Pendant Functional Group Copolyether Sulfones. II. Modified Copolyether Sulfones with Aminoazobenzene Units

ANTON AIRINEI, ELENA BUTUC, VASILE COZAN

Petru Poni Institute of Macromolecular Chemistry, Aleea Grigore Ghica Vodă, 41 A, 6600 Iaşi, Romania

ABSTRACT: Modified copolyether sulfones with bulky azo pendant groups were synthesized by a polycondensation reaction of some polysulfones containing aldehyde groups with *p*-aminoazobenzene. The corresponding model compound and an azo oligomer were also prepared to compare their properties. The structure of the resulting compounds was confirmed by IR, ^{1}H-NMR spectra, and elemental analyses. The polymers were characterized by reduced viscosity, thermogravimetric analysis, and differential scanning calorimetry. The photochemical behavior of the azoaromatic chromophores was followed by UV-visible absorption spectroscopy. Two kinds of photoreactions (photoisomerization and photodecoloration) operate in these polymers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2009–2016, 2000

Key words: modified copolyether sulfones; azobenzene pendant groups; synthesis; photosensitive polymers; thermal stability

INTRODUCTION

Poly(aryl ether sulfone)s are a family of aromatic amorphous thermoplastics that possess unique high performance properties as engineering materials. The aromatic polysulfones are recognized as polymers that have a variety of desirable characteristics including high thermooxidative and dimensional stability, excellent mechanical properties, and good hydrolytic stability.[1,2] They have been extensively used as membrane materials, electrical isolating components, and so forth.

Aromatic polysulfones are sometimes functionalized in order to extend the range of their utility. The principal methods of homogeneous modification of polysulfones are sulfonation,[3,4] halomethylation,[5,6] lithiation,[7,8] carboxylation,[9] bromination,[7] and aminomethylation.[10]

Functional aromatic polyether sulfones containing pendant groups have received much attention in the last 16 years.[11–14] Thus, polysulfones with pendant aldehyde groups have been obtained by direct oxidation of the halomethylated polysulfone benzyl halide groups with dimethyl sulfoxide or tetrabutyl ammonium dichromate.[5] Also, in our previous work new functional copolyether sulfones with pendant aldehyde groups were synthesized by the classical polycondensation reaction between bis(4-chlorophenyl)sulfone and different bisphenols.[15]

These chemical modifications of aromatic polysulfones may allow us to obtain new polysulfones containing photoreactive groups along the polymer main chain. The incorporation of the photosensitive pendant units in the polymer backbone was expected to affect the properties of polymers. The photoresponsive polysulfones are most widely used as membranes, where the transport can be controlled by light.[14,16]

Until now there has been little information concerning aromatic polysulfones bearing pendant azobenzene photosensitive groups. There are also few reports on the investigation of the behavior of some azoaromatic compounds dispersed in a polysulfone matrix.[17–19]

The present article describes the synthesis and characterization of new copolyether sulfones containing a photoreactive azobenzene chromophore in a side chain of the polysulfone backbone. Some model compounds with the same chromophore were prepared. The photobehavior in solution of these compounds was followed by absorption UV-visible (UV-vis) spectroscopy.

EXPERIMENTAL

Materials

5,5′-Methylene bis-salicylaldehyde (**1**) was prepared as described in the literature.[20] 4-Amino-azobenzene (Merck, **2**) was used as obtained. The oligomer (**3**) was synthesized by treating salicyl-aldehyde with 37% formaldehyde (molar ratio 1:1) under basic conditions according to methods published previously.[21,22] The preparation of the copolyether sulfones with aldehyde pendant groups (**4, 5**) was based on the polycondensation reaction of bis(4-chlorophenyl)sulfone and bisphenols such as 5,5′-methylene bis-salicylaldehyde and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) in the presence of dimethyl sulfoxide (DMSO), chlorobenzene, and anhydrous potassium carbonate.[15] The DMSO (Merck), chloroform (Merck), benzene (Chimopar Bucureşti), and methanol (Chimopar Bucureşti) were used as received.

General Equipment

The UV-vis spectra were obtained on a Carl Zeiss Jena SPECORD M42 spectrophotometer in chloroform solutions using 10-mm quartz cells fitted with poly(tetrafluoroethylene) stoppers. The IR absorption spectra were recorded on a Carl Zeiss Jena SPECORD M80 spectrophotometer with KBr pellets. The ^{1}H-NMR spectra were recorded on a Jeol C60-HL spectrometer using CDCl$_3$ or DMSO-d_6 as solvents and tetramethylsilane as an internal standard. The softening points were measured with a Gallenkamp hot-block melting point apparatus. Thermogravimetric (TG) measurements were made at a heating rate of 12°C/

min in air using a MOM derivatograph. Differential scanning calorimetry (DSC) was performed with a Mettler TA DSC 12E instrument with a heating rate of 10°C/min. The second heating cycle was used to determine the glass-transition temperature (T_g). Reduced viscosity determinations were carried out in N-methyl-2-pyrrolidone (NMP) at 25°C with a sample concentration of 0.2%.

UV irradiations were performed with a 350-W high-pressure mercury arc lamp at room temperature in the π–π* absorption band of the azo chromophore, and a suitable glass filter (365 nm) was used to obtain the irradiation light. The initial absorbance of the samples under study in the absorption band maximum was kept between 0.9 and 1.0.

Chemical Syntheses

Model Compound (I)

A mixture of 5,5′-methylene-bis-salicylaldehyde (**1**, 2.5 g, 0.01 mol), 4-aminoazobenzene (**2**, 3.95 g, 0.02 mol), and benzene (50 mL) were refluxed under stirring in a 250-mL round-bottomed flask (fitted with a Dean–Stark trap) until the calculated amount of water was collected. The reaction mixture was cooled and the crude product was then filtered, dried, and recrystallized from methanol (m.p. 259–264°C).

ANAL. Calcd for C$_{39}$H$_{30}$N$_6$O$_2$: C, 76.20%; H, 4.88%; N, 13.67%. Found: C, 75.97%; H, 4.73%; N, 14.33%. IR (KBr, cm^{-1}): 3450 (OH); 1625 (C=N); 1600, 1570, 1495 (C=C, aromatic); 855, 825 (aromatic ring). ^{1}H-NMR (CDCl$_3$, ppm): δ 10.82 (s, 2H, OH); 8.60 (s, 2H, CH=N); 8.25–6.80 (m, 24 H, aromatic); 3.97 (s, 2H, CH$_2$).

Preparation of Azo Oligomer (II)

Oligomer (**3**, 1.34 g, 0.01 mol), 4-aminoazobenzene (3.15 g, 0.016 mol), and benzene (50 mL) were added into a 250-mL flask fitted with a magnetic stirrer and a Dean–Stark trap. Previously the reaction mixture was stirred vigorously and allowed to react for 8 h at room temperature. Then the temperature was increased to 80°C and the system was maintained under reflux until the calculated amount of water was collected. The reaction mixture was cooled to room temperature, poured into methanol (50 mL), and filtered. The product was heated in methanol under reflux for 0.5 h. After filtration and washing thoroughly

with methanol, the final product (**II**) was dried at 50°C in a vacuum for 20 h.

ANAL. Calcd for $C_{20}H_{15}N_3O$): C, 76.66%; H, 4.82%; N, 13.41%. Found: C, 76.47%; H, 4.95%; N, 10.78%. IR (KBr, cm^{-1}): 3450 (OH); 1625 (C=N); 1580, 1500 (C=C, aromatic); 1280 (phenolic OH, in-plane bending), ^{1}H-NMR (CDCl$_3$, ppm): δ 8.55 (s, 1H, CH=N); 8.20–6.70 (m, 11H, aromatic); 3.95 (s, 2H, CH$_2$).

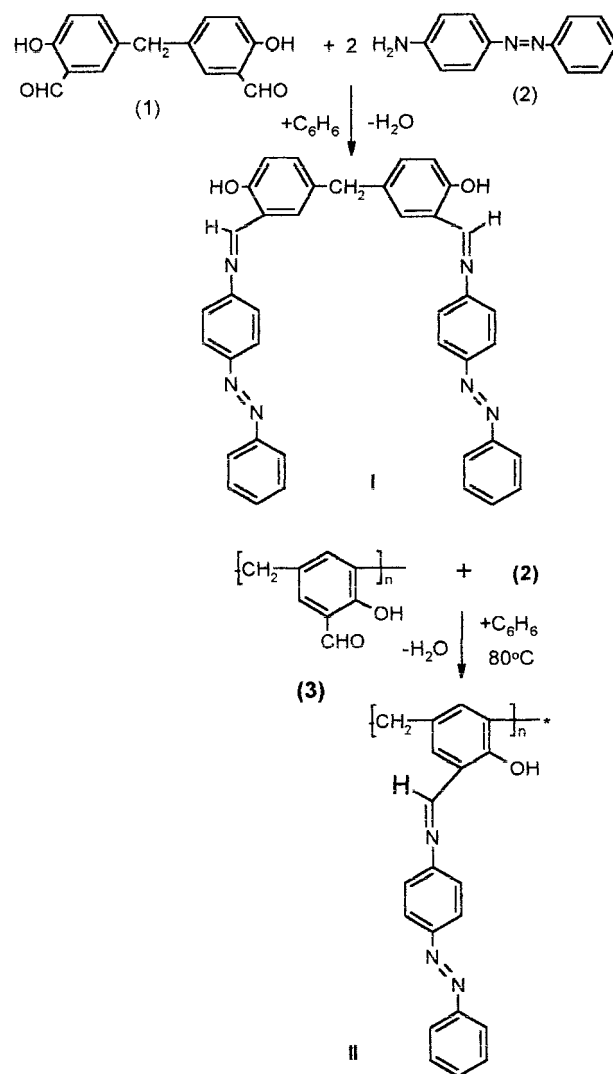### *Preparation of Azo Copolyether Sulfones (III, IV).*

These polymers were synthesized according to the same general procedure. A typical synthesis was conducted in a 250-mL round-bottomed flask equipped with a magnetic stirrer and Dean–Stark trap. A detailed synthetic method used to obtain polymer **III** is described below. The flask was charged with a mixture of polysulfone (**4**, 5.43 g, 0.01 mol), DMSO (50 mL), 4-aminoazobenzene (4.95 g, 0.026 mol), and chlorobenzene (20 mL). The reaction mixture was stirred at room temperature for 10 h and then at 40°C for 3 h. The purification procedure was similar to that described above for the azo oligomer. **III;** IR (KBr, cm^{-1}): 1625 (C=N); 1590, 1495 (C=C, aromatic); 1300 (SO$_2$, asymmetric); 1250 (aromatic ether); 1160 (SO$_2$, symmetric); 840 (aromatic ring). ^{1}H-NMR (CDCl$_3$, ppm): δ 8.60 (s, 2H, CH=N); 8.10–6.70 (m, 32 H, aromatic); 3.95 (s, 2H, CH$_2$). **IV:** IR (KBr, cm^{-1}): 1630 (sh, C=N); 1590, 1500 (C=C, aromatic); 1300 (SO$_2$, asymmetric); 1250 (aromatic ether); 1160 (SO$_2$, symmetric); 875, 840, 810 (aromatic ring).

RESULTS AND DISCUSSION

5,5′-Methylene bis-salicylaldehyde (**1**) was used as the starting material for the synthesis of the new copolyether sulfones.[15] The preparation of model compound **I** and azo oligomer **II** was performed by a synthetic procedure as represented in Scheme 1. The azobenzene modified polysulfones **III** and **IV** were obtained by continuous azeotropic solution condensation of the parent polysulfones bearing aldehyde pendant groups with 4-aminoazobenzene in the DMSO/chlorobenzene system (Scheme 2).

The yields and some properties of the products are listed in Table I. The synthesis of azo oligomer **II** was readily performed in benzene, because of the good solubility of the starting oligomer. The

Scheme 1 The preparation of model compound **I** and azo oligomer **II**.

DMSO/chlorobenzene system was chosen as the solvent in the synthesis of polymers **III** and **IV**, because copolyether sulfones **4** and **5** were insoluble in benzene. The resulting polymers were soluble in chloroform, dichloromethane, DMSO, and dimethylformamide, and insoluble in methanol, benzene, and toluene. The reduced viscosities of the azo polymers determined in NMP at 25°C are given in Table I and range from 0.1 to 0.2 dL/g, which is lower than those of the starting polysulfones.

The thermal properties of the compounds under study were monitored by DSC and TG analysis. DSC measurements revealed that while the model compound (**I**) had a melting temperature
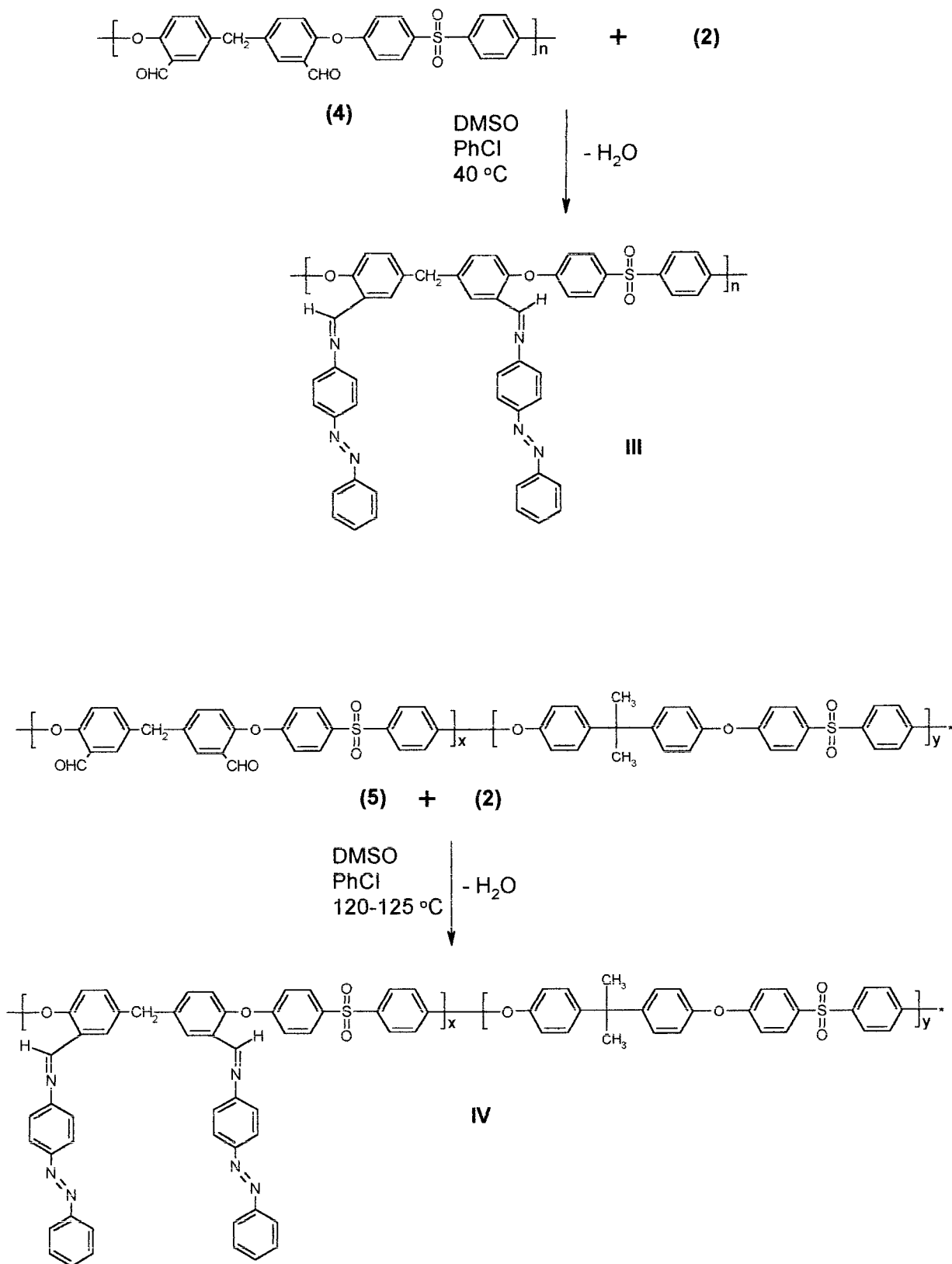
Scheme 2 The preparation of azo copolyether sulfones.

Table I   Analytical Data of Model Compound and Azopolymers

Sample	Yield (%)	Softening Range (°C)	η_{red} (dL/g)	T_g^{DSC} (°C)	λ_{max} (nm)	Temp. Corresponding to wt. loss (°C)	
						10%	50%
I	95	259–264	—	255[a]	371.0	313	640
II	85	140–155	0.10	123	369.5	350	650
III	70	148–162	0.17	124	371.0	380	560
IV	78	180–220	0.20	170	369.5	383	570

[a] Melting point.

(255°C), the other products **II–IV** exhibited glass transition temperatures correlated with η_{red} values (Table I). The T_g values were arranged in the series of **II** < **III** < **IV**, which was probably due to the increase of the chain rigidity for polymer **IV** as compared to polymers **II** and **III**. Weight loss–temperature profiles determined from TG data are shown in Figure 1 for the azo model compound and polymers **II–IV**. The temperatures corresponding to 10 and 50% weight loss are also given in Table I. The results of TG analysis evidenced that the polymers showed no significant weight losses before 230°C and the azo model exhibited a higher initial decomposition temperature than the azo polymers. The incorporation of the ami-noazobenzene side groups along the polysulfone backbone decreased the thermal stability of these polymers relative to the polysulfones containing carbonyl pendant groups.[15]

The thermal degradation occurs in a two-step process for these samples. The polymer decomposition temperature was determined for a temperature at which 10% weight loss was observed. This temperature decreases in the following order; azo model **I** > oligomer **II** > **III** > **IV**. The weight loss in the first stage of degradation is greater for the azo model (16.5%) and becomes smaller for the polymers (5.0% for **III** and **IV**, 11.5% for **II**).

The photochemical behavior of the azo model and polymers **II–IV** was studied in chloroform solutions by means of UV-vis absorption spectroscopy. The electronic absorption spectra of these compounds containing azobenzene moieties are characterized by an absorption band at about 370 nm (Table I), which is assigned to a very intensive $\pi-\pi^*$ transition of the azobenzene chromophore.[23]

Similar spectral changes were observed for azo model **I** and azo oligomer **II** when they were exposed to 365-nm light. The UV irradiation of these compounds determines a small decrease of the $\pi-\pi^*$ absorption band intensity, corresponding to a conversion of about 15% after 300 s of irradiation. At the same time, the maximum of the $\pi-\pi^*$ absorption band is shifted to shorter wavelengths of 368.5 (azo model) and 364 nm (**II**), respectively. However, the system does not achieve a photostationary state because at continued irradiation the intensity of this absorption band will increase again. Also, the thermally induced return (66°C) takes place in 40 min with the restoring of the initial absorption band.
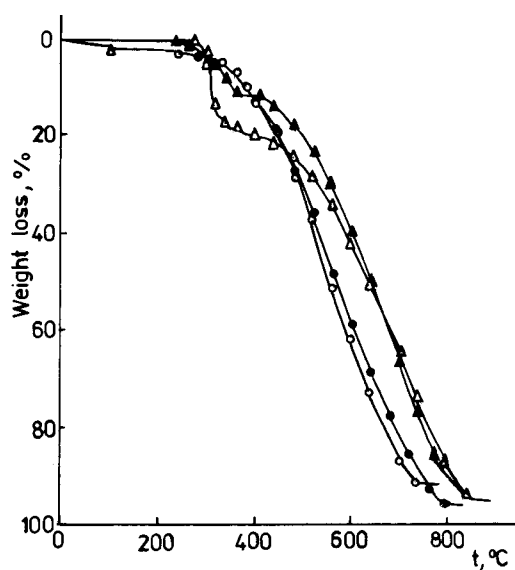

Figure 1 Thermogravimetric traces of model compound **I** and polymers **II–IV**: (△) **I**, (▲) **II**, (○) **III**, and (●) **IV**.
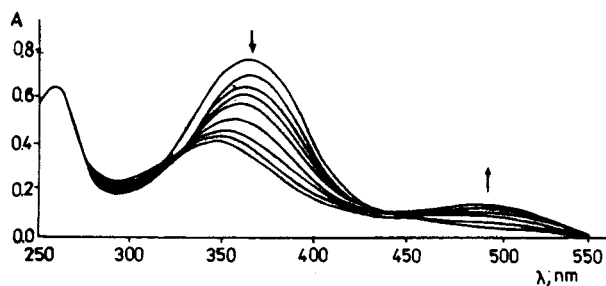
Figure 2 The change in UV spectral characteristics during UV irradiation of oligomer **II** at different intervals of time; the curves correspond to irradiation times of 0, 15, 34, 48, 63, 100, 144, 192, and 260 min.

Figure 3 The dependence of the relative absorbance on irradiation time for azo model **I** and azo oligomer **II**.

By standing in the dark for 24 h, the electronic absorption spectra of **I** and **II** have a new pattern. Thus, the $\pi-\pi^*$ absorption band becomes narrower and is located now at 367 nm for **I** and 365 nm for the azo oligomer. A new absorption band appears at 260 nm in the absorption spectra of both derivatives. The absorption band at about 365 nm is also sensitive to UV irradiation in both products. During UV exposure this band diminishes in intensity and an absorption band at longer wavelengths (around 490 nm) is observed (Fig. 2). The absorption band at longer wavelengths is due to an $n-\pi^*$ transition of the azobenzene unit. At the same time, the UV irradiation of the chloroform solutions of **I** and **II** results in a blueshift of the absorbance at 365 nm, as seen in Figure 2. The intensity of the absorption band at 490 nm increases until 150 min of irradiation and after 220 min this band becomes a shoulder and decreases in intensity. At high irradiation times the absorption band at 365 nm decreases less and less in intensity. During UV exposure the intensity of the absorption band at about 260 nm is practically not modified.

Following the plots of relative absorbance, A/A_0 (where A_0 is the absorbance before irradiation and A is the absorbance after irradiation at time t), as a function of time, the photolysis proceeds almost identically in the two cases (Fig. 3), suggesting no significant influence of the polymer chain structure on the phototransformation of the azobenzene chromophore. The plot is divided into two parts corresponding to different stages of the photoprocess. The first stage may be ascribed to a trans-cis photoisomerization process and in the second stage a photodecoloration process occurs at a very slow rate. The thermal cis-trans recovery does not take place because maintaining the
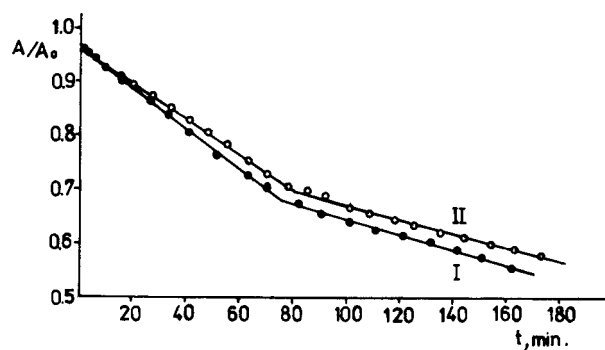
sample at 66°C for 980 min does not change the spectral pattern.

On irradiation at 365 nm, the intensity, shape, and position of the absorption bands of azo polymers **III** and **IV** were modified. The progress of the photoprocess determined by the photochemical transformations of the azochromophore as a function of irradiation time is shown in Figure 4 for the copolyether sulfone **III**. There is a decrease in the intensity of the absorption band at about 370 nm that is due to the $\pi-\pi^*$ transition and an evident blueshift of this band. The fact that no well-defined isosbestic points appeared (Fig. 4) indicates that during UV irradiation of the chloroform solution of **III** at least two different photoprocesses can occur. Thus, at the beginning a trans-cis photoisomerization reaction takes place, when approximately 50% of the azobenzene moieties occupy the higher energy cis configurations. The absorbance of the $n-\pi^*$ band
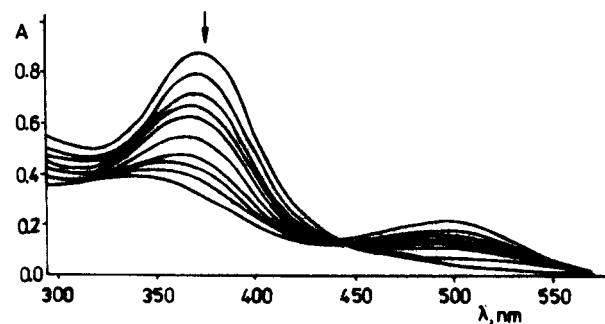

Figure 4 The change in the electronic absorption spectra during UV irradiation of azo chromophores in copolyether sulfone **III**; the curves correspond to irradiation times of 0, 1, 6, 10, 15, 27, 43, 55, 80, and 125 min.
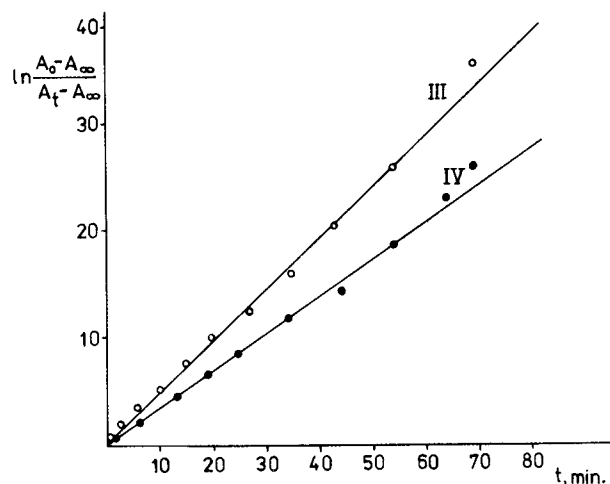
Figure 5 First-order plots for trans-cis photoisomerization of azo copolyether sulfones in chloroform solution.

at 495 nm reaches a maximum for conversion of 50%, and then it decreases during continued UV irradiation.

In the case of polysulfone **IV** a retardation in the formation of cis isomers was observed, which was due to restrictions in the chromophore mobility within the free volume of the microenvironment of the azobenzene chromophore. Table I shows that polysulfone **IV** has a high T_g and the motion of azochromophores becomes more difficult because of less free volume available for the isomerization process. When irradiation was stopped at the end of the first stage and the samples were kept at 63°C, the absorbance of the $\pi-\pi^*$ band of these compounds did not reach the starting value before irradiation. The recovery degree corresponds to 81.0 and 74.0% for polysulfones **III** and **IV**. The kinetic photoisomerization data were fitted to a monoexponential decay (Fig. 5). The rate constants of the photoisomerization of azochromophores were found to be 5.71 and 7.90 10^{-4} s^{-1} for copolyether sulfones **III** and **IV**.

The gradual decrease in intensity of the absorption bands due to $\pi-\pi^*$ and $n-\pi^*$ transitions, as well as their shift to shorter wavelengths at the later stages of photolysis, can be attributed to photodecoloration reactions occurring in these polymers. However, the rate of this process is very slow. After 200 min of 365-nm light irradiation, the position of the $\pi-\pi^*$ absorption band was located at 336 nm and a new absorption band appeared at 256 nm for polysulfone **III**. The same

photodecoloration process also took place for polysulfone **IV**, but after 100 min of UV exposure the $\pi-\pi^*$ absorption band became a shoulder. The UV-vis absorption spectra of the irradiated copolyether sulfones were unchanged by keeping them at 65°C for different times, suggesting that the observed photodecoloration process is irreversible even at higher temperatures.

CONCLUSIONS

Photoreactive modified copolyether sulfones bearing azobenzene pendant groups were prepared in good yields by polycondensation. A corresponding low molecular weight model compound and an azo oligomer were also synthesized. Their photoinduced transformations in dilute solutions were monitored by electronic absorption spectra under 365-nm light irradiation. The trans-cis photoisomerization in azo copolyether sulfones obeyed the first-rate law. The azobenzene modified polymers possessed relatively high glass-transition temperatures and displayed good thermal stabilities up to about 350–380°C.

REFERENCES

1. Robeson, L. M.; Crisafulle, S. T. J Appl Polym Sci 1983, 28, 2925.
2. El-Hibri, M. J.; Nazabal, J.; Equiazabal, J. I.; Arzak, A. In Handbook of Thermoplastics; Olabisi, O.; Ed.; Dekker: New York, 1997, p 893.
3. Nolte, R.; Ledjeff, K.; Bauer, M.; Muelhaupt, R. J Membr Sci 1993, 83, 211.
4. Shibuya, N.; Porter, R. S. Polym Mater Sci Eng 1992, 67, 421.
5. Warshawsky, A.; Kahana, N.; Deshe, A.; Gottlieb, H. E.; Arad-Yellin, R. J Polym Sci Part A Polym Chem 1990, 28, 2885.
6. Avram, E.; Butuc, E.; Luca, C.; Druţă, I. J Macromol Sci Pure Appl Chem 1997, A34, 1701.
7. Guiver, M. D.; Kutowy, O.; ApSimon, J. W. Polymer 1989, 30, 1137.
8. Hinke, E.; Staude, E. J Appl Polym Sci 1991, 42, 2951.
9. Lau, W. W. Y.; Guiver, M. D.; Matsuura, T. J Appl Polym Sci 1991, 42, 3215.
10. Kahana, N.; Arad-Yellin, R.; Deshe, A.; Warshawsky, A. J Polym Sci Part A Polym Chem 1990, 28, 3303.
11. Mohanti, D. K.; Sachdeva, Y.; Hedrick, J. L.; Wolfe, J. F.; McGrath, J. E. Polym Prepr 1984, 25(2), 19.

12. Park, S. J.; Lyle, G. D.; Mercier, R.; McGrath, J. E. Polym Bull 1992, 29, 477.

13. Ueda, M.; Toyota, H.; Ouchi, T.; Sugiyama, J.; Yonetake, K.; Masuko, T.; Takero, T. J Polym Sci Part A Polym Chem 1993, 31, 853.

14. Ratner, J.; Kahana, N.; Warshawsky, A.; Krongauz, V. Ind Eng Chem Res 1996, 35, 1307.

15. Cozan, V.; Butuc, E.; Stoleriu, A.; Caşcaval, A.; Ni, Y.; Ding, M. J Macromol Sci Pure Appl Chem 1995, A32, 1067.

16. Koch, T.; Ritter, H. Macromol Chem 1993, 194, 1483.

17. Diakoumakos, C. D.; Mikroyanidis, J. A. J Appl Polym Sci 1997, 64, 921.

18. Matsuoka, Y.; Suzuki, A. Kobunshi Ronbunshu 1994, 51, 442.

19. Lor, S. K.; Hiraoka, H.; Yu, P.; Cheng, L. T.; Wong, G. K. L. J Mater Res 1995, 10, 2693.

20. Marvel, C. S.; Tarkoy, N. J Am Chem Soc 1957, 79, 6000.

21. Patel, B. K.; Patel, M. M. Angew Makromol Chem 1989, 165, 47.

22. Patel, B. K.; Patel, M. M. J Indian Chem Soc 1988, 65, 651.

23. Rau, H. In Photochemistry and Photophysics; Rabek, J. F., Ed.; CRC Press: Boca Raton, FL, 1990; Vol. 2, 119.