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Azobenzene modified poly(aryl ether ketone amide)s. I. Synthesis and physical properties*

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A series of azobenzene modified poly(aryl ether ketone amide)s was prepared by the low temperature polycondensation of *trans*-azobenzene-4,4′-dicarbonyl chloride with bis-1,4-(3-aminophenoxy-4′-benzoyl)-benzene and other aromatic diamines containing ether and keto groups. The polymers were amorphous, possessed glass transition temperatures between 167 and 218°C and displayed good thermal stabilities under nitrogen and air up to about 400°C. They dissolved readily in a number of organic solvents giving stable solutions. By employing conventional solvent casting techniques, mechanically robust polymer films were obtained with excellent levels of optical clarity. The poly(aryl ether ketone amide)s described here appear to be well suited for photochemical studies in both the solid state and in solution. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: photo-responsive polymers; polymer films; polymer solubility)

INTRODUCTION

Polymers characterised by stimuli-responsive molecular architectures comprise an interesting and rapidly expanding class of materials. Notable advances in this arena have led to macromolecules with thermo-, photo-, and redox-regulated behaviors[1–3]. Not surprisingly, polymers of this kind are increasingly viewed as attractive candidates for a variety of 'smart' materials applications.

Among the most extensively studied polymers in this category are azobenzene modified derivatives which undergo large changes in geometry and polarity owing to *trans-cis* isomerization about their rotoresistant nitrogen double bonds[4]. For polymers with main-chain azobenzene linkages, photo- and thermo-induced isomerization reactions may have a profound impact on the global conformations assumed by the macromolecule. Perturbations in polymer geometry are often accompanied by significant changes in the physical behavior of these materials. These changes tend to be most pronounced for polymers having high levels of azobenzene incorporation and relatively rigid geometries, which effectively transmit molecular motion afforded by the isomerization process up and down the polymer backbone[5,6].

In an effort to develop new high performance materials endowed with stimuli-responsive properties, we prepared a series of poly(aryl ether ketone amide)s containing main-chain *trans*-azobenzene linkages. In contrast to azobenzene-modified polyaramides, the polymers possessed enhanced levels of solubility and tractability due to the presence of conformationally restricted aryl ether ketone segments in the polymer backbone. 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 this paper we describe the synthesis and physical properties of a new series of polymers. The *trans-cis* isomerization behavior of these materials is reported more extensively in the following communication.

EXPERIMENTAL

Materials

Anhydrous *N,N*-dimethylacetamide (DMAC) (Aldrich) and *N*-methyl-2-pyrrolidone (NMP) (Aldrich) were stored under Ar over 4A molecular sieves. Terephthaloyl chloride (99%, Aldrich) and sebacoyl chloride (99%, Aldrich) were fractionally distilled under reduced pressure before use. 4,4′-Diaminobenzophenone (98%, Fluka), 4,4′-diaminobiphenyl (97%, Fluka) and 4,4′-diaminodiphenyl ether (99%, Fluka) were twice recrystallized from methanol/DMAC (90:10 v:v). All other reagents and solvents (> 98%) were supplied by Aldrich and were used without further purification.

Monomer syntheses

trans-Azobenzene-4,4′-dicarboxylic acid-dipotassium salt (**1**) was synthesized according to a modified procedure of Tomlinson[7]. To a magnetically stirred solution of p-nitrobenzoic acid (13.0 g, 77.8 mmol), NaOH (50.0 g, 1250 mmol) and water (225 mL) at 50°C was added a warmed solution of α-D-glucose (100 g, 555 mmol) in water (150 mL) over a 1 h period. A stream of air was vigorously bubbled into the light brown solution for 12 h, ultimately affording a viscous, dark brown mixture. On cooling to room temperature, the mixture was acidified with glacial acetic acid to pH 6, after which a mud-like precipitate was collected by filtration. The solid was twice recrystallized from hot aqueous K_2CO_3, giving 8.0 g (59%) of **1** as bright orange needles: m.p.: > 300°C (decomp); ^{1}H NMR: (D_2O, 300 MHz) δ 7.99 (d, 4H), 7.83 (d, 4H); Anal. Calcd. for $C_{14}H_8N_2O_4K_2$: C, 48.54; H, 2.33; N, 8.09. Found: C, 48.63; H, 2.22; N, 8.09.

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* Contribution no. 7570.

trans-Azobenzene-4,4'-dicarbonyl chloride (**2**) was prepared by treating **1** with thionyl chloride in the dark as described by Tomlinson[7]. The product was isolated (90%) as dark red needles: m.p.: 164.5–165°C (lit[7] m.p.: 164°C); ^{1}H NMR: ($CDCl_3$, 300 MHz) δ 8.33 (d, 4 H), 8.06 (d, 4 H); MS (e.i.): m/e (rel. int.) 307.9921 (37, M^+), 271.0234 (78), 166.9972 (72), 138.9982 (100).

Bis-1,4-(4-fluorobenzoyl)benzene (**3**) was synthesized according to standard literature procedures[8]. The product was isolated (83%) as a white crystalline solid: m.p.: 221–222°C (lit[8] m.p.: 218.5–219.5°C); ^{1}H NMR (TFD, 300 MHz) δ 7.95–8.05 (m, 8 H), 7.29 (m, 4 H); MS (e.i.) m/e (rel. int.) 322.0573 (57, M^+), 227.0519 (59), 123.0122 (100).

Bis-1,4-(3-aminophenoxy-4'-benzoyl)benzene (**4**). A magnetically stirred solution of **3** (2.00 g, 6.21 mmol), 3-aminophenol (2.70 g, 24.7 mmol) and K_2CO_3 (1.54 g, 11.1 mmol) in DMAC (150 mL)/toluene (10 mL) was heated to reflux under Ar for 2.5 h, during which time water was removed via a Dean-Stark trap. The hot solution was filtered into a large volume (400 mL) of water. A tan solid was collected by filtration and recrystallized twice from hot acetone/water (80:20 v:v), affording 2.7 g (84%) of **4** as a tan, crystalline solid: m.p.: 162–163°C; ^{1}H NMR: (TFD, 300 MHz) δ 8.00–8.06 (m, 8 H), 7.63–7.71 (t, 2 H), 7.35–7.44 (m, 6 H), 7.18–7.27 (d, 4 H); MS(fab): m/e 501.26 (MH^+).

Synthesis of polymers

In a typical polymerization reaction, a mechanically stirred solution of diamine (0.400 mmol) and acid chloride (0.400 mmol) in DMAC (10–20 ml) was cooled to 0°C for 1 h under Ar and then warmed to 45°C for 2–3 hours. The viscous solution was poured into water (250 ml), giving a stringy solid. The solid was vigorously extracted with water (2 × 100 ml), methanol (2 × 100 ml) and acetone (1 × 50 ml) and then dried *in vacuo* at 60–70°C for 48 h. Unless otherwise noted, all azobenzene-modified polymer samples were prepared and manipulated under ambient room light.

Polymer film formation

A poly(aryl ether ketone amide) (1.0 g) was slowly dissolved into DMAC (25 mL) over 24 h and then allowed to stand in the dark for an additional 24 h period. The viscous solution was poured onto a level, dust-free, non-stick teflon surface, covered with a large inverted funnel and then warmed in the dark to 32 ± 2°C for 24 h during which time the DMAC slowly evaporated away. The resulting film was carefully peeled from its plastic base, loosely taped to a supporting frame and then dried *in vacuo* at 60–80°C for 72 h. Films were typically 10–20 microns thick.

Analytical methods

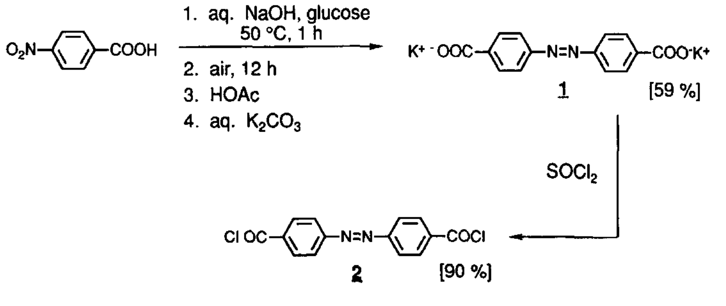
Melting points were determined in open capillary tubes with a Laboratory Devices (Holliston, MA) Mel-Temp unit and are uncorrected. A heating rate of 2°C/min was consistently employed. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained at 300 MHz on a General Electric QET spectrometer. Tetramethylsilane was used as a standard. Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 series Fourier transform infrared spectrophotometer. Samples were measured in thin film form. UV-visible (UV-Vis) 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. High resolution electron impact mass spectra (MS ei) were obtained with a VG 70–250SE double-focusing mass spectrometer. Fast atom bombardment mass spectra (MS fab) were provided by a VG ZAB-E double-focusing mass spectrometer equipped with a xenon-ionization gun. Elemental analyses were performed by Galbraith Laboratories (Knoxville TN).

Inherent viscosity measurements were obtained in sulfuric acid at 30°C with a polymer concentration of 0.5%. Gel permeation chromatography (GPC) was performed with a Waters HPLC 150C equipped with a refractive index detector. Polymer samples were dissolved in DMAC containing trace amounts of Ionol (antioxidant) and toluene sulfonic acid and were analyzed at 135°C. Narrow molecular weight polystyrene standards were employed for GPC calibration. Thermal gravimetric analyses (TGA) were obtained with a TA Instruments TGA 2950 Thermo-gravimetric Analyzer. Differential scanning calorimetry (DSC) was performed with a TA Instruments DSC 2910. Both instruments were interfaced to a TA Instruments Thermal Analyzer 2100. Polymer samples were heated at 20°C/min under N_2 unless otherwise noted. Mechanical (tensile) testing measurements were acquired at room temperature with an Instron Model 1123 using a series IX Automated Testing System. A crosshead speed of 1.3 cm/sec was utilized for all measurements.

RESULTS AND DISCUSSION

Synthesis of monomers and polymers

trans-Azobenzene-4,4'-dicarbonyl chloride (**2**) was prepared in several steps (*Scheme 1*), by a glucose-mediated bimolecular reduction of 4-nitrobenzoic acid to initially give the 4,4'-diacid of hydrazobenzene. Air oxidation and a subsequent aqueous K_2CO_3 crystallization step then furnished *trans*-azobenzene-4,4'-dicarboxylic acid as the



Scheme 1

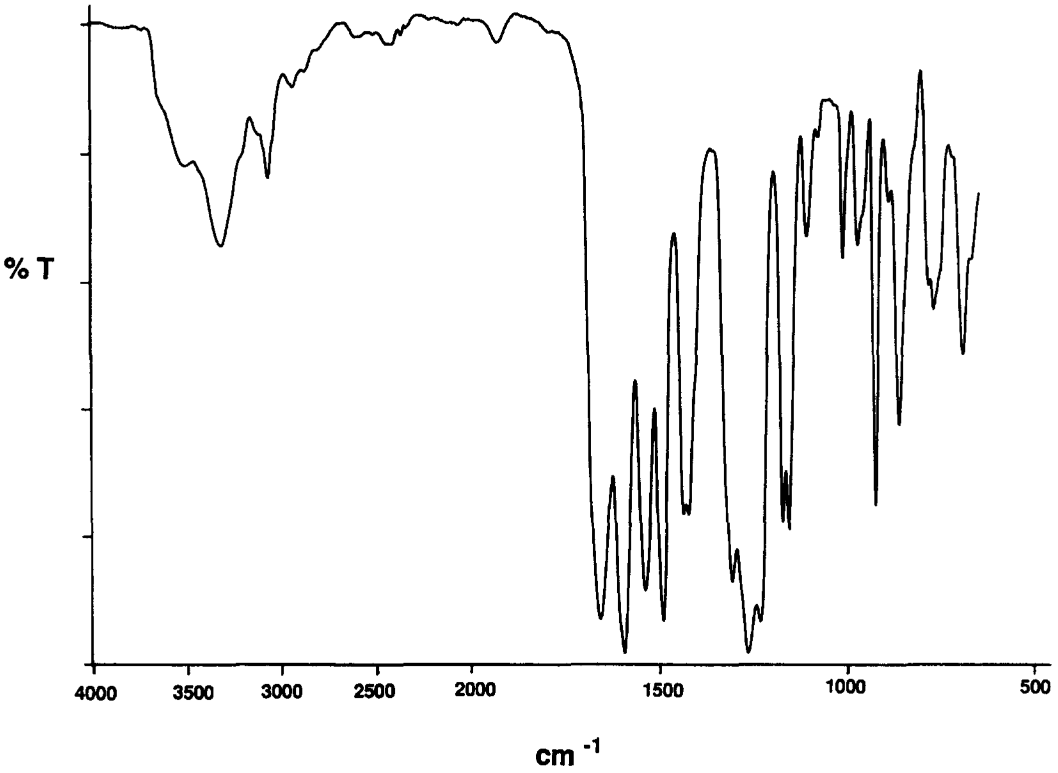


Figure 1 Infrared spectrum of polymer **5** in thin-film form

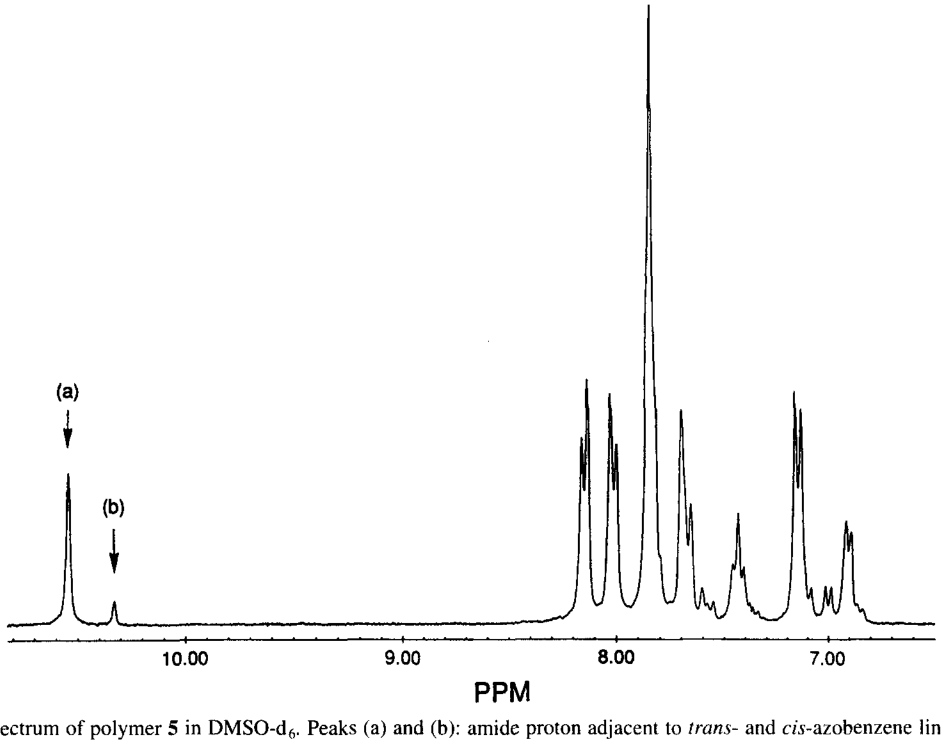


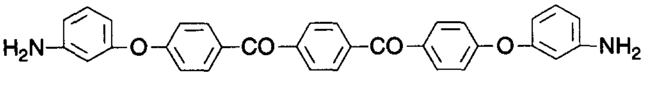
Figure 2 ^{1}H NMR spectrum of polymer **5** in DMSO-d$_6$. Peaks (a) and (b): amide proton adjacent to *trans*- and *cis*-azobenzene linkage, respectively

di-potassium salt (**1**). The air oxidation step originally reported by Tomlinson[7] was extended to 12 hours, in an effort to limit the presence of residual hydrazobenzene species in the reaction mixture. In acidic media, hydrazobenzenes can undergo benzidine or semidine rearrangements[9] to yield a variety of side products which greatly complicate the isolation of the desired monomer. The treatment of **1** with thionyl chloride in the dark gave diacid chloride **2** with an approximate 53% overall yield. Monomer **2** was devoid of azoxybenzene or hyrazobenzene contaminants as evidenced by ^{1}H NMR and mass spectroscopies.

The chemical ellaboration of bis-1,4-(4-fluorobenzoyl)-benzene (**3**) with 3-aminophenol provided access to an additional monomer, bis-1,4-(3-aminophenoxy-4′-benzoyl)benzene (**4**). The diamine was purified by a series of acetone/water recrystallization steps until a sharp melting point was observed.

Table 1 Polymer composition, inherent viscosity and molecular weight data

Polymer	Wt. % azobenzene	η_{inh} (dL/g)	M_n	M_w/M_n
5	24.5	1.77	80,400	2.30
6	13.2	1.92	—	—
7	5.5	1.99	—	—
8	2.8	2.33	—	—
9	0	1.54	83,200	1.98
10	22.3	1.23	51,400	2.06
11	18.8	0.82	31,500	1.95
12	12.9	1.80	69,800	2.09
13	27.2	1.85	87,100	1.92
14	30.5	1.62	84,600	2.11
15	34.8	2.06	—	—
16	40.4	4.26	—	—
17	25.6	1.91	—	—
18	27.3	1.70	—	—



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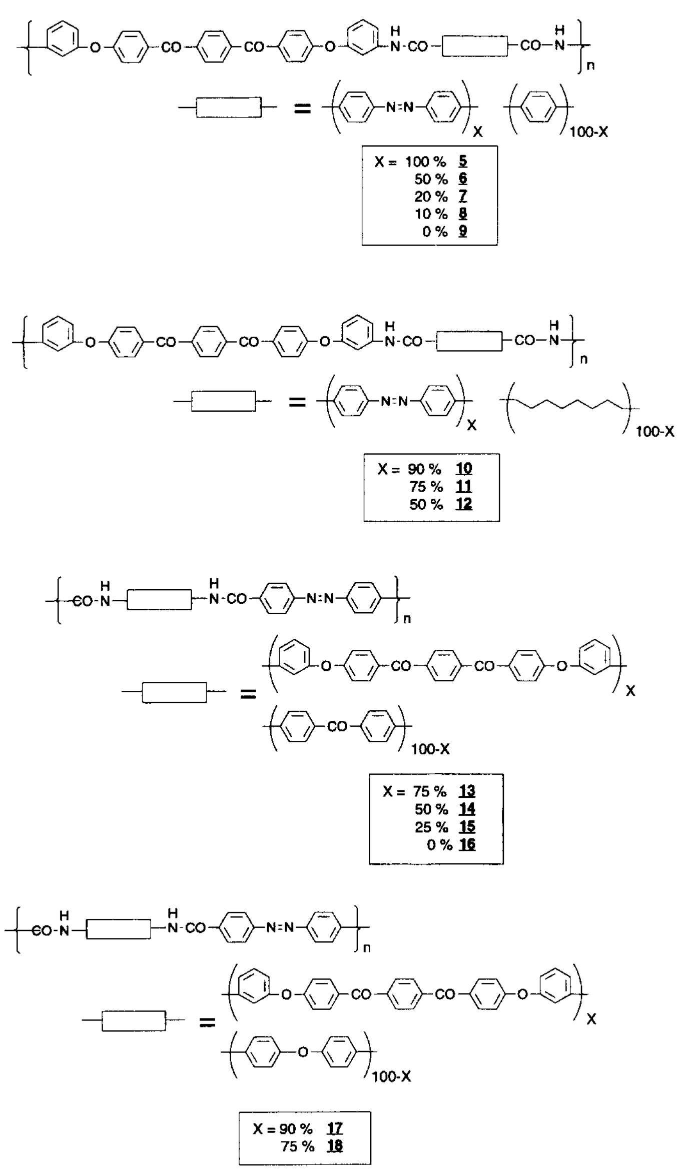
A low temperature polycondensation of diamine **4** with *trans*-azobenzene-4,4′-dicarbonyl chloride was carried out in DMAC to afford the parent poly(aryl ether ketone amide) (**5**). The resulting polymer was precipitated by pouring the DMAC solution into water, giving a fibrous solid that was extracted with methanol and acetone and then rigorously dried *in vacuo* to remove residual solvent. Polymer **5** possessed a deep orange color with nearly 25 wt.% azobenzene loading along its backbone.

The structure of the resulting poly(aryl ether ketone amide) was consistent with data gleaned from IR spectroscopy. An infrared spectrum for polymer **5** as a thin film is provided in *Figure 1*. Amide I (carbonyl stretching) and amide II (NH bending) bands are visible in the spectrum at 1656 and 1536 cm^{-1}, respectively. An additional absorption centered at 3320 cm^{-1} due to NH stretching is also apparent. The breadth and position of this third band suggest a considerable degree of hydrogen bonding within the polymer sample, as would be expected for a IR spectrum obtained in the solid state[10]. Taken together, these data confirm the existence of secondary amide groups within the polymer which have their genesis in the polycondensation reaction. Notably absent from the IR spectrum in *Figure 1* are absorptions specific to the azobenzene chromophore. As has been discussed elsewhere[11], the nitrogen double bond stretching frequencies for aromatic azo compounds generally fall within the 1450–1380 cm^{-1} range. However, these bands are weak and tend to be obscured by other aromatic absorptions as is the case here[12,13]. An examination of the polymer by NMR spectroscopy was also informative. A ^1H NMR spectrum for **5** is shown in *Figure 2*. Proton resonances for the aryl ether ketone and azobenzene chain segments are evident between 6.8–7.9 and 8.0–8.2 ppm, respectively. The polymer's amide protons gave rise to two additional signals further down field, depending upon on whether they are situated adjacent to *trans*- or *cis*-azobenzene linkages. The photostationary state of the polymer can thus be determined by integrating appropriate peak areas. Under ambient room light, approximately 5% of the azobenzene moieties in **5** occupy the higher energy *cis* configuration at any given time. As will be demonstrated in a following paper[14], ^1H NMR spectroscopy provides a convenient means for quantifying *trans-cis* isomerization in azobenzene modified polymers of this kind.

Poly(aryl ether ketone amide)s with reduced azobenzene contents were prepared by employing other diacid chlorides in the low temperature polycondensation reaction (*Table 1*). The use of terephthaloyl chloride and sebacoyl chloride as comonomers furnished two series of copolymers shown in *Scheme 2*. Other copolymers with altered backbone architectures and higher azobenzene loadings, were obtained when 4,4′-diaminobenzophenone or 4,4′-diaminodiphenyl ether were partially substituted for diamine **4** during the polymerization step (*Scheme 2*). In contrast, the use of 1,4-phenylenediamine or 4,4′-diaminobiphenyl as comonomers generally failed to afford high molecular weight materials due to the precipitation of the growing chain species from the polymerization medium (*vide infra*). The molar mass characteristics of a number of polymers were determined by GPC and are provided in *Table 1*, along with inherent viscosity data. As can be noted, the poly(aryl ether ketone amide)s prepared in this study were generally high molecular weight materials. Molecular weight distributions were unimodal with the first polydispersity index (M_w/M_n) falling near two for those polymer samples evaluated. The backbone compositions of **6–18** were consistent with ^1H NMR spectroscopic data (not shown). When prepared and manipulated under room light, all of the azobenzene modified polymers exhibited photostationary states similar to that observed for polymer **5** as evidenced by NMR. Consistently, about 5% of the azobenzene moieties contained within these polymers actually reside in the higher energy *cis*-state at any given time. Polymers devoid of measurable *cis*-azobenzene content in the solid state were obtained by heating samples dissolved in DMAC in the dark, followed by a precipitation step. However, carrying out this thermally driven cis → trans isomerization process did not significantly alter the physical properties of these materials.

Polymer solubility

A principal driving force behind the synthesis of the polymers depicted in *Scheme 2* was to gain access to a series



Scheme 2

of azobenzene-modified derivatives having enhanced organosolubilities. Polyaramides constructed from *trans*-azobenzene-4,4′-dicarbonyl chloride tend to be poorly soluble in DMAC, DMSO and other aggressive organic solvents[15,16]. This behavior is especially apparent for aromatic polymers that occupy rod-like geometries. In our laboratory, the solution (DMAC) polycondensation of **2** with 1,4-phenylene diamine, 4,4′-diaminobiphenyl or other 'rigid' diamines routinely furnished low molecular weight materials with poor physical properties. In all cases, these polymers precipitated during their polymerization reactions. The premature precipitation of the growing polyaramide chains was blocked to some extent by the addition of lithium chloride (2–3%) to the DMAC solutions. However, after isolation and drying, the resulting polymers were soluble only in strong acids like H_2SO_4; precluding their fabrication into thin films useful for spectroscopic and optical studies.

It is widely appreciated that the introduction of ether linkages and other flexible 'pivot points' into a polymer backbone can enhance the solubility characteristics of rigid polyaramides[17]. For example, a number of poly(aryl ether amide)s recently prepared by Hedrick and coworkers were reported to have improved solubilities when compared to more conventional aromatic polyamides[18]. We speculated that the incorporation of conformationally restricted aryl ether ketone segments into our *trans*-azobenzene modified polyaramides might lead to a new family of photo- and thermo-responsive materials with an improved range of physical properties. The use of bis-1,4-(3-aminophenoxy-4′-benzoyl)benzene (**4**) in conjunction with other commercially available aromatic diamines as comonomers, provided a convenient opportunity to introduce both aryl ether and keto linkages into the polyaramide chain.

A qualitative description of the solubility behavior of polymers **5–18** is provided in *Table 2*. As expected, poly(aryl ether ketone amide) **5** was highly soluble in a variety of aggressive organic solvents. In anhydrous DMAC or NMP, one gram of this polymer dissolved readily in as little as 12 mL of solvent, giving extremely viscous solutions with a gel-like appearance. When stored in the dark, these solutions remained homogeneous for several weeks before some precipitation of the polymer occurred. Precipitation of **5** was greatly accelerated when the DMAC or NMP solutions were exposed to ambient levels of moisture. For polymers **6–12**, in which terephthaloyl chloride or sebacoyl chloride were partially substituted for

Table 2 Polymer solubilities at 25°C

Polymer	Solvent medium					
	H_2SO_4	DMAC	NMP	DMSO	$(CF_3)_2CHOH$	CH_3OH
5–12	+ + +	+ + +	+ + +	+ + +	+ +	–
13–14	+ + +	+ +	+ +	+ +	+	–
15–16	+ +	+	+	+	+	–
17	+ + +	+ +	+ +	+ +	+	–
18	+ +	+	+	+	+	–

+ + + very soluble; + + soluble; + slightly soluble; – insoluble

Table 3 Polymer thermal properties

Polymer	T_g (°C)[a]	Tazo (°C)[a]	Onset of weight loss (°C)[b]	
			5%	50%
5	218	426	439	> 700
6	214	416	430	> 700
7	208	427	452	623
8	204	409	453	> 700
9	208	absent	470	695
10	206	404	414	> 700
11	190	394	438	> 700
12	167	386	425	> 700
13	190	431	430	561
14	185	429	410	500
15	183	440	411	517
16	173	443	420	491
17	195	412	436	539
18	201	420	422	520

[a] DSC; 20°C/min under nitrogen
[b] TGA; 20°C/min under nitrogen

trans-azobenzene-4,4′-dicarbonyl chloride during the polymerization reaction, solubility behavior was little changed as compared to polymer **5** (*Table 2*). In stark contrast, substituting diamine **4** with 4,4′-diaminobenzophenone or 4,4′-diaminodiphenyl ether, afforded polymers with significantly diminished solubilities. The solubility drop observed for **13–18** is consistent, in part, with an overall reduction in the number of ether and keto groups residing along the polymer chain. The loss of meta backbone linkages afforded by monomer **4** may also contribute to this behavior. Indeed, for a related series of poly(aryl ether ketone amide)s prepared from the isomeric bis-1,4(4-aminophenoxy-4′-benzoyl)benzene monomer, polymer solubilities were significantly diminished as compared to those reported here[19].

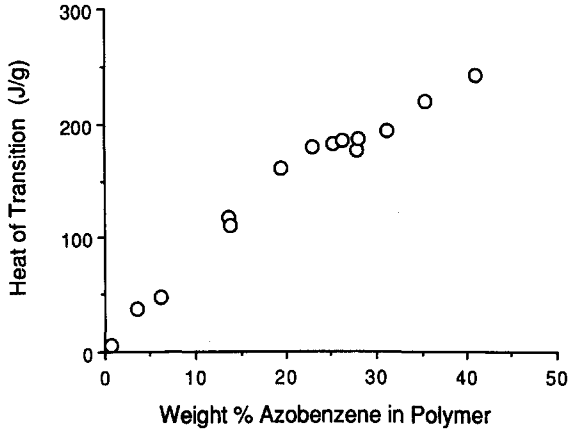
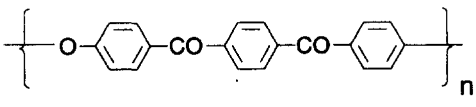


Figure 3 Heat of T_{azo} transition in DSC vs. weight % of azobenzene along polymer backbone for **5–18**

Thermal properties

DSC and TGA were used to probe the thermal characteristics of the polymers shown in *Scheme 2*. Poly(aryl ether ketone amide) **5** exhibited a glass transition temperature near 218°C. Glass transition values for the other wholly aromatic polymers ranged from about 173°C to 214°C (*Table 3*). It is interesting to note that these values are considerably higher than those recorded for polymers in the aryl ether ketone family, which lack main-chain amide bonds. For example, the T_g for all the para isomer of poly(aryl ether ketone ketone) (p-PEKK) lies near 165°C, or about 53° below that measured for polymer **5** under identical conditions[20]. As expected, the introduction of flexible octamethylene spacers into the poly(aryl ether ketone amide) backbone, had a dramatic impact on the glass transition values associated with these materials with the T_g for polymer **12** falling to near 167°C (*Table 3*). Well-defined melting transitions were not observed by DSC for any of the polymers prepared in this study, suggesting an absence of



p-PEKK

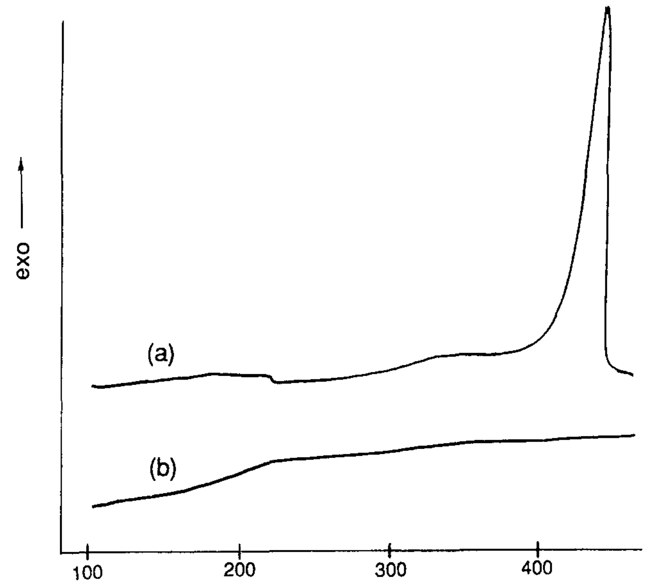


Figure 4 DSC thermogram for polymer **5** under nitrogen. Trace (a): first heat; trace (b): second heat

crystallinity from these materials. Attempts to induce some degree of crystallinity into **5** by carefully annealing the polymer above its glass transition temperature for 24 hours were unsuccessful. Similar results were obtained for the 100% *trans*-isomer of **5**, indicating that trace amounts of the *cis*-azobenzene linkage normally present along the polymer backbone were not responsible for the amorphous nature of these materials. That the non-azobenzene-containing polymer **9** was also devoid of crystallinity as evidenced by DSC lends further support to this notion.

Poly(aryl ether ketone amide)s containing the azobenzene chromophore also exhibited an exothermic transition (T_{azo}) in the DSC between 386 and 443°C (*Table 3*). Similar observations have been reported for other azobenzene containing materials[15–22]. It is anticipated that extrusion of molecular nitrogen from the polymer backbone is responsible for this behavior[15,16]. Indeed, for polymers **5–18**, the heat associated with this exothermic transition appears to correlate well with azobenzene content as demonstrated in *Figure 3*. When **5** was heated to 450°C, cooled and then reheated in the DSC, the exothermic peak centered near 426°C was absent from the second scan (*Figure 4*), consistent with an irreversible loss of the azo group from the polymer sample. Exotherm temperatures displayed in *Table 3* were highly dependent upon the heating rates employed during the DSC measurements. For example, for polymer **5**, a systematic drop in heating rate from 25°C/min to 5°C/min afforded a gradual shift in the position of the exotherm from 429°C to 395°C. Based on these data, the activation energy (E_{act}) for this thermally driven decomposition process was approximated from the following expression[23]:

$$E_{act} = \frac{-R\Delta Ln\rho}{1.052\Delta(1/T_p)} \qquad (1)$$

where T_p is the peak exotherm temperature recorded in the DSC at scan rate ρ and R is the gas constant. For the poly(aryl ether ketone amide)s prepared here, activation energies calculated in this manner ranged from 38 to 42 kcal mol^{-1} with that for polymer **5** falling near 41.5 kcal mol^{-1}. These values are in fair agreement with those recently reported by Mohanty *et al.*[22] for a series of azoaromatic polyethers (average E_{act} = 34.2 kcal mol^{-1}).

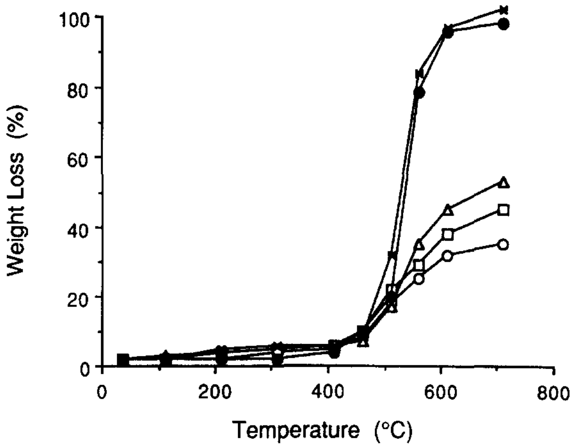


Figure 5 Weight loss: temperature profiles for polymers **5** [○], **9** [△], **12** [□] and **14** [X] under nitrogen and **5** [●] under air

When evaluated under a nitrogen atmosphere, all of the poly(aryl ether ketone amide)s exhibited good thermal stabilities up to about 400°C. Weight loss–temperature profiles constructed from TGA data are provided in *Figure 5* for selected polymers. As can be seen, a number of these materials were quite robust, with half of the polymer mass remaining above 700°C. Polymer residues recovered after heating were highly discolored and were insoluble in all of the solvent media listed in *Table 2*. Temperatures for 5% and 50% weight loss under nitrogen are tabulated in *Table 3*. It is interesting to note that for all of the azo-modified polymers described here, the potential loss of the azo group (DSC) and the onset of significant weight loss (TGA), both occur in the same temperature window. It is plausible that extrusion of molecular nitrogen from the polymer backbone may be directly involved in the thermal decomposition of these materials. Similar suggestions have been made for other families of azobenzene modified polymers, including polyaramides[15,16], organosilicon-based polyamides[21], poly aryl ethers[22] and polybenzimidazoles[24]. As expected, the poly(aryl ether ketone amide)s described here exhibited diminished thermal stabilities in the presence of air when evaluated above 500°C. A weight loss: temperature profile for **5** under air is included in *Figure 5* for comparison. Other wholly aromatic polymers shown in *Scheme 2* behaved similarly.

Polymer films and their properties

Polymers were fabricated into thin films suitable for optical and mechanical studies by solvent casting methods. DMAC was typically employed as a solvent. As detailed in the experimental section, an inverted funnel placed over the samples was utilized to slow the rate of DMAC evaporation and to reduce air turbulence above the film specimens. Using this approach, uniform film samples with an average thickness ranging between 10 and 20 microns were routinely obtained. The thin films prepared from the azobenzene modified polymers were optically transparent and possessed an intense orange colour owing to a broad, structureless n-π^* transition of the *trans*-azobenzene chromophore centered near 440 nm. When examined by optical spectroscopy at wavelengths above 600 nm, the polymer films transmitted nearly 100% of the incident light.

Table 4 Tensile properties of selected polymer films at 25°C[a]

Polymer	Modulus (Kpsi)	Toughness (psi)	Elongation at yield (%)	Elongation at break (%)
5	350	9300	4.5	98
9	225	5720	4.4	66
12	294	7300	4.5	94
13	376	6160	3.5	60

[a] All data typically ± 15%

This optical clarity can be attributed to a lack of light scattering by the sample and is consistent with DSC results, which indicate an absence of crystallinity from these materials. Because of their high surface to volume ratios, polymer films were prepared in the dark to minimize *trans* → *cis* isomerization of the backbone azobenzene moieties.

Stress–strain measurements were carried out for a number of different film specimens. At room temperature, all of the poly(aryl ether ketone amide)s evaluated underwent plastic-like deformations in response to tensile elongations. Polymer **5** suffered elongations ranging between 70–90% before breaking with an initial modulus of 350 Kpsi and a measured toughness near 9000 psi. At extensions of 4–5%, the polymer also exhibited a yield point. Further elongation resulted in cold-drawing and necking of the film samples. For amorphous polymers, this type of ductile behavior is most often attributed to molecular rearrangements between entanglement points, rather than to longer range molecular flow[25]. Thin films fabricated from other *trans*-azobenzene modified poly(aryl ether ketone amide)s exhibited similar stress-strain behavior. Measured values for initial modulus, toughness, elongation at yield and elongation at break, are provided in *Table 4* for several different backbone compositions.

CONCLUSIONS

The low temperature polycondensation of *trans*-azobenzene-4,4′-dicarbonyl chloride with bis-1,4-(3-aminophenoxy-4′-benzoyl)benzene and other aromatic diamines containing ether and keto groups, afforded a series of poly(aryl ether ketone amide)s with a good mix of physical properties. As prepared, the azobenzene-modified polymers were amorphous, possessed relatively high glass transition temperatures and displayed good thermal stabilities under nitrogen and air up to about 400°C. The polymers dissolved readily in a number of organic solvents giving stable solutions. By employing conventional solvent casting techniques, mechanically robust polymer films were obtained with excellent levels of optical clarity. The poly(aryl ether ketone amide)s described here appear to be well suited for a variety of photochemical studies in both the solid state and in solution.

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