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Polymer Vol. 36 No. 15, pp. 3019–3025, 1995
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0032-3861/95/$10.00+0.00

Azoaromatic polyethers

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(Received 20 August 1994; revised 8 February 1995)

A series of high molecular weight azoaromatic polyethers was prepared by the reaction of bisphenols with 4,4′-difluoroazobenzene in *N*-methylpyrrolidinone in the presence of anhydrous potassium carbonate. The activating influence of the aromatic azo group towards nucleophilic displacement reactions was first established by appropriate model compound studies. The polymers were amorphous in nature and tough films could be obtained upon solution casting from chloroform. The azoaromatic polyethers exhibit well defined glass transition temperatures and undergo thermal crosslinking at elevated temperature. Photoviscosity effects due to *cis–trans* isomerism of the azo groups were also investigated.

(Keywords: azoaromatic polyethers; properties; *cis–trans* isomerism)

INTRODUCTION

Aromatic polyethers belong to a family of macromolecules known as engineering thermoplastics[1–3]. They are of commercial importance and have been studied extensively in both academic and industrial laboratories[4–12]. Nucleophilic aromatic substitution reactions are one of the ways by which aromatic polyethers are prepared[4]. Activated bishalides containing a variety of functional groups including sulfone, sulfoxide, ketone, azo, oxadiazole[4], imine[13], azine[14], fused heterocycles and perfluoroalkyls[15] have been used in these reactions as one of the components, along with a wide array of bisphenols. Although Johnson *et al.*[4] found the azo group to have the necessary activating influence to afford polymers, detailed discussion of the synthesis and characterization of azoaromatic polyethers is lacking. Furthermore, an aromatic azo group is a photoisomerizable chromophore. Under ultraviolet irradiation the more stable *trans* form is converted to the *cis* form, which returns to the initial state thermally. Therefore photoinduced isomerization of the azo group is expected to induce conformational change in the polymer backbone. Azoaromatic polyamides[16–19] and polyureas[20] have been studied extensively to observe such changes. Aromatic polyesters containing azo linkages in the main chain, as possible polymeric non-linear optical substrates, have been prepared[21]. In addition, the thermal stability of azo groups containing polybenzimidazole has been examined[22]. In this paper we report the synthesis of suitable monomer, azoaromatic polyethers, model compound studies and the effects of photoisomerization on the solution viscosity behaviour of the polymers. The polymers have been characterized by spectroscopic, thermal and thermomechanical means.

EXPERIMENTAL

Materials

N-methylpyrrolidinone (NMP) and 4-fluoroaniline were dried over calcium hydride and then distilled at reduced pressure. 4,4′-Isopropylidenediphenol (bisphenol-A), kindly supplied by Dow Chemical, was purified by recrystallization from toluene. Tetramethyl bisphenol-A was prepared according to a reported procedure[23]. 4,4′-Sulfonyldiphenol (bisphenol-S) and *tert*-butylhydroquinone were recrystallized from acetone and ether/hexanes, respectively. 9,9′-Bis(4-hydroxyphenyl)fluorene, a gift from Ken Seika Corporation, was used as received. Manganese dioxide was either prepared in the laboratory[24,25] or procured from commercial sources. All other reagents were used without further purification.

4,4′-Difluoroazobenzene

To a reaction vessel consisting of a 2 l three-necked round-bottomed flask equipped with a nitrogen inlet, an overhead stirrer and a Dean–Stark trap fitted with a condenser and a drying tube were added toluene (500 ml) and 4-fluoroaniline (48.64 g, 0.45 mol). The reaction mixture was stirred vigorously and manganese dioxide (228.5 g, 2.6 mol) was added. The entire mixture was heated to reflux and water, the by-product of the reaction, was removed via the Dean–Stark trap by azeotropic distillation. The reaction was held at reflux for 24 h and then allowed to cool. The contents of the flask were filtered through Celite and the filtrate was distilled to remove toluene. The residue was dissolved in small amounts of hexane and eluted on a silica gel column with hexane to afford **1** in 57% yield. The orange coloured solid was purified further by recrystallization from hexane to obtain monomer grade material. **1**: m.p. 103°C (d.s.c.), (lit.[26] m.p. 101°C). ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 7.25 (m, 4H), 7.95 (m, 4H). ^{13}C n.m.r. ($CDCl_3$) δ (ppm): 164.39 (J_{CF}, 253 Hz), 161.5 (J_{CF}, 250 Hz), 149.03

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(J_{CF}, 3 Hz, 124.31 (J_{CF}, 9 Hz), 122.60 (J_{CF}, 9 Hz), 116.22 (J_{CF}, 22 Hz), 116.34 (J_{CF}, 22 Hz). I.r. (KBr) ν (cm^{-1}): 1498 (C–N). Mass spectrum *m/e*: 218 (M$^+$), 95. Elemental analysis for $C_{12}H_8N_2F_2$: calculated C, 66.06; H, 3.67; N, 12.87; F, 17.43. Found: C, 65.72; H, 3.77; N, 12.79; F, 17.12.

4,4′-Dichloroazobenzene

To a reaction vessel consisting of a 2 l three-necked round-bottomed flask equipped with a nitrogen inlet, an overhead stirrer and a Dean–Stark trap fitted with a condenser and a drying tube were added toluene (500 ml) and 4-chloroaniline (51.02 g, 0.40 mol). The reaction mixture was stirred vigorously and manganese dioxide (208.95 g, 2.4 mol) was added. The entire mixture was heated to reflux and water, the by-product of the reaction, was removed via the Dean–Stark trap by azeotropic distillation. The reaction was held at reflux for 24 h and then allowed to cool. The contents of the flask were then filtered through Celite and the filtrate was distilled to remove toluene. The residue was dissolved in small amounts of hexane and eluted on a silica gel column with hexane to afford **2** in 68% yields. The orange coloured solid was purified further by recrystallization from hexane to obtain monomer grade material. **2**: m.p. 187°C (d.s.c.). ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 7.5 (m, 4H, 7.95 (m, 4H). ^{13}C n.m.r. ($CDCl_3$) δ (ppm) 150.76, 137.21, 129.38, 124.18. I.r. (KBr) ν (cm^{-1}) 1477 (C–N). Mass spectrum *m/e*: 251 (M$^+$), 139, 111. Elemental analysis for $C_{12}H_8N_2Cl_2$: calculated C, 57.37; H, 3.19; N, 11.16; Cl, 28.29. Found: C, 57.55; H, 3.16; N, 11.18.

4,4′-(4-tert-Butylphenoxy)azobenzene

To a 100 ml three-necked round-bottomed flask fitted with a nitrogen inlet, a magnetic stirrer, a thermometer and a Dean–Stark trap fitted with a condenser and a drying tube, 4-*tert*-butylphenol (0.30 g, 0.002 mol), **1** (0.22 g, 0.001 mol) and anhydrous potassium carbonate (0.48 g, 0.0034 mol) were added. The weighing pans were washed with 25 ml of NMP and 15 ml of toluene with solvents flowing directly into the reaction vessel. The reaction mixture was heated to reflux and the reaction was allowed to continue at the reflux temperature (150°C). The progress of the reaction was monitored by thin layer chromatography (t.l.c.). After completion of the reaction (18 h), the reaction mixture was cooled and diluted with 50 ml of ethyl acetate. It was then filtered and the filtrate was distilled at reduced pressure to remove all solvents. The crude solid was recrystallized from hexane to afford **3** in 85% yield. **3**: m.p. 151°C (d.s.c.). ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 1.85 (s, 18H), 7.05 (m, 8H), 7.40 (m, 4H), 7.90 (m, 4H). ^{13}C n.m.r. ($CDCl_3$) δ (ppm): 159.10, 152.80, 147.25, 146.02, 125.71, 123.39, 118.16, 117.18, 33.38, 30.47. I.r. (KBr) ν (cm^{-1}): 1490 (C–N), 1240 (C–O–C). Mass spectrum *m/e*: 480 (M$^+$), 225, 210. Elemental analysis for $C_{30}H_{34}N_2O_2$: calculated C, 80.33; H, 7.11; N, 5.86. Found: C, 80.26; H, 7.32; N, 5.81.

General procedure for the preparation of azoaromatic polyethers

Polymerization reactions were carried out in a 100 ml four-necked round-bottomed flask fitted with a nitrogen inlet, a thermometer, an overhead stirrer and a Dean–Stark apparatus in a heated oil bath. The following representative procedure was used for the preparation of **6a**. Bisphenol-A (2.8532 g, 0.0125 mol) and **1** (3.7562 g, 0.0125 mol) were weighed and carefully transferred into the reaction vessel. Anhydrous potassium carbonate (3.75 g, excess) along with NMP (30 ml) and toluene (20 ml) were added to the reaction vessel. The reaction mixture was heated until toluene began to reflux (140°C); this was periodically removed from the Dean–Stark trap along with water (by-product of the reaction). It took ~ 4–6 h for the complete removal of water. The colour of the reaction mixture turned deep orange and the viscosity increased gradually. The reaction was allowed to continue at 140°C for 24 h. The reaction mixture was then coagulated in ~ 10× volume of acetone. The polymer was collected by filtration and washed with acetone, water and then acetone again in a Soxhlet apparatus. The polymer was then dried in a vacuum oven at 80°C for 24 h.

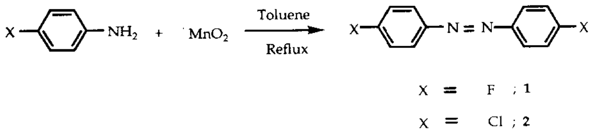
Measurements

^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.) spectra were recorded using a General Electric QE-300 instrument. Infra-red (i.r.) spectra were obtained with a Perkin–Elmer Series 1600 FT-IR spectrophotometer. Absorption spectra were recorded with a Varian Cary 219 spectrophotometer. Thermal transition temperatures were measured by differential scanning calorimetry (d.s.c.), either with a Du Pont DSC 2100 or Perkin–Elmer DSC-7 at a heating rate of 10°C min^{-1} unless otherwise indicated. The transition temperatures are reported as the maxima and minima of their endothermic and exothermic peaks. Glass transition temperatures (T_g) were taken as the mid-point of the change in slope of the baseline. Thermogravimetric analysis (t.g.a.) of polymer samples was conducted at a heating rate of 10°C min^{-1} in nitrogen. Intrinsic viscosity measurements were made on NMP solutions at 25°C using a Cannon–Ubbelohde dilution viscometer. Polymer solutions in NMP were irradiated using a 400 W, 120 V mercury lamp (General Electric). During irradiation the chamber was cooled by a fan and the solutions were cooled using a cold finger.

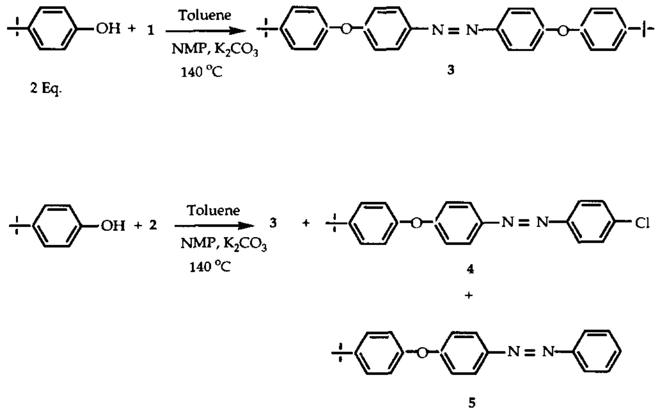
RESULTS AND DISCUSSION

Monomer synthesis

Both 4,4′-difluoroazobenzene, **1**, and 4,4′-dichloroazobenzene, **2**, have been used for the synthesis of aromatic polyethers in dimethylsulfoxide (DMSO)[4]. High molecular weight polymers could be prepared using the difluoride. On the other hand, the reaction time was significantly longer and oligomeric products were prepared when the dichloride was used[4]. We have prepared both of these compounds in order to gain a better understanding as to why the dichloride affords only oligomeric products. The monomers were synthesized by oxidative coupling reactions of 4-haloanilines (*Scheme 1*) by manganese dioxide according to a reported general procedure[23]. Toluene was used as the



Scheme 1



Scheme 2

solvent and water, the by-product of the reaction, was removed by azeotropic distillation. The yield of the dichloroazo compound was significantly lower (30%) than that of the fluorinated analogue (50%). The purity of these compounds was assessed by d.s.c. ^{13}C n.m.r. analysis of **1** revealed the presence of both *cis* and *trans* isomers. On the other hand, the presence of only one isomer (*trans*) was evident from a similar analysis of **2**. This is consistent with our earlier observations with bishalides containing ketimine groups[13]. For example, the reaction product of 4-phenylenediamine and two equivalents of 4-chlorobenzophenone in the presence of molecular sieves consisted exclusively of the *trans* isomer whereas a similar reaction with 4-fluorobenzophenone afforded a mixture of *cis* and *trans* isomers. We are unable to offer a rational explanation for this phenomenon since arguments based on steric constraints cannot be justified.

Model compound studies

Model compound studies were undertaken in order to establish appropriate reaction conditions for polymer synthesis from **1** and a bisphenol. Also, it was important to gain an understanding as to why **2** affords only oligomeric products under similar reaction conditions when it is allowed to react with a bisphenol. These reactions were conducted in NMP at 140°C (*Scheme 2*) in the presence of anhydrous potassium carbonate. Toluene was used to remove water, the by-product of the reaction. It was possible to prepare the desired bisether, **3**, in quantitative yield, when two equivalents of 4-tert-butylphenol was allowed to react with **1** under these reaction conditions. In contrast, a similar reaction with **2** afforded a mixture of products. These compounds were separated on a silica gel column and identified. The mixture consisted of the bisether, **3**, the mono-substituted compound, **4**, and the dehalogenated derivative of the mono-substituted product, **5** (*Scheme 2*).

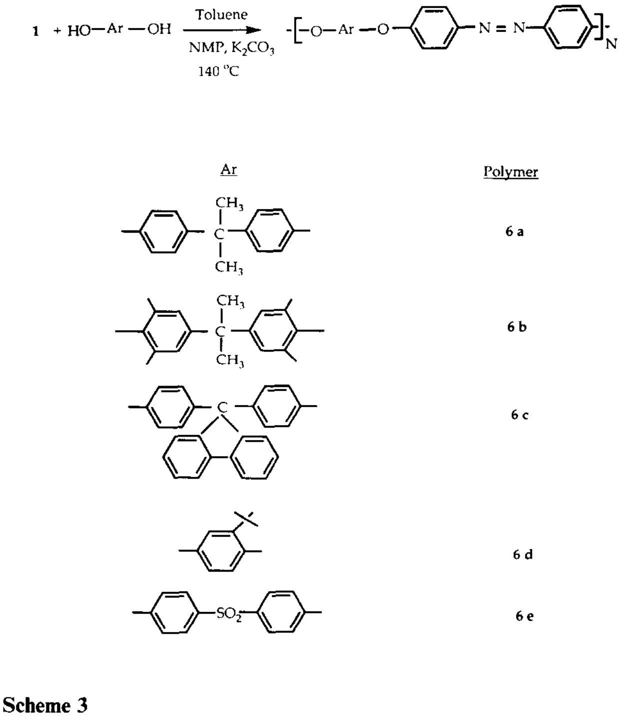
This is consistent with earlier observations that both S$_N$AR and S$_{RN}$1 reactions compete during aromatic polyether formation[11,27–32]. The S$_{RN}$1 reactions compete effectively when the combination of a weak nucleophile and a substrate with poor leaving groups (e.g. chloride anion in the present case) is used. Furthermore, the choice of solvent plays an important role[30]. Our observation suggests that the nucleophilicity of the 4-tert-butylphenoxide anion in NMP is somewhat similar to the poor nucleophilicity exhibited by a phenoxide anion (a weaker base) in dimethylacetamide (DMAc).

Dehalogenation reactions are one of the consequences of S$_{RN}$1 processes. In this instance, the presence of dehalogenated compounds **5** indicates that S$_{RN}$1 reactions must be taking place when the bischloride is used. Therefore, during polymerization reactions with **2**, dehalogenation generates stoichiometric imbalance and only oligomeric products are formed. It should be pointed out that we were unable to detect the presence of azobenzene in the product mixture. On the other hand, it was possible to isolate the same when phenol was allowed to react with **2** under similar reaction conditions. On the basis of these findings, **1** was chosen as the monomer for polymerization reactions.

To shorten the reaction time between **1** and 4-tert-butylphenol, the reaction was carried out at 160°C. Unfortunately, the colour of the reaction mixture turned brown above a reaction temperature of 150°C and the desired bisether, **3**, could not be detected. T.l.c. analysis indicated the presence of highly polar base-line products possibly due to side reactions involving carbonate anion attack on the carbon bearing the fluorine atom. This was confirmed by conducting the same reaction in the absence of 4-tert-butylphenol. A t.l.c. analysis of the reaction mixture indicated the loss of the bisfluoride and the presence of similar products as before within 2 h. This led us to conclude that the actual polymerization reactions should be conducted at 140°C, albeit for the longer reaction time.

Polymer synthesis and characterization

The polymerization of the difluoride, **1**, with a series of bisphenols was carried out in NMP/toluene (2:1 v/v) solvent mixture in the presence of anhydrous potassium carbonate (*Scheme 3*). The reaction temperature was maintained at 140°C and water (formed during phenoxide formation) was removed by azeotropic distillation with toluene. The reaction was allowed to continue at



Scheme 3

Table 1 Values of intrinsic viscosity (η), glass transition temperature (T_g), exotherm peak temperature (T_p), activation energy for crosslinking (E_a) and activation energy for thermal recovery from *cis* to *trans* isomer (E_a) for polymers **6a–e**

Polymer	η^a (dl g^{-1})	$T_g{}^b$ (°C)	$T_p{}^c$ (°C)	$E_a{}^d$ (kcal mol^{-1})	$E'_a{}^e$ (kcal mol^{-1})
6a	0.80	175	377	31.2	23.6
6b	0.91	235	351	34.3	26.4
6c	1.02	229	393	34.8	26.7
6d	0.50	187	359	34.8	26.0
6e	0.52	222	364	36.1	24.6

[a] Solvent NMP at 25°C
[b] Second heating; heating rate = 10°C min^{-1}
[c] Heating rate = 10°C min^{-1}
[d] Mean = 34.2 kcal mol^{-1}; standard deviation = 1.8 kcal mol^{-1}
[e] Mean = 25.5 kcal mol^{-1}; standard deviation = 1.3 kcal mol^{-1}

this temperature for 24 h with vigorous stirring. During this time the viscosity of the bright orange coloured reaction mixture increased significantly. At completion of the reaction, the hot reaction mixture was poured into rapidly stirring acetone in a blender. The fibrous polymer that coagulated was filtered and washed with acetone. The polymer was subsequently extracted with acetone, water and acetone, in that order, in a Soxhlet apparatus. It was possible to obtain high molecular weight fibrous polymers (**6a–e**) (*Scheme 3*) by using this procedure. On the other hand, the polymerization reactions failed when more rigid bisphenols such as hydroquinone or biphenol were used. Oligomeric products precipitated out of the reaction mixture at early stages of the reaction. Increasing the temperature of the reaction mixture above 150°C resulted in discoloration and decomposition of the products.

Polymers **6a–e** produced clear, finger-nail creasable films upon solution casting from chloroform, except **6e** which was insoluble in chloroform. Intrinsic viscosity measurements for the polymers in NMP at 25°C produced values from 0.50 to 1.02 dl g^{-1} (*Table 1*). The azoaromatic polyether **6e** exhibited exceptional solvent resistance. It was sparingly soluble in a series of common solvents (hot) including dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), tetrahydrofuran (THF) and DMSO. It was soluble in NMP, DMAc and trifluoromethanesulfonic acid only. I.r. (KBr) was used to identify the ether and sulfone groups. Since sulfone is a polar moiety, the resulting inter- and intrachain forces contribute to the exceptional solvent resistance of this polymer. The solubility behaviour of polymers **6a–e** is shown in *Table 2*. Surprisingly, the polymers exhibit a low degree of solubility in DMSO.

Table 2 Solubility behaviour[a] of polymers **6a–e**

Polymer	CH_2Cl_2	$CHCl_3$	THF	DMAc	DMSO	NMP
6a	sp*	s	s	sp*	sp*	s
6b	s	s	s	sp*	i	s
6c	sp*	s	s	i	i	s
6d	sp*	s*	s	s*	sp*	s
6e	sp*	sp*	i	s	i	s

[a] s, soluble at room temperature; s*, soluble (hot); sp*, sparingly soluble (hot); i, insoluble (hot)

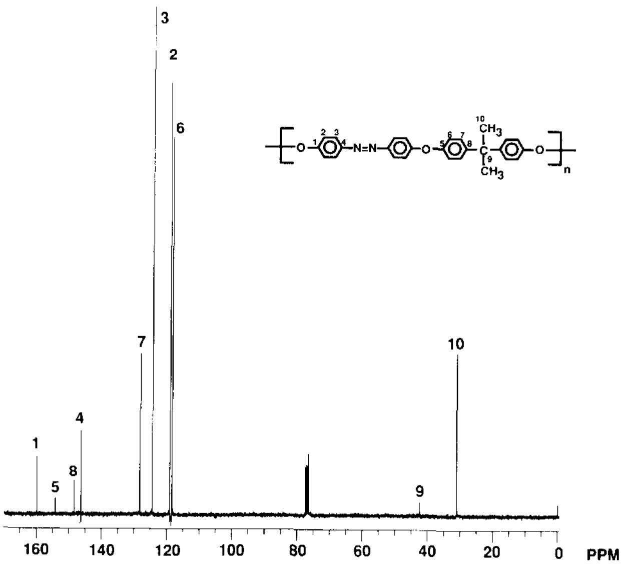


Figure 1 ^{13}C n.m.r. spectrum ($CDCl_3$) of azoaromatic polyether, **6a**

Except for **6e**, the polymer repeat units were characterized by ^{13}C n.m.r. ($CDCl_3$) and i.r. (film) analysis. The ^{13}C n.m.r. spectrum of polymer **6a** is shown in *Figure 1*. It was possible to assign the absorbances to various carbon atoms of the polymer repeat unit[33,34]. An examination of the spectrum indicates the presence of only the more stable (*trans*) isomer in contrast to the monomer **1**, which consisted of a mixture of both *cis* and *trans* isomers. A solution of **6e** in trifluoromethanesulfonic acid was used to obtain the ^{13}C n.m.r. spectrum Deuterium oxide in a sealed tube served as the internal standard. The total number of absorbances contained in the n.m.r. spectrum of **6e** agreed with the expected number based on the structure of the repeat unit. However, it was not possible to assign the various carbon atoms to the observed peaks, due to a lack of readily available chemical shift constants for the solvent system used to collect the spectrum. The *FT*-i.r. (film) of the polymers established the presence of ether linkages.

The T_gs of polymers **6a–e**, listed in *Table 1*, ranged from 175 to 235°C depending on the nature of the bisphenol used. Polymers **6a–d** were amorphous in nature while polymer **6e** exhibited a melt endotherm at 248°C (10.80 J g^{-1}) in the first heating and did not recrystallize upon slow cooling. All polymers, **6a–e**, exhibited a large exotherm on further heating above their respective T_g. The peak temperatures (T_ps) are also displayed in *Table 1*. Polymers recovered from the d.s.c. pans were discoloured and insoluble in the common solvents in which the virgin polymers were initially soluble. This is consistent with earlier observations regarding the decomposition of azoaromatic polymers at elevated temperature with the elimination of nitrogen gas[16,22]. It was possible to calculate the energy of activation (E_a) for these crosslinking reactions (*Table 1*) by conducting the d.s.c. scans at five different heating rates (2.5, 5, 10, 15 and 20°C min^{-1}) and measuring the exotherm peak temperatures (T_ps)[35]. D.s.c. exotherms obtained in this manner for polymer **6a** are shown in *Figure 2*. An examination of the data in *Table 1* reveals that, within experimental error, the E_a values are essentially identical irrespective of the nature of the polymer backbone. The calculated mean value of 34.8 kcal mol^{-1} is similar to the activation energy value of 30.8 kcal

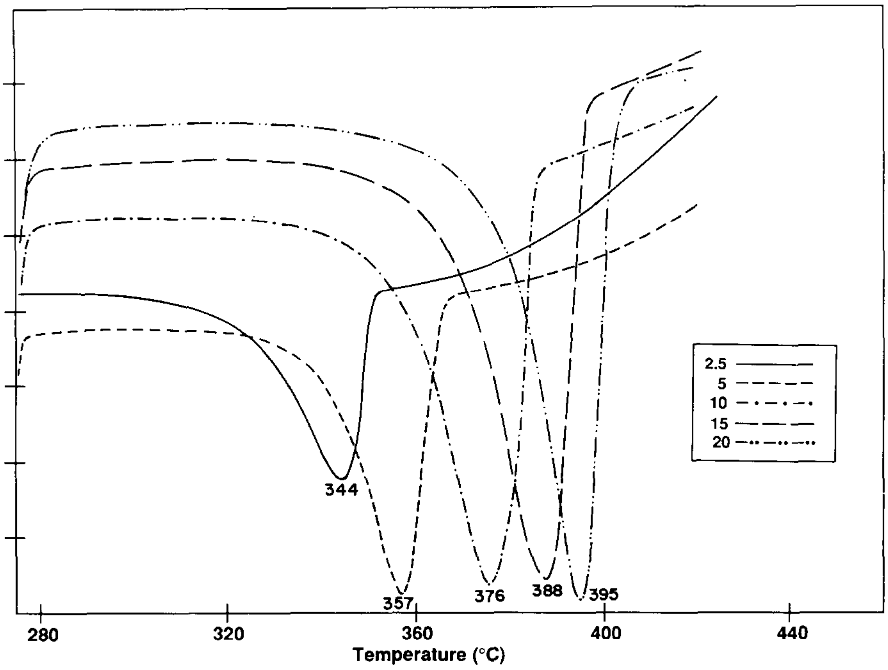


Figure 2 Cure exotherms of **6a** at different heating rates (°C min^{-1})

mol^{-1} reported for the decomposition of azoisobutyronitrile[36].

Attempts at preparing polymer films by compression moulding were unsuccessful except in the case of **6a**. Since the polymers were high molecular weight in nature, it was necessary to maintain the temperature of the plates at at least 100°C above the T_g to obtain homogeneous films. As expected, under these conditions, polymers **6b–e** underwent crosslinking reactions. Because of the relatively low T_g (175°C), it was possible to compression mould a tough, clear, bright orange coloured, finger-nail creasable film of **6a**.

The thermal stability of these polymers was further assessed by t.g.a. in both isothermal and dynamic modes. The variable temperature t.g.a. curves are shown in *Figure 3*. An examination of this figure indicates that the onset of decomposition ranges from 327 to 408°C, significantly lower than for the more conventional poly(aryl ether ketone)s and poly(aryl ether sulfone) which have higher onset temperatures (~450°C). The inferior thermal stability can once again be attributed to the presence of thermally labile azo linkages. On the other hand, polymers **6a–e** exhibit excellent char yields at 750°C, in the range 30 to 65%. This may indicate good flame-retardant characteristics associated with these polymers[37]. A weight loss of < 10% was observed by isothermal t.g.a. at 300°C after only 1 h (*Table 3*). It was highest with polymer **6d** with the tert-butyl substituent.

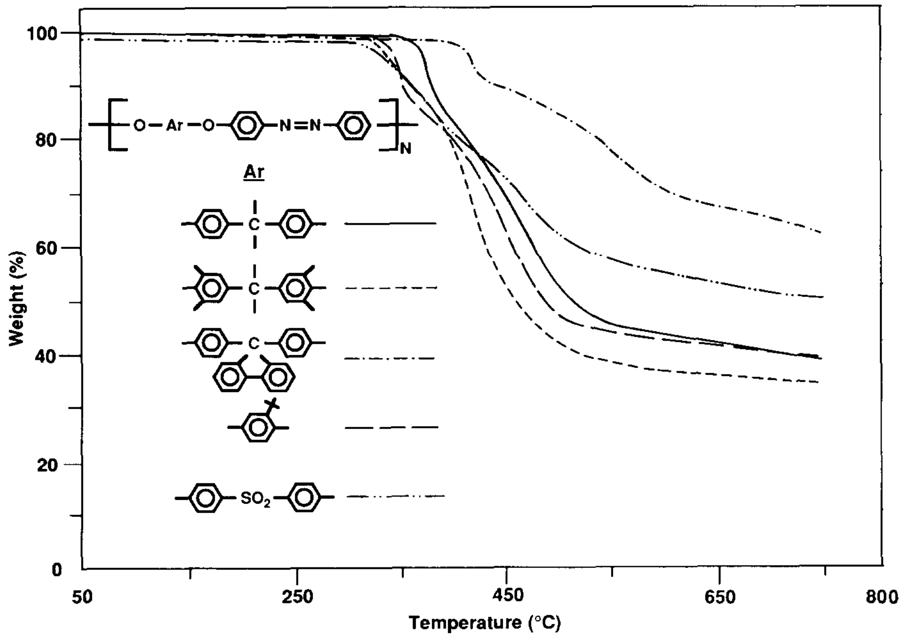


Figure 3 T.g.a. thermograms of polymers **6a–e**

Table 3 Thermogravimetric analysis (in nitrogen) of polymers **6a–e**

Polymer	Wt loss in isothermal ageing at 300°C (wt% h^{-1})	Onset of decomposition temperature (°C)	% Residue at 750°C
6a	5.8	366	39
6b	4.6	327	35
6c	1.4	408	63
6d	9.3	340	40
6e	4.0	341	54

Photo-viscosity effect

Azobenzenes are characterized by reversible transformation from the stable *trans* form to the less stable *cis* form upon ultraviolet irradiation. The intense absorption at 320 nm due to the $\pi - \pi^*$ transition decreases during this transformation. The photogenerated *cis* form undergoes thermal reversal in the dark to the *trans* form. This can be followed spectroscopically. *Figure 4* represents the spectral profile (**6a** in NMP) of thermal reversal. Similar observations have been made with azoaromatic polyureas[38] and polyamides[18]. The thermal isomerization from the photogenerated *cis* form to the *trans* form for **6a–e** in NMP was followed spectroscopically by monitoring the increase in the absorption intensity at 360 nm with time at room temperature in the dark after removal of the light source. The isomerization follows first-order kinetics and the slope of the plot of log $(A_\infty - A_t)$ against time gives the rate of isomerization, where A_∞ and A_t are absorbances at 360 nm before photoirradiation and at time t, respectively. The isomerization was followed at six different temperatures, i.e. 26, 29, 30, 33, 35 and 39°C, and the activation energies (E'_a) obtained from the Arrhenius plots are summarized in *Table 1*. An examination of these values indicates that they are essentially identical irrespective of the nature of the bisphenol used for the preparation of the polyether. Furthermore, these values are similar to those obtained for a variety of polyureas[38] and polyamides[18]. The low molecular weight model bisether, **3**, was also subjected to a similar analysis and the activation energy was determined to be 22.9 kcal mol^{-1}; a value similar to that for the higher molecular weight polymers. This is consistent with earlier observations by Paik and Morawetz for low molecular weight model amides and high molecular weight polyamides containing a smaller number of azobenzene residues[39].

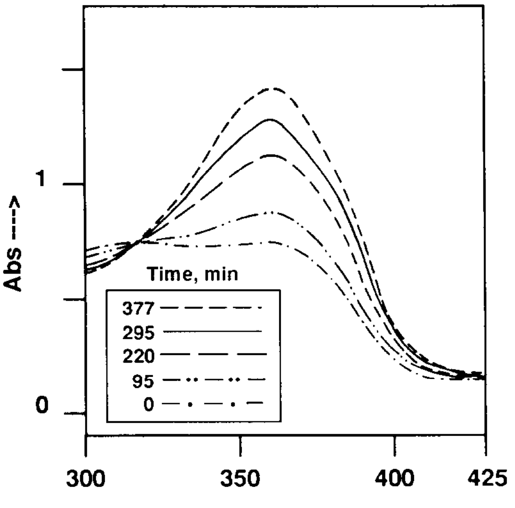


Figure 4 Absorption spectra of **6a** in NMP showing thermal recovery after irradiation

A direct consequence of the conversion of *trans* to *cis* form upon irradiation is the decrease in the intrinsic viscosity of the polymer samples. Decreases of as much as 60% with polyamides and 40% for polyureas have been reported[18,37] This concentration independent photodecrease has been ascribed to the change in conformation of the polymer sample and not from interchain interaction. The solution viscosity of polymer **6a** in NMP decreases upon irradiation to 57% of the original value at the photostationary state immediately after irradiation. The viscosity of the polymer solution returns to its initial value in the dark at room temperature in ~21 days.

CONCLUSIONS

A series of novel, high molecular weight, aromatic azoethers has been prepared. Most of these polymers afford tough, transparent, highly coloured films upon solution casting. The polymers undergo crosslinking reactions at elevated temperature and exhibit *cis–trans* photoisomerization in solution. The polymer solution viscosity, which decreases as a consequence of the *trans* to *cis* isomerization, returns slowly to its original value in the dark at room temperature.

ACKNOWLEDGEMENTS

The authors acknowledge partial support of this project by Grant #62811 made available to D.K.M. by the Department of Chemistry and the Michigan Polymer Consortium, Grant #48450 from the FRCE committee, Central Michigan University, and Grant #62845 from the Research Excellence Fund, State of Michigan. A University Research Professorship award to D.K.M. by Central Michigan University was extremely helpful. Partial support for the purchase of the GE QE-300 n.m.r. spectrometer used in this work was provided by NSF/ILI Grant #USE-8852049. Special thanks are due to Professors M. Spartz and A. Sharma for helpful discussions.

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