

Synthesis and Thermal Stability, Dielectric, and Conductivity Characteristics of Some Carbazole-Bearing Pendant and Backbone Sulfones

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SYNOPSIS

A group of poly(*N*-vinylcarbazole) pendant polysulfones has been prepared by reacting it with benzene, toluene, *p*-chlorobenzene- and *p*-nitrobenzenesulfonyl chloride and *N*-methyl carbazole, 3,6-disulfonyl chloride by the Friedel Crafts reaction. Carbazole-based backbone polysulfones have also been prepared by the reaction of *N*-methyl carbazole, 3,6-disulfonyl chloride and biphenyl, naphthalene, anthracene, and carbazole in presence of anhydrous aluminum chloride. The various sulfone polymers, thus prepared, have been structurally characterized by elemental analysis and IR spectroscopy. Detailed analyses of thermal stability, dielectric, and conductivity characteristics have revealed certain significant differences between these two types of sulfone polymers.

INTRODUCTION

In view of the very limited information^{1,2} available on polysulfone-bearing heterocyclic moieties, the preparation of carbazole-based polysulfones appeared to be of considerable significance. It was expected that the marked thermal stability of carbazole-containing polymers vis-à-vis their outstanding photophysical electrical and conductivity characteristics³ might be reflected in these polysulfones.

Two structural varieties of the sulfone polymers were envisaged (Fig. 1): (a) carbazole-based polysulfones with the sulfone groups in the polymer backbone and (b) poly(*N*-vinylcarbazole)-based pendant sulfonyl derivatives of benzene, toluene, *p*-chloro- and *p*-nitrobenzene, and carbazole. The research described in this article was aimed at (i) developing synthetic conditions for these two types of sulfones, (ii) characterizing their structure by spectral and elemental analysis, and (iii) elucidating their thermal stability, dielectric, and conductivity behavior.

EXPERIMENTAL

Materials and Solvents

Carbazole and *N*-vinylcarbazole (BASF, Germany) were purified by recommended methods. Poly(*N*-vinylcarbazole) (PNVC) ($M_n = 6000$) was prepared by a method of Biswas and Mitra.⁴ The sulfonyl chlorides of benzene, toluene, *p*-nitrobenzene, and *p*-chlorobenzene were supplied by Aldrich and used as such.

Preparation of PNVC-based Pendant Sulfones (Scheme 1, Fig. 1): Benzenesulfonyl Derivative of PNVC (PNVC-BSC)

Nitrobenzene (30 mL), anhydrous aluminum chloride (1.1 g, 0.008 mol), and benzenesulfonyl chloride (1.3 g, 0.08 mol) were introduced under nitrogen into a carefully dried 250 mL reaction vessel and the mixture was stirred for 45 min at room temperature. A solution of PNVC (0.75 g, 0.004 mol of repeating unit) in nitrobenzene (15 mL) was slowly added to the stirred reaction mixture for 20 min. The color changed from pale yellow to red, which darkened with time. The total reaction mixture was stirred for 36 h at room temperature and then poured into a mixture of ice and 10% hydrochloric acid.

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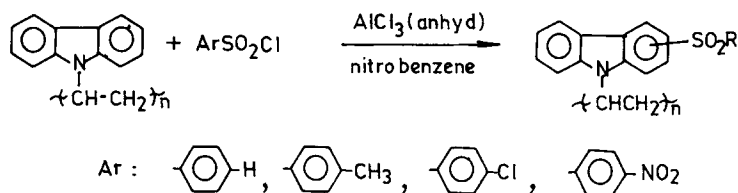
After the ice had melted, the organic layer containing the reaction product was separated and slowly added to methanol. The precipitate thus obtained was filtered, washed thoroughly with water to free the product off the acid or AlCl_3 , if any. The product was vacuum-dried at 50°C and finally washed thoroughly with methanol, benzene, and tetrahydrofu-

ran, after which the product was vacuum-dried at 60°C for 12 h.

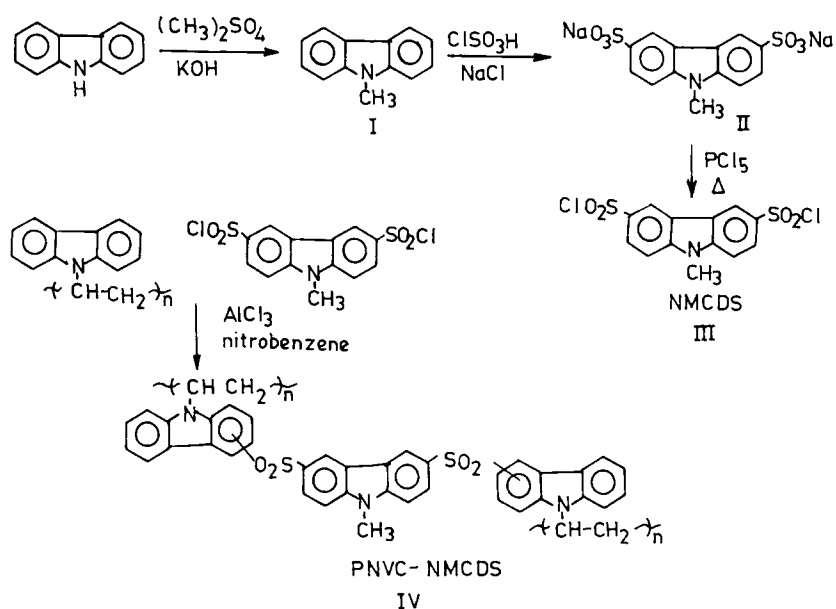
The same reaction was repeated with a 1 : 4 mol ratio of PNVC: benzenesulfonyl chloride: aluminum chloride, *p*-toluene, *p*-chlorobenzene and *p*-nitrobenzene derivatives of PNVC.

These were prepared by identical procedures used

SCHEME 1



SCHEME 2



SCHEME 3

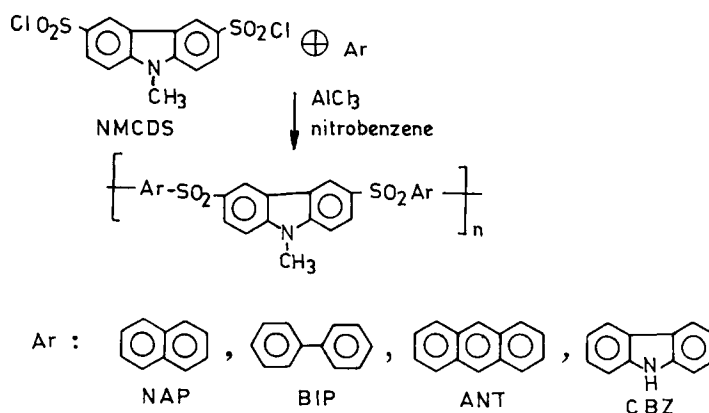


Figure 1 Synthetic routes for various carbazole-based pendant and backbone sulfone polymers.

for PNVC-BSC with selected mol ratios of the reactants in the presence of anhydrous AlCl_3 .

Preparation of *N*-Methylcarbazole-3,6-disulfonic Acid (Sodium Salt) II (Scheme 2)

Chlorosulfonic acid (12 mL) was preheated to 65–70°C in a Pyrex reaction vessel provided with a guard tube. *N*-Methylcarbazole (6 g) was added portionwise with continuous vigorous stirring. The reaction mixture was then heated to 78–80°C for 4 h, cooled, and added to ice. After the ice had melted, sodium bicarbonate solution (20%) was added to the mixture to make it partially neutral. The whole solution was then boiled for 15 min. Under this condition, the solution was saturated with sodium chloride. It was then cooled to 5–7°C to precipitate out the product. The product thus obtained was filtered and dried under vacuum at 40°C.

Preparation of *N*-Methylcarbazole-3,6-disulfonyl Chloride (NMCDS) III (Scheme 2, Fig. 1)

N-Methylcarbazole-3,6-disodium sulfonate (7 g, 0.018 mol) was mixed with PCl_5 (15 g, 0.073 mol) and shaken well to mix thoroughly in a Pyrex reaction flask provided with reflux condenser and a guard tube. After heating the mixture at 100–110°C for 6 h with occasional stirring, POCl_3 was distilled off *in vacuo* and the residual product was poured into ice. The precipitate thus obtained was filtered, washed thoroughly with water, and vacuum-dried at 40°C for 12 h to yield *N*-methylcarbazole-3,6-disulfonyl chloride (NMCDS).

Yield: 75%.

Found: C, 41.01% (41.48%); H, 2.25% (2.40%); N, 3.66% (3.70%); S, 16.72% (16.95%), the values in parentheses being the calculated values.

Preparation of *N*-Methylcarbazole Disulfone Derivative of PNVC (PNVC-NMCDS) IV (Scheme 2)

The method of preparation of PNVC-NMCDS polysulfone was exactly as that described for PNVC-BSC above. The reactants PNVC and NMCDS were taken in a 1 : 1 mol ratio.

Preparation of NMCDS-based copolysulfones (Scheme 3, Fig. 1): NMCDS-co-naphthalene Polysulfone

Nitrobenzene (25 mL), anhydrous AlCl_3 (1.34 g, 0.01 mol), and NMCDS (1.5 g, 0.004 mol) were in-

roduced under nitrogen into a carefully dried Pyrex reaction vessel. The mixture was stirred for 45 min at room temperature. A solution of naphthalene (1.28 g, 0.01 mol) in nitrobenzene (10 mL) was slowly added to the stirred reaction mixture for 20 min. During the addition, a characteristic color change was observed. The content was stirred for 36 h at room temperature and then poured into a mixture of ice and 10% hydrochloric acid. The organic layer containing the reaction product was separated and slowly added to methanol. The precipitate thus obtained was filtered and washed thoroughly with water followed by methanol. The product was then dried under vacuum at 50°C. The polymeric product was purified by digesting it with chloroform and THF followed by filtering and vacuum drying at 50°C for 12 h. (Yield: 65%.)

Preparation of NMCDS-based Biphenyl, Anthracene, and Carbazole-Copolysulfones (NMCDS-BIP, NMCDS-ANT, and NMCDS-CBZ, respectively)

The methods of preparation of all these copolysulfones were essentially identical to that for the NMCDS-NAP with the same molar ratio of the reactants and other reagents.

CHARACTERIZATION

Elemental Analysis

Carbon and hydrogen were estimated by a Heraeus C-H Analyzer. Nitrogen was determined by the Micro-Dumas method. Sulfur and chlorine were estimated by standard methods.

Infrared Spectra

IR spectra of the various polymers dispersed in KBr pellets were recorded on a Perkin-Elmer 237B IR spectrophotometer.

Thermal Stability

TG analyses were performed on a Stanton-Redcroft analyzer in air at a heating rate of 10°C/min in the range ambient–1000°C.

Dielectric and ac Conductivity

Dielectric constant, dielectric loss ($\tan \delta$), and ac conductivity measurements were made with an

impedance bridge HP A4192. The samples were used as pellets coated on both surfaces with silver paint.

Electrical Conductivity

Conductivity, dc, was measured at room temperature with a cell containing a guard ring and stainless-steel electrodes. A Keithley 6105 resistivity adaptor was used with a circuit consisting of HP 6144 precision power supply and a Keithley 6105 solid-state electrometer. The polymers were used as pellets with silver paints on either surface.

RESULTS AND DISCUSSION

The PNVC-based pendant polysulfones are insoluble powdery materials exhibiting characteristic colors (Table I). Table I shows the variation in the elemental sulfur content among the polysulfones. Evidently, PNVC-BSC polysulfone (reactants mol ratio 1 : 4) exhibits maximum incorporation of sulfur, thereby proving benzenesulfonyl chloride to be the most reactive of all toward PNVC. Nitrobenzenesulfonyl chloride is the least reactive, and the order, in general, is BSC > PTSC > CBSC > NBSC. The higher electron-withdrawing effect of the —Cl and —NO₂ groups might have caused the respective derivatives to be less reactive than the benzene derivative. Further, the elemental analyses data (Table

I) of PNVC-NMCDs-based polysulfone are very consistent with the theoretical values calculated on the basis of the proposed cross-linked structure (IV, Scheme 2).

The polysulfones reveal an antisymmetric doublet at 1290 and 1320 cm⁻¹ and a strong symmetric O=S=O absorption at 1150 cm⁻¹. The presence of —Cl and —NO₂ groups in the chloro- and nitro-based polysulfones, respectively, is also confirmed.

All the NMCDs-based main-chain copolysulfones, NMCDs-NAP, NMCDs-BIP, NMCDs-ANT, and NMCDs-CBZ, are also insoluble in common organic solvents. The elemental analysis data (Table I) are found to be in good agreement with the theoretical values calculated on the basis of the structures proposed (Scheme 3). All these copolysulfones exhibit characteristic IR absorption at 1280–1300 and 1160–1165 cm⁻¹, thus confirming the formation of sulfone linkage in the polymers.

Thermal Stability

Figures 2 and 3 are representative of the thermal behavior of all the pendant polysulfones, i.e., those from 1 : 2 and 1 : 4 molar ratios of the reactants and also PNVC-NMCDs-based polysulfones. Except for PNVC-CBSC (Fig. 3), all other polysulfones are thermally less stable than the unmodified PNVC, up to a decomposition of 10–25% of the corresponding polymers. Evidently, PNVC-CBSC exhibits superior thermal stability to PNVC. For example, for 10% decomposition, the order is

Table I Physical Characteristics of PNVC-based Polysulfones and NMCDs-based Copolysulfones

Polymer	Color	Percent Content of the Elemental				
		Carbon	Nitrogen	Sulfur	Hydrogen	Chlorine
PNVC-BSA ^a	Brown	72.08	4.21	9.51	5.01	—
PNVC-BSC ^b	Grey	65.88	3.18	12.02	4.38	—
PNVC-PTSC ^a	Grey	77.10	4.98	6.98	5.12	—
PNVC-PTSC ^b	Grey	77.51	3.85	9.89	4.88	—
PNVC-CBSC ^a	Green	74.42	5.13	5.12	4.62	6.00
PNVC-CBSC ^b	Green	60.32	4.09	7.78	3.92	8.91
PNVC-NBSC ^a	Green	77.21	7.31	4.21	4.72	—
PNVC-NBSC ^b	Green	68.17	7.35	7.39	3.13	—
PNVC-NMCDs ^c	Brown	70.33	6.71	8.79	4.21	—
NMCDs-NAP	Brown	63.02	3.10	14.98	3.34	—
NMCDs-BIP	Dark brown	64.76	2.98	13.51	3.56	—
NMCDs-ANT	Deep brown	66.64	3.00	13.03	3.17	—
NMCDs-CBZ	Deep green	63.10	5.61	13.62	3.28	—

^a Mol ratio 1:2 (PNVC:aromatic sulfonyl chloride).

^b Mol ratio 1:4 (PNVC:aromatic sulfonyl chloride).

^c Mol ratio 1:1 (PNVC:NMCDs).

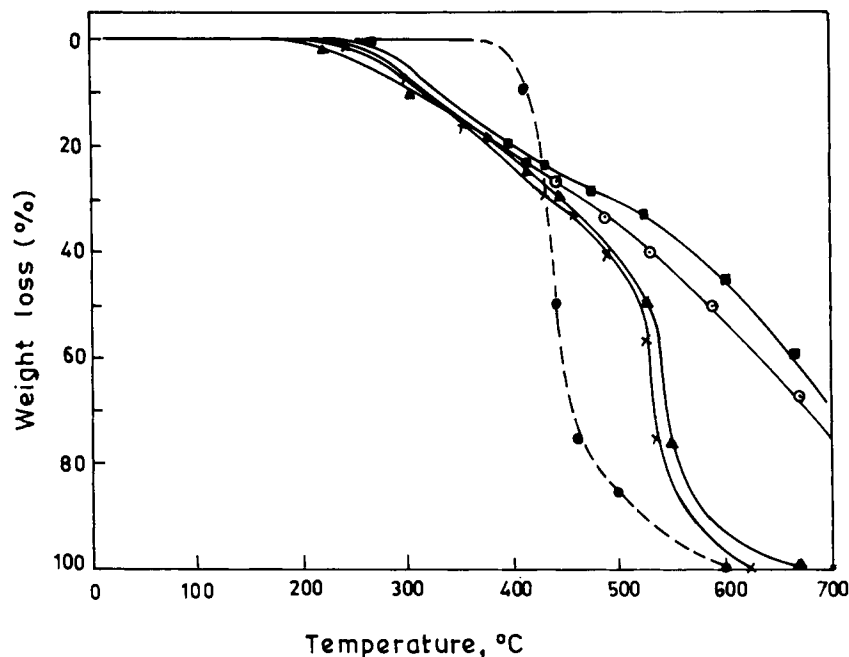


Figure 2 Thermogravimetric analysis curve of (●) PNVC, (*) PNVC-BSC, (○) PNVC-PTSC, (■) PNVC-CBSC, and (▲) PNVC-NBSC in 1 : 2 molar ratio of the reactants.

PNVC-CBSC (460°) > PNVC (410°)
 > PNVC-PTSC (365°) > PNVC-NBSC (350°)
 > PNVC-BSC (345°)

However, the trend in thermal stability for both (1 : 2) and (1 : 4) types of PNVC-based polysulfones is identical, i.e.,

PNVC-CBSC > PNVC-PTSC
 > PNVC-NBSC > PNVC-BSC

The thermal stability of PNVC-NMCDS (Fig. 4) is somewhat comparable to that of other aromatic sulfone derivatives of PNVC, bearing higher percentages of the sulfone group. This is due presumably to the formation of the cross-linked rigid structure in PNVC-NMCDS (**IV**, Scheme 2), where NMCDS may act as a bridge between the PNVC chains.

From the results, it appears that with an increase in the sulfone group content in a particular polysulfone the stability increases. The degradation in the range 350–425°C may be tentatively ascribed to the homolytic scission of C—S linkage.⁵ Reportedly,⁶ the decomposed product in such cases has been found to be SO₂,⁷ produced in a yield comparable to that for C—S scission. The second step of degradation may be due to oxidative degradation

occurring in the PNVC chains. In the light of various results available on carbazole polymers, it seems that stripping of monomeric carbazoles⁸ and oxidative degradation of the aromatic counterparts to form quinonoid structures⁸ may occur in the thermal degradation process.

Figure 5 describes the thermal stability of the main-chain copolysulfones where NMCDS-CBZ is found to be most stable out of all the four copolysulfones throughout the whole degradation process. Typically, the stability trend for ca. 25% decomposition is

NMCDS-NAP (450°) < NMCDS-BIP (475°)
 < NMCDS-ANT (510°) < NMCDS-CBZ (535°)

This indicates that inclusion of the heterocyclic moiety, e.g., the carbazole or anthracene moiety, induces comparatively higher stability in the resultant copolysulfones than those with naphthalene or biphenyl. Significantly, this is also the order in the variation of the resonance stabilization energy of BIP < NAP < ANT < CBZ.

Dielectric Characteristics

Table II presents the dielectric constant and loss behavior of the polysulfones at frequencies 1 and 10

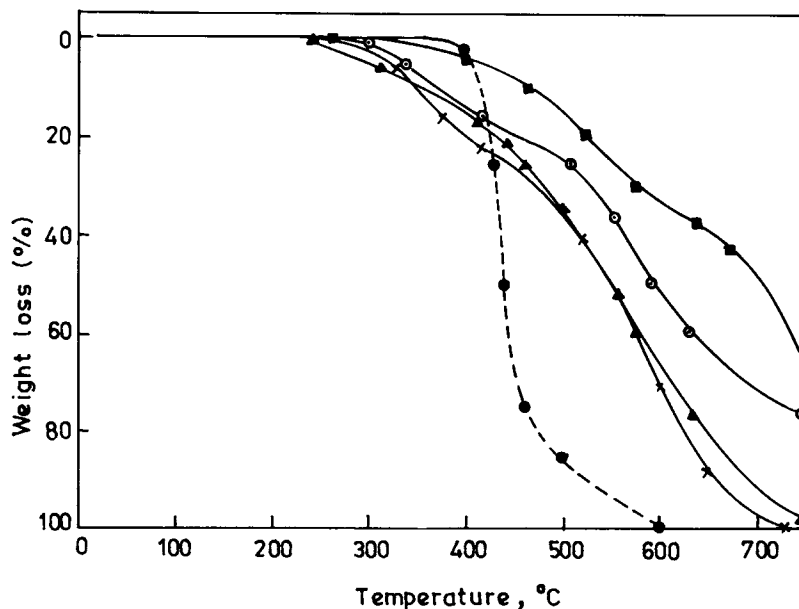


Figure 3 Thermogravimetric analysis curve of (●) PNVC, (*) PNVC-DSC, (○) PNVC-PTSC, (■) PNVC-CBSC, and (▲) PNVC-NBSC in 1 : 4 molar ratio of the reactants.

kHz. Evidently, frequency variation has a very little effect both on the dielectric constant and loss of the polysulfones. However, polysulfones produced from a 1 : 4 mol ratio of the reactants exhibit somewhat higher dielectric constant values than those from a 1 : 2 mol ratio of the same. This indicates that an increase in the extent of incorporation of sulfone groups into the PNVC chain results in an increase in the dielectric constant of the modified PNVC. Thus, the aryl-SO₂- moiety seems to be respon-

sible for an increase in the polarization in the modified PNVC system, thereby exhibiting an increase in the dielectric constant value at lower frequency. The polar —NO₂ and —Cl groups in the aromatic sulfonyl moiety further facilitate the polarizability, and as a result (Table II), PNVC-NBSC and PNVC-CBSC exhibit higher dielectric constant values compared to the BSC- and PTSC-modified PNVC sulfones. This effect of increased polarity is also reflected in the dielectric loss values, where a

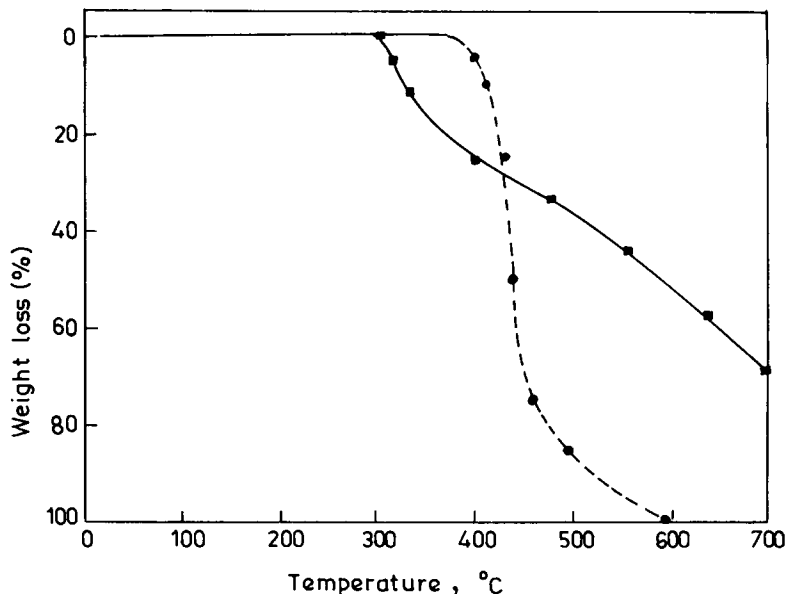


Figure 4 Thermogravimetric analysis curve of (●) PNVC and (■) PNVC-NMCDs.

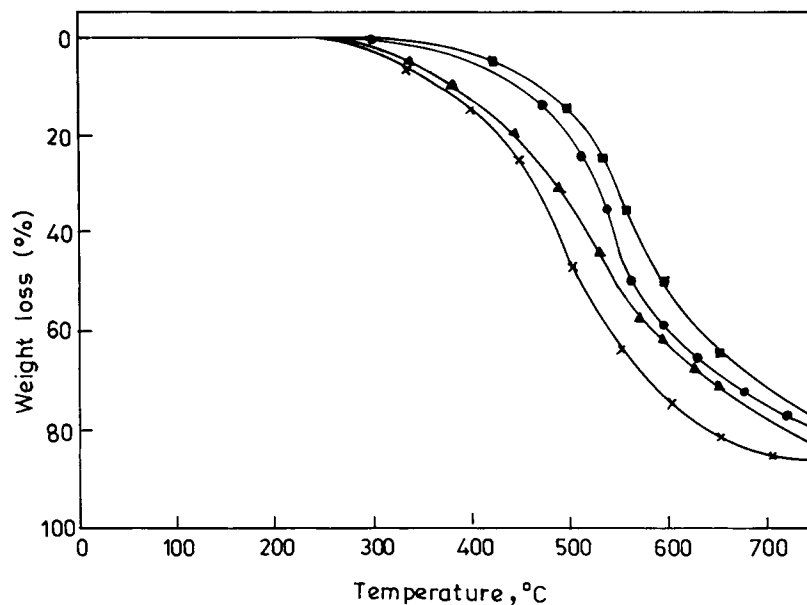
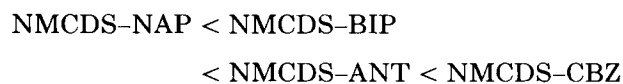


Figure 5 Thermogravimetric analysis curve of (*) NMCDS-NAP, (▲) NMCDS-BIP, (●) NMCDS-ANT, and (■) NMCDS-CBZ.

sharp decrease in loss values is observed with an increase in frequency. This feature is typical of polymers with polar groups where orientation polarization predominates at lower-frequency ranges.⁹

High dielectric constant and loss values (Table II) observed for the PNVC-NMCDS polysulfones may be attributed to the greater extent of polarization,¹⁰ provided tentatively through cross-linking of two polar PNVC chains by the carbazole disulfonyl moiety (IV, Scheme 2).

All the *N*-methylcarbazole-3,6-disulfone (NMCDS)-based main-chain copolysulfones exhibit (Table II) high dielectric constant values compared to the pendant ones, the order being

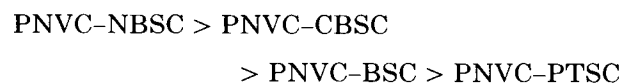


The density of the π -electron system and the resonance stabilization energy vary in the same order for the aromatic and the heterocyclic moieties. Accordingly, electron polarizability in the presence of an applied field, hence, the dielectric constant, will be expected to vary in the same order.

dc Conductivity Characteristics

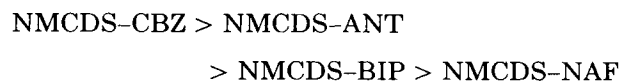
The aromatic sulfonyl derivatives of PNVC exhibit dc conductivity (Table III) of the order of 10^{-7} (ohm-cm)⁻¹, whereas the PNVC-NMCDS disulfone derivative exhibits a hundredfold higher conductiv-

ity, i.e., 10^{-5} (ohm-cm)⁻¹. The higher extent of π -electron conjugation in the proposed cross-linked structure of PNVC-NMCDS as well as the higher resonance stabilization expected due to the presence of a larger number of carbazole moiety in the chain seem to be responsible for its high conductivity value. The trend in the conductivity values for the aromatic sulfonyl-based PNVC systems is



with either 1 : 2 or 1 : 4 mol ratio of the reactants, although the variation is only very slight. However, PNVC-NBSC shows the highest value due to the highest resonance stabilization¹¹ provided to the system by NMSC through the $-\text{NO}_2$ group, relative to others, i.e., $-\text{Cl}$, $-\text{H}$, or $-\text{CH}_3$.

The dc conductivities of NMCDS-based main-chain copolysulfones at room temperature (Table III) are of the order of 10^{-5} (ohm-cm)⁻¹ and the trend is



As explained, extended π -conjugation in the group of copolysulfones is likely to be responsible for the observed high conductivity value. The highest con-

ductivity in all these four polymers is exhibited by NMCDs-CBZ, which probably results from the preponderance of the heterocyclic groups in the chain that enhances the resonance stabilization and, hence, the conductivity.

CONCLUSION

Thermal stability, dielectric, and conductivity characteristics of poly(*N*-vinylcarbazole) pendant sulfonyl derivatives of benzene, toluene, *p*-chloro- and *p*-nitrobenzene, and carbazole show significant variations in the series. A comparison of these properties with those of carbazol-based backbone polysulfones from biphenyl, naphthalene, anthracene, and carbazole also reveals characteristic differences arising out of structural variations.

Table II Dielectric Characteristics of PNVC-based Pendant Polysulfones and NMCDs-based Copolysulfones

Polymer	Dielectric Characteristics			
	Dielectric Constant at Frequency (kHz)		Dielectric Loss at Frequency (kHz)	
	1	10	1	10
PNVC-BSC ^a	10.61	10.53	0.006	0.001
PNVC-PTSC ^a	10.58	10.45	0.007	0.001
PNVC-CBSC ^a	10.77	10.37	0.030	0.002
PNVC-NBSC ^a	11.49	11.22	0.010	0.009
PNVC-BSC ^b	12.47	11.71	0.010	0.006
PNVC-PTSC ^b	12.31	11.43	0.010	0.007
PNVC-CBSC ^b	16.15	15.72	0.020	0.002
PNVC-NDSC ^b	17.25	16.17	0.020	0.005
PNVC-NMCDs	—	146.51	—	0.126
NMCDs-NAP	—	78.81	—	0.089
NMCDs-BIP	—	81.32	—	0.092
NMCDs-ANT	—	124.52	—	0.108
NMCDs-CBZ	—	142.60	—	0.112

PNVC (unmodified) dielectric constant = 4.96 and dielectric loss = 0.0027 at 100 kHz.

^a Mol ratio 1:2.

^b Mol ratio 1:4.

Table III dc Conductivity Characteristics of PNVC-based Pendant Polysulfones and NMCDs-based Copolysulfones

Polymer	dc Conductivity (ohm-cm) ⁻¹ at Room Temperature
PNVC-BSC ^a	1.44×10^{-7}
PNVC-PTSC ^a	1.42×10^{-7}
PNVC-CBSC ^a	1.47×10^{-7}
PNVC-NBSC ^a	1.96×10^{-7}
PNVC-BSC ^b	2.36×10^{-7}
PNVC-PTSC ^b	2.21×10^{-7}
PNVC-CBSC ^b	2.82×10^{-7}
PNVC-NBSC ^b	3.23×10^{-7}
PNVC-NMCDs	2.32×10^{-5}
NMCDs-NAP	1.01×10^{-5}
NMCDs-BIP	1.31×10^{-5}
NMCDs-ANT	3.40×10^{-5}
NMCDs-CBZ	1.94×10^{-5}

^a Mol ratio 1:2.

^b Mol ratio 1:4.

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REFERENCES

- S. K. Das and M. Biswas, *Polymer*, **23**, 1713 (1981).
- M. Biswas, A. Mazumdar, and P. Mitra, *Polym. Bull.*, **20**, 323 (1989).
- R. C. Penwell, B. N. Ganguly, and T. W. Smith, *J. Polym. Sci. Macromol. Rev.*, **13**, 63 (1978).
- M. Biswas and P. Mitra, *J. Appl. Polym. Sci.*, to appear.
- M. J. Bowden et al, *Macromolecules*, **15**, 1417 (1982).
- M. J. Brown and J. H. O'Donnel, *Macromolecules*, **5**, 109 (1972).
- T. N. Bowmer and J. H. O'Donnel, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 45 (1981).
- J. Y. C. Chu and M. Stolka, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 2867 (1975).
- A. Tager, *Physical Chemistry of Polymers*, 2nd ed, Mir, Moscow, 1978, pp. 273-286.
- H. Meier, *Organic Semiconductors*, Verlag-Chemie, 1974, Vol. 2, p. 227.
- I. L. Finar, *Organic Chemistry*, 6th ed. Longman, UK, 1973, Vol. 1, p. 590.

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