polymer backbones. The aryl ketone groups incorporated into these polymers also provide additional sites through which photochemical reactions can be triggered in conjunction with the isomerization process.

In the present study, the photo- and thermo-responsive behaviour of these materials was examined in dilute solution using a variety of analytical techniques. Reversible *trans–cis* isomerization reactions within the polymers were followed by optical absorbance spectroscopy. For each polymer, kinetic parameters associated with the thermally induced *cis* → *trans* isomerization process were determined and compared to those for several lower molecular weight analogues. Additional insight into the nature of the isomerization reaction and its longer range impact on the global dimensions of the azobenzene modified poly(aryl ether ketone amide)s was provided by ^{1}H n.m.r. spectroscopy and size exclusion chromatography.

EXPERIMENTAL

Materials

Anhydrous *N,N*-dimethylacetamide (DMAC) (Aldrich) was stored under Ar over 4A molecular sieves. 4-Aminobenzophenone (97%, Pfaltz and Bauer) and 3-phenoxyaniline (98%, Aldrich) were dried *in vacuo* at 60°C for 48 h. All other reagents and solvents (> 98%) were

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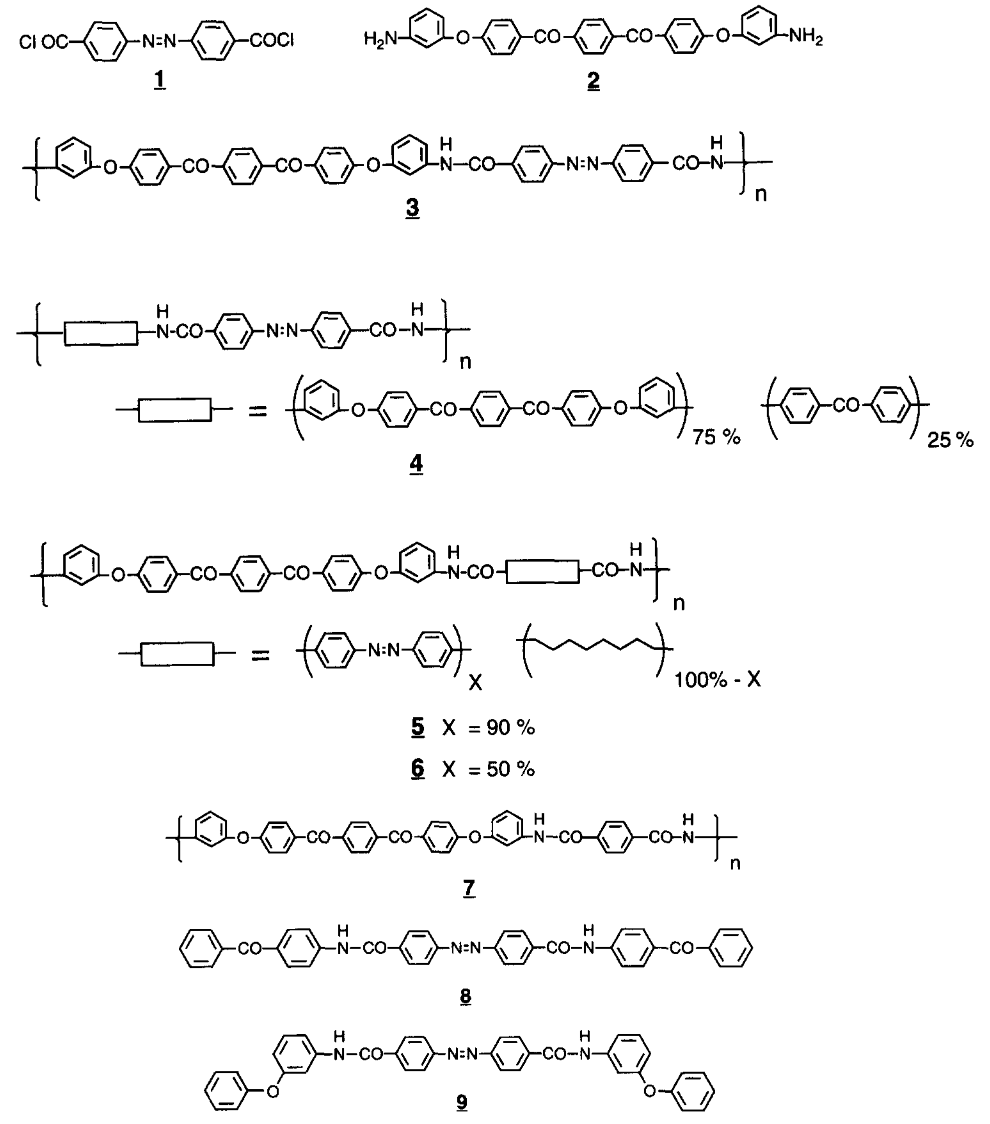

Scheme 1

supplied by Aldrich and were used without further purification. *trans*-Azobenzene-4,4′-dicarbonyl chloride (1) and polymers 3–7 were prepared according to methods described previously[9].

Model compound syntheses

Bis-amide from 1 and 4-aminobenzophenone (8). To a magnetically stirred solution of 4-aminobenzophenone (1.00 g, 5.07 mmol) in DMAC (50 ml) was added a solution of 1 (0.74 g, 2.41 mmol) in DMAC (30 ml) over a 30 min period. The reaction mixture was stirred at 40°C under Ar for an additional hour and then concentrated to half of its original volume with a nitrogen stream. The resulting cherry red solution was cooled to 5°C, eventually affording an orange crystalline solid. Further concentration of the mother liquor provided additional solid. The solids were combined and then recrystallized from hot methanol/ DMAC (90:10 v:v), furnishing 1.12 g (74%) of 8 as a bright orange crystalline solid: m.p.: > 320°C (decomp.); ^{1}H n.m.r. (TFD, 300 MHz) δ 11.55 (s, 2H), 8.16–8.24 (m, 8H), 8.06–7.84 (m, 12H), 7.73–7.82 (m, 2H), 7.56–7.66 (m, 4H); MS (fab): *m/e* 629.15 (MH$^+$). Anal. calcd. for $C_{40}H_{28}N_4O_4$3/4H_2O: C, 74.81; H, 4.63; N, 8.72. Found: C, 74.80; H, 4.57; N, 8.88.

Bis-amide from 1 and 3-phenoxyaniline (9). To a magnetically stirred solution of 3-phenoxyaniline (1.00 g, 5.40 mmol) in DMAC (30 ml) was added a solution of 1 (0.82 g, 2.67 mmol) in DMAC (30 ml) over a 30 min period. The reaction mixture was stirred at 40°C for an additional hour and then concentrated *in vacuo* to give a crude orange solid. The solid was recrystallized from hot methanol/DMAC (90:10 v:v), furnishing 1.40 g (87%) of 9 as an orange crystalline solid: m.p.: 259–262°C; ^{1}H n.m.r. (DMSO-d$_6$, 300 MHz) δ 10.59 (s, 2H), 8.10–8.20 (d, 4H), 8.00–8.10 (d, 4H), 7.50–7.65 (m, 4H), 7.35–7.47 (m, 6H), 7.02–7.10 (m, 6H), 6.75–6.81 (m, 2H); MS (fab): *m/e* 605.16 (MH$^+$). Anal. calcd. for $C_{38}H_{28}N_4O_4$1/4H_2O: C, 74.92; H, 4.72; N, 9.20. Found C, 74.85; H, 4.81; N, 9.28.

Analytical methods

Melting points were determined in open capillary tubes with a Laboratory Devices (Holliston, MA) Mel-Temp unit and are uncorrected. A heating rate of 2°C/min was consistently employed. Routine proton nuclear magnetic resonance (^{1}H n.m.r.) spectra were obtained at 300 MHz on a General Electric QET spectrometer. Tetramethylsilane was used as a standard. High temperature ^{1}H n.m.r. measurements were acquired with a General Electric Omega

300 MHz spectrometer. UV–visible (UV–Vis) absorbance spectra were obtained with a Perkin-Elmer Lambda 2 UV–Vis spectrophotometer interfaced to a Digital 316sx DECstation or with a Hewlett Packard 8451A Diode Array UV–Vis spectrophotometer. Fast-atom bombardment mass spectra (MS fab) were furnished by a VG ZAB-E double-focusing mass spectrometer equipped with a xenon-ionization gun. Elemental analyses were provided by Galbraith Laboratories (Knoxville, TN).

Size exclusion chromatography (SEC), utilized to probe the hydrodynamic volumes of polymers before and immediately following irradiation experiments, was performed with a Hewlett Packard Model 1050 autosampler and pump connected to two 300 mm × 7.5 mm columns packed with PLGel mixed-bed 5 μm particle size cross-linked polystyrene (Polymer Laboratories, Amherst MA). A Waters Model 410 differential refractometer and a Hewlett Packard Model 1050 UV spectrophotometer were employed as detectors. Chromatography columns were maintained at 40°C using a DuPont Instruments column oven. The columns were calibrated with narrow MWD polystyrene standards (Polymer Laboratories) and molecular weight distributions were calculated relative to polystyrene using a TriSEC SEC software package (Viscotek Corp., Houston TX). In all cases, spectrophotometric grade DMAC (Aldrich) with 0.1% LiCl served as a mobile phase. Polymer samples were dissolved in the mobile phase at a concentration of 0.2%. Injected sample volumes were typically 0.1 ml.

Table 1 Polymer composition, inherent viscosity and molecular weight data

Polymer	Wt% azobenzene	η_{inh} (dl/g)[a]	M_n[b]	M_w/M_n[b]
trans-3	24.5	1.77	80400	2.30
trans-4	27.2	1.85	87100	1.92
trans-5	22.3	1.23	51400	2.06
trans-6	12.9	1.80	69800	2.09
7	0	1.54	83200	1.98

[a] Measured in sulfuric acid at 30°C. Polymer concentration = 0.5 wt% (data from Ref. 9)

[b] Measured by GPC in DMAC at 135°C (data from Ref. 9)

Low intensity UV irradiations were carried out with a Black-Ray Long Wavelength UV Lamp (San Gabriel, CA; model B 100 AP) with a maximum intensity centred near 360 nm. Higher intensity UV irradiations were effected with a 450 W medium-pressure quartz mercury arc (Ace-Hanovia, Vineland, NJ; model 7883-14) equipped with a model 7830-60 power source. The lamp was fitted with an aluminium reflector having a reflectivity of 85%. Lamp-to-sample pathlength was typically 10 cm. When desired, a combination of optical cut-on and band-pass filters (Oriel Corp., Stratford, CT) were employed to furnish radiation within a desired spectral window.

RESULTS AND DISCUSSION

trans-Azobenzene modified poly(aryl ether ketone amide)s 3–6 were prepared by a series of low temperature polycondensation reactions in DMAC as described previously[9]. The reaction of *trans*-azobenzene-4,4′-dicarbonyl chloride (1) with bis-1,4-(3-aminophenoxy-4′-benzoyl) benzene (2) furnished the parent poly(aryl ether ketone amide) 3 with a 25 wt% azobenzene loading along its polymer backbone. The use of terephthaloyl chloride, sebacoyl chloride and 4,4′-diaminobenzophenone as comonomers afforded an opportunity to modify the composition and rigidity of the polymer chain (*Scheme 1*). An additional poly(aryl ether ketone amide) (7) devoid of azobenzene linkages was obtained by treating diamine 2 with terephthaloyl chloride. All of these polymers were high molecular weight materials as evidenced by tandem SEC and inherent viscosity measurements (*Table 1*)[9]. Several lower molecular weight model compounds (8 and 9) mimicking portions of the polymer backbone in 3–6 were also prepared by capping the diacid chloride monomer 1 with two equivalents of either 4-aminobenzophenone or 3-phenoxyaniline.

Trans–cis isomerization as monitored by optical absorbance spectroscopy

Reversible *trans–cis* isomerization reactions in azobenzene modified polymers can be readily probed by optical absorbance spectroscopy. A spectrum for *trans*-3 dissolved in DMAC is provided in *Figure 1*. Absorbance bands

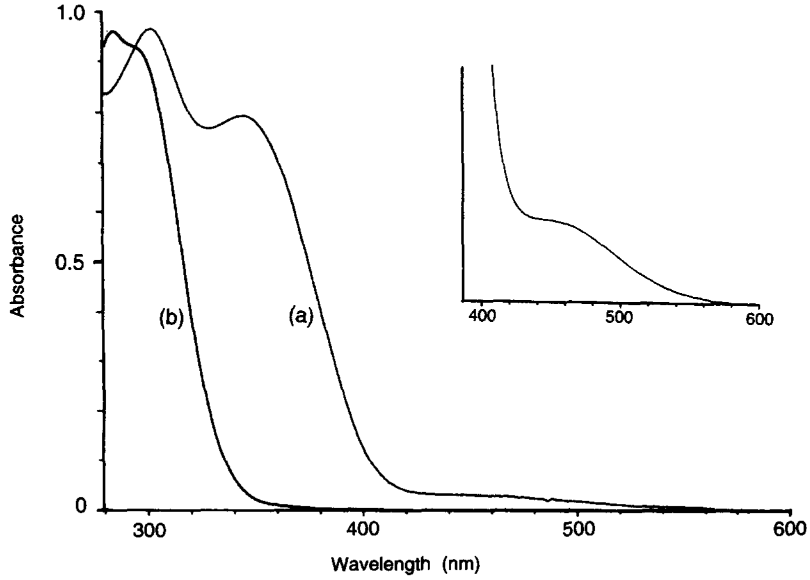

Figure 1 Optical absorbance spectra in DMAC. Spectrum (a): *trans*-3; spectrum (b): 7; inset: enhanced view of n–π^* transition in *trans*-3

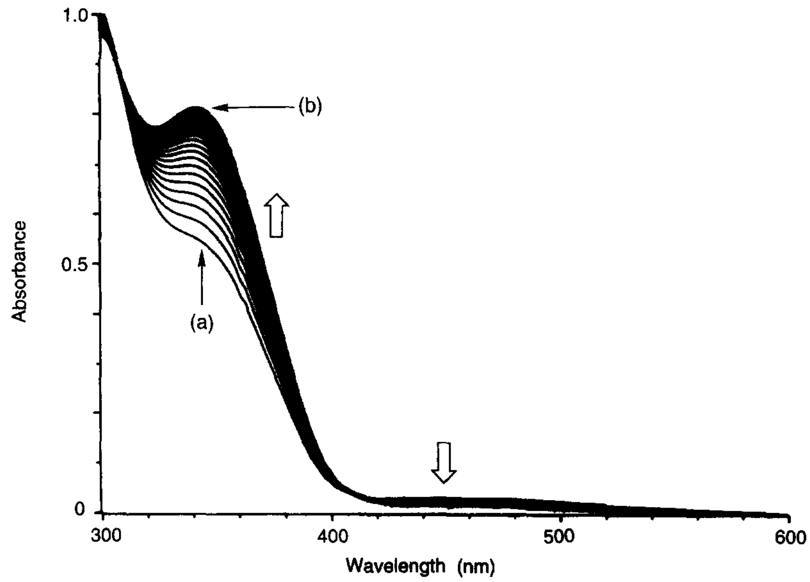

Figure 2 Optical absorbance overlay spectra showing *cis* → *trans* recovery in 3 in DMAC at 70°C. Spectrum (a): 65% *cis*/35% *trans*. Spectrum (b): 100% *trans*. (Scanning frequency: 1 scan/5 min)

for both the $\pi-\pi^*$ and forbidden $n-\pi^*$ transition within the backbone *trans*-azobenzene chromophores are present at 344 and 438 nm, respectively. The aryl ketone linkages in polymer 3 give rise to an additional poorly resolved $n-\pi^*$ band centred near 302 nm. *trans*-Azobenzene modified poly(aryl ether ketone amide)s 4–6 afforded absorbance spectra that were qualitatively similar when evaluated in DMAC. For comparison, an absorbance spectrum for polymer 7 devoid of azobenzene groups is also displayed in *Figure 1*. In this case, only the aryl ketone $n-\pi^*$ band is observed above 300 nm.

That two distinct chromophoric groups are present in these materials has important implications. Irradiation of 3–6 with broad-spectrum, i.e. unfiltered, ultraviolet light will trigger dual photoprocesses centred at both the *trans*-azobenzene and aryl ketone chromophores located in the polymer backbone. Although numerous reports have established that the azobenzene moiety is not prone to undergoing irreversible photochemical transformations in neutral media[5,6,10,11], photoinduced crosslinking reactions have been widely documented in polymers containing main-chain aryl ketone groups[12–14]. Indeed, when exposed to higher energy radiation ($280 < \lambda < 320$ nm), the polymers described here underwent a complex series of photochemical transformations that remain to be fully characterized. Under certain conditions, reduction of the main-chain azobenzene chromophores by ketyl (or other) radical intermediates and a loss of molecular weight along the polymer chain were both observed[15]. Preliminary results have further hinted that the outcome of these photomediated reactions may be dependent on the global conformation or 'compactness' of the polymer coil that is independently regulated by the *trans–cis* isomerization reaction. In an effort to isolate reversible photoprocesses centred exclusively at the azobenzene chromophore and avoid crosslinking or degradation reactions in the polymer backbone, optical filters were employed in the current study to furnish ultraviolet radiation above 370 nm. When illuminated in this manner, the polymer solutions exhibited reversible photochromic behaviour consistent with the *trans–cis* isomerization process as will be demonstrated below. Irreversible perturbations in the higher energy (< 320 nm) portions of their u.v. absorbance spectra, or permanent alterations in the solution viscosities for these materials were not observed.

Photoinduced *trans* → *cis* isomerization of the azobenzene linkages in polymers 3–6 was effected with filtered ($370 < \lambda < 400$ nm) ultraviolet light supplied by a 450 W medium-pressure quartz mercury arc. Irradiation experiments were carried out in DMAC at room temperature for 10 min. Photostationary states achieved under these conditions were largely independent of polymer structure, with approximately 65–70% of the azobenzene residues in 3–6 ultimately occupying the higher energy *cis* configuration. An optical absorbance spectrum for 3, obtained immediately after the irradiation process, is provided in *Figure 2* (spectrum (a)) and can be contrasted to the spectrum shown in *Figure 1* for the non-irradiated sample. The absorbance intensity at 344 nm attributable to the $\pi-\pi^*$ transition for the *trans*-azobenzene linkage is much reduced with the band for the newly formed *cis* chromophore shifted to higher energies (< 300 nm). Also apparent in *Figure 2* are perturbations in the lower energy side of the spectrum. The weak $n-\pi^*$ band for the *cis*-azobenzene chromophore is blue-shifted slightly relative to that for the *trans*-azobenzene link and is also somewhat more intense, consistent with reports for other azobenzene modified species having similar structures[16].

For each of the polymers studied, *cis* → *trans* or 'reverse' isomerization of the azobenzene linkages in the polymer backbone was triggered by either photochemical or thermal means. The irradiation of 3 (in DMAC) having a photostationary state composition of 70% *cis*/30% *trans* with visible light above 420 nm brought about an immediate reduction in *cis*-azobenzene content within the polymer. Under the conditions employed here, the isomerization reaction was nearly complete after 15 min at room temperature. Thermally induced *cis* → *trans* isomerization rates were strongly dependent on temperature as expected. For example, complete reorganization of the polymer backbone in 3 via the thermal or 'dark' isomerization reaction required a period of several weeks when carried out at 0°C but only 10 min at temperatures near 100°C. *Cis* → *trans* isomerization in 3 at 70°C was followed spectroscopically as shown in *Figure 2*. Scans were repeated every 5 min in the dark over a 3 h period following the acquisition

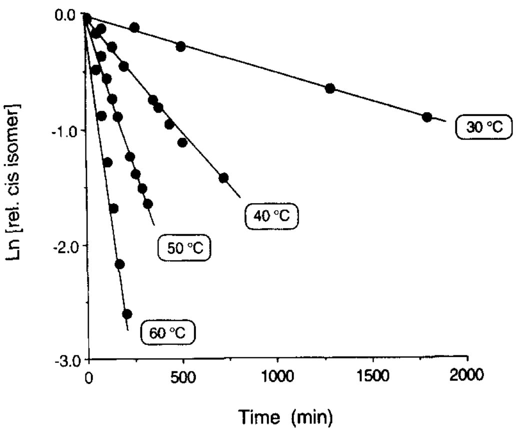

Figure 3 First-order plots for *cis* → *trans* in 3 at four different isotherms as determined by optical absorbance spectroscopy

Table 2 Kinetic data for thermally induced *cis* → *trans* isomerization in 3 as a function of temperature in DMAC[a]

Isotherm (°C)[b]	$k \times 10^3$ (min^{-1})	$\tau_{1/2}$ (h)
30.0	0.410	28.1
40.0	1.69	6.84
50.0	4.01	2.88
60.0	11.0	1.05

[a] Polymer concentration = 4×10^{-5} mol l^{-1}
[b] Values ± 0.1°C

Table 3 Calculated activation parameters for thermally induced *cis* → *trans* isomerization in azobenzene modified polymers and model compounds in DMAC

Species	E_{act}^a (kcal mol^{-1})	$\Delta S\ddagger^b$ (cal deg^{-1} mol^{-1})	$\Delta G\ddagger^b$ (kcal mol^{-1})
3	21.6	− 12.8	24.9
4	19.5	− 19.1	24.7
5	20.8	− 15.2	24.8
6	20.8	− 15.6	24.9
8	20.7	− 15.2	24.7
9	21.0	− 15.5	25.1

[a] Values typically ± 1%
[b] Values for $\Delta S\ddagger$ and $\Delta G\ddagger$ were calculated for 30°C isotherm[17]

of spectrum (a) which corresponds to the photostationary state for this system. Twin isosbestic points at 310 and 409 nm are apparent in *Figure 2* and are consistent with a shifting *cis–trans* isomeric ratio in the polymer backbone. The final spectrum (spectrum (b)) in this series is identical to that provided in *Figure 1* for the non-irradiated sample of trans-3 and serves to establish the overall reversibility of the isomerization process. Similar results were obtained for poly(aryl ether ketone amide)s 4–6.

An analysis of spectroscopic data confirmed that thermal *cis* → *trans* reorganization in 3 followed the first-order rate law. First-order plots for four different isotherms are displayed in *Figure 3*. Rate constants and calculated half-life values for the isomerization process in 3 are given in *Table 2*. As can be noted, these values are strongly temperature sensitive. When carried out at 30°C, thermally induced *cis* → *trans* isomerization of the azobenzene linkages in 3 proceeded slowly, with a calculated *cis* half-life near 28 h. Raising the temperature by 30° resulted in a much more rapid return to the more stable *trans* configuration with the half-life for the isomerization reaction shortened to only 63 min. Based on the rate constant data listed in *Table 2*, an activation energy (E_{act}) of 21.6 kcal mol^{-1} was calculated for this process using the standard Arrhenius equation. Associated values for the free energy ($\Delta G\ddagger$) and entropy ($\Delta S\ddagger$) of activation were determined to be 24.9 kcal mol^{-1} and −12.8 cal deg^{-1} mol^{-1}, respectively[17]. Similar evaluations were carried out for thermally driven *cis* → *trans* return in azobenzene-modified polymers 4–6 and the two model compounds 8 and 9. Relevant data are summarized in *Table 3*.

The results given in *Table 3* merit several comments. In spite of significant differences in the backbone composition and rigidity of polymers 3–6 the 'dark' isomerization reaction within these materials is characterized by remarkably similar E_{act} and $\Delta G\ddagger$ values. This non-variance in the data suggests that the *cis* → *trans* isomerization reaction in the polymer backbone is not significantly influenced by either its immediate environment (flanking sequences) or by its more global environment (polymer random coil). In dilute solution, conformational adjustments within the macromolecule appear to occur with sufficient speed to accommodate the geometrical demands imposed by 'local' *cis* → *trans* isomerization reactions that take place along the main chain. That the low molecular weight model compounds 8 and 9 are characterized by nearly identical E_{act} and $\Delta G\ddagger$ values lends additional support to this notion. Similar findings have been reported for other azobenzene modified polymers and model compounds[18–22]. The nature of the transition state associated with the isomerization process is also worth noting. Activation entropies calculated for these derivatives are all strongly negative as indicated in *Table 3*. Whether following an inversional[23–25] or, less likely, a rotational[26] pathway, thermally driven *cis* → *trans* return in these materials clearly proceeds through a transition state geometry that is more highly organized and less random than that associated with the *cis* form of the molecule. These data are in excellent accord with those communicated for other azobenzene modified derivatives that have been evaluated in dilute solution[27,28].

Trans–cis isomerization as monitored by proton n.m.r. spectroscopy

The geometries, dipole moments[6,29] and basicities[30–32] of azobenzene derivatives all undergo significant changes during the isomerization process. When triggered within a polymer backbone, *trans–cis* isomerization reactions have the potential to perturb the chemical environments of protons which are localized in close proximity to the azobenzene linkage. For cases where these perturbations are of sufficient magnitude, proton n.m.r. spectroscopy can be effectively utilized to independently track the course of the isomerization process.

A ^{1}H n.m.r. spectrum for *trans*-3 dissolved in perdeuterated DMSO (DMSO-d_6) is provided in *Figure 4*. Proton resonances for the aryl ether ketone and azobenzene chain segments in the polymer backbone are evident between 6.8–7.9 and 8.0–8.2 ppm, respectively. The polymer's amide protons flanking the *trans*-azobenzene group give rise to an additional signal further downfield near 10.5 ppm. As can be noted in *Figure 5* (spectrum (a)), irradiation of the polymer solution with filtered ($370 < \lambda < 400$ nm) ultraviolet light resulted in the emergence of a number of new signals in both the aromatic and amide regions of the n.m.r. spectrum. Of particular significance here is the appearance of a new singlet near 10.3 ppm along with a concomitant reduction in signal intensity at 10.5 ppm. When taken together, these changes indicate the presence of a new chemical environment for some of the amide protons

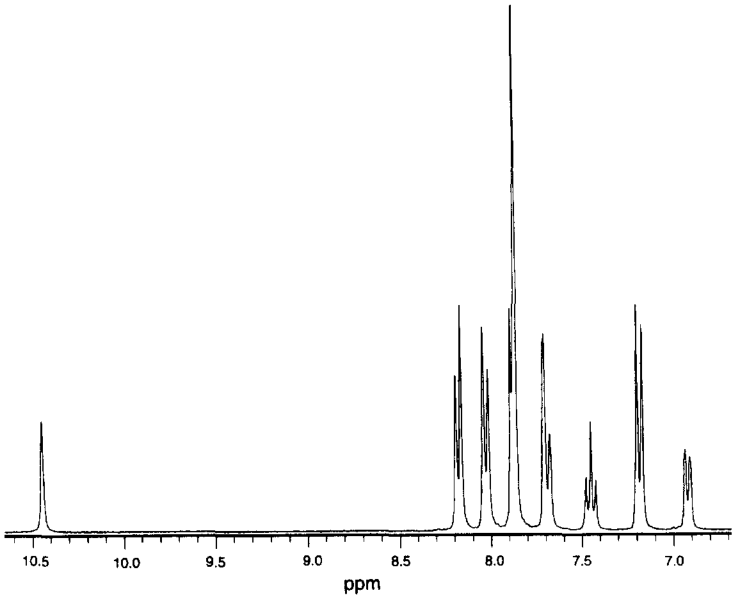

Figure 4 ^{1}H n.m.r. spectrum for *trans*-3 in DMSO-d$_6$

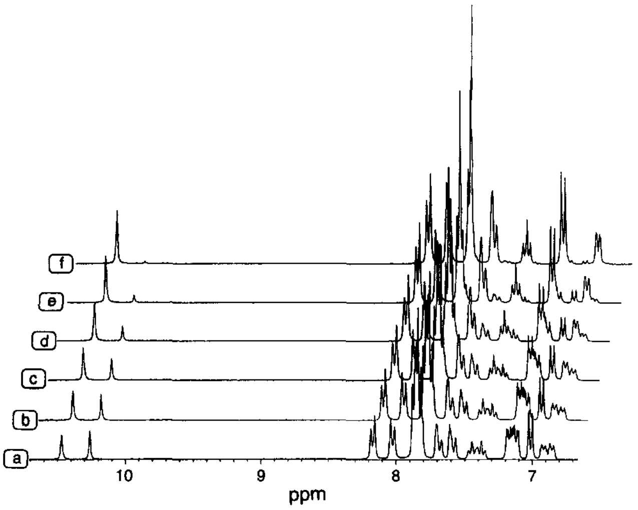

Figure 5 Time resolved ^{1}H n.m.r. spectra showing *cis* → *trans* return in 3 in DMSO-d$_6$ at 55.7°C. Spectrum (a): 65% *cis*/35% *trans*. Spectrum (b): 0.97 h; (c): 2.1 h; (d): 4.4 h; (e): 8.9 h; (f): 17.5 h after irradiation

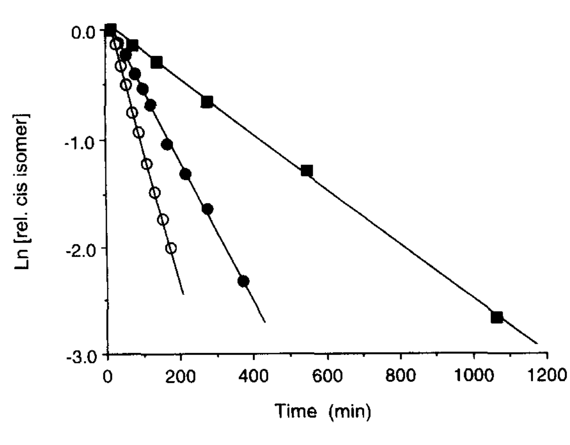

Figure 6 First-order plots for *cis* → *trans* return in 3 as determined by ^{1}H n.m.r. spectroscopy. DMSO-d$_6$ at 55.7°C [■]; DMSO-d$_6$ at 64.6°C [●]; DMF-d$_7$ at 64.6°C [○]

Table 4 Kinetic data for thermally induced *cis* → *trans* isomerization in 3 as determined by ^{1}H n.m.r. spectroscopy

Solvent	Temp (°C)^a	$k \times 10^3$ (min^{-1})	$\tau_{1/2}$ (h)
DMSO-d$_6$	55.7	2.61	4.42
DMSO-d$_6$	64.6	6.56	1.76
DMF-d$_7$	64.6	12.8	0.90

^{a} Values ± 0.2°C

located along the polymer backbone, i.e. protons that are located immediately adjacent to the newly formed *cis*-azobenzene linkages. As expected, these perturbations in the n.m.r. data were fully reversible. Warming the polymer solution to 55.7°C directly in the n.m.r. probe to drive the 'dark' *cis* → *trans* isomerization reaction provided an opportunity to monitor changes within the polymer in real time. A series of spectra acquired at different time intervals for polymer 3 are displayed in *Figure 5* (spectra (b)–(f)). Spectrum (f), obtained after 17.5 h of heating, was nearly identical to that shown in *Figure 4* for the non-irradiated sample of *trans*-3. By integrating appropriate peak areas for the amide protons, the relative amount of *cis* isomer present in the backbone of polymer 3 could be determined for any time following the photoinduced *trans* → *cis* reaction.

An analysis of the n.m.r. data described above again revealed that thermally driven *cis* → *trans* reorganization within the poly(aryl ether ketone amide) backbone obeyed the first-order rate law. A series of first-order plots for isomerization in 3 are shown in *Figure 6* for two different solvents and two separate isotherms. Rate constants and corresponding half-life values extracted from the line slopes of these plots are given in *Table 4*. As can be noted for the DMSO-d$_6$ solvent system, the calculated isomerization rate constants were strongly dependent on temperature as expected. A 9° temperature rise more than doubled the velocity for *cis* → *trans* return in the polymer. Moreover, the rate data were also dependent on the nature of the solvent medium used to conduct the n.m.r. experiment. Perdeuterated dimethylformamide (DMF-d$_7$) afforded a two-fold rate enhancement over that observed for DMSO-d_6 at the 64.6°C isotherm. That the thermally driven *cis* → *trans* isomerization reaction is solvent dependent has been demonstrated before for a series of lower molecular weight azobenzene derivatives[25,27]. It is also interesting to compare the rate constant data obtained here for polymer 3 with that gleaned from optical absorbance spectroscopy reported in *Table 2*. Although a direct comparison is not possible, results for the DMF-d_7 (64.6°C) and DMAC (60.0°C) solvent systems are very similar, with calculated *cis* half-life values for the polymer near 1 h for both cases.

The reversible perturbations in the aromatic n.m.r. signals displayed in *Figure 5* are also worthy of some discussion. The irradiation of polymer 3 in DMSO-d_6 generated a large number of new peaks between 6.8 and 7.9 ppm. This change was also accompanied by a reduction in the signal intensity for the aromatic protons (8.0–8.2 ppm) located on the *trans*-azobenzene chromophore. Similar results were obtained for model compound 9 when it was evaluated in the same deuterated solvent. These data suggest that the effects of the isomerization process are far reaching. Reversible changes in the chemical environments along the poly(aryl ether ketone amide) backbone apparently extend well beyond the twin amide protons that flank the azobenzene linkage. Two-dimensional n.m.r. experiments are currently underway with a series of oligomeric model compounds that mimic different lengths of the polymer backbone in an effort to gain a better understanding of this phenomenon. An intriguing and as yet untested possibility exists that longer range conformational changes in the polymer that accompany the isomerization process may be responsible for some of the perturbations observed in the n.m.r. spectra shown in *Figure 5*. As will be discussed in greater detail below, photoinduced *trans* → *cis* isomerization in 3 will lead to a more compact polymer coil in which through-space interactions between different segments of the polymer backbone become increasingly probable. In such an 'intimate' environment, the reversible stacking of aromatic rings or other physical bonding interactions could lead to minor changes in the n.m.r. signals observed within the aromatic portion of the n.m.r. spectrum. Indeed, up-field shifts in the aromatic signals obtained for paracyclophanes and other aromatic structures that adopt stacked or tightly packed geometries have been widely reported[33–36].

***Trans–cis* isomerization as followed by size exclusion chromatography**

For many azobenzene modified macromolecules suspended in solution, the configurational and conformational features of the polymer backbone are strongly intertwined. That local *trans–cis* isomerization reactions were likely to have a profound impact on the global conformations assumed by some of the polymers described in this study was predicted by the inspection of CPK (Corey–Pauling–Koltun) molecular models. A model representing a 4900 dalton fragment of 3 containing six 'linear' *trans*-azobenzene residues occupied an extended geometry when viewed in three-dimensional space. On converting four of the six azobenzene residues into a 'kinked' *cis* configuration (to model a photostationary state composition not unlike that observed for 3 by optical absorbance and n.m.r. spectroscopies), the same oligomeric fragment adopted a much more compact geometry. Such perturbations predicted for three-dimensional structure are likely to be even more dramatic when they occur along a higher molecular weight polymer backbone.

In an effort to gain a somewhat more quantitative understanding of how the global dimensions of the azobenzene modified poly(aryl ether ketone amide)s were altered in response to the isomerization reaction, several of the macromolecules described in this study were evaluated by size exclusion chromatography (SEC). The full details concerning the SEC measurements are provided in the experimental section of this report. Twin chromatograms for poly(aryl ether ketone amide) 3 before and after light exposure are displayed in *Figure 7*. These data suggested that irradiation of the polymer solution with filtered ultraviolet light ($370 < \lambda < 400$ nm) had a dramatic impact on the global geometry adopted by the polymer coil in the DMAC environment.

As is widely recognized, the SEC technique separates a polymer in solution based on its hydrodynamic volume. The concentrations of eluting polymer species are typically recorded as a function of elution volume. A calibration curve is then employed to convert elution volumes into molecular weight values, ultimately furnishing a molecular weight distribution for the polymer sample. The SEC columns employed in this study were calibrated using polystyrene reference samples and so reported molecular weight averages are all relative to polystyrene. When the azobenzene modified polymer 3 undergoes a photo-stimulated change in conformation, there is an apparent shift in the molecular weight distribution as measured by SEC which corresponds to an actual change in the hydrodynamic volume of this polymer. Based on the results shown in *Figure 7*, the *apparent* number-average (M_n) and weight-average (M_w) molecular weights for 3 were reduced to about one-sixth of their original values following the irradiation procedure (*Table 5*).

The intrinsic viscosities ($[\eta]$) of the polystyrene SEC reference samples in DMAC can be expressed as a function of their known molecular weights (M) using the Mark–Houwink relationship which is valid for the DMAC solvent system[37]:

$$[\eta] = 1.54 \times 10^{-4} M^{0.677}\ \mathrm{dl/g} \qquad (1)$$

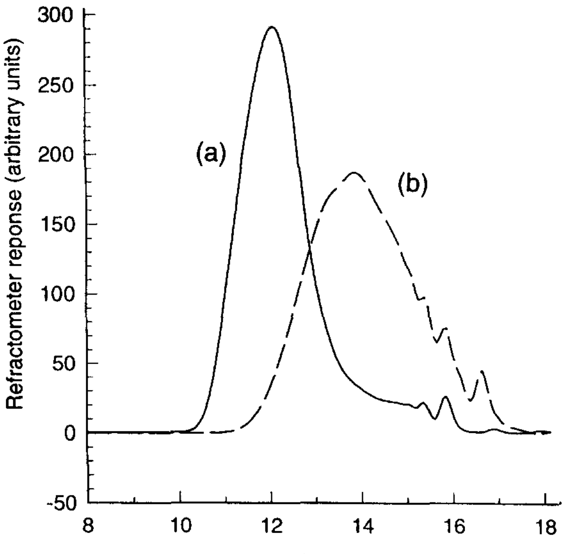

Figure 7 Size exclusion chromatograms for 3 (a) before and (b) after irradiation

Table 5 Hydrodynamic radii (R_h) and apparent M_n and M_w values measured by SEC for polymers 3 and 6 before ($-h\nu$) and after ($+h\nu$) irradiation[a]

	$-h\nu$			$+h\nu^b$			
Polymer	R_h (nm)	M_n	M_w	R_h (nm)	M_n	M_w	$R_h(-h\nu)/R_h(+h\nu)$
3	15.8	90000	302000	5.8	14000	50000	2.7
6	16.3	82000	320000	10.9	38000	155000	1.5

[a] In DMAC with 0.1% LiCl at 40°C

[b] Measured within 4 h after achieving a photostationary state composition of *ca.* 70% *cis*/30% *trans*

In this study, calculated intrinsic viscosity values derived from equation (1) were used to determine the individual hydrodynamic radii (R_h) for the polystyrene standards by employing equation (2) where N_A is Avogadro's number:

$$R_h = (3[\eta]M/10\pi N_A)^{1/3} \qquad (2)$$

In this way, a new calibration curve was constructed linking the hydrodynamic radii of the polystyrene standards to their elution volumes measured during the SEC experiment. The hydrodynamic radii for the azobenzene modified polymer 3 before and after irradiation were then estimated from their own elution profiles using this calibration curve. As is indicated in *Table 5*, the R_h for 3 (based on weight-average molecular weight) decreased by a factor of 2.7 in response to light exposure. In other words, data gleaned from the SEC experiment suggested that the hydrodynamic volume of the polymer coil contracted by a factor of 20 during the irradiation process. Interestingly, the magnitude of photostimulated response in polymer 6 was much less dramatic (*Table 5*). Here, the SEC experiment suggested a drop in R_h by a factor of 1.5, corresponding to a volume contraction of only 3.4 under similar irradiation conditions. It should be noted that, in contrast to 3, polymer 6 is endowed with a more flexible polymer backbone and has a smaller number of azobenzene linkages residing along its main-chain which are available to drive the photoresponse.

The results derived from the SEC experiment, although preliminary in nature, are nevertheless consistent with dilute solution viscosity measurements carried out independently for a number of these polymers. Poly(aryl ether ketone amide) 3, endowed with a conformationally restricted polymer backbone, displayed large photoviscosity effects when evaluated in DMAC. In certain cases, intrinsic viscosities measured for 3 were reduced by more than half in response to light exposure. These effects were strongly dependent on the composition of the photostationary state achieved during illumination. In stark contrast, significant changes in solution viscosity were never observed for its more flexible polymeric cousins like 6. These observations are consistent with other reports in the literature for azobenzene modified polyamides[22] and polyureas[19,20] and strongly suggest that photoinduced property changes in materials of this kind will be best realized for those derivatives that are endowed with large numbers of conformationally restricted backbone segments. More sophisticated studies using dynamic light scattering techniques and 2D-n.m.r. spectroscopy are planned in an effort to further track the photoinduced volume contractions observed for the poly(aryl ether ketone amide)s described in this study.

CONCLUSIONS

A number of azobenzene modified poly(aryl ether ketone amide)s with differing backbone geometries were evaluated for their reversible photo- and thermo-regulated behaviour in dilute solution. Photoinduced *trans* → *cis* isomerization reactions were carried out by irradiating the polymer samples with ultraviolet light wavelengths between 370 and 400 nm. Photostationary state compositions achieved under these conditions typically consisted of 65–70% of the higher energy *cis* isomer distributed along the polymer main chain. Reverse *cis* → *trans* isomerization of the backbone azobenzene moieties was triggered by either photochemical or thermal means and was monitored by optical absorbance and ^{1}H n.m.r. spectroscopies. Thermally induced *cis* → *trans* return in each of the polymers obeyed the first-order rate law. Activation energies calculated for the 'dark' isomerization reaction fell near 21 kcal mol^{-1} for each of the polymer samples evaluated. These values were not dependent on the overall structure or molecular weight of the polymer backbone and were nearly identical to those determined for several lower molecular weight model compounds. Calculated half-lives for the isomerization of *cis*-azobenzene linkages buried in the polymer backbone ranged from 1 day near room temperature to about 1 h at the 60°C isotherm. Data gleaned from SEC experiments suggested that polymers endowed with conformationally restricted geometries underwent a 20-fold reduction in hydrodynamic volume in response to ultraviolet light exposure. Photo-contractions in more flexible polymer chains appeared to be less dramatic consistent with molecular modelling and dilute solution viscosity measurements.

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