Synthesis and Thermal Stability, Dielectric and Conductivity Characteristics of Some Aromatic Anhydride-Modified Carbazole Polymers

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SYNOPSIS

Copolycondensates have been prepared from carbazole, poly(N-vinylcarbazole) and various aromatic anhydrides, e.g., phthalic anhydride, trimellitic acid anhydride, pyromellitic dianhydride, naphthalene tetracarboxylic dianhydride, and benzophenone tetracarboxylic dianhydride in presence of the Friedel–Crafts catalyst anhydrous zinc chloride at high temperature. The polymers have been characterized by elemental analyses and IR spectroscopy. Thermal stabilities, dielectric, and conductivity behaviors of these polymers have also been evaluated and it has been observed that these properties show interesting differences depending upon the nature of the anhydride.

INTRODUCTION

Carbazole-based polymer systems have received much research attention[1,2] because of their interesting thermal, electrical and photophysical properties. In continuation of our attempts[3,4] to improve upon these properties of carbazole polymers by chemical modification, we have now prepared and evaluated a series of polycondensates from carbazole/poly(N-vinylcarbazole) and aromatic anhydrides (Fig. 1). The latter includes phthalic anhydride (PA), trimellitic acid anhydride (TMA), pyromellitic dianhydride (PMDA), naphthalene tetracarboxylic dianhydride (NTDA), and benzophenone tetracarboxylic dianhydride (BTDA). Evidently, the resultant copolycondensates would experience interesting structural variations arising out of the differences in bulkiness, functionality, reactivity, resonance stability, and conjugation in the various moieties. As a result, the bulk properties as above would be modified. Salient features of this research are now highlighted in this article.

EXPERIMENTAL

Materials

Carbazole (BDH), phthalic anhydride (Sarabhai Chemicals), trimellitic anhydride (Fluka AG), pyromellitic dianhydride (Fluka AG), 1,4,5,8-naphthalene tetracarboxylic dianhydride (Aldrich), and benzophenone tetracarboxylic dianhydride (Aldrich) were used directly as supplied. Poly(N-vinylcarbazole) (PNVC, $\bar{M}_n$ = 3300) was prepared from N-vinylcarbazole (BASF) following a standard method,[5] reprecipitated twice from the THF solution of PNVC by methanol and finally dried off the solvent in vacuum. Anhydrous zinc chloride (Merck) was used as the catalyst.

Synthesis

Carbazole–Anhydride Copolycondensates

Carbazole (CBZ), phthalic anhydride (PA), and anhydrous $ZnCl_2$ were intimately mixed together in the mole ratio of 1 : 1 : 2 in a mortar. The mixture was heated gradually to 265 ± 5°C in a Pyrex flask under nitrogen for 18 h. At the end of this reaction
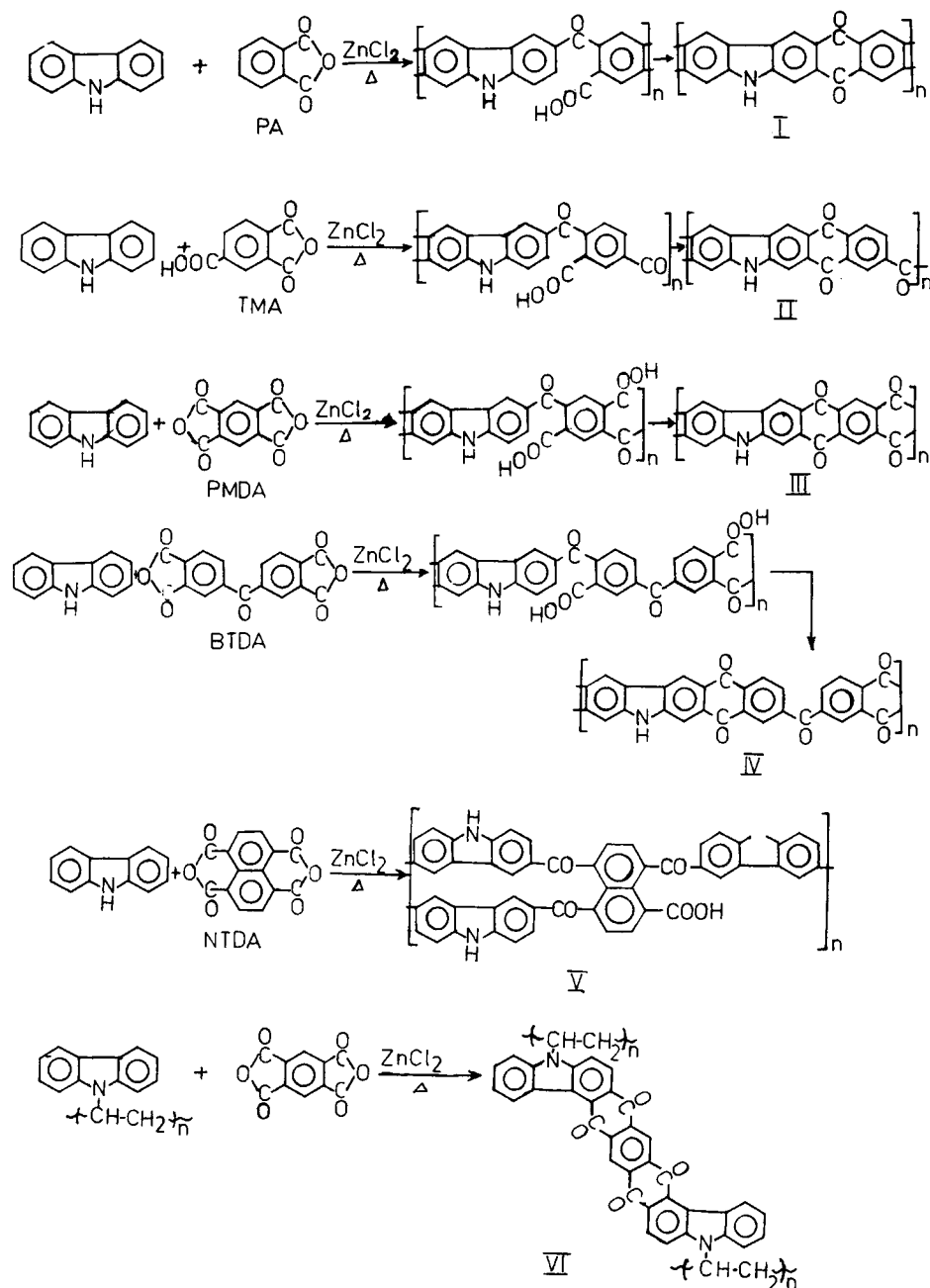
Figure 1   Tentative structures and modes of formation of the PNVC/CBZ–anhydrides copolycondensates.

time, a black mass was obtained, which was digested with 2N HCl, filtered, and washed several times with distilled water, until it became free from Zn ions and the acid. The mass was then washed thoroughly with methanol, chloroform, and THF successively, filtered, and oven-dried. Finally the product was dried in vacuum at 100°C for 12 h, yielding a black insoluble powdery polymeric mass (CBZ–PA).

A similar procedure was adopted for preparing other carbazole based condensates i.e., carbazole–trimellitic anhydride (CBZ–TMA), carbazole–pyromellitic dianhydride (CBZ–PMDA), carbazole–1,4,5,8-naphthalene tetracarboxylic dianhydride (CBZ–NTDA), and carbazole–benzophenone tetracarboxyl dianhydride (CBZ–BTDA) copolycondensates.

PNVC–Anhydride Copolycondensates

The respective PNVC–anhydride copolyconden-sates, i.e., PNVC–PA, PNVC–TMA, PNVC–PMDA, PNVC–NTDA, and PNVC–BTDA, were prepared by a similar procedure using a molar ratio of 1 : 1 : 2 (1 mole of the repeating unit of PNVC per anhydride). In all the cases black insoluble powdery masses were obtained. The condensates were freed of unreacted PNVC, $ZnCl_2$, and anhydrides by repeated treatment with 2 N HCl, water, benzene, chloroform, and THF.

Characterization

Elemental Analyses

Carbon and hydrogen contents of the polymers were estimated by a Heraeus C—H analyzer. Nitrogen was quantitatively estimated by the micro-Dumes method.

IR Spectra

IR spectra of the copolycondensates were recorded on a Perkin-Elmer 237B spectrophotometer.

Thermal Analyses

Thermogravimetry and differential thermal analyses of the polymers were studied with a Stanton Red-croft thermal analyzer under static air at a heating rate of 10°C/min.

Dielectric Properties

The dielectric constant (ϵ) and dielectric loss (tan δ) were measured by an impedance analyzer (HP, A4192) at room temperature. Measurements of the polymers were carried out in the pellet form with silver coatings on the surfaces.

dc Conductivity

dc conductivities of the polymers were measured with the variation in temperature by a 1666 dc resistance bridge (General Radio) with silver-coated samples in the pellet forms.

RESULTS AND DISCUSSION

General Features and Structural Characteristics

All the polycondensates were isolated as black powdery masses which were insoluble in common solvents including DMF, DMSO, DMAc, and concd. H_2SO_4.

The conventional mode of the reaction between carbazole and the anhydrides is schematically shown in Figure 1.

The elemental analytical data for carbon, hydrogen, and nitrogen for the various polycondensates are presented in Table I. The values in parantheses represent the theoretical percentages of the elements on the basis of the proposed structures. In general, the agreement between the theoretical and the experimental values are fairly convincing considering

Table I Characterization of the Carbazole Poly(N-Vinylcarbazole)–Anhydride-Based Copolycondensate

Polycondensates	Yield (%)	Percentage Contents of Elements			Characteristic IR-Absorption Peaks (cm⁻¹)
		Carbon	Hydrogen	Nitrogen	
CBZ–PA	70	82.91 (81.91)	2.51 (2.39)	4.66 (4.78)	3340 (NH stretching), 1679 (quinone)
CBZ–TMA	70	81.50 (78.26)	1.59 (2.48)	4.20 (4.35)	3340 (—NH stretching), 1679 (quinone)
CBZ–PMDA	75	77.74 (75.65)	2.10 (2.00)	4.09 (4.01)	3400 (—NH stretching), 1690 (quinone)
CBZ–NTDA	78	87.87 (80.21)	2.61 (3.47)	5.59 (5.61)	3400 (—NH stretching), 1710, 3200, 1420, 1270 (—COOH group), 1580, 1450 (C==C aromatic)
CBZ–BTDA	75	79.87 (76.82)	2.61 (2.42)	3.95 (3.09)	3420 (—NH stretching), 1690 (quinone), 1700 (ketonic), 1580, 1440 (C==C aromatic)
PNVC–PA	75	84.27 (82.75)	2.77 (2.82)	3.85 (4.39)	1680 (quinone)
PNVC–TMA	75	81.15 (79.31)	3.36 (2.87)	3.90 (4.02)	1680 (quinone)
PNVC–PMDA	80	79.75 (76.80)	2.18 (2.40)	4.14 (3.73)	1679 (quinone)
PNVC–NTDA	80	88.01 (81.35)	4.25 (3.87)	4.73 (5.08)	1710, 1420, 1265 (—COOH group)
PNVC–BTDA	75	81.47 (77.66)	2.87 (2.71)	3.97 (2.92)	1080 (quinone), 1700 (ketonic)

the uncertainties involved in the analysis of insoluble organic systems. IR absorption data (Table I) confirm the presence of N–H and quinonic linkages expected for these polycondensates (Fig. 1).

Structure of CBZ–NTDA Polycondensate

The conventional mode of condensation between CBZ and NTDA involving quinonic structure is unlikely on several counts: (i) It will give rise to a seven-membered-ring system the stability of which under the high temperature used in the synthesis is questionable. (ii) IR absorptions rule out the presence of quinonic groups, but suggest the presence of the free carboxylic group. Recently, a similar observation has been confirmed[6] in anthraquinone–NTDA-based condensates. (iii) The elemental analysis data differ widely for such a structure from the expected values. Considering the above, it seems reasonable to suggest the CBZ–NTDA structure as shown in Figure 1. The elemental nitrogen percentage agrees reasonably well with the expected value, while C and H percentage values show some deviations.

However, the general insolubility of polycondensates renders an unambiguous structure determination extremely difficult—an experience shared by other investigators[7-9] in this field. Consequently, these suggestions are to be regarded as tentative ones.

Structure of PNVC–Anhydride Condensates

Apparently, as shown with the PNVC–PMDA system (structure V, Fig. 1), interchain crosslinks are established in the reaction of PNVC with various anhydrides. The formation of insoluble crosslinked network during the reaction of PNVC and PA has been confirmed earlier.[10] In the case of the PNVC–NTDA system, the crosslinks between the PNVC chains may be readily introduced by the anhydride moiety through ketonic links (structure V, Fig. 1). Apparently in this system a crosslink possibility is appreciably higher than in the others.

Thermal Stability Characteristics

The thermal stabilities of the various polycondensates have been compared in Table II and the data suggest the following trends:

(i) With either CBZ or PNVC, initial decomposition temperature and the overall stability depend on the anhydride moiety

$$NTDA > BTDA > PMDA > TMA > PA$$

(ii) With a fixed anhydride, initial decomposition temperature and the overall stability vary in the order PNVC > CBZ.

(iii) In general, polycondensation of PNVC by anhydrides improves the thermal stability of the base polymer.

These trends appear reasonable from structural considerations. The NTDA moiety itself is expected to possess higher inherent stability as a condensed hydrocarbon anhydride with considerably greater resonance stabilization than benzene derivatives. Moreover, the structure V in Figure 1 proposed for CBZ–NTDA is expected to be more rigid and can

Table II Thermal Stabilities of the CBZ/PNVC–Anhydride-Based Copolycondensates

| Polycondensate | Temperature (°C) with Corresponding Weight Loss (%) | | | | | DTA Peak (Endo.) at Temp (°C) |
	Initial Decomposition	5	25	50	Complete (%)	
CBZ–PA	300	325	405	465	585 (98%)	470
PNVC–PA	370	415	420	500	640 (98%)	490
CBZ–TMA	305	330	410	475	600 (97%)	460
PNVC–TMA	370	415	425	505	680 (98%)	495, 658
CBZ–PMDA	310	340	415	500	610 (98%)	475
PNVC–PMDA	375	420	470	540	700 (95%)	495, 656
CBZ–NTDA	330	430	515	545	620 (98%)	500
PNVC–NTDA	400	470	530	596	806 (97%)	518
CBZ–BTDA	315	420	480	535	620 (96%)	480
PNVC–BTDA	375	425	495	550	732 (97%)	495, 677
PNVC	375	420	430	440	520	—

Table III Isothermal Stability of Carbazole/PNVC–Anhydride-Based Polycondensates

Polymer	Total Weight Loss (%) after Heating in Air for							
	8 h at		12 h at		16 h at		24 h at	
	280°C	350°C	280°C	350°C	280°C	350°C	280°C	350°C
CBZ–PMDA	4.92	20.96	12.66	21.61	15.22	23.59	19.33	—
PNVC–PMDA	4.84	22.62	12.89	20.76	14.87	22.69	17.85	—
CBZ–BTDA	4.66	19.08	11.12	23.48	14.12	26.73	18.36	—
PNVC–BTDA	5.10	16.39	10.32	20.12	13.01	25.83	15.66	—
CBZ–NTDA	3.46	6.48	8.01	12.97	12.69	18.00	17.84	—
PNVC–NTDA	3.59	7.00	8.52	13.01	11.23	17.61	13.43	—

induce interchain crosslinks through pendant —COOH groups. Repeat-unit-wise, CBZ–NTDA possesses a greater amount of N, implying greater incorporation of carbazole moiety, which by virtue of its inherent thermal stability should also contribute to the overall stability.

The second and third features are best interpreted by the manifestation of a crosslinked polymer network through the anhydride moieties linking up different PNVC chains (cf. structure VI, Fig. 1). Such crosslinked systems will be thermally stable by virtue of their rigid structure, the relative stabilities of the various systems will obviously depend on the extent of such interchain crosslinks, introduced in the polycondensates.

Isothermal Stability. Table III compares the isothermal degradation stability of pairs of polycondensates, discussed above. These data nicely confirm the high thermal stability of NTDA over the others (NTDA > BTDA > PMDA) as discussed earlier.
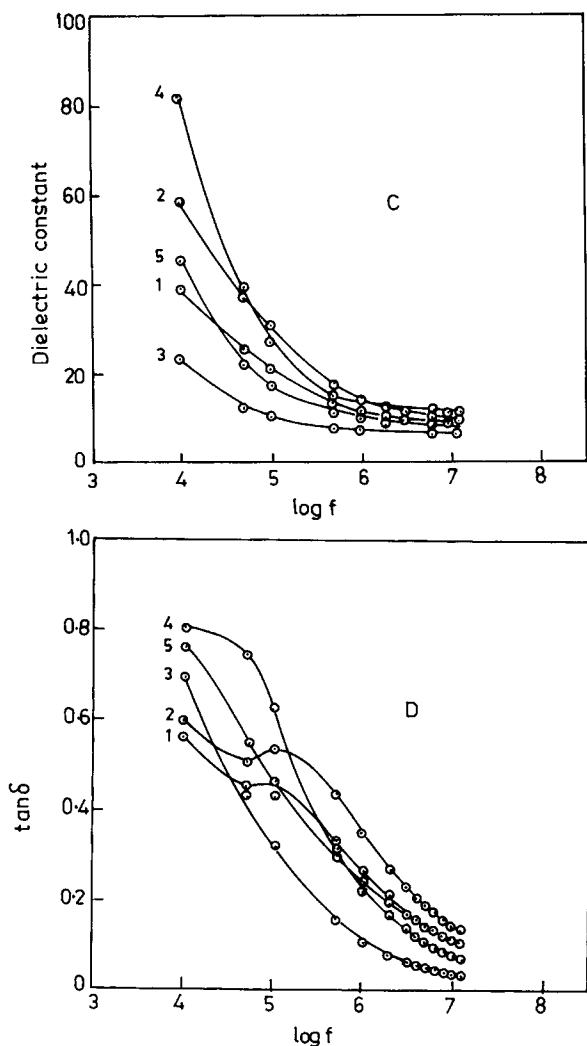
Dielectric Behavior

The variation of the dielectric constant and the dielectric loss parameters with frequency for all the CBZ and PNVC/anhydride polycondensates is presented in Figures 2 and 3 (A–D) respectively. The following features are noteworthy: (i) the dielectric constant values decrease sharply with an increase in frequency. At low frequency ($f = 10^4$ Hz) the dielectric constants depend on the nature of the anhydride moiety in the order: NTDA > TMA > BTDA > PA > PMDA both in the case of CBZ and PNVC systems. (ii) The magnitudes of the dielectric constants at low frequencies (10^4–10^5 Hz) are appreciably higher in the case of PNVC/anhydrides systems than in the CBZ/anhydrides systems. In general, these values are much higher compared to those for most organic molecules (2–10).[11]

(iii) All these polycondensates exhibit broad dielectric loss over the frequency range 10^4–10^7 Hz [Figs. 2(B) and 3(D)].

The relatively high frequency-dependent dielectric constants realized with these polymers appear to be consistent with the conjugated structures pos-
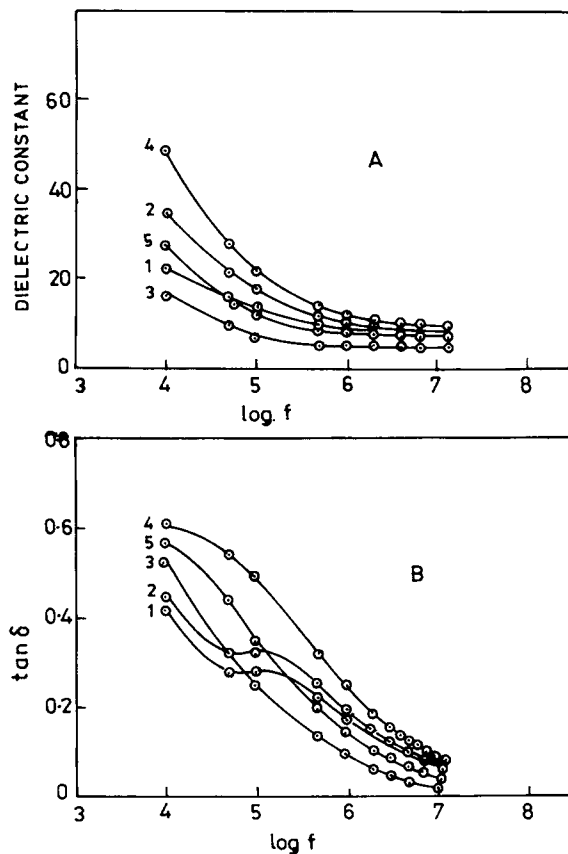
Figure 2 Dielectric constant (A) and dielectric loss (tan δ) (B) vs. log(frequency) plots of the copolycondensates: (1) GBZ–PA; (2) CBZ–TMA; (3) CBZ–PMDA; (4) CBZ–NTDA; (5) CBZ–BTDA.

**Figure 3** Dielectric constant (C) and dielectric loss (tan δ) (D) vs. log(frequency) plots of the copolycondensates: (1) PNVC–PA; (2) PNVC–TMA; (3) PNVC–PMDA; (4) PNVC–NTDA; (5) PNVC–BTDA.

sible for these systems. Relevantly, very similar behavior has been observed by us[6] with anthracene–anhydride-based polycondensates. Conjugation will facilitate frequency-induced dielectric polarization which will be further enhanced by polar groups. NTDA-based polymers evidently possess a highly conjugated π-electron-rich structure compared to the others and, as mentioned earlier, relatively higher incorporation of heterocyclic carbazole moiety in NTDA-based system should further facilitate greater electron polarization. NTDA/TMA-based systems may be expected to be more crosslinked intermolecularly through —COOH group compared to either BTDA or PMDA and PA. As such, conjugation should be enhanced to result in

high electron polarizability. The lower dielectric constant values in BTDA- or PMDA-based systems may result from the possibility that steric restrictions imposed by the bulky groups will control the formation of very long chain conjugated structures, thereby affecting electron polarizability. Relevantly, Hodgkin and Heller[12] reported that copolycondensation of tetraamines with PMDA and NTDA is favored more with NTDA than with PMDA due to stereochemical reasons.

DC Conductivity Characteristics

All these polycondensates exhibit temperature-dependent conductivities (Table IV). As expected, PNVC/CBZ–NTDA systems exhibit the highest conductivity in the series. The activation energies for conduction (Table IV) as obtained from log σ vs. 1/T plot (Fig. 4) depend on the anhydride moiety in the order: NTDA < TMA < BTDA < PA < PMDA. Barring TMA, this order is consistent with decreasing number of rings or π-electrons in the structure.[13] The exceptional behavior of TMA has been reported by Pohl et al. with regard to conductivity characteristics of anthracene/phenazene/phenanthrene–PMDA/TMA polycondensates. It appears that the —COOH moiety enhances intermolecular hydrogen bonding or ionic interactions
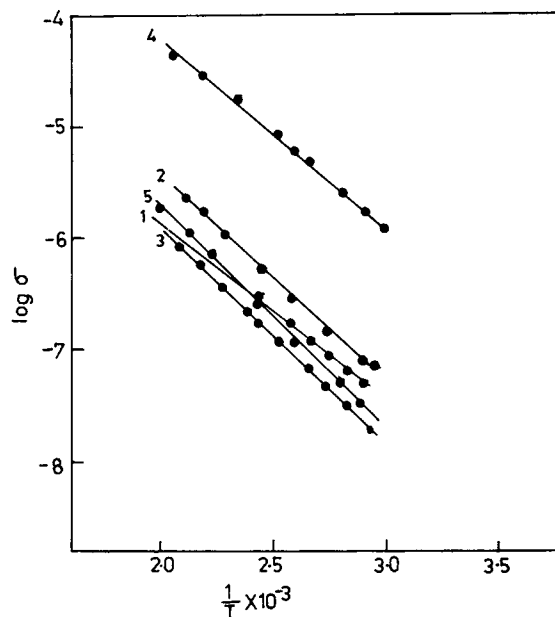
Figure 4 DC conductivity, log(σ), vs. temperature (1/T × 10⁻³) plot of the PNVC-based copolycondensates: (1) PNVC–PA; (2) PNVC–TMA; (3) PNVC–PMDA; (4) PNVC–NTDA; (5) PNVC–BTDA.

Table IV   DC Conductivities and the Activation Energies of the Carbazole/PNVC–Anhydride-Based Copolycondensates

Polymer	DC Conductivity at Room Temperature (27°C) (Ω^{-1} cm^{-1})	DC Conductivity at 200°C (Ω^{-1} cm^{-1})	Thermal Activation Energy E_a(eV)	Energy Interval E_g [$=2E_a$] (eV)
PNVC–PA	2.71×10^{-8}	9.33×10^{-7}	0.329	0.658
PNVC–TMA	5.34×10^{-8}	2.61×10^{-6}	0.306	0.612
PNVC–PMDA	7.63×10^{-9}	7.32×10^{-7}	0.397	0.794
PNVC–NTDA	3.40×10^{-7}	3.95×10^{-5}	0.294	0.598
PNVC–BTDA	1.23×10^{-8}	1.37×10^{-6}	0.317	0.634
CBZ–PA	1.32×10^{-8}	6.73×10^{-7}	0.362	0.724
CBZ–NTDA	1.91×10^{-7}	1.76×10^{-5}	0.273	0.546
CBZ–BTDA	1.40×10^{-7}	1.66×10^{-5}	0.297	0.595

(with other —COOH moieties), thereby reducing intermolecular conduction barriers.[14]

A point of further interest is that the conductivities in PNVC-based polycondensates are appreciably higher than those for CBZ-based systems. This feature again implies a more conjugated and intermolecularly crosslinked structure which, as discussed before, is tentatively represented by structure VI (Fig. 1).

The term E_g (energy gap) in Table IV needs some comments. Unlike the well-established semiconducting systems, organic semiconductors pose some problems in the evaluation of the so-called band gap energy. In fact, the term energy gap in this system is restricted by the question whether or not the particular sample meets the theoretical requirement in the use of the term energy gap. Pohl et al.[7,8] have considered that question while formulating the thermal activation energy in organic semiconductors and recommended the use of the term "energy interval" E_g, in place of the conventional energy gap or forbidden band gap. E_g is given by $2E_a$ and will thus provide a comparison of the semiconductor behavior of the present systems with other well-understood semiconductors.

CONCLUSIONS

Polycondensates derived from poly(N-vinylcarbazole) and carbazole through reaction with PA, TMA, PMDA, NTDA, and BTDA show interesting and characteristic differences in thermal stability, dielectric, and conductivity behavior. These properties are enhanced to the maximum extent in NTDA-based polycondensates.

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