

Azoxyaromatic polyethers

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Moderate to high molecular weight azoxyaromatic polyethers have been prepared by the reactions of four bisphenoxides with 4,4'-difluoroazoxybenzene in *N*-methylpyrrolidinone. The polymers are amorphous and undergo crosslinking reactions at elevated temperatures. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Aromatic polyethers have been investigated extensively by both industrial and academic laboratories^{1–3}. Nucleophilic aromatic substitution reactions of activated bisphenoxides with bisphenoxides have been used as one of the preparative techniques for the synthesis of these polyethers^{4–11}. The activation of the bisphenoxide is achieved by the introduction of an electron-withdrawing group including sulfone, ketone¹², phosphineoxide¹³, fused heterocycles, perfluoroalkyls¹⁴ and imine, azine^{15,16} in *para* orientation to the halogen atoms. Johnson *et al.* had identified the azo group to possess the necessary activating influence on the halogens towards nucleophilic aromatic substitution reactions⁴. However, high molecular weight polymers were not prepared and detailed discussion regarding polymer properties was lacking. Recently we have reported the syntheses and characterization of azoaromatic polyethers¹⁷. These polymers are photoresponsive. They undergo *trans*–*cis* isomerization in solution when irradiated with light. This results in a dramatic drop in the solution viscosity of the polymer. The viscosity reverts to its original value in the dark. Furthermore, the azoaromatic polyethers undergo crosslinking reactions at elevated temperatures with the elimination of nitrogen gas.

The synthesis and characterization of related azoxyaromatic polyethers have not been reported. On the other hand, a plethora of liquid crystalline azoxyaromatic polyesters have been prepared and studied extensively¹⁸. The azoxy group is expected to behave in a somewhat similar fashion to the azo group. In addition, aromatic azoxy compounds are known to undergo an interesting photochemical transformation in which the oxygen atom of the azoxy group migrates to produce a phenolic group¹⁹. This would allow one to prepare azoxyaromatic polyethers and to convert them subsequently to azoaromatic polyethers with pendant phenolic substituents. This is significant because the phenolic groups can be used for metal coordination or a variety of other post-reactions. We now report the

preparation, characterization and photochemical rearrangements of azoxyaromatic polyethers.

Results and discussion

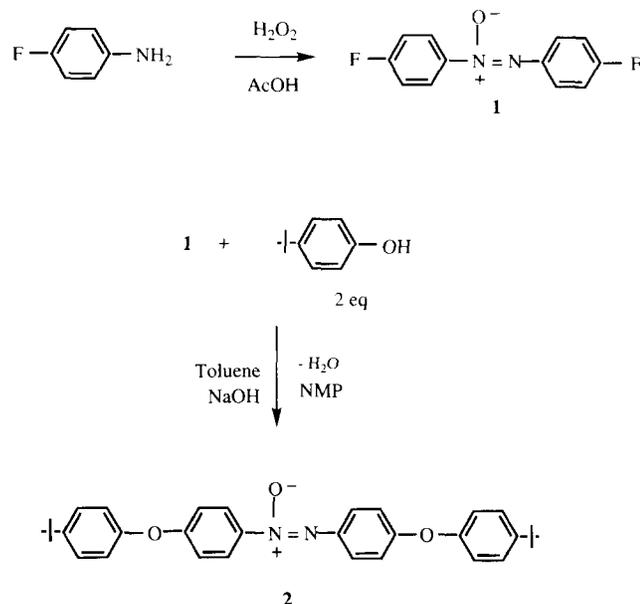
The bisfluoride, 4,4'-difluoroazobenzene was used as a suitable monomer for the preparation of a series of high molecular weight polyethers¹⁷. Only low molecular weight polymers were formed when the corresponding dichloride was used due to competing side reactions¹⁷. The difluoroazoxy monomer, **1**, was synthesized by the oxidation of 4-fluoroaniline with hydrogen peroxide in glacial acetic acid solution (*Scheme 1*). Compound **1** was purified by column chromatography followed by recrystallization from hexanes. Model compound studies were undertaken to establish the feasibility of using **1** as a suitable monomer for the preparation of high molecular weight azoxyaromatic polyethers. Reactions of 4-*tert*-butylphenol (2 eq.) with **1** in *N*-methylpyrrolidinone (NMP) in the presence of excess anhydrous K₂CO₃ at 140°C resulted in the formation of a series of products. A controlled reaction of **1** with K₂CO₃ under similar reaction conditions led to complete loss of the difluoride. The desired model ether, **2** (*Scheme 1*), could be prepared by the reactions of 4-*tert*-butylphenoxide anion with **1** in (NMP) at a reaction temperature of 130°C. The reaction was conducted for 48 h. An aqueous solution of sodium hydroxide was used to prepare the phenoxide anion prior to the addition of **1** to the reaction mixture. Toluene was used to azeotropically dehydrate the system. At higher reaction temperatures (> 140°C), besides the bisether, other side products were obtained. As in case of the azoaromatic polyethers, the desired model bisether was not obtained in quantitative yield when 4,4'-dichloroazoxybenzene was used instead of the bisfluoride. The ¹³C n.m.r. spectrum of **2** is shown in *Figure 1*. An examination of the figure indicates that the spectrum contains nineteen absorbances. It was possible to assign the absorbances to the various carbon atoms based on substituent chemical shift constants (CSCs)^{20,21}.

Polymerizations‡ of **1** with a variety of bisphenols were performed under the same conditions as the model reactions. The polymers (**4a–d**) were coagulated in

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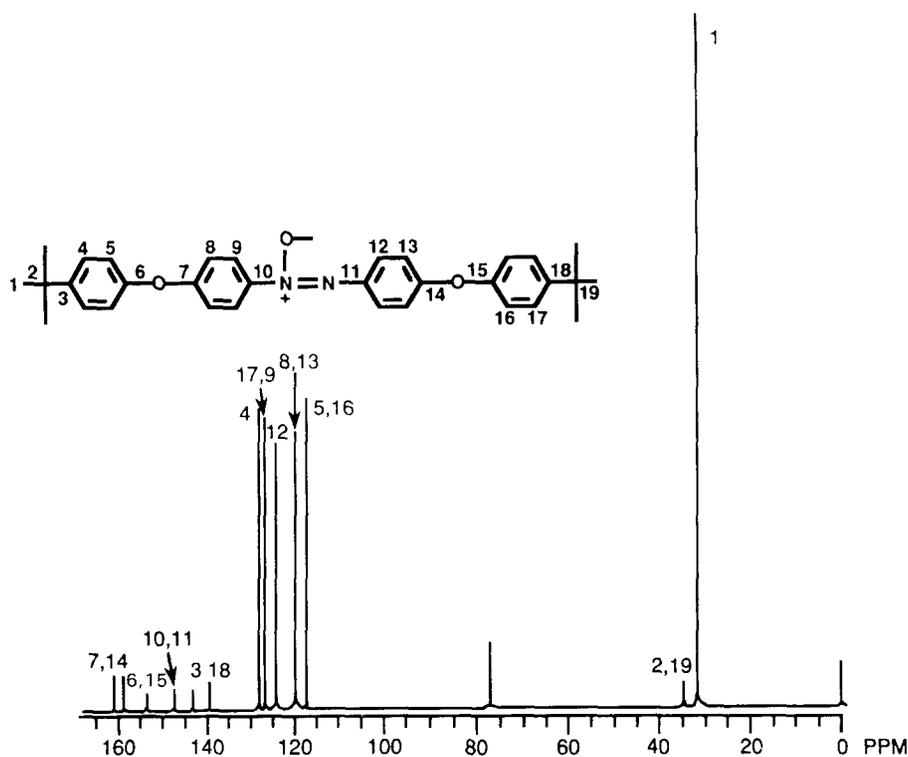
acetone, filtered. The polymers were then extracted in a Soxhlet apparatus, first with acetone, then with water and finally with acetone. High molecular weight polymers were formed when Bisphenol-A (**3a**),



Scheme 1

Tetramethylbisphenol-A (**3b**), 3,3'-dihydroxybiphenyl (**2c**) and Bisphenol-F (**3d**) were used. On the other hand, only oligomeric products were obtained when either rigid bisphenols such as hydroquinone or 4,4'-dihydroxybiphenyl or a weak nucleophile generated from 4,4'-dihydroxydiphenylsulfone were used under these reaction conditions. As expected from the model compound studies, attempts at conducting these polymerizations at elevated reaction temperatures led to discoloration of the reaction mixture and noticeable increase in the solution viscosity were not observed.

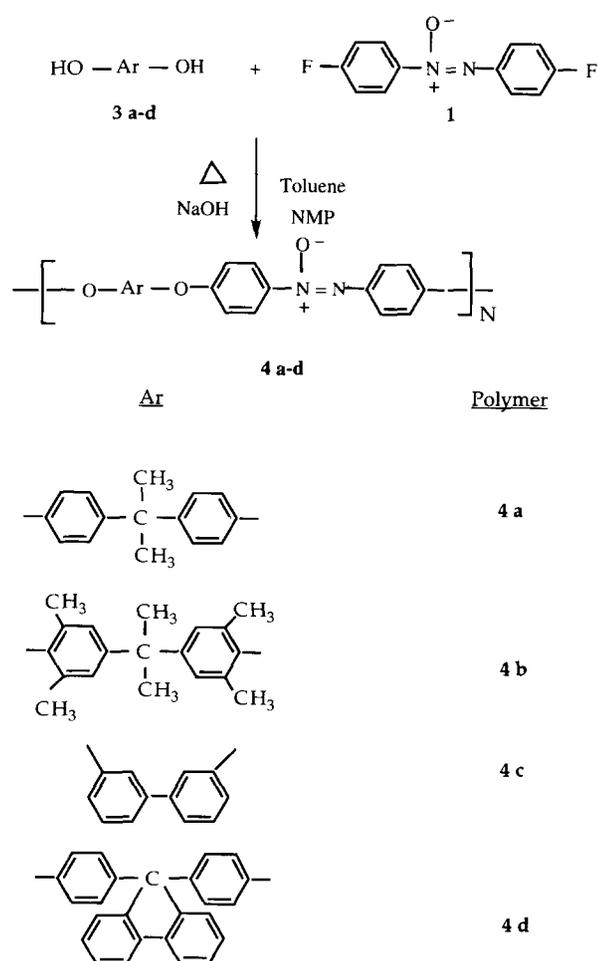
The azoxyaromatic polyethers (**4a-d**) were soluble in a variety of organic solvents including chloroform, dichloromethane and tetrahydrofuran (THF). It was possible to obtain transparent, coloured and tough films upon solution casting. The high to moderate molecular weight nature of these polymers was assessed by intrinsic viscosity measurements in chloroform (*Table 1*). The glass transition temperatures (T_g s) of these polymers ranged from 125 to 256°C. As expected, polymer **4d**, derived from Bisphenol-F, exhibited the highest T_g , consistent with the trend observed with azoaromatic polyethers¹⁸. Furthermore, as in case of the azoaromatic polyether, polymers **4a-d** undergo crosslinking reactions at elevated temperature. Samples recovered after the first heat were highly discoloured and they were insoluble in solvents in which the virgin polymers were soluble. In contrast to the azoaromatic polyethers, polymers **4a-d**

Figure 1 ^{13}C n.m.r. spectrum (CDCl_3) of model azoxyaromatic compound, **2**

‡ The reaction vessel consisted of four necked round-bottomed flask fitted with an overhead stirrer, a thermometer, a nitrogen inlet and a Dean-Stark trap fitted with a condenser. Bisphenol-A (6.1942 g, 0.02717 mol) was added to the reaction vessel along with 50 ml of toluene. The reaction mixture was warmed with an external oil bath until complete dissolution occurred. Aqueous sodium hydroxide solution (25 ml, 0.05433 mol) was added to the reaction mixture using a volumetric pipette. The reaction mixture was heated to reflux (112°C). Water, the by-product of the reaction mixture, was continuously removed via the Dean-Stark trap. The reflux temperature was maintained for 4 h. The bisphenoxide precipitated out of the reaction mixture. The reaction mixture was cooled to room temperature and 4,4'-difluoroazoxybenzene (6.3572 g, 0.0271 mol) was added to the reaction vessel along with 60 ml of NMP. The reaction mixture was then heated to 135°C for 96 h. The viscosity of the reaction mixture increased gradually. It was then cooled, diluted with chloroform, filtered and the filtrate was precipitated from a 10-fold excess of methanol. The precipitated polymer was filtered, and the residue was extracted with acetone, water and then acetone in a Soxhlet apparatus. The polymer was finally dried in a vacuum oven at 80°C for 2 days.

Table 1 Intrinsic viscosity values, glass transition temperatures, exotherm peak temperatures, T_p and T_p' and activation energies, E_a and E_a' (crosslinking) values for polymers **4a–d**

Polymer	η^a (dl g ⁻¹)	T_g^b (°C)	T_p^c (°C)	T_p'	E_a^d (kcal mol ⁻¹)	$E_a'^e$ (kcal mol ⁻¹)
4a	0.52	152	328	363	34.6	36.1
4b	0.45	220	321	340	32.7	36.1
4c	0.30	125	319	362	33.3	35.2
4d	0.36	256	335	384	40.5	47.4

^a Solvent chloroform at 25°C^b Second heating; heating rate 10°C min⁻¹^c Heating rate 10°C min⁻¹^d Mean = 35.2 kcal mol⁻¹; SD = 3.5^e Mean = 38.7 kcal mol⁻¹; SD = 5.8**Scheme 2**

exhibited two cure exotherms. The reasons for this behaviour are not clear at present. The T_g s and the differential scanning calorimetry (d.s.c.) exotherm peak temperatures are displayed in *Table 1*. Activation energies (*Table 1*) associated with each of the cure exotherms were calculated from the peak temperatures by conducting the d.s.c. experiments at five different heating rates²².

The photochemical transformation of the model bisether **2–5** (*Scheme 3*) was conducted in solution. A 10% (w/v) solution of **2** in a 90/10 (v/v) mixture NMP and glacial acetic acid was irradiated with a 400 W mercury arc lamp. During irradiation, the solution was

cooled with a cold finger. Conversion of the azoxy to the azo group could be achieved after 21 days. The desired product was isolated in 89% yield after percolating the crude product through a silica gel column with dichloromethane to remove base line impurities. The presence of the phenolic hydroxyl group in **5** was ascertained by infra-red (i.r.) (weak, broad, ~ 3400 cm⁻¹). The ¹H n.m.r. spectra of **4** and **5** are shown in *Figure 2*. The assignments of absorbances to the various hydrogen atoms were made after conducting ¹H–¹H COSY and ¹H–¹³C correlation spectral analyses. An examination of the figure indicates the loss of a set of absorbances at 8.25 ppm (*Figure 2a*) due to H_c and H'_c (compound **4**) and the appearance of absorbances at 13.4 ppm due to the phenolic hydroxyl group, at 7.8 ppm (*Figure 2b*) due to H_c and H'_c, at 6.7 ppm due to H_d and at 6.5 ppm due to H_{d'} (compound **5**). A considerable longer period of irradiation time (42 days) was necessary to convert the azoxy groups of polymer **4a** to azo groups (*Scheme 4*) under similar conditions. The progress of the reaction was monitored by ¹H n.m.r. spectroscopy. Samples were removed periodically and after precipitation from a non-solvent, spectra were obtained. The ¹³C n.m.r. spectrum of the resulting polymer, **5a**, contained a large number of absorbances, significantly higher than the number based on the expected repeat unit. The product was powdery in nature and exhibited an intrinsic viscosity value of 0.07 dl g⁻¹ (chloroform, 25°C), which is considerably lower than the value of 0.52 dl g⁻¹ (chloroform, 25°C) for polymer **4a**. This suggests that under these reaction conditions the polymer backbone undergoes chain scission. This was further confirmed by gel permeation chromatography (g.p.c.) analysis of polymer **4a** and product **5a** in THF. The chromatogram of polymer **4a** was unimodal, in contrast to **5a** which was multimodal. Furthermore **4a** eluted at a lower volume than **5a**. Thus we were unable to achieve quantitative transformations without backbone degradation under these reaction conditions. It is likely that the chain scission under these conditions proceeds with the elimination of the azoxy moieties via radical intermediates. Acetic acid, a good source of a hydrogen radical, was used as the cosolvent. We believe it would be possible to substitute acetic acid with another polar cosolvent to suppress chain scission. We have attempted to irradiate a solid film of **4a** to bring about azoxy to azo transformation reactions. However, detectable conversion (¹H n.m.r.) was not observed. Reaction variables, including the solvent system and the time period of irradiation, are being modified to achieve a partial conversion of the azoxy to the azo moiety without altering the molecular weight or the molecular weight distribution of the starting polymer. Findings from these studies will be reported shortly. It was important to ascertain whether the first d.s.c. exotherm was due to the azoxy to azo transformation followed by a second true cure exotherm. This did not turn out to be the case. Samples obtained from the d.s.c. experiments at various points along the first exotherm were discoloured and they were insoluble, characteristics of crosslinking reactions.

Conclusions

A series of novel, high molecular weight, azoxyaromatic polyethers has been prepared. The polymers afford

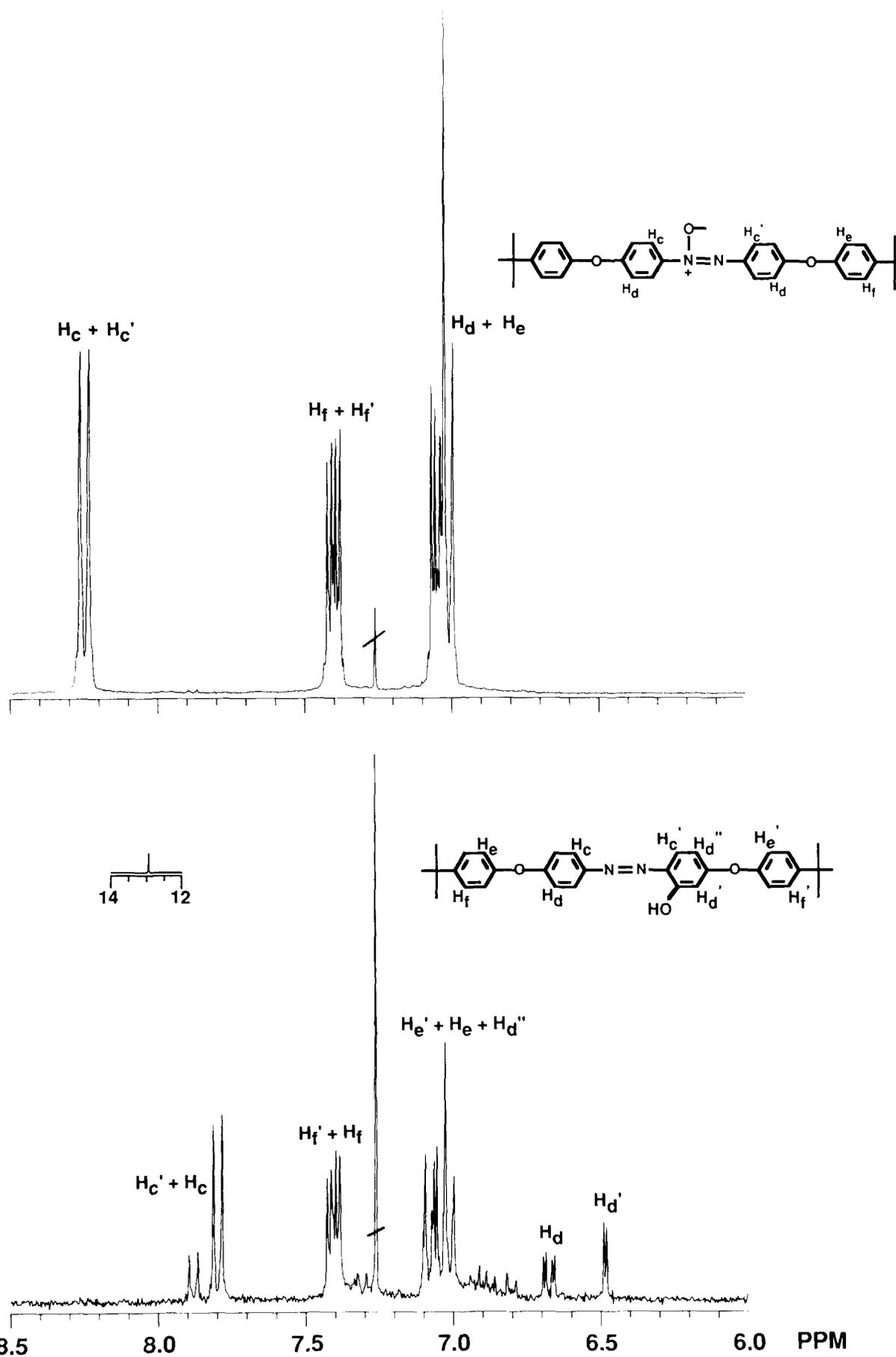
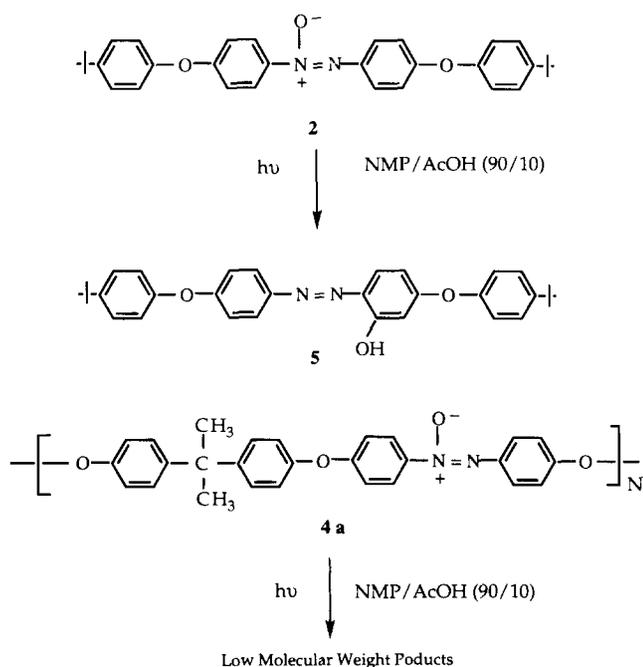


Figure 2 ¹H n.m.r. spectra (CDCl₃) of compounds 2 and 5


Scheme 3

transparent, coloured films upon solution casting and undergo crosslinking reactions at elevated temperatures.

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