Synthesis and Thermal Stability, Dielectric, and Conductivity Characteristics of Polymers with Pendant and Backbone Anthracene Sulfonyl Groups

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SYNOPSIS

Anthracene-mono- and disulfonyl derivatives of polystyrene and poly(N-vinylcarbazole) have been prepared and the thermal stability, dielectric, and conductivity of these polymer pendant sulfones have been evaluated. The anthracene-based benzene, naphthalene, anthracene, and biphenyl copolysulfones have also been prepared and characterized in regard to the above-cited properties. Interesting variations in these properties between these two classes of polymers carrying pendant and backbone sulfonyl groups have been noted and rationalised from structural considerations.

INTRODUCTION

Polymer pendant sulfones offer an interesting structural variation from the conventional polysulfones prepared by the usual polycondensation reactions which may lead to characteristic differences in desirable properties such as thermal stability, dielectric, and conductivity behavior. A facile way of preparing polymer pendant sulfones is by Friedel Crafts reaction between a polymer and the appropriate sulfonyl chloride derivative. This procedure was successfully used by Dasgupta et al.[1] for the preparation of arylsulfone derivatives of polystyrene and by us[2] for the benzene and anthraquinone sulfone derivatives of poly(N-vinylcarbazole) (PNVC). In this article, we report the preparation (Fig. 1) of anthracene-mono- and disulfonyl derivatives of polystyrene (III and IV), poly(n-vinylcarbazole) (V and VI), and anthracene-based copolysulfones of benzene, naphthalene, anthracene, and biphenyl (VIIa–d). Detailed evaluation of thermal stability, dielectric, and conductivity characteristics of these polysulfones has revealed a number of interesting features, which will be highlighted here.

EXPERIMENTAL

Materials

Poly(N-vinylcarbazole) ($\bar{M}_n$ = 3300) was prepared by a method of Biswas and Kamannarayana,[3] reprecipitated twice from THF by hot methanol, and finally dried off the solvent. Polystyrene ($\overline{DP}$ = 480, Polychem India Ltd.) was used in all experiments. Anthracene, naphthalene, and biphenyl were purified by the usual procedure. Anthraquinone-2-sulfonic acid, anthraquinone-2-6-sulfonic acid (sodium salt), and anhydrous aluminum-chloride (Fluka) were used as such.

Synthesis

Preparation of Anthracene-2-Sulfonyl Chloride (I) and Anthracene-2,6-Disulfonyl Chloride (II)

Anthracene-2-sulfonic acid was prepared from anthraquinone-2-sulfonic acid (Na-salt) by the same procedure as described elsewhere.[4]

Ten grams of anthracene-2-sulfonic acid was mixed with PCl_5 (3 g) and heated in water bath (60–70°C) for 2 h with occasional shaking. The contents were poured into crushed ice and filtered after the melting of ice. The residue was washed thoroughly with water and ethanol respectively. The product (I) was recrystallized from dichloromethane and characterized.
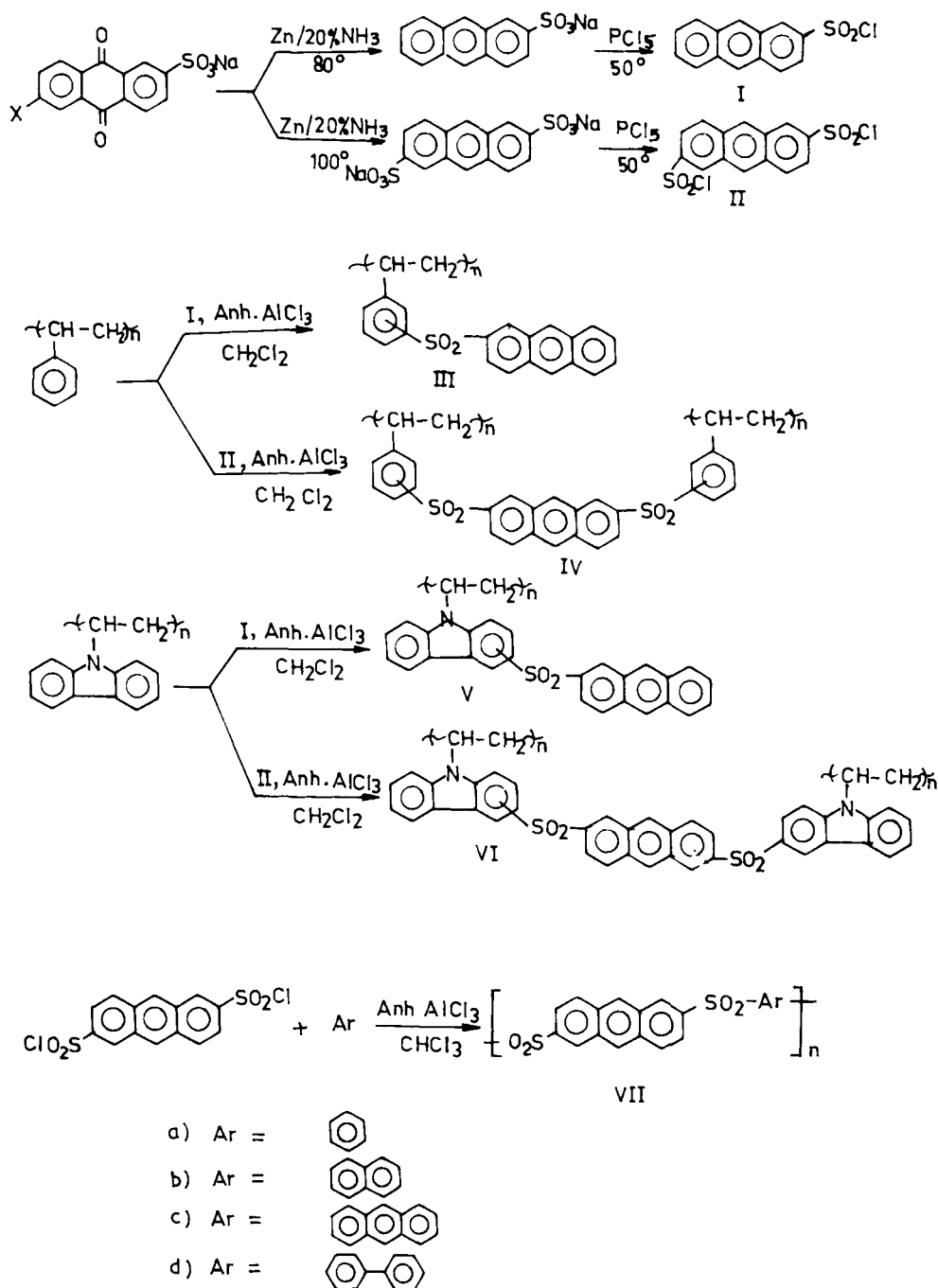
Figure 1 Reaction schemes and tentative structure of the polycondensates.

Ten grams of anthraquinone-2,6-disulfonic acid (sodium salt) and 8 g pure zinc-dust were taken in a round-bottomed flask provided with a condenser. Ten percent ammonia solution was poured into the mixture to obtain a colored mass. It was heated in a steam bath with constant stirring for 12 h, until the color turned to light yellow. The mass was subsequently poured into 200 cc water with constant stirring and finally filtered. The filtrate was acidified with dilute acetic acid. The anthracene-2,6-disulfonic acid was precipitated out by adding the requisite amount of sodium chloride. The residue was filtered and washed with 20% NaCl solution.

II was prepared from anthracene-2,6-disulfonic acid, sodium salt by a similar procedure as described for I.

Anthracene-Sulfone Derivatives of Polystyrene and Poly(n-Vinylcarbazole)

I (0.02 mol) and anhydrous $AlCl_3$ (0.02 mol) in chloroform (50 cc) were reacted under nitrogen for 30 min at 27°C. A solution of polystyrene (0.014 mol of repeating units) in chloroform was slowly added to the stirred solution for 30 min. The color gradually darkened with time. The mixture was stirred at 27°C for a definite time (12, 24, and 36 h) and poured into ice-containing 10% HCl solution. The organic layer containing the solid product was poured into methanol, filtered, washed with water, ethanol, chloroform, respectively, and dried in vacuum. The product was characterized (Table I) as III.

The same procedure was adopted for the synthesis of anthracene-monosulfone derivatives of PNVC. The anthracene-disulfone derivatives of polystyrene and poly(N-vinylcarbazole) were prepared by reacting anthracene-2-6-disulfonyl chloride with the corresponding polymers using the earlier procedure adopted for III.

Synthesis of Anthracene-co-Benzene (VIIa), Anthracene-co-Naphthalene (VIIb), Anthracene-co-Anthracene (VIIc), and Anthracene-co-Biphenyl (VIIb) Polysulfones

Anhydrous $AlCl_3$ (0.04 mol) was mixed with a solution of II (0.02 mol) in chloroform and stirred for 30 min under nitrogen atmosphere. Benzene (0.02 mol) was slowly added to it and mixture was stirred for 36 h at 27°C. The resultant solution was poured into crushed ice, the aqueous phase was separated out, and methanol was added to the organic layer. The precipitate was filtered and washed thoroughly with chloroform, methanol, water, and ethanol, re-

Table I   Characterization of Compounds

Code No.	Compound	Yield (%)	Elemental Analysis				Characteristic IR Absorption (cm^{-1})
			S (%)		N (%)		
			Calcd[c]	Found	Calcd[c]	Found	
I	Anthracene-2-sulfonyl chloride[a]	70	11.57	11.43	—	—	1320, 1140 (—S=O stretching), 1580 (aromatic —C=C stretching)
II	Anthracene-2,6-disulfonyl chloride[a]	60	17.66	17.02	—	—	1320, 1145 (—S=O stretching), 1580 (aromatic —C=C stretching)
III	Anthracene-monosulfonyl derivatives of polystyrene[b]	70	6.32	9.30	—	—	1300, 1150 (—S=O stretching), 1600 (C=C aromatic stretching), 3020 (=C—H stretching), 700, 750 (for 5 adjacent H atoms)
IV	Anthracene-disulfonyl derivatives of polystyrene[b]	60	7.15	12.54	—	—	1300, 1150 (—S=O stretching), 1590 (—C=C aromatic stretching), 3000 (=C=H stretching), 700, 740 (for 5 adjacent H atoms)
V	Anthracene-monosulfonyl derivatives of poly(N-vinylcarbazole[b]	65	7.42	4.30	3.20	4.44	1320, 1145 (—S=O stretching), 1604 (aromatic —C=C stretching)
VI	Anthracene-disulfonyl derivatives of poly(N-vinylcarbazole[b]	60	6.80	9.30	4.04	5.03	1320, 1145 (—S=O stretching), 1604 (aromatic —C=C stretching)
VIIa	Anthracene-co-benzene polysulfone[b]	35	16.84	16.20	—	—	1150, 1300 (—S=O stretching), 1610 (—C=C aromatic stretching)
VIIb	Anthracene-co-naphthalene polysulfone[b]	40	14.81	14.30	—	—	1150, 1300 (—S=O stretching), 1610 (—C=C aromatic stretching)
VIIc	Anthracene-co-anthracene polysulfone[b]	40	13.33	12.95	—	—	1145, 1290 (—S=O stretching), 1620 (—C=C aromatic stretching)
VIId	Anthracene-co-biphenyl polysulfone[b]	45	14.03	15.38	—	—	1145, 1300 (—S=O stretching), 1600 (—C=C aromatic stretching)

[a] Soluble in organic solvents like $CHCl_3$, THF, DMF, etc.
[b] Insoluble in common organic solvent such as THF, DMSO, DMF, $CHCl_3$.
[c] Calculated on the basis of their tentative structure as in Figure 1.

spectively, and finally dried in vacuum and it was characterized as VIIa (Table I).

Essentially similar procedures were adopted for the syntheses of anthracene-co-naphthalene (VIIb), anthracene-co-anthracene (VIIc), and anthracene-co-biphenyl polysulfones (VIId).

CHARACTERIZATION

Elemental Analysis

Estimation of sulfur and nitrogen was done by standard methods.

Infrared Spectra

Infrared spectra of the samples dispersed in KBr pellets were recorded on a Perkin-Elmer 237B infrared spectrophotometer.

Thermal Stability

Thermal stability measurements were made on a Stanton-Redcroft analyzer with the sample under air at a heating rate of 10°C/min. The temperature was 0–1000°C.

Dielectric Measurements and ac Conductivity

Permittivity or dielectric constant (ϵ) and dielectric loss factor (tan δ) and ac conductivity measurements were made with an impedance bridge (HP, A4192). The samples were used in pellet forms coated (both surface) with silver paint.

Electrical Conductivity

Electrical conductities were obtained by using a cell containing guard ring and electrodes made of stainless steel disc. The special mounting device of Keithley 6105 resistivity adoptor was used for the measurements. The circuit consisted of HP 6144 precision power supply and Keithley 610C solid state electrometer.

RESULTS AND DISCUSSION

The general properties and the relevant analytical data for polystyrene and poly(N-vinylcarbazole) pendant anthracene sulfones are presented in Table I. The maximum yield was realized when the reaction was continued for 24 h. The IR spectra for com-

pounds III and IV show two sharp bands at 1300 and 1150 cm^{-1} (absent in pure polystyrene) which correspond to S=O stretching bands of the sulfone linkages. The presence of the S=O group in anthracene-sulfonyl derivatives of poly(N-vinylcarbazole) (V and VI) is also well endorsed by the IR data (1320 and 1145 cm^{-1}) (Table I). Elemental analyses (N and S) of all compounds (III–VI) reveal that the condensation between the polymers and anthracene-sulfonylchloride (I and II) did not take place quantitatively. Assuming that every phenyl or carbazole moiety is derivatized, the theoretical % S for compound III and % S and % N for compound V should be 6.32 and 7.42 and 3.20, respectively; accordingly, the observed values indicate that condensation by I occurs with 65% of the polystyrene repeating units and 60% of poly(N-vinylcarbazole) repeating units, respectively. This is also well endorsed from the IR spectra. The compound III shows the IR absorption at 750 and 700 cm^{-1} like pure polystyrene, which reveals the presence of five adjacent atoms. This is possible only if some unreacted polystyrene repeating units are present in anthracene sulfone derivatives of polystyrene (III).

It is expected that interchain crosslinking via sulfonyl linkages may occur in the case of the anthracene disulfonyl derivatives of polystyrene and poly(N-vinylcarbazole) (as in structures IV and VI in Fig. 1). In fact, these sulfones (IV and VI) contain a very negligible amount of Cl, indicating participation of both the SO$_2$Cl groups of II in the condensation. Further, such crosslinking should be expected to make the polymer structure more rigid. The relatively higher thermal stability of IV and VI may possibly result from such interchain crosslinking. In the same vein, lesser dielectric loss (Figs. 4 and 5) and frequency stable dielectric constant for these structures are more reasonable.

The copolycondensed products anthracene-co-benzene (VIIa), anthracene-co-naphthalene (VIIb), anthracene-co-anthracene (VIIc), and anthracene-co-biphenyl (VIId) were recovered as insoluble (in common organic solvent) colored compounds. The optimum reaction time for all these reactions was 36 h. The structures of these copolysulfones as shown in Figure 1 (structure VIIa–d) are reasonably endorsed by IR spectra and elemental analyses (Table I).

Thermal Stability

Figures 2 and 3 compare thermal stabilities of anthracene-monosulfone and anthracene-disulfone derivatives of polystyrene and poly(N-vinylcarba-
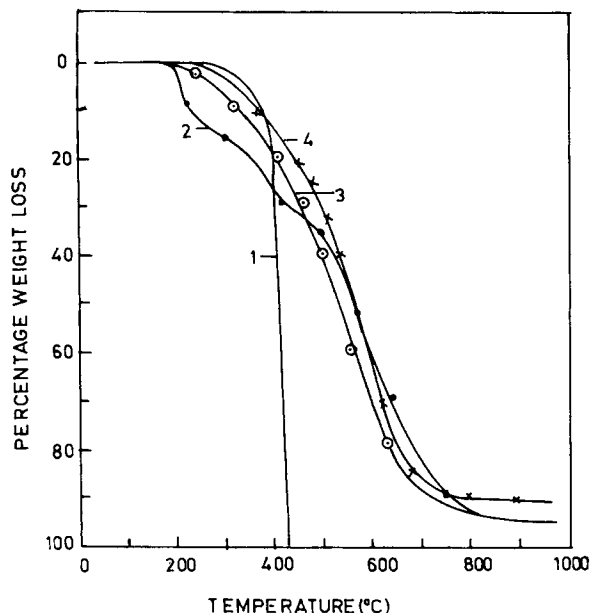
Figure 2 Thermograms of: (1) polystyrene; (2) anthracene-monosulfone derivatives of polystyrene; (3) anthracene-disulfone derivatives of polystyrene; (4) anthracene-co-benzene polysulfone.

zole) (III, IV, V, and VI) with their respective base polymers, polystyrene, and poly(N-vinylcarbazole). The initial decomposition temperatures of all these polymer pendant sulfones (III-VI) are lower than their corresponding base polymer, the trend being

polystyrene (320°C) > IV (250°C) > III (200°C)

poly(N-vinylcarbazole) (330°C)

> VI (300°C) > V (250°C)

It is further noted that the overall thermal stability (beyond 25% decomposition) of all these pendant polymeric sulfones is significantly improved relative to their base polymer. Both polystyrene and PNVC undergo most of the decomposition (5-80%) in a very narrow temperature range (400-450°C) whereas their sulfone derivatives do so with a slower rate over a wider temperature range (~ 600°C). The initial decrease in thermal stability of polystyrene- and poly(N-vinylcarbazole)-based sulfones (III-VI) relative to their corresponding base polymers is believed to be due to the manifestation of the weakness of carbon–sulfur linkages, which has already been noted for an aryl-sulfonated polystyrene as well as benzene and anthraquinone sulfone derivatives of poly(N-vinylcarbazole).[1,2]

Throughout the thermal degradation process both the anthracene disulfone derivatives of polystyrene

and poly(N-vinylcarbazole) (IV and VI) exhibit higher thermal stability over their respective monosulfone derivatives (III and V) due to the interchain crosslinking through the sulfone linkages.

Figures 2 and 3 (curves nos. 4 and 4, respectively) represent the thermal degradation pattern of the anthracene-co-benzene and carbazole-co-naphthalene polysulfones, respectively, where the sulfone ($-SO_2-$) linkages are in the main chain. The initial decomposition temperatures of these two copolysulfones are higher than their corresponding polymer pendant sulfones, i.e., anthracene-mono- and disulfone derivatives of polystyrene and poly(N-vinylcarbazole). However, the overall trend of their thermal decomposition is similar to the polymer pendant sulfones. It was noted that the initial decomposition of both the copolysulfones (VIIa-d) as well as pendant polysulfones (III-VI) take place via degradation of sulfone linkages which is supported by the isothermal studies. As, for example, on heating at 200 and 350°C for 30 min, the compounds III and VIIa suffer 1.2 and 4.1% and 0.41 and 2.2% loss in sulfur content, respectively. It is interesting to note that, though both the compounds IV and VIIa contain phenyl $-SO_2-$ anthracene linkages as well as follow essentially the same degradation path, their initial decomposition temperatures are not the same. This possibly results from the fact that in the case of the polymer pendant sulfones the pendant moi-
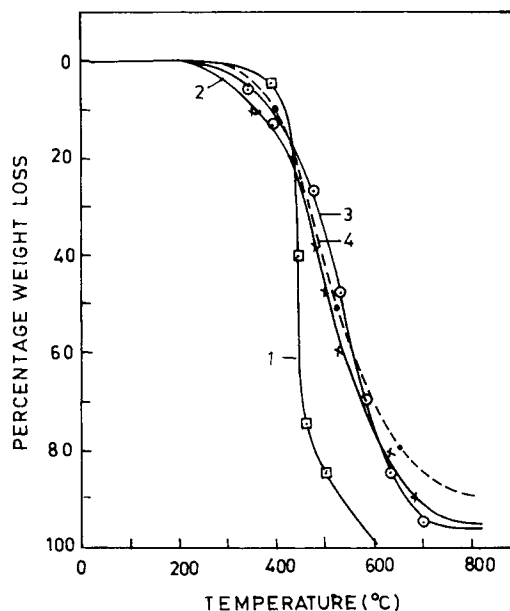

Figure 3 Thermograms of: (1) PNVC; (2) anthracene-monosulfone derivatives of PNVC; (3) anthracene-disulfone derivatives of PNVC; (4) carbazole-co-naphthalene polysulfones.
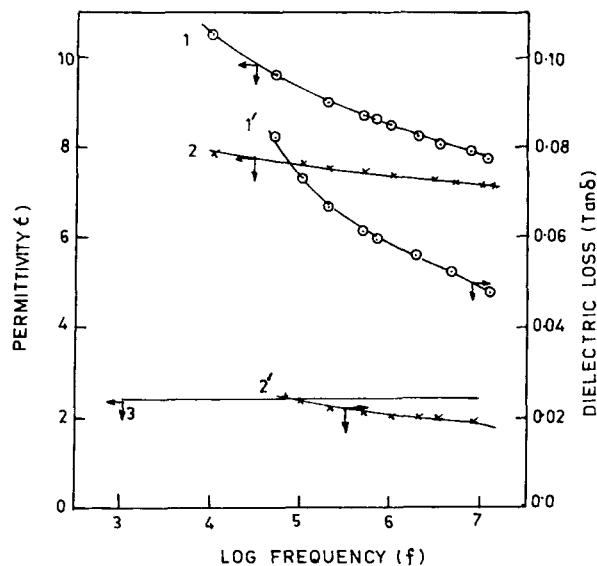
Figure 4 Permittivity and tan δ versus frequency plots for: (1,1') anthracene-monosulfone derivatives of polystyrene; (2,2') anthracene-disulfone derivatives of polystyrene; (3) polystyrene.

eties make the polymer certainly more strained than what is to be expected for the straight chain copolysulfones.

Dielectric Characteristics

Figures 4-6 represent the variation of permittivity and dielectric loss parameters with applied frequency for polystyrene and anthracene-mono- and disulfone derivatives of polystyrene (III and IV), poly(N-vinylcarbazole) and its anthracene-mono- and disulfonyl derivatives (V and VI) and four copolysulfones (VIIa-d), respectively. The following features are significant: (i) The dielectric constant and the loss parameter remain independent of the applied frequency for polystyrene. However, inclusion of anthracene as monosulfone derivatives (III) leads to a higher value of permittivity as well as the dielectric loss, both tending to fall with the applied frequency. For the disulfone derivatives (IV) the permittivity values are lower than those for III, whereas the loss parameter is reduced appreciably both tending to be
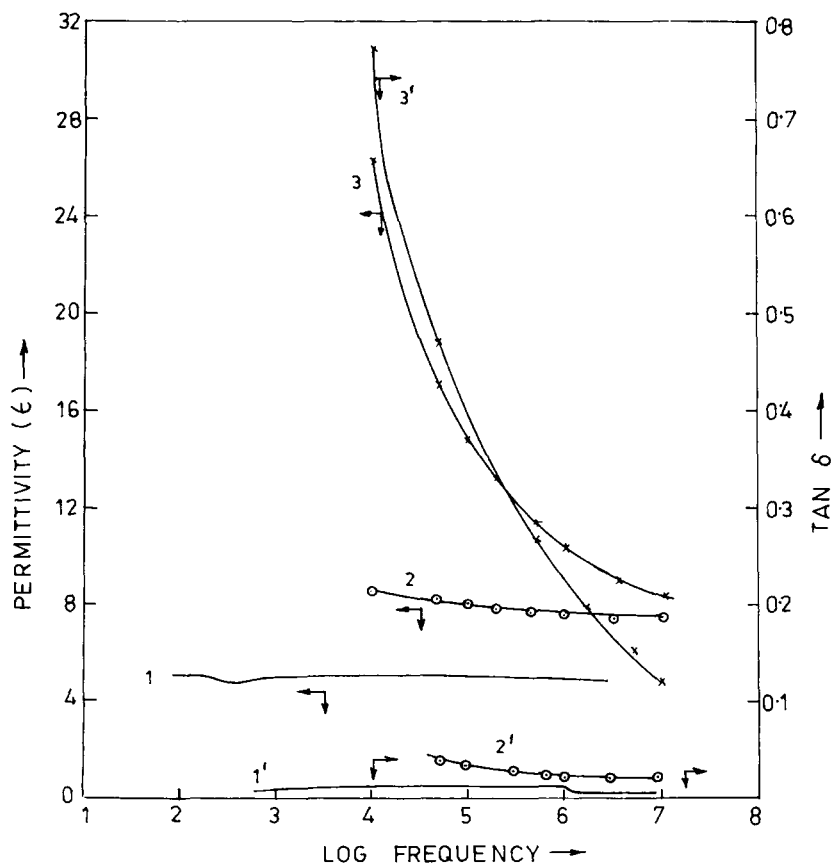

Figure 5 Permittivity and tan δ versus frequency plots for: (1,1') PNVC; (2,2') anthracene-sulfone derivatives of PNVC, (3,3') anthracene-monosulfone derivatives of PNVC.
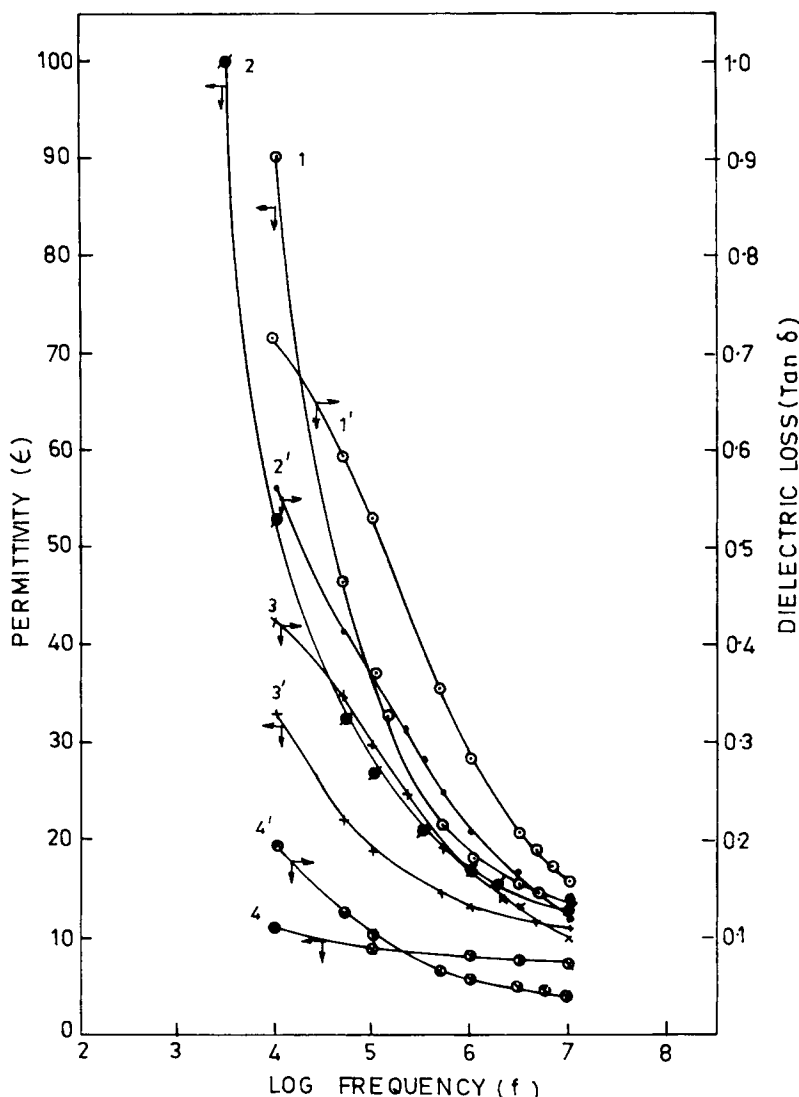
Figure 6   Permittivity and tan δ versus frequency plots for: (1,1′) anthracene-co-anthracene; (2,2′) anthracene-co-naphthalene; (3,3′) anthracene-co-benzene; (4,4′) anthracene-co-biphenyl polysulfones.

independent of the frequency. (ii) The permittivity and loss parameter for poly(N-vinylcarbazole) remain low and frequency-independent. For anthracene-mono-sulfone derivatives of poly(N-vinylcarbazole) (V) as with the corresponding polystyrene derivatives (curves nos. 1,1′ of Fig. 4) both the permittivity value and loss factor reveal a sharp fall with the applied frequency. However, for the corresponding anthracene disulfone derivatives (VI) the permittivity and loss parameter tend to become frequency-independent—a behavior very similar to that exhibited by the corresponding polystyrene derivatives. (iii) The permittivity and tan δ of the copolysulfone (VIIa-d) show a fall with the applied

frequency. However, at any particular frequency between 10^4 and 10^7 Hz, the order in the decrease of the permittivity and loss parameter is

$$\text{VIIc} > \text{VIIb} > \text{VIIa} > \text{VIId}$$

The aforementioned results suggest that the introduction of polar groups in the polymer chain, in general, enhances the dielectric constant and loss parameter,[5] which is clearly due to the greater extent of polarization in the molecule facilitated by polar group and more polarizable delocalized π-electrons of anthracene moiety. Further, the polar anthracene-sulfone pendant moieties are apparently flexible in

Table II Conductivities of Polysulfones

Polymer Code No.	dc Conductivity at 27°C (Ω^{-1} cm^{-1})	ac Conductivity at 27°C (Ω^{-1} cm^{-1} at 50 kHz)
Polystyrene	2.8×10^{-16}	—
III	6.4×10^{-10}	—
Poly(N-vinylcarbazole)	4.2×10^{-16}	—
VI	2.0×10^{-8}	—
VIIa	6.9×10^{-10}	1.7×10^{-7}
VIIb	1.37×10^{-9}	2.1×10^{-6}
VIIc	2.6×10^{-9}	2.16×10^{-6}
VIId	2.82×10^{-7}	2.16×10^{-6}

nature; consequently, they can orient themselves in the direction of the electrical field easily at the low frequency of alternation, which explains the high dielectric constant. With the increasing frequency of alternation, the polar groups do not find sufficient time to orient themselves along the field direction, which leads to a drastic fall in the permittivity value. As for the disulfone derivatives (IV and VI), the polar anthracene sulfonyl moieties are more rigidly bound via interchain crosslinking, thereby restricting the orientation of these groups with the applied frequency. Accordingly, low and frequency stable permittivity and loss values are reasonable.

As for the copolysulfones (VIIa–d), the observed trend appears to be consistent with the increase in the extent of conjugation through delocalized π-electrons from a to c. Interestingly, anthracene-*co*-anthracene and anthracene-*co*-naphthalene (VIIb–c) polysulfones exhibit rather high dielectric values ~ 100 at low frequency (10^3–10^4 Hz), which is possibly a manifestation of the greater polarization possibility of the highly delocalized system. Relevantly, very high polarizability and dielectric values were obtained in the case of anthracene-based polyacenoquinone radical type polymers.[6,7]

Some comments[†] are perhaps desirable on how conjugation is likely to be affected by the geometry of the —SO_2— fragment linking up two aromatic systems. Sulfur in these sulfones is bonded to two carbon atoms and to two terminal oxygens in a tetrahedral arrangement which is readily deformable.[8,9] Further, the structure will correspond to a "crossed conjugated system" involving the interaction of each aromatic moiety with a corresponding $-\overset{\overset{\displaystyle O}{\|}}{\underset{\|}{S}}-$ of

the sulfonyl moiety. In addition, the high polarity of the sulfur–oxygen bond will give rise to a large dipole moment.[8] Consequently, enhanced electron polarization in these sulfones and hence a high dielectric constant may be envisaged—as observed with the pendant sulfones.

As for the backbone sulfones, which exhibit much higher dielectric polarization, the crossed conjugation will be operative. In addition, some interaction of the π-electron systems of the involved aromatic moieties present in the chain cannot possibly be ruled out. Relevantly, slight interactions with the aromatic ring in aryl sulfones are indicated when UV is used.[8]

Conductivity Characteristics

dc Conductivity

The inclusion of high electron rich moieties in polystyrene and poly(N-vinylcarbazole) and the preponderance of such groups in the straight chain copolysulfones obviously imply the manifestation of electronic conductivity in these systems. In fact, the conductivity data (Table II) endorse the expectations convincingly. The effect of conjugation is amply clear in anthracene copolysulfones of benzene, naphthalene, and anthracene, the dc conductivity increasing in the order. Interestingly, the corresponding anthracene copolysulfone of biphenyl (VIId) exhibits higher dc conductivity, though, from steric considerations, the reverse should have been expected. It is suggested that additional Friedel–Crafts sulfonation through the available ortho positions in the biphenyl moiety may be possible which will introduce more conjugation by a similar mechanism discussed earlier. Relevantly, the sulfur percentage actually found in these biphenyl sulfones are higher than what would be expected on the basis

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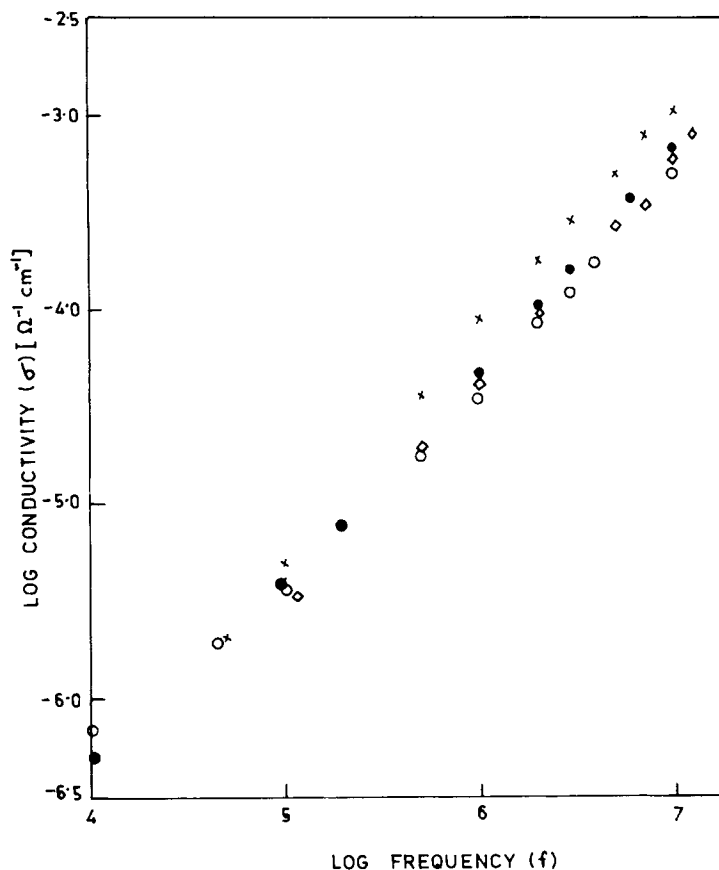[†] Thanks are due to a referee for raising this point.

Figure 7 Log conductivity versus log frequency plots for: ($\lozenge$) anthracene-*co*-benzene; ($\bullet$) anthracene-*co*-naphthalene; ($\bigcirc$) anthracene-*co*-anthracene; (X) anthracene-*co*-biphenyl polysulfones.

of structure (VIId). This feature also endorses our proposition about additional anthracene sulfone linkages through ortho position in VIId. Of course, the extent of such possible addition would be controlled by steric restrictions.

ac Conductivity

The ac conductivity of the copolysulfones shows a linear dependence on the applied frequency (Fig. 7). A similar trend has been observed for a broad class of disordered semiconductors,[10] polyacenoqui-none radical type of polymers reported by us[7] and for *cis*-polyacetylene by Epstein et al.[11] These data imply that conduction is predominantly by a hopping[12,13] mechanism, although details explaining contributions of surface barriers and ionic dipoles to such conduction cannot be elucidated on the basis of these data only. Table II further suggests that ac conductivity at any frequency is higher than the dc conductivity, which implies higher hopping rate of electrons between the available sites.[13,14]

CONCLUSION

Anthracene-sulfonyl derivatives of polystyrene and poly(*N*-vinylcarbazole) show higher overall thermal stability, higher dielectric constant, and significantly higher conductivity relative to their corresponding base polymer. Copolymers of anthracene with benzene, naphthalene, anthracene, and biphenyl containing backbone sulfonyl groups reveal comparable thermal stability similar to the polymer pendant sulfones of polystyrene, high dielectric constant and dielectric losses, strongly dependent on the applied frequency and the extent of π-electron delocalization in the copolycondensates.

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