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Thermal stability, dielectric and conductivity characteristics of 9,10-anthracene-diol-anhydride polycondensates

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SUMMARY

Four polycondensates have been prepared from 9,10-anthracene-diol and succinic anhydride, phthalic anhydride, pyromellitic dianhydride and 1,4,5,8-naphthalene tetracarboxylic dianhydride. Thermal stabilities, dielectric and conductivity characteristics of these condensates indicate that these properties are influenced by the nature of the anhydride moiety.

INTRODUCTION

During our work with anthracene based polymer systems [1,2] the idea occurred to us that properties such as thermal stability, dielectric and conductivity characteristics of anthracene - anhydride polycondensates might perhaps be modified by changing the anhydride moiety from aliphatic, aromatic to condensed aromatics with progressively increasing delocalized π-electrons and resonance stabilization. Accordingly, we report here the synthesis of polycondensates from 9,10-dihydroxyanthracene (AHQ) and succinic anhydride (SA), phthalic anhydride (PA), pyromellitic dianhydride (PMDA) and 1,4,5,8-naphthaline tetracarboxylic dianhydride (NTDA), and their characterization in regard to the above properties.

EXPERIMENTALS

Materials

Anthraquinone (BDH), pyromellitic-dianhydride (Fluka), phthalic anhydride (Fluka), succinic anhydride (BDH) and 1,4,5,8-naphthalene tetracarboxylic dianhydride (Aldrich) were used without further purification. Zince chloride, Dry (Merck) was again dried at 100°C for 24 h. All other chemicals and solvents were reagent grade and used without purification.

Synthesis

Preparation of anthracene-9,10-diol (anthrahydroquinone) [AHQ] :

Anthraquinone (5 g) and zinc-dust (4 g) were taken in a two necked round-bottomed flask provided with a thermometer and a condenser. 40 ml of 10% NaOH solution was poured into the mixture which was

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stirred and heated to 60°C for 3 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered under nitrogen and the filtrate was quickly acidified to precipitate the product which was very unstable in the presence of traces of oxygen. The precipitate was filtered under nitrogen, washed thoroughly with water, dried carefully under high vacuum at 100°C, and recrystallised from acetone.

Synthesis of the AHQ-acid-anhydride polycondensates :

An intimate mixture of AHQ(3 g) and zinc chloride (excess) was heated at a temperature 225°C for 3 h under nitrogen atmosphere in a Pyrex flask (250 ml). The resulting mass was extracted with water, filtered and washed thoroughly with water, 2% HCl and ethanol respectively and dried at 100°C under N_2. Elemental analysis of the product is given in Table-1.

An intimate mixture of (I), (3 g), zinc chloride (6.5 g) and pyromellitic dianhydride (3.4 g) was heated at 250°C for 12 h under nitrogen atmosphere. The black mass was extracted with water, filtered, and washed thoroughly with water, 2% HCl, water, ethanol and THF respectively. The resultant mass was dried at 100°C under nitrogen.

Essentially, the same procedure was adopted for other acid-anhydrides such as, succinic anhydride (SA), phthalic anhydride (PA) and 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), respectively.

Characterization :

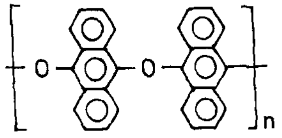
Elemental analyses for C,H were done by the Heraus Commbustion (Micro) apparatus. IR spectra were recorded on a Perkin-Elmer 237 B spectrometer in KBr Pellets. TG measurements were done on a Stanton Redcroft Analyzer (air; 0-1000°C; 15°C/ min). Dielectric constant, loss factor (tan δ) and A.C. conductivity were measured on an Impedance Bridge (HPA 4101). D.C. Conductivity was directly measured by a 1666 D.C. Resistance bridge (General Radio). The samples were used as pellets silver painted on either surface.

RESULTS AND DISCUSSION :

Structural Features

Table 1 presents some relevant properties of the polymers. All the AHQ-anhydride polycondensates are intractable so that an unambiguous structure elucidation becomes difficult. On the basis of elemental analysis and infrared absorption data of the polymers along with the corresponding information on the xanthene model polymers [4] tentative structures for the AHQ-anhydride polycondensates are shown in Figure 1.

The existence of an ether linkage (Ar-O-Ar) is confirmed by IR peaks at 1260 cm^{-1} in I-V (Figure 2). Furthermore, IR spectra reveal that the nature of the functional groups present in all of the polymers (II, III and IV) is almost the same except in polymer V, AHQ-NTDA condensates. It implies that the mode of condensation of NTDA with



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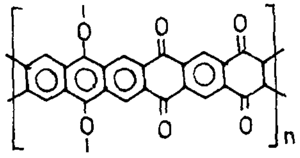

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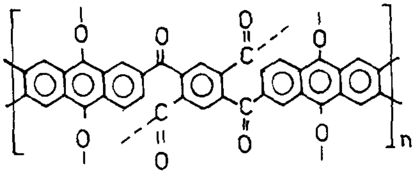

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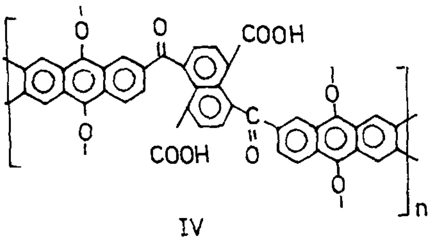

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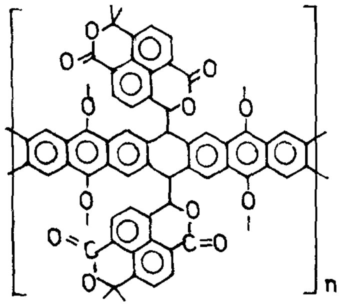

V

Fig. 1 Probable structures of the condensates: I-AHQ$_n$; II-AHQ-PMDA$_n$; III-AHQ-PMDA$_n$; IV & V-AHQ-NTDA$_n$.

AHQ is quite different from the condensation of SA, PA and PMDA. In case of polymers containing SA, PA and PMDA, the main types of linkages are quinone or ketone (IR absorption : 1640 cm^{-1}) whereas in AHQ-NDTA condensates the majority of the linkages comprise ketones and but also lactone type (IR absorption, 1670, 1700, 1770 cm^{-1}). The possibility of quinone formation in case of AHQ-NTDA)$_n$ (V) polymer is very unlikely because it will lead to a seven membered ring structure which is expected to be very unstable particularly at high temperature.

Further, the difference between the total acidity of the polymer as determined by alkali absorption also supports the above fact. The polymer containing NTDA absorbed 2.5 meq/gm alkali whereas PMDA containing polymer absorbed 0.41 meq/gm alkali. This difference suggests thaty lactones or acid group which are present in NTDA complex can react with alkali. Relevantly, McNeill and Weiss [4]

TABLE 1

Characterization of AHQ-Anhydride Condensates

Compound	Color	Solubility	%C	%H	%H	Characteristic IR Absorption [cm^{-1}]
$(AHQ)_n$	Ash	+ in DMF, THF, DMSO	85.0 (87.5)	3.9 (4.1)		1260(aryl C-O Str), 1590 (aromatic C=C Str)
$(AHQ-SA)_n$	Black	-	77.5	5.0		1650(C=O Str), 1590 (aromaticC=C Str), 1265 (Aryl C-O Str)
$(AHQ-PA)_n$	Black	-	84.2	4.0		1630(C=O Str), 1590 (aromatic C=C Str), 1270 (Aryl C-O Str)
$(AHQ-PMDA)_n$	Black	-	85.2	2.3		1630 (C=O Str), 1580 (aromatic C=C Str), 1270 (Aryl C-O Str)
$(AHQ-NTDA)_n$	Black	-	84.3	2.4		1770(C=O Str of lactone), 1700(C=O Str of acid), 1670 (C=O Str of ketone) 1580 (aromatic C=C Str), 1270 (aryl C-O Str) 1350 (O-H deformation)

TABLE 2

Specific Conductivity and Activation Energy for AHQ-ANHYDRIDE and other Polymers

Polymer	Thermal Stability	Dielectric Constant	Conductivity ohm^{-1} cm^{-1}	Activation Energy (eV)	Reference
AHQ-NTDA	-	-	$1.54X10^{-4}$	$\Delta E_1 = 0.38$ $\Delta E_2 = 0.78$	This work
AHQ-PMDA	-	-	$2.52X10^{-5}$	$\Delta E_1 = 0.46$ $\Delta E_2 = 0.93$	"
AHQ-PA	-	-	$6.48X10^{-5}$	$\Delta E_1 = 0.49$ $\Delta E_2 = 0.55$	"
AHQ-SA	-	-	$1.35X10^{-7}$	$\Delta E_1 = 0.55$ $\Delta E_2 = 1.09$	"
Xanthene (Hydroquinone - PA/PMDA)	-	-	$1.4 X10^{-4}$	-	4
Anthraquinone-PMDA	extensive chenges at 600°C	50-900 (depending on frequency)	$1.1 X10^{-8}$	-	3,5

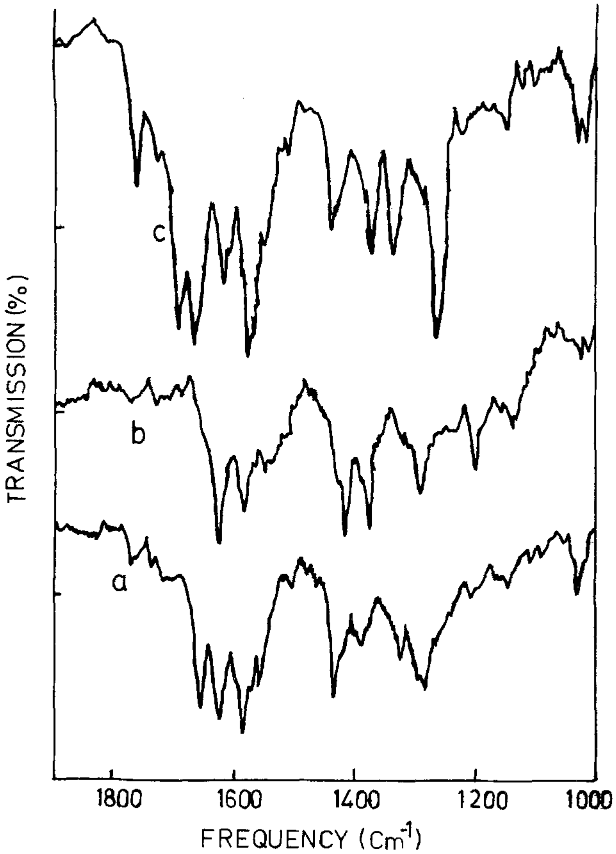

Fig.2 IR spectra of (a)-PA; (b)-PMDA & (c)-NTDA based polycondensates.

reported such alkali absorption behaviour with xanthane polymer from benzohydroquinone and PMDA.

Thermal Stability

Figure 3 shows that PAHQ has the lowest stability and the aliphatic anhydride (SA) modified polymer shows a significant gain in stability compared to the base polymer PAHQ. The effects of PMDA, NTDA and PA on the stability are more or less similar, the AHQ-NTDA polycondensate showing ultimately higher stability than that for AHQ-PMDA. Between 400-500°C, AHQ-NTDA shows a lower stability than AHQ-PA/PMDA, due presumably to dicarboxylation via the lactone ring or any free COOH group. The ultimate gain in stability for AHQ-NTDA over the others probably reflects the order in thermal energy required for complete oxidative degradation of the matrix containing AHQ and PA/PMDA/NTDA possessing different amounts of inherent thermal stability.

The common exothermic DTA peak noted in AHQ-PA, AHQ-PMDA and AHQ-NTDA around 450°C corresponds probably to oxidative degradation of the aromatic moieties in all the polycondensates. Pohl et al reported extensive oxidative degradation of PAQR polymers around 600°C due, specutatively, to volatization of H, CO and CO_2 etc from the polymer. It is likely that similar degradation products will result in the prestnt system from the oxidative rupture of the aromatic nuclei present.

Dielectric Behaviour

The dielectric constant values (Figure 4) for the anhydride modified

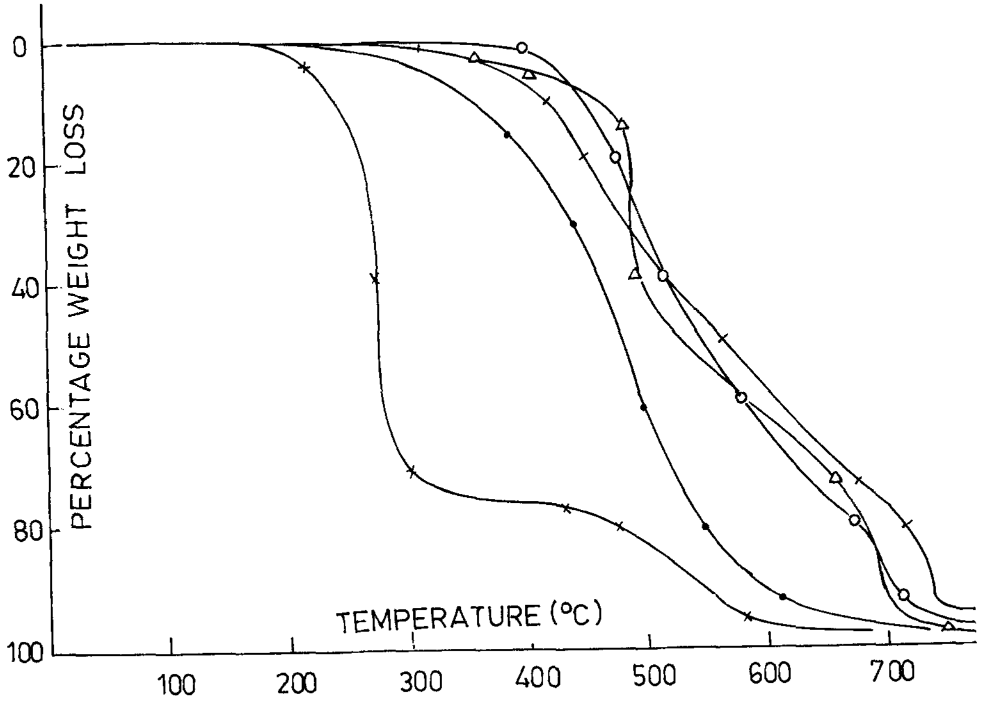

Fig.3 Thermograms of $(AHQ)_n$-X, $(AHQ\text{-}SA)_n$- , $(AHQ\text{-}PA)_n$- , $(AHQ\text{-}PMDA)_n$ and $(AHQ\text{-}NTDA)_n$-

condensates are seen to be unusually high (~ 500) at low frequency relative to conventional organic semiconductors and fall to the limiting value (~ 10) at high frequency. For the self-condensed PAHQ, the diielectric constant values are low and remain independent of the applied frequency. At a frequency of 1 KHz, the dielectric constant values follow the sequence :

AHQ-NTDA	>	AHQ-PMDA	>	AHQ-PA	>	AHQ-SA	>	PAHQ
(500)		(300)		(250)		(125)		(10)

Pohl and Rosen explained [6] similar high dielectric constants (50 -900) for the polyacene quinone radical polymers from pyrin-PMDA and anthraquinone-PMDA polycondensates by the concept of hyperelectronic polarization due to a thermally generated plasma of electrons and holes each locally mobile in extended regions of associated π -orbitals on the molecule. The present results appear reasonable when viewed in the light of the suggestion of Pohl and Rosen. Furthermore, increasing exttent of conjugation in the series PA, PMDA and NTDA enhances the polarization of the polymers to different extents as evidenced by the trend in dielectric constants. The ((tan δ) parameter exhibits a broad shoulder falling sharply with the applied frequency. However, AHQ-NTDA exhibits a typical

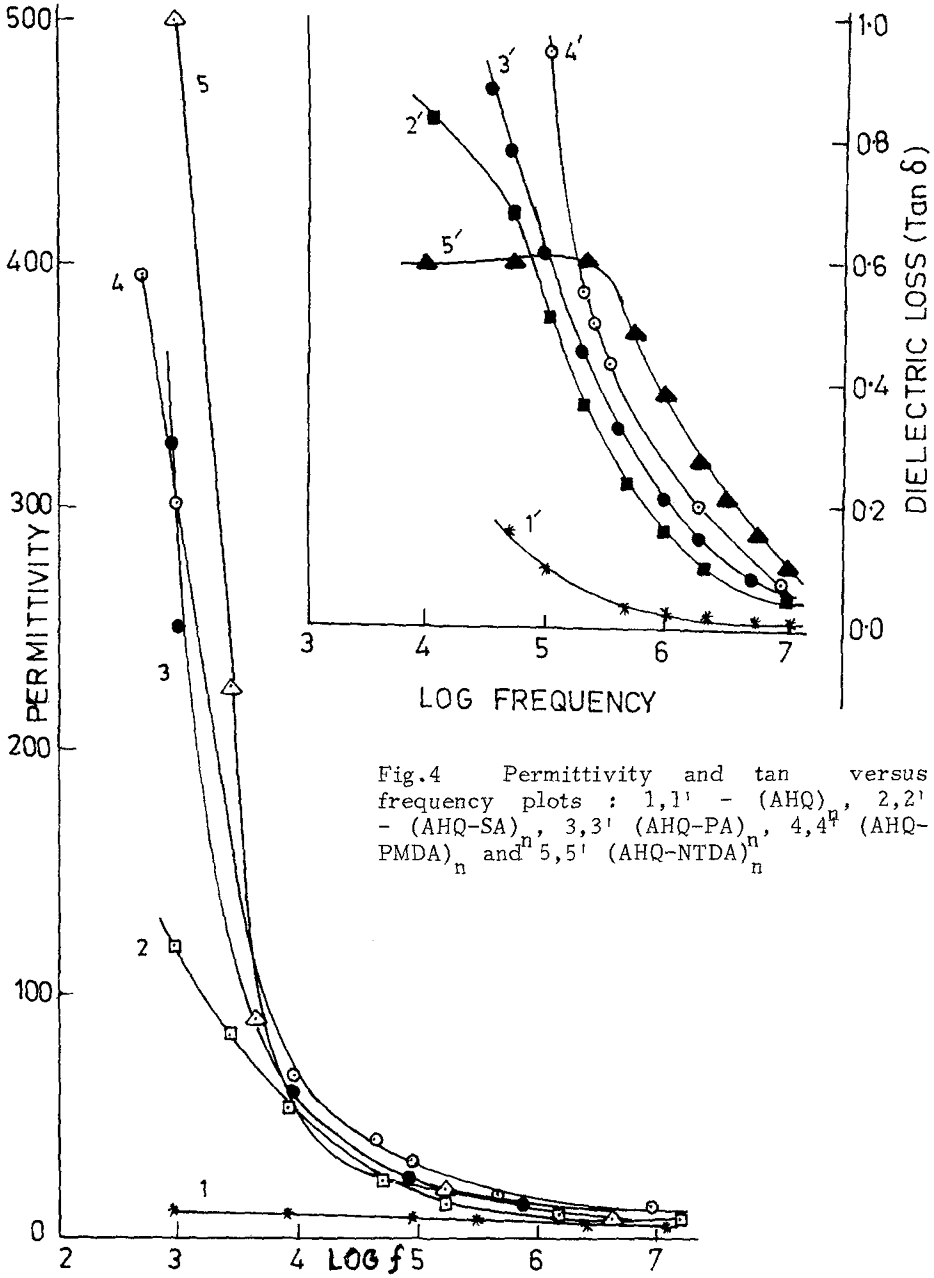

Fig.4 Permittivity and tan versus frequency plots : 1,1' - (AHQ)$_n$, 2,2' - (AHQ-SA)$_n$, 3,3' (AHQ-PA)$_n$, 4,4' (AHQ-PMDA)$_n$ and 5,5' (AHQ-NTDA)$_n$

maximum in tan-δ frequency graph. AHQ-NTDA may be regarded as being composed of chains of AHQ cross-linked with the NTDA moiety carrying polar - COOH as pendant groups, which are likely to undergo dielectric polarization under applied frequency.

Conductivity Characteristics

The specific conductivities depend on the anhydride : SA $<$ PA $<$ PMDA $<$ NTDA - which is the order for increasing conjugation; these values are also higher than those reported for anthracene based semiconductors (Table II). Log σ -1/T plot reveals a slope change implying contribution of extrinsic (ΔE_1) and intrinsic conduction (ΔE_2, and the trend : SA $>$ PMDA $>$ NTDA $>$ PA. The lowest value (0.55) for $(AHQ\text{-}PA)_n$ contradicts the expected trend, the reason being obscure. Relevantly, Pohl et al [3] also reported a similar lower activation energy for PA - 2 Bromo - 4 phenyl phenol and PA - 1, 4-dihydroxynaphthalene that 1,8 naphthalic anhydride-2-bromo-4 phenyl phenol and 1,8 naphthalic anhydride - 1,4 dihydroxynaphthalene respectively.

AHQ-PMDA polycondensate exhibits A.C. conductivity which increases with applied frequency. Typically, at 6 X 10^3 KHz, the A.C. conductivity (2.28 X 10^{-3} is higher than the d.c. conductivity (3 X 10^{-5}) which implies a higher hopping rate of electrons between available sites (7,8).

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