

Benzene and anthraquinone sulfone derivatives of poly(N-vinylcarbazole)

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SUMMARY

Benzene and anthraquinonesulfonyl chlorides were reacted with poly-N-vinylcarbazole in presence of Friedel-Crafts catalyst to form the corresponding sulfonyl derivatives. The sulfonated poly-N-vinylcarbazoles were characterized by elemental analyses, IR spectroscopy, thermogravimetric analysis and evaluation of permittivity and loss-tangent behaviour with varying applied frequencies.

INTRODUCTION

Carbazole-based thermally stable polysulfones have been synthesized (1, 2) through polycondensation of 3, 6-carbazole disulfonyl chloride with benzene, toluene and diphenyl ether in presence of $AlCl_3$, $FeCl_3$ and polyphosphoric acid. In continuation of our studies (2, 3) on chemical modification of poly-N-vinylcarbazole (PNVC) we now report the synthesis (Scheme 1) and some physico-chemical properties of hitherto unreported benzene and anthraquinone sulfone derivatives of PNVC via a Friedel-Crafts reaction between PNVC and the respective sulfonyl chlorides. Harwood et al. (4) applied a similar procedure for the synthesis of arylsulphone derivatives of polystyrene. The choice of benzene and anthraquinone is significant in view of our recent observation (5) that PVC modified with the latter moiety exhibits appreciably higher overall thermal stability and different dielectric behaviour relative to PVC, unmodified as well as modified by aromatic groups.

EXPERIMENTAL

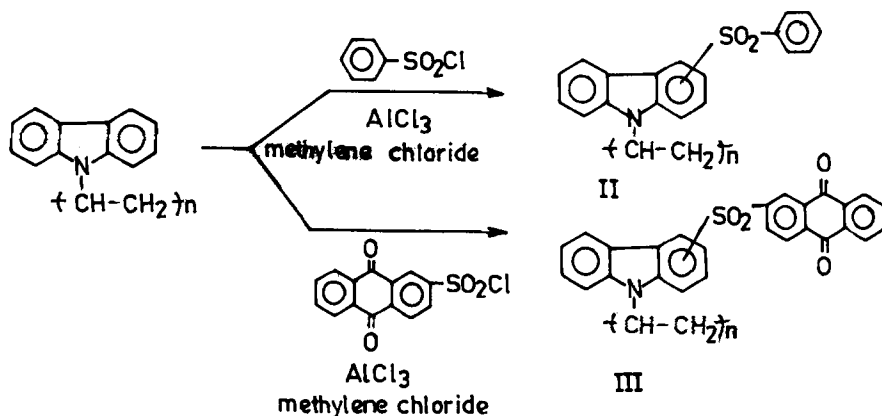
Materials

PNVC ($\bar{M}_n = 3300$) was prepared by a method of Biswas and Kamannarayanaⁿ (6), reprecipitated twice from THF by hot methanol and finally dried off the solvent. Anthraquinone 2-

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sulfonic acid (sodium salt), benzene sulfonyl chloride, PCl_5 and anhydrous AlCl_3 , all Fluka A R materials, were used directly.

SCHEME 1



Synthesis

1. Anthraquinone - 2-sulfonyl chloride

Anthraquinone 2-sulfonic acid, sodium salt (0.02 mol) was reacted with PCl_5 (0.015 mol) at 150° for 10h with occasional shaking. The contents were poured into crushed ice, and the residue was washed with methanol and ethanol respectively. The crude product was recrystallized from dichloromethane. Yield 60%; calc: C = 54.77 H = 2.28 S = 10.21; found: C = 55.20, H = 2.13, S = 10.43. I.R (KBr) : 1140 cm^{-1} (O = S = O symmetric stretching), 1280 cm^{-1} and 1310 cm^{-1} (O = S = O, antisymmetric doublet).

2. Benzene Sulfonyl derivative of PNVC (II)

Methylene chloride (50 ml), anhydrous AlCl_3 (0.02 mol) and benzene sulfonyl chloride (0.02 mol) were reacted under nitrogen for 30 min at 27°C . A solution of PNVC (0.014 mol of repeat units) in methylene chloride was slowly added to the stirred solution for 30 min when the pale yellow

colour immediately changed from orange to red, darkening with time. The mixture was stirred at 27°C for 48 h, poured into ice containing 10% HCl solution. The organic layer containing the solid product was poured slowly into methanol, filtered, washed with water and methanol and dried. Finally, it was kept in benzene at 60°C for 12 h, filtered, washed with benzene and dried in vacuum. Found: C = 71.91, H = 4.23, N = 4.11 and S = 9.95. Calc. C = 72.07, H = 4.50, N = 4.20 and S = 9.61. I.R.(KBr): 700 cm⁻¹, 770 cm⁻¹ (5 adjacent H vibration of aromatic ring), 1130 cm⁻¹ (O = S = O asymmetric stretching), 1360 cm⁻¹ (O = S = O, symmetric stretching), 1450 cm⁻¹ (aromatic ring stretching).

3. Anthraquinone Sulfonyl derivative of PNVC(III)

The procedure adopted was essentially similar to 2. Found: C = 77.21, H = 3.45, N = 4.31 and S = 4.61; Calc. C = 72.53, H = 4.31, N = 3.02 and S = 6.91. I.R.(KBr): 1145 cm⁻¹ (O = S = O symmetric stretching), 1215 cm⁻¹ (C-N vibration), 1320 cm⁻¹ (O = S = O antisymmetric stretching), 1590 cm⁻¹ (aromatic ring vibration), 1670 cm⁻¹ (C = O stretching).

Characterization

Thermogravimetric analyses were performed on a Stanton Redcroft Analyzer under static air with a heating rate of 10°C/min.

Permittivity and dielectric loss factor were measured on a Impedance Bridge (Hewlett Packard, A4192) at 27°C. The samples were taken in a pellet form coated with silver paint on both surface.

RESULTS AND DISCUSSION

General Features

The benzene and anthraquinone derivatives of PNVC (II and III) were recovered as dark powdery masses insoluble in all solvents common to PNVC, including DMF, DMSO or acetonitrile. The results of elemental analyses for II and III confirm the presence of both N and S in the polymers, and the elemental C and H percentages are different from those for unmodified PNVC. The calculated values for C, H, N and S, as shown above are on the basis of structures II and III, assuming that condensation between PNVC and R-SO₂Cl occurs in the ratio 1:1. On this basis the observed elemental compositions for II and III indicate that the corresponding ratios are 1:1(II) and 2:1(III) respectively. The analysis of the I.R. absorptions (4) also endorses the presence of the sulfone linkages in II and III.

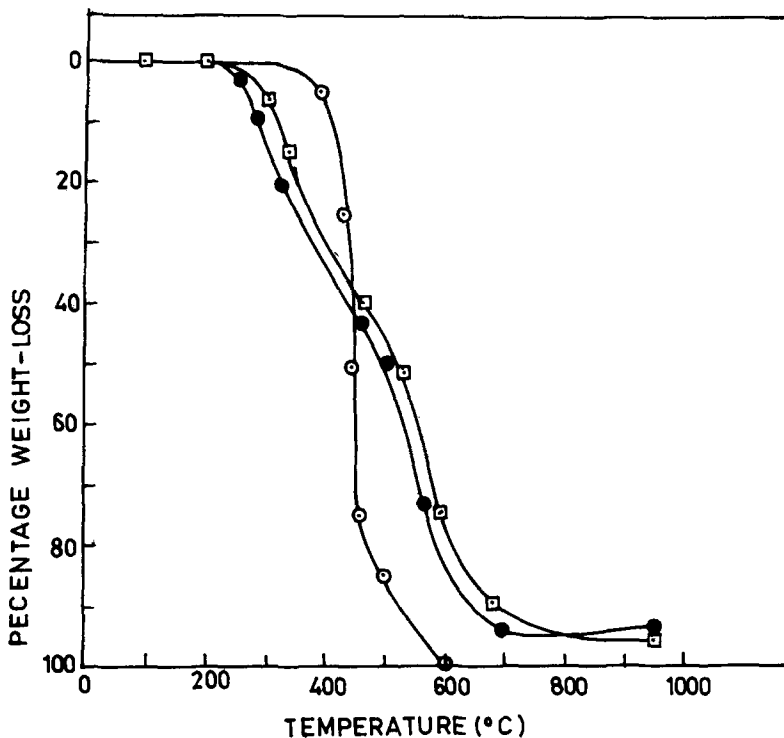


Fig. 1: T.G. Curves of PNVC(○), Benzene sulphonyl(●) and Anthraquinone sulphonyl(◻) derivatives of PNVC.

Thermal Stability

Figure 1 suggests that the initial decomposition temperatures for the sulfone derivatives follow the trend: PNVC (330°C) > III (260°C) > II (230°C). Beyond 40% decomposition, the order in thermal stability becomes III > II > PNVC. Both II and III leave ca. 5% residues beyond 650°C . Further, PNVC undergoes most of the decomposition (5-85%) within a very narrow temperature gap ($400\text{--}500^{\circ}\text{C}$), while II and III do so with a slower rate over a wider temperature range ($300\text{--}600^{\circ}\text{C}$).

The initial decrease in thermal stability of II and III relative to PNVC is believed to be due to a manifestation of the weakness of carbon-sulfur linkages, which has already been noted for polysulfones prepared by condensation polymerization, as also for arylsulfonated polystyrenes (4). The observed trend beyond 40% weight-loss is difficult to explain. At this stage, the polymers II and III are expected to comprise partially decomposed matrices of II and III together with moieties from benzene or anthraquinone

fragments. Obviously, the relative thermal stabilities of these entities will control the overall trend in stability as displayed in the thermogravimetric analysis.

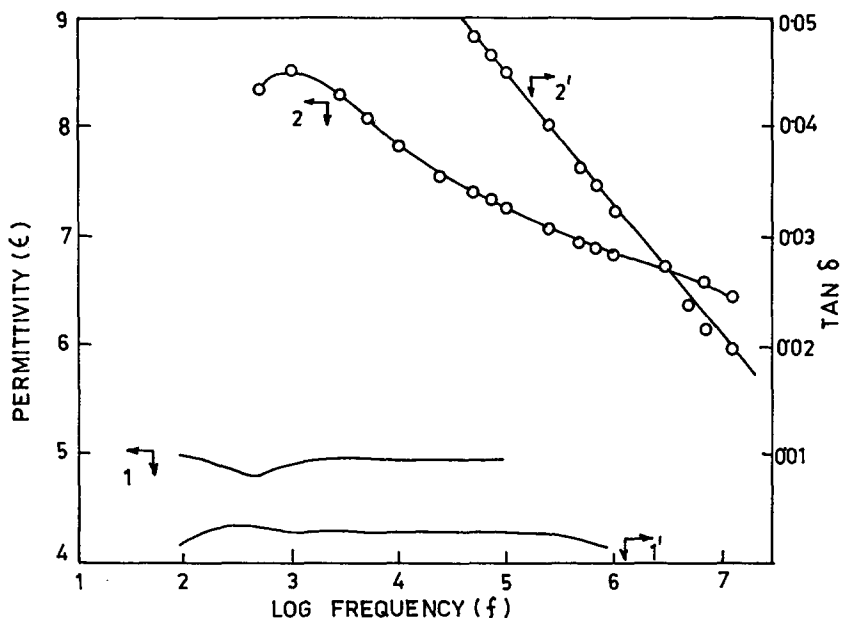


Fig. 2: Permittivity and $\tan \delta$ versus frequency plots for (1,1')-PNVC, (2,2')-Anthraquinone sulphonyl derivative of PNVC.

Dielectric Characteristics

In view of our recent experience (5) that anthracene groups enhance the dielectric properties of PVC, we were interested to examine the dielectric characteristics of III. Figure 2 clearly reveals that the permittivity of III is nearly double the corresponding value for PNVC at an applied frequency of 10^3 Hz. With increasing frequency (10^3 - 10^7 Hz) the permittivity of III shows a gradual fall, while that for PNVC remains essentially constant (≈ 5). The dielectric loss parameter for III likewise reveals a sharp fall at high frequency (10^3 - 10^7 Hz). The usual loss tangent maximum corresponding to an inflection in the permittivity-frequency curve (7) is absent. These features are similar to our earlier observations with PVC-anthraquinone and PVC-anthrol polycondensates (5). The large volume of the anthraquinone moiety in III permits of appreciable electron polarization with varying applied frequencies (5) and the observed trend in Figure 2 may be explained from this consideration (5).

As for the $\tan \delta$ -frequency behaviour of III, it seems that the loss of electrical energy by conversion to thermal energy at low frequency is too small to be detected, but it shows up only at some intermediate frequencies when electron polarization coincides with the rate and frequency of alternation in the electric field. This manifests as a broad relaxation in the higher frequency side as in Figure 2, with no maximum.

CONCLUSION

The benzene and anthraquinone sulfones of poly-N-vinylcarbazole show enhanced overall thermal stability and distinct dielectric behaviour relative to the unmodified polymer. However, general insolubility of these sulfonated polymers limits their scope. We have already observed that the benzene and anthraquinone sulfonyl derivatives of polystyrene are soluble in usual solvents. While their in-depth characterization is under way, concerted efforts are also being made to produce soluble sulfones of poly-N-vinylcarbazole. Details of these researches will be published in due course.

ACKNOWLEDGEMENT

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