Synthesis and curing of bis[4(3'-ethynyl phenyl amino)-3-nitrophenyl]sulphone

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A new acetylene terminated nitrophenyl sulphone (ATNPS) has been synthesized by nucleophilic displacement reaction between bis(4-chloro-3-nitrophenyl)sulphone and 3-ethynyl aniline. ATNPS is characterized by elemental analysis, IR and ¹H-NMR spectroscopies. On heating at ca. 250°C or above ATNPS becomes crosslinked due to the presence of the acetylenic end group. The thermal behaviour has been studied by DSC and DTA techniques. The kinetic study of the curing has been carried out by both differential and integral methods by use of a computational programing.

In recent years acetylene terminated oligomers have received considerable attention because of their inexpensive synthetic route, information on chemical structure-property relationships, excellent thermal and chemical stability of cured resins and broad scope of resin products for various applications[1]. The chemistry of acetylene terminated materials permits the tailoring of systems to provide cured resins with a unique combination of properties. The terminated acetylene group reacts under various conditions. For example, the thermal curing of acetylene end groups leads to linear chain extension, branching and crosslinking. There are various methods used for synthesis of acetylene terminated monomers, oligomers and polymers. The nucleophilic displacement reaction of an activated nitro or a halogen group by ethynyl phenoxide is widely used to introduce the ethynyl group. By using this method, the synthesis of acetylene terminated sulphone[2] (ATS) and its polymerization have offered a low cost route for significant commercial application.

Very recently, ethynyl terminated polyethers through halo/nitro displacement reaction forming new end-capping agents have been reported by Delfort et al[3].

$$R = -SO_2-; \{-O$$
$$X = F; Cl; NO_2$$
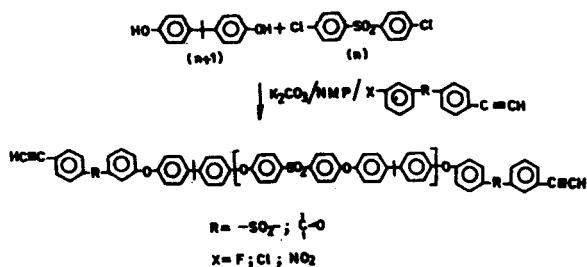
The acetylene terminated (ATI) imide oligomers are also well known because the early work[4] on ATIs led to the development of a material called HR-600 (trade name, Thermid-600). The ethynyl substituted aromatic amine, namely 3-ethynyl aniline, is widely used in these purposes.

However, 3-ethynyl aniline as an end capping agent has not so far been used via nucleophilic displacement reaction for synthesis of reactive oligomers. The use of aromatic diamines for preparation of poly(aryl amines) from bis(4-chlorophenyl) sulphone (BCPS) is reported elsewhere[5]. But it is seen that the reactivity of diamines with BCPS is rather poor (producing very low molecular weight polymers) whereas the introduction of nitro groups into the *meta* position of the aromatic dichloride greatly enhances[6] the reactivity of BCPS for the polycondensation reaction with aromatic diamines (η_{inh} values in the range of 0.10-0.42 dL/g).
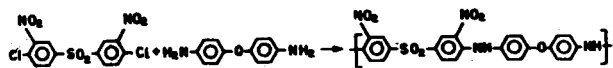
This result encouraged us to develop a new reactive oligomer from nitro substituted BCPS, namely bis(4-chloro-3-nitrophenyl)sulphone (BCNPS) with 3-ethynyl aniline following the principle of activated nucleophilic displacement reaction.

Materials and Methods

Bis(4-chlorophenyl)sulphone (BCPS) (Fluka A.G., Switzerland) was of 95% purity. It was purified by recrystallization (m.p. 146-148°C). 3-Ethy-

nyl aniline was received as a gift from USA and used as received. Triethylamine (S.D. Fine Chem.), nitric acid, conc. AR (Viswabharati) sulphuric acid, conc. 98%, AR (Viswabharati), acetic acid, AR (S.D. Fine Chem.) were used without further purification. Methanol was purified by distillation.

Preparation and characterization of bis(4-chloro-3-nitrophenyl)sulphone (BCNPS)

BCNPS was prepared according to the method described by Korselt and coworkers[7]. BCPS, (10 g, 0.0348 M) was dissolved in conc. H_2SO_4 (50 ml), then conc. HNO_3 (50 ml) was added slowly and the reaction mixture was heated on a boiling water bath for 2 h. Afterwards, the solution mixture was cooled and poured into cold water. The precipitate was filtered and repeatedly washed with water. The light yellow powder, BCNPS, was recrystallized from acetic acid. The light yellow needle shaped BCNPS was dried in vacuo at 110°C for 16 h. Yield = 11.8 g (90%), m.p., 200°C (lit. value[7] 202°C). The IR spectrum (KBr): 1540 and 1360 cm^{-1} ($\bar{v}_{NO_2}$), 1340 and 1170 cm^{-1} (v_{SO_2}) and 779 cm^{-1} ($\bar{v}_{Cl}$).

Synthesis of acetylene terminated nitrophenyl sulphone (ATNPS): bis[4(3'-ethynyl phenyl amino)-3-nitrophenyl]sulphone

BCNPS (0.943 g, 0.0025 M) 3-ethynyl aniline (0.585 g, 0.005 M) triethylamine (Et$_3$N) (0.70 ml, 0.005 M) and DMAC (5 ml) were taken in a three necked flask and the reaction mixture was stirred for 12 h at 80°C followed by quenching in 30 ml of methanol-water mixture (50:50, v/v). The resultant solid was washed with water and finally refluxed with methanol and dried in vacuo at room temperature. Yield = 2.28 g (90%); colour: yellow.

Materials analysis and characterization

Elemental analysis viz. carbon, hydrogen and nitrogen was carried out by a Heraeus Carbo Erba 1108 elemental analyzer. Element sulphur was analyzed by the Schoniger Combustion flask method. IR spectrum was recorded with a KBr pellet using a Perkin-Elmer Model 837 spectrophotometer. ^{1}H-NMR spectrum was recorded with a Varian EM 360, 90 MHz NMR spectrometer using DMSO-d_6 as solvent and trimethyl silane as internal standard.

Curing study was carried out in a temperature controlled oven. Thermal analysis was done by TGA and DSC techniques. TGA and DSC were made with a Stanton Redcroft, Model 625 thermal analyzer in air at a heating rate of 10°C/min for TGA and 5, 10, 20 and 40°C/min for DSC.

Curing of ATNPS

A 5% solution of ATNPS in DMF was cast on a glass plate using a doctor blade. The wet film was dried under vacuum at 30°C for 6 h. The tack-free film on glass was transferred to a forced-air oven and dried in stages to a temperature at 100°C for 0.5 h, 200°C for another 1 h. Further drying was performed in vacuo at a final temperature of 250°C for 1 h. The film was removed from the glass plate in water and used to study the crosslinking behaviour.

Results and Discussion

Synthesis of acetylene terminated nitrophenyl sulphone (ATNPS)

Synthesis of the acetylene terminated sulphone i.e., ATNPS was achieved by condensation of 3-ethynyl aniline with BCNPS. BCNPS was prepared[7] by a reaction of BCPS with HNO_3/H_2SO_4.
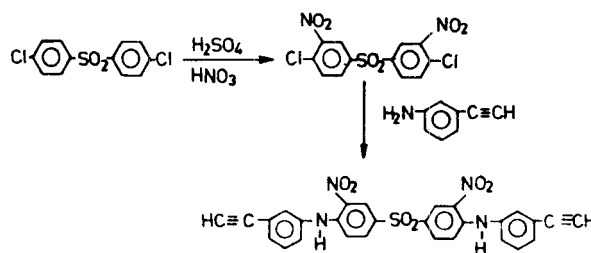
Scheme 1—Synthesis of ATNPS

The amine is a nucleophile but due to the enhanced reactivity of BCNPS, the reaction becomes possible[6]. The purified ATNPS is a yellow solid and soluble in many organic solvents such as chloroform, DMSO, DMF, DMAc, NMP, HMPA, etc. However, the solubility of ATNPS decreases when the compound is exposed to light (UV-radiation) or heat over a long period of time owing probably, to slight crosslinking of the acetylenic groups.

Characterization of ATNPS

The results of elemental analysis is in good agreement with the proposed structure for ATNPS: Calc. for ($C_{28}H_{18}N_4O_4S$): C, 66.40; H, 3.56; N, 11.07; S, 6.32. Found: C, 67.10; H, 3.98; N, 10.87; S, 6.18.

The IR spectrum of ATNPS is given in Fig. 1(a). The most characteristic IR absorption bands for the detection of acetylenic group ($-C \equiv CH$) are the stretching vibrations of the hydrogen-carbon and carbon-carbon bonds which usually appear at 3300, 3080, and 2100 cm^{-1}, respectively[8].
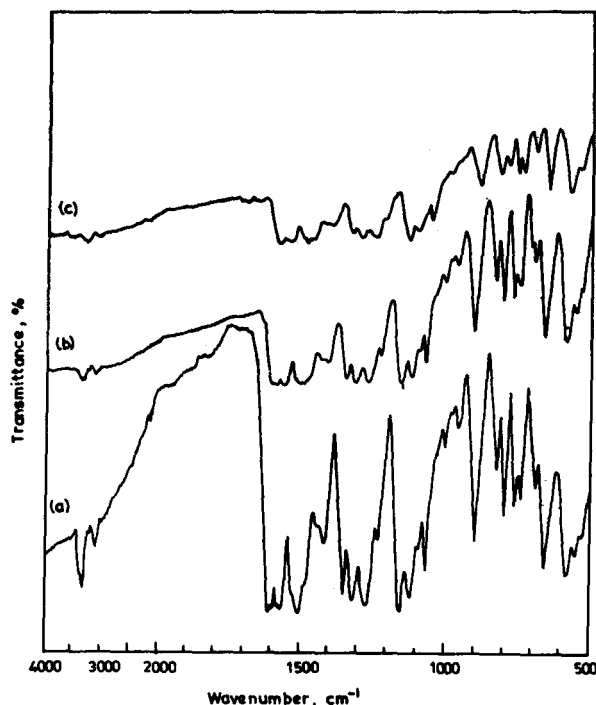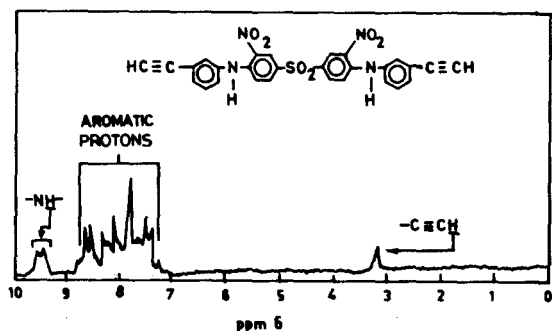
Fig. 1—IR spectra of ATNPS and its cured products

Fig. 2—^{1}H-NMR spectrum of ATNPS

Fig. 3—The intensity ratio of the IR bands at 3300 cm^{-1} and 1100 cm^{-1} versus curing temperature of ATNPS

ATNPS shows a strong, sharp absorption band at 3310 cm^{-1} and weak bands at 3080 and 2100 cm^{-1} [Fig. 1(a)], indicating the presence of the acetylenic group in ATNPS.

The ^{1}H—NMR spectrum of ATNPS is shown in Fig. 2. The singlet at 3.10 δ is assigned to the acetylenic (-C ≡ C-H) proton[9]. The signal of aromatic protons of the phenylene groups from dinitro-diphenyl sulphone moiety appears in the region of 7.6-8.8 δ and that of ethynyl aniline moieties[10] is in the region of 7.2-7.5 δ. The proton of the (-NH-) group[11] appears in the region 9.2-9.4 δ.

Curing study of ATNPS

The ATNPS was cured at elevated temperatures to yield a crosslinked material. When heated at 30°C to 200°C, the colour of the oligomer
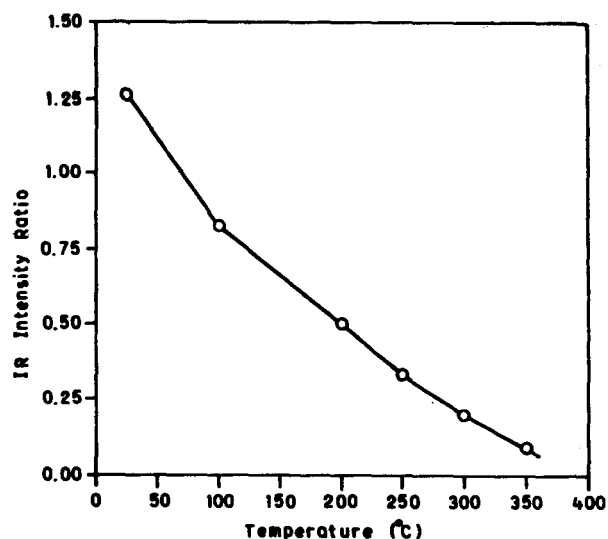
changed from yellow to brown. In the IR spectra [Fig. 1(b) and (c)] of the cured ATNPS, the intensities of the acetylenic C—H and the C ≡ C stretching bands at 3300 and 3080 cm^{-1} are decreased gradually with the rise of curing temperature. The intensity ratio of the bands at 3300 cm^{-1} and 1100 cm^{-1} is plotted against the curing temperature, as shown in Fig. 3. The results indicate that after curing (up to 350°C), most of the acetylenic groups were reacted to give a cross-linked material. This observation is consistent with the curing study of hexakis (4-ethynyl anilino) cyclotriphosphazene[12]. It is well-known that thermal crosslinking of acetylenic groups leads to various conjugated species including aromatic rings and some conjugated linear chains[13,14].

The resultant material (cured at up to 250°C) is insoluble in common organic solvents, even in conc. H_2SO_4, indicating formation of the cross-linked polymer[15]. After curing at temperatures up to 350°C, the material became a brownish black powder. No melting was observed in the temperature range of 30-350°C.

Thermal behaviour of ATNPS

Differential scanning calorimetry (DSC) was performed on the ATNPS in air (Fig. 4a). There is one exothermic peak at 360°C. The onset temperature for the exotherm is ~ 300°C. The DSC of the oligomer ATNPS also shows lack of a clear melting process. No significant weight loss of ATNPS in the temperature range of 50-250°C in air is indicated by the TGA of ATNPS (Fig. 5). However, the TGA shows a small weight gain (ca,

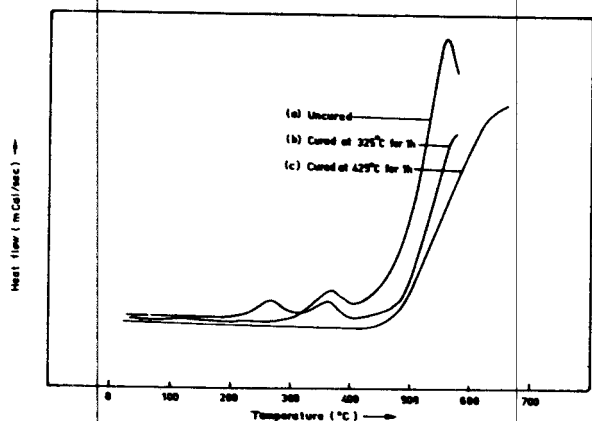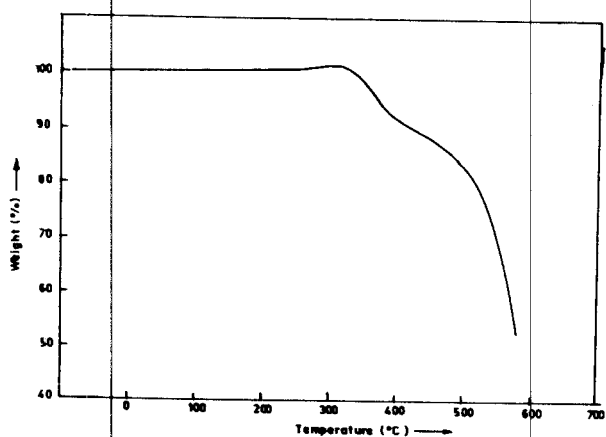Fig. 4—DSC thermograms of ATNPS and its cured products

Fig. 5—TGA thermogram of ATNPS

Fig. 6—DSC thermograms of ATNPS at different heating rates
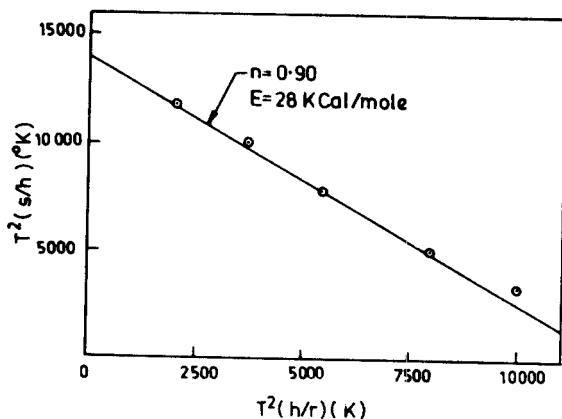
Fig. 7—A typical Ellerstein plot of ATNPS (heating rate 20K/min)

2%) in the temperature range of ~250-300°C. This indicates that oxidation of ATNPS by oxygen occurs in this temperature range. During thermal curing free radicals and/or other reactive species are generated[16,17], which react with oxygen and lead to formation of carbonyl and other oxygen-containing groups. The oxidation reactions seem to start at ~250°C. As the temperature is further increased, more carbonyl and other oxygen-containing species are produced, which are responsible for the weight gain in the TGA thermogram.

This is confirmed by the IR studies of ATNPS after thermal curing under various conditions. It should be noted in Fig. 3 that the thermal cross-linking of the acetylene groups almost reaches completion at 350°C. This is consistent with the fact that the thermal crosslinking reactions are responsible for the exothermic peak at 350°C in the DSC thermogram of ATNPS (Fig. 4a).

The new exotherm in the DSC curve appears as a shoulder at Ca. 250°C when ATNPS is cured at 325°C (Fig. 4b). This exotherm is presumed to be due to oxidation of ATNPS during the curing of ATNPS at 325°C for 1 h. Further curing of

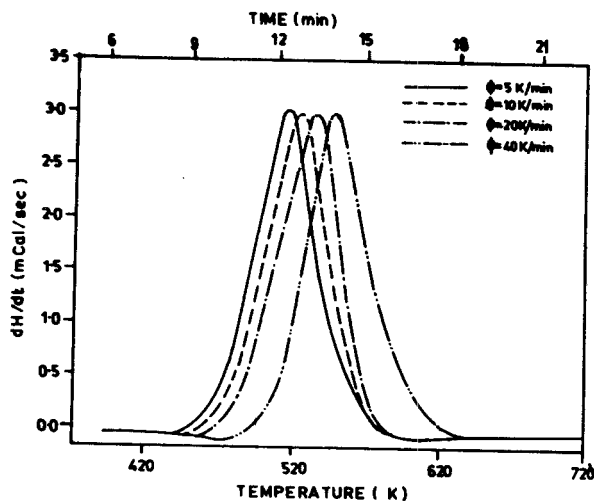ATNPS at 425°C for 1 h eliminates both these exotherms (Fig. 4c). Similar kind of curing in male-omido-terminated polyimide has also been observed by a group of Chinese workers[18].

Kinetic study of curing of ATNPS

Among various methods of curing kinetics[19], the differential/integral analysis of the DSC curve has been proved as an elegant and rapid technique[20]. The determination of kinetic parameters such as activation energy, E, the kinetic order, n, and heat of polymerization (or crosslinking), ΔH_p, by such thermal analysis techniques has been applied mainly in structural adhesives and fiber reinforced materials. The analysis of curing kinetics in reactive oligomers has not been studied well. Two analytical methods for evaluating the activation energy, E, and kinetic order, n, during the polymerization (or crosslinking) of the reactive oligomer, ATNPS, from the DSC curves have been used in this study.

Table 1—DSC analysis during curing of ATNPS from the first exotherm

ϕ (K/min)	T^* (K)	ΔH_p (Cal/g)	E (kcal/mol)	n	E/n
5	514	71	27.6	0.85	32.47
10	525	76	29.6	0.86	34.42
20	537	70	28.0	0.90	31.10
40	549	72	36.0	1.00	36.00
Average values :		72.25	32.50	0.90	33.48
Standard values :		±5.18	±3.37	±0.09	±2.16
% Deviation :		±7.17	±11.00	±10.00	±6.45
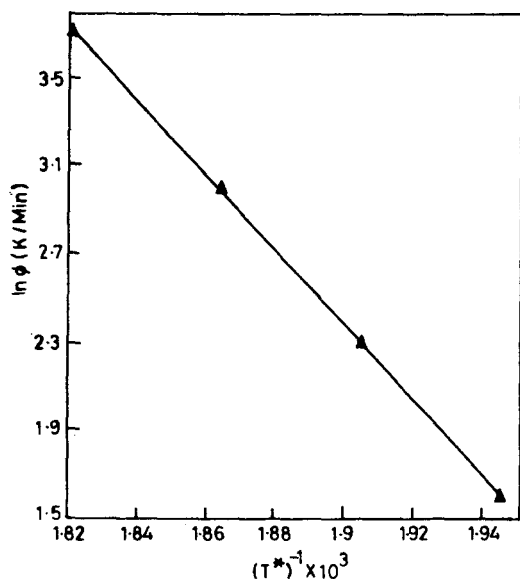
Fig. 8—Correlation of ln ϕ versus $(T^*)^{-1}$ for four scan rates of ATNPS

The first method utilizes a detailed differential analysis of a single DSC curve to isolate E, n, and ΔH_p as suggested by Ellerstein[21].

$$T^2(S/h) = E/R - nT^2 \ (h/r) \qquad \ldots (1)$$

The second method is based on the relationship (2).

$$\frac{d\ln\phi}{d\left(\dfrac{1}{T^*}\right)} = -\left[\frac{1}{n}\frac{E}{R} + 2T^*\right] \qquad \ldots (2)$$

A plot of ln ϕ versus $(T^*)^{-1}$ from several DSC curves will give a straight line with slope $(-E/nR)$ where $E/nR \gg 2T^*$ and $\phi = dT/dt$.

The resultant thermogram at heating rate of 20 K/min (Fig. 6) was analyzed by Eq. 1. The base line was obtained by drawing the best smooth curve connecting the beginning and the ending of the exothermic peak. The calculations were made by a computational programming[22]. Recently, a group of Chinese workers[18] also reported the use

of DSC thermograms for determination of the kinetic parameters of the maleimidoterminated polyimide with the help of a computational programming.

A typical Ellerstein plot is shown in Fig. 7 (heating rate: 20 K/min). It is evident from Fig. 7 that application of Eq. 1 produces an effective linearization of the DSC curves showing activation energy, $E = 28$ kcal/mol and the order of the reaction, $n = 0.90$. Four different scan rates (ϕ) has been performed (Fig. 6) and the values of T^* are shown in Table 1. The E/n ratio obtained from the slope of ln ϕ versus $1/T^*$ according to Eq. 2 (Fig. 8) is 34 kcal/mol. The activation energy of this method is only comparable to the first method when $n > 1$. From this discussion it is clear that the order of the reaction will be as follows: $0.85 < n < 1.074$. Similarly, the comparison of the first method with the second shows the activation energy will be higher when the value of n will be less than one.

Acknowledgement

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