RESEARCH ARTICLE

Synthesis, characterization and dielectric properties of sulfonated poly(1,3,4-oxadiazole-ether) sulfone copolymer with functional pendant carboxylic acid groups

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Abstract This work reports the synthesis and electrical characterization of sulfonated copolymer with flexible carboxylic acid pendants with 1,3,4-oxadiazole unit in the main polymer structure contrived successfully via nucleophilic displacement polycondensation among 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (BFPOx), 4,4′-Bis(4-hydroxyphenyl) valeric acid (BPV) and Disodium-3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (S-DCDPS). The molecular structural characterization of the copolymer was achieved by NMR spectroscopic studies, TGA was performed to verify the thermal stability, dielectric studies were executed by compressing the copolymer sample in to tablets and results were discussed.

Keywords Sulfone · Oxadiazole · Dielectric loss · Loss tangent · AC conductivity

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Introduction

Aromatic heterocyclic polymers, especially poly(arylene-oxadiazole)s, are best known to exhibit excellent thermal stability [1–4], this rigid moiety in the polymer structure, due to the delocalization of π-electrons, makes them insoluble in organic solvents and infusible, and their processing and practical use is very limited [2]. Modification to poly(1,3,4-oxadiazole)s with flexible ether and sulfone linkages are in practice to improve solubility and lower the glass transition temperature in beneficial to easy processing in solution and to adopt them in various technical applications exclusively in PEMFCs by the introduction of ionic groups laterally to the polymer chain [5–8]. These high performance polymers with oxadiazole moieties due to richness in its structure and semiconducting properties received considerable attention in many areas of modern chemistry and physics of hybrid materials owing to the microelecronic applications as electrochemical sensors. In this sense, many dielectric studies on the properties of poly(1,3,4-oxadiazole)s have been carried out [9, 10]. There is indeed a great amount of interest by varying the properties of poly(1,3,4-oxadiazole)s by inserting flexible mesogenic segments [11–13], furthermore, several ionic transport materials can be imputed to a polymer backbone in the main chain or as pendant groups [14–16]. In view of previous studies, we believe it to be very important to design and synthesize sulfonated copolymer with 1,3,4-oxadiazole unit in the main polymer chain with flexible carboxylic acid pendants and intended to examine the dielectric properties and the effect of ionic groups on to the polymer backbone.

In this paper, a one-pot, high temperature polycondensation method was used to synthesize sulfonated poly(1,3,4-oxadiazole-ether) sulfone copolymer containing flexible sulfone and ether linkages with reactive carboxylic acid pendants to study the effect of ions on the structure and dielectric properties.

Experimental

Materials

4,4′-Dichlorodiphenyl sulfone (DCDPS), 4,4′-Bis(4-hydroxyphenyl) valeric acid, 4-fluoro benzoic acid and fuming sulfuric acid (27 % SO$_3$) were used as received from Sigma-Aldrich. N-methyl pyrolidinone (NMP) was purchased from Merck was purified by distillation over phosphorous pentoxide under reduced pressure. Potassium carbonate was purchased from HIMEDIA Chemicals. All other solvents and reagents were analytical grade quality, purchased from S.D. Fine Chem. Ltd., Mumbai, India and were used without any further purification. Double distilled water was used throughout the study.

Instrumentation

The Fourier transform infrared (FT-IR) spectra were recorded by a Thermo Nicolet -5700, USA spectrometer (diamond window method). The ^{1}H & ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard reference. Thermogravimetric analysis (TGAs) was performed on a

PerkinElmer Diamond TGA/DTA thermogravimetric analyzer at a heating rate of 10 °C/min in a nitrogen atmosphere.

Synthesis

Monomer synthesis

The monomers 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (BFPOx) and Disodium-3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (S-DCDPS) was synthesized from previously described synthetic protocols [17, 18]. NMR (^{1}H, ^{13}C & ^{19}F) spectra of monomers were presented in Supplementary Material.

2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (BFPOx)

Yield: 85 %. MP: 203.2–203.8 °C. ^{19}F NMR (δ, DMSO-d_6): −107.28 (s, 2F, para to Ox). ^{1}H NMR (δ, DMSO-d_6): 7.43–7.48 (m, 4H), 8.15–8.18 (m, 4H), ^{13}C NMR (δ, DMSO-d_6): 165.38 (F attached to C), 163.28 (2C, Ox), 162.90 (F attached to C), 129.42 & 129.33 (2C, attached to Ox), 119.97 & 119.94 (4C, ortho to Ox), 116.76 & 116.51 (4C, meta to Ox).

   FT-IR (diamond window): 1652 (C=N of Ox ring), 1560, 1504, 1422, 1364, 1320, 1214, 1104, 1038, 992, 845, 821, 779, 749, 709 cm^{-1}.

   Mass Spectrum (LCMS): 259.0 (MH$^+$);

   Elemental Analysis Calcd.: C, 65.12; H, 3.12; F, 14.7; N, 10.85; O, 6.20. Found: C, 65.04; H, 3.01; N, 10.68.

Disodium-3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (S-DCDPS)

Yield: 70 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.32 ppm (d, 2H), 7.82 ppm (dd, 2H), 7.64 ppm (d, 2H); ^{13}C NMR (δ, DMSO-d_6): 138.99, 137.35, 132.83, 129.24, and 127.94.

   FT-IR (KBr) 1,021 cm^{-1} (S=O, sulfonic acid, sym.), 1,078 cm^{-1} (S=O sulfonic acid, asym.), 1,164 cm^{-1} (S=O, sulfone).

   Mass Spectrum (LCMS): 468.7 (S-DCDPS-Na$^+$);

   Elemental Analysis Calcd.: C, 27.3; H, 1.15; S, 18.2; Na, 8.72. Found: C, 27.5; H, 1.20; S, 19.1; Na, 9.38.

Copolymer synthesis

Synthesis of sulfonated poly(1,3,4-oxadiazole-ether) sulfone copolymer (DSVPOx)

The synthesis of DSVPOx copolymer with pendant carboxylic acid groups was achieved from direct copoymerization of oxadiazole activated bis(fluoride) monomer (BFPOx), Disodium-3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (S-DCDPS) and 4,4′-Bis(4-hydroxyphenyl) valeric acid (BPV). In a typical reaction, three necked 100 ml flask was equipped with a mechanical stirrer, Dean-Stark trap, condenser, and a nitrogen inlet/outlet, was charged with BPV (2.217 g,

7.74 mmol), monomer BFPOx (1.0 g, 3.87 mmol), monomer S-DCDPS (1.902 g, 3.87 mmol) and potassium carbonate (1.926 g, 13.93 mmol). Then 15 ml N-Methyl pyrollidine and 10 ml toluene were added to the flask under moisture free nitrogen, the reaction mixture was heated to 120 °C for 2 h until the toluene was all condensed in the Dean–Stark trap. Upon dehydration, the reaction mixture was heated to 180 °C for 10 h, the viscous solution was cooled to 80 °C and poured in to 200 ml Hydrochloric acid (0.05 M) solution. The precipitated polymer was repeatedly washed with excess of hot deionized water and dried in vacuum at 60 °C (Yield: 74 %).

## Results and discussions

Synthesis and characterizations

The synthetic route for DSVPOx copolymer with pendant carboxylic acid moiety was depicted in Fig. 1 was achieved via conventional aromatic nucleophilic substitution polymerization technique from 4,4′-Bis(4-hydroxyphenyl) valeric acid, 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole, and Disodium-3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (S-DCDPS). The polycondensation was carried out at elevated temperature in NMP/Toluene azeotrope in presence of anhydrous pulverised potassium carbonate as catalyst. The inclusion of these in a sequence leading to diversely substituted sulfonated oxadiazole copolymer will then be delineated by NMR spectroscopy. Signal broadening of the ^{1}H NMR spectrum of the polymer DSVPOx was due to polymerization and is presented in Fig. 2. The peaks in the range 8.27–8.34 ppm were assigned to the hydrogen atoms adjacent to the sulfonic acid group. The peak at 12.06 ppm was assigned to the hydrogen atoms of carboxylic acid group; aliphatic side chain signals resonates at 2.49, 1.89–1.98 and 1.51 ppm. Further signal at 174.50 δ in ^{13}C NMR spectra (Fig. 3) confirms the carboxylic acid carbon and two methylene carbons at 29.91 δ and 36.25 δ, peak at 165.43 δ was assigned to carbons of oxadiazole ring.

Thermogravimetric analysis

TGA measurement was performed for DSVPOx and pattern (Fig. 4) showed two degradation steps with onset decomposition at 170 °C. The initial weight loss step
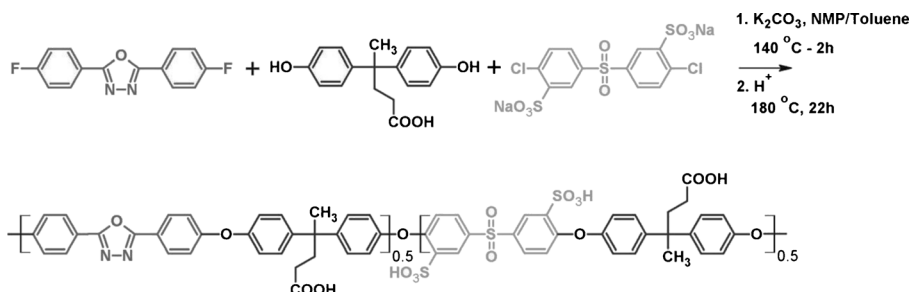
Fig. 1 Synthetic route to synthesize DSVPOx copolymer
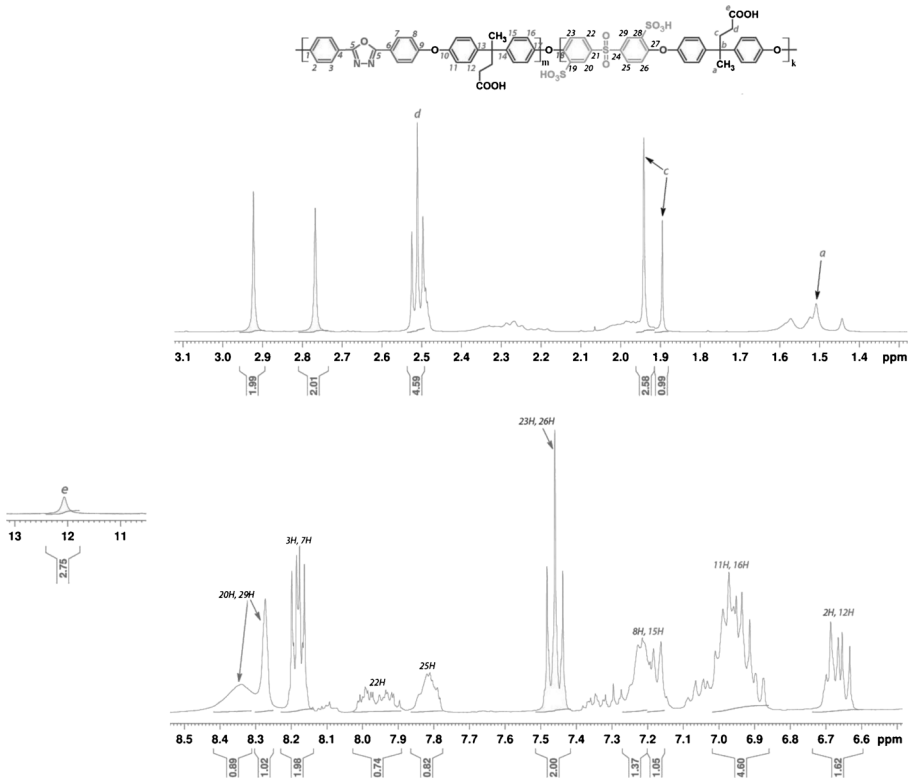
Fig. 2 ^{1}H NMR (DMSO-d$_6$) spectrum of DSVPOx copolymer

started at around 170–410 °C was attributed to the desulfonation of sulfonic moities, where –SO$_3$H was easily exterminated by releasing H$_2$O, SO$_2$ and other sulfur oxides, second degradation step is in the range of 490–610 °C can be accounted for the main polymeric chain. The degradation in the temperature below 150 °C can be accounted for the loss of moisture. Broido's method [19] was employed to determine kinetic and thermodynamic parameters and results were tabulated in Table 1. Plots of Ln(ln(−1/Y)) versus 1/T (where Y is the fraction of the compound undecomposed) were developed for the decomposition segment. From the plot (Fig. 5) the activation energy (Ea) and frequency factor (ln A) were evaluated. The enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) have been calculated.

Dielectric measurements

The copolymer DSVPOx was pressed in to pellets of nearly similar thickness and subjected to the dielectric measurements, Sandwiched polymer sample between two silver-plated stainless steel electrodes were analyzed by impedance analyzer model HIOKI 3352-50 HiTESTER Version 2.3. Where silver paint (ELTECKS preparation No. 1228-C) was coated on both flat surfaces of the pressed tablet and the electrical contacts to the samples were made using the same silver paint to the silver electrodes. The electrical contacts were checked to verify the ohmic connection. The measurements were carried out at room temperature in between the 50Hz–
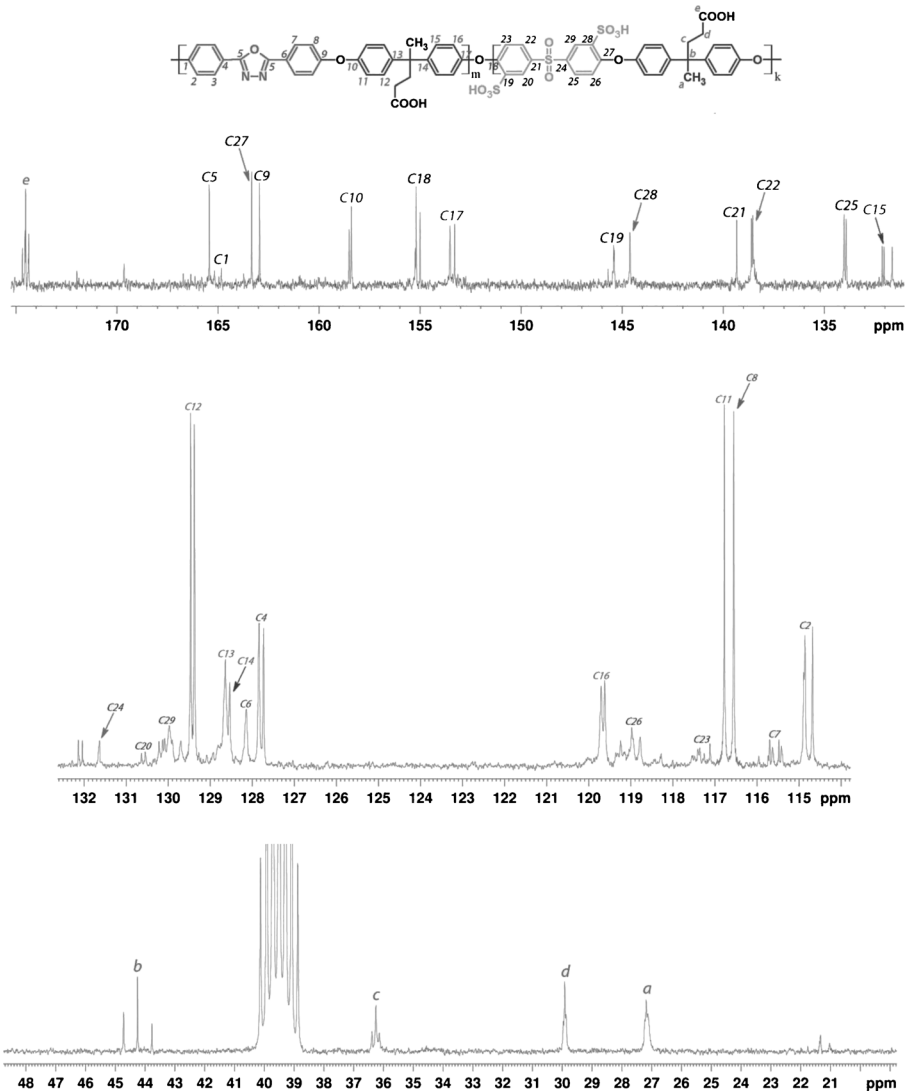
Fig. 3 ^{13}C NMR (DMSO-d$_6$) spectrum of DSVPOx copolymer

5MHz frequency range. The capacitance value (C), and ac conductance (G) were directly obtained from the apparatus. The dielectric constant (ε') and ac conductivity (σ_{ac}) values are calculated using the relations $\varepsilon' = C_p d/\varepsilon_o A$ and $\sigma_{ac} = Gd/A$ respectively. Where, 'd' is the thickness of the polymer pellet and 'A' is the cross-section area and ε_o is the permittivity of the free space. All these measurements were made under dynamic vacuum.

Figure 6 shows the variation of dielectric constant (ε') on log (frequency) at room temperature. It is clear from the figure that ε' decreases with the increase in frequency. The dielectric constant is associated with the polarization of the material under the influence of sub-switching ac field [20]. At low frequencies
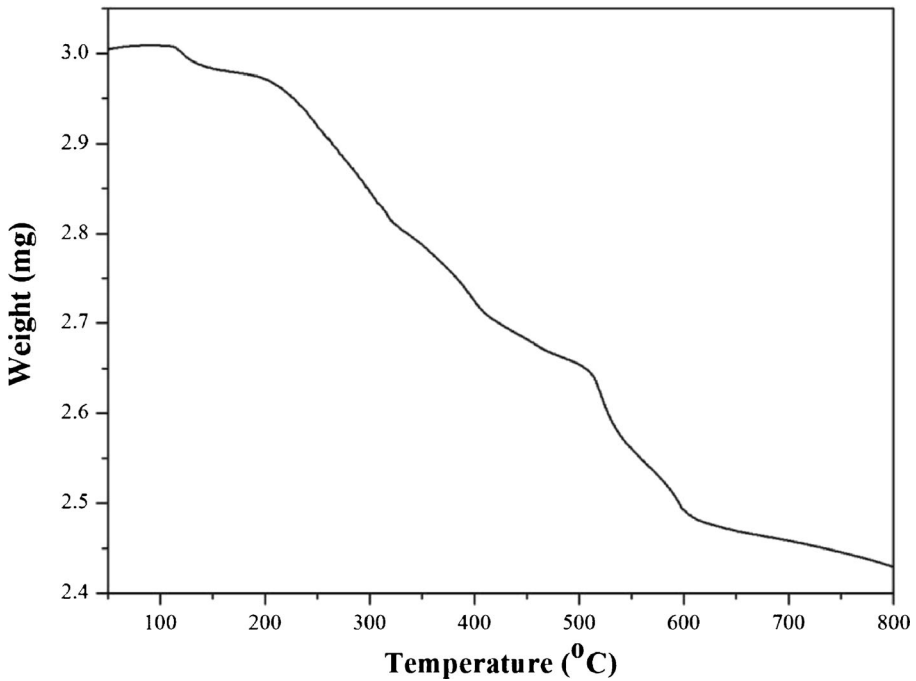
Fig. 4 TGA Plot of DSVPOx copolymer at a heating rate of 10 °C/min under a nitrogen atmosphere

the dielectric constant ε' for polar materials is due to the contribution of both deformational polarization (electronic and ionic polarization) and relaxation polarization (orientational and interfacial polarization) [21]. When the frequency is increased, the dipoles will no longer be able to rotate quickly, so that their oscillations begin to lag behind those of the field. At higher frequency, the dipole will be completely incapable to follow the applied field and the orientation polarization notably stopped, so ε' decreases at higher frequencies approaching a constant ε' value due to the interfacial or space charge polarization only [22, 23]. The dielectric loss (tanδ) was also found to be decreased (Fig. 7) exponentially with increase of frequency up to 90 kHz and attains the constant value due to interfacial polarization.

The frequency dependence of the ac conductivity for DSVPOx was shown in Fig. 8. The plot reveals that conductivity increases with increase of frequency is due to frequent charge motion with in the polymer sample which is supporting the view that can be explained by hopping-type conduction mechanism [24, 25].

Table 1 Kinetic and thermodynamic parameters of DSVPOx copolymer

Sample	Decomposition range (°C)	Ea (kJ/mol)	lnA	ΔH (kJ/mol)	ΔS kJ/K	ΔG kJ/mol
DSVPOx	170–410	0.000546	−11.1113	−4.69647	−163.486	92.3573
	490–610	0.001777	−9.76614	−6.86559	−160.779	132.796
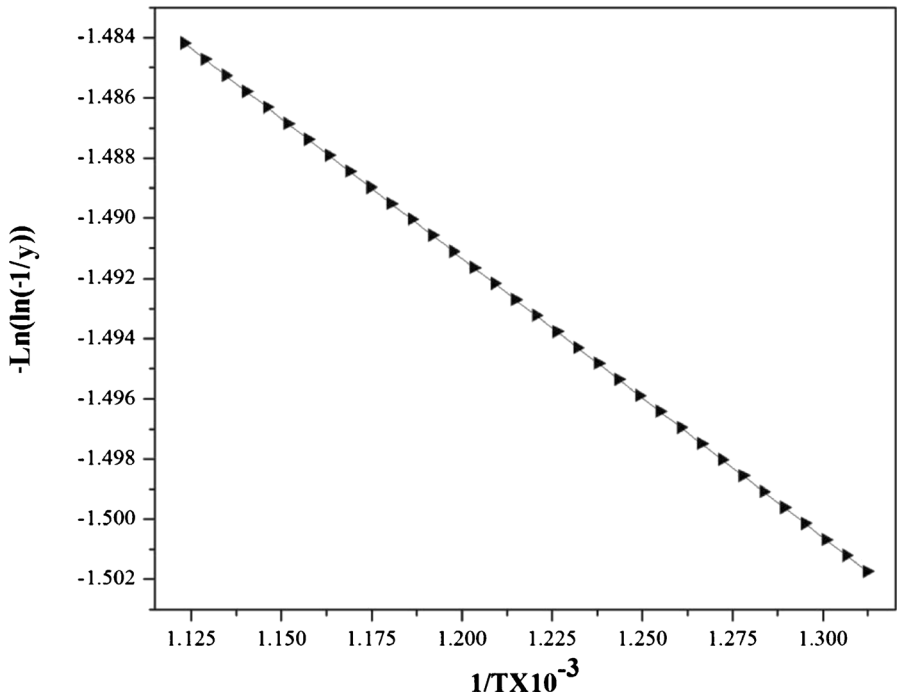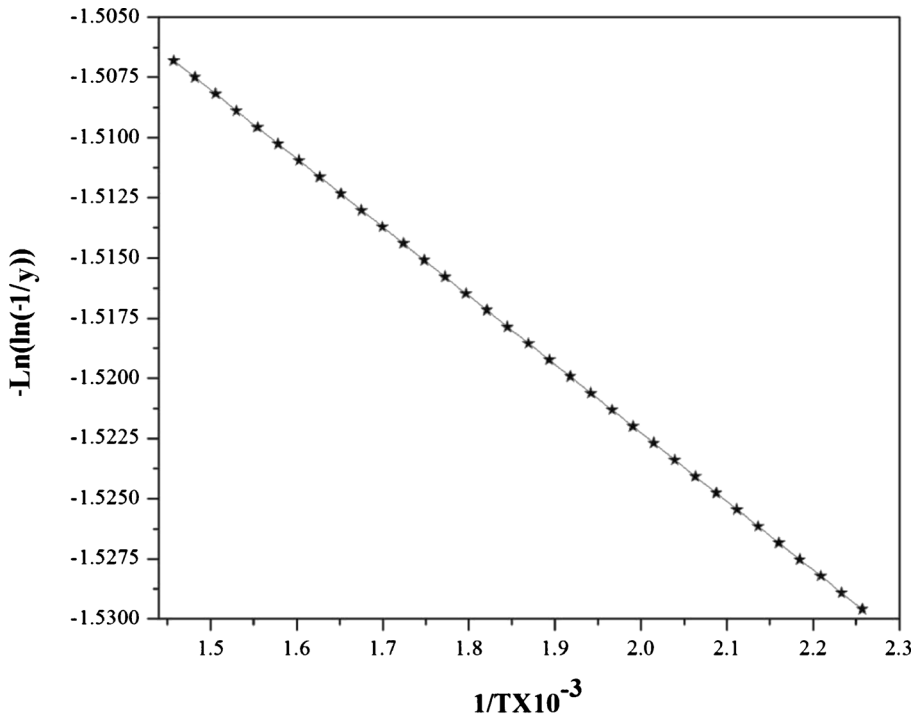
Fig. 5 Plots of -Ln(ln(−1/y)) vs 1/T × 10^{-3} for the decomposition step of DSVPOx in the range **a** 170–410 °C. **b** 490–610 °C
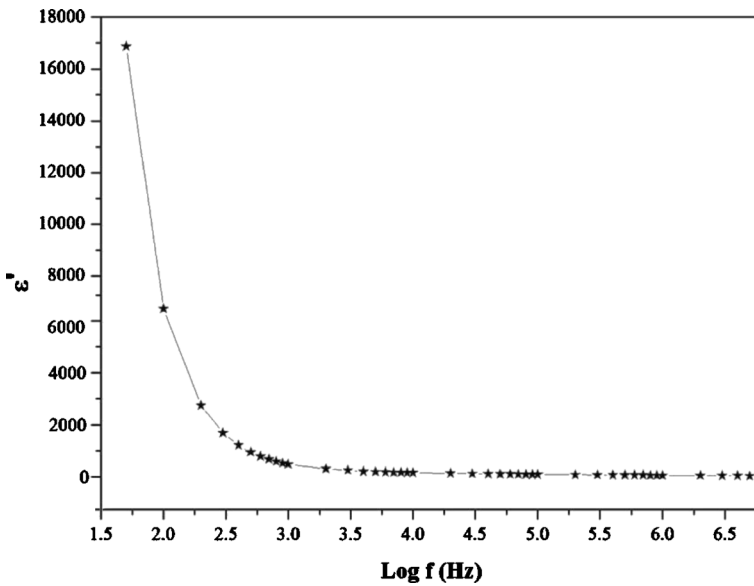
Fig. 6 Variation of dielectric constant (ε') with log (frequency) of DSVPOx at room temperature

Conclusions

Sulfonated poly(1,3,4-oxadiazole-ether) sulfone copolymer with pendant carboxylic acid groups was synthesized and well characterized by NMR spectroscopic technique. Further, using Broido's method, kinetic and thermodynamic parameters were calculated from thermogravimetric analysis plots. Ac conductivity of DSVPOx was measured as a
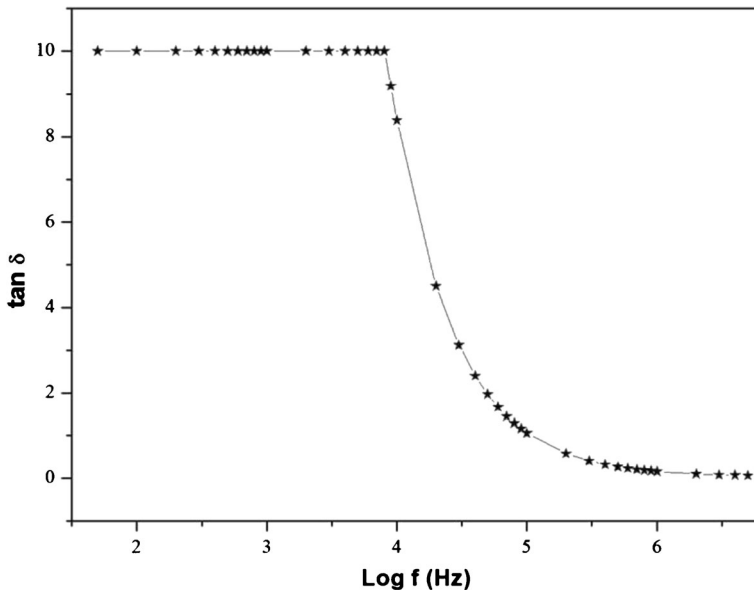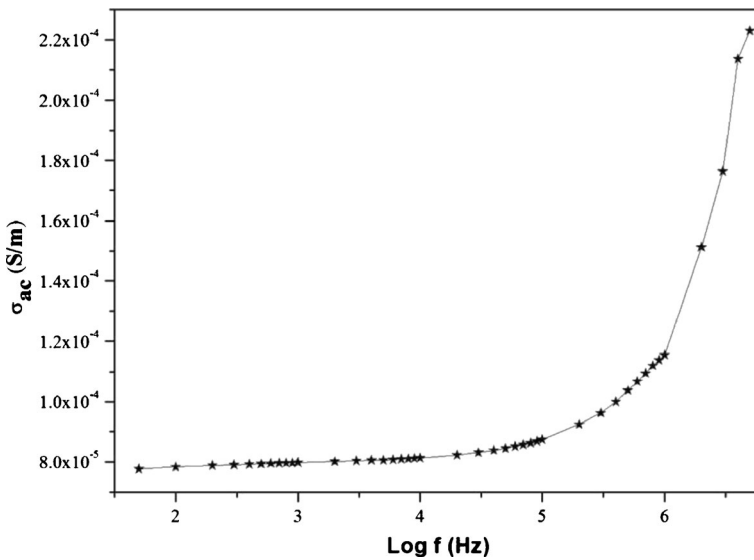

Fig. 7 Variation of loss tangent on log (frequency) for DSVPOx at room temperature

Fig. 8 Variation of AC conductivity on log (frequency) for DSVPOx at room temperature

function of frequency, with ohmic silver electrodes. The dielectric constant (ε') was found to decrease with the increase in frequency. The dielectric loss (tanδ) was also found to be decreased with the increase in frequency, such behaviours reveals that bulk DSVPOx sample exists in the form of molecular dipoles and suggests that ionic and polymer segmental motions are strongly coupled.

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