

Research Article

Poly(Arylene Ether Sulfone)s with HEPES Pendants: Synthesis, Thermal, and Dielectric Studies

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Polyethersulfone with active carboxylic acid pendants was prepared from solution polymerization via nucleophilic displacement polycondensation reaction among 4,4'-dichlorodiphenyl sulfone (DCDPS) and 4,4'-bis(4-hydroxyphenyl) valeric acid (BHPA). The conditions necessary to synthesize and purify the polymer were investigated in some details. The synthesized polyethersulfone comprises sulfone and ether linkages in addition to reactive carboxylic acid functionality; this reactive carboxylic acid group was exploited to hold the HEPES moiety via ester linkage and is achieved by simple DCC coupling condition at ambient temperature. Without impairing the primary polymeric backbone, three modified polymers were prepared by varying the stoichiometric ratio of HEPES. Characterization of the polymers by ¹H & ¹³C NMR, FT-IR, and TGA demonstrated that HEPES was quantitatively incorporated into the prime polymer. All the prepared polymers were pressed into tablets, and electrical contacts were established to study the dielectric properties. Finally, the influence of the HEPES on the dielectric properties was examined.

1. Introduction

The field of ionomers has expanded over the past few decades and has become fundamental to the science of polymer technology; the intriguing properties and the wide range technological interests have been an ever increasing stimulus to fully focus on specialized applications such as electrochemical sensors [1, 2], polymer electrolyte fuel cells (PEMFCs) [3–5]. In recent years, there have been a multitude of new simple synthetic methodologies developed to aid in the construction of high performance polymers with suitable ionic groups [6]. Concurrently with these developments, the field of ionomers has matured within the last few decades; the richness of physical and chemical properties of these polymers finds its fundamental and potential response to technical field. In order to attain controlled charge separation and ion mobility, a variety of chemical modifications to

the high performance Udel poly(ethersulfone) polymer are in lively practice via appended ionic pendants in PEMFCs application [7, 8]. Modification reactions create the enormous diverse applications providing new linkages with different functionalities.

There is an on-going uncertainty about the best way to mitigate the synthetic pathway by changing the basic monomer scaffolds to attain efficient synchronized properties of resulting polymers and copolymers. Much effort to synthesize relatively inexpensive and thermally stable macromolecules including sulfonated and phosphonated polysulfones, poly(arylene ether)s [9–11], polybenzimidazoles [12], polyphenylenes [13] and poly(oxadiazole)s [14] have been initiated, and several of the above mentioned polymers have gained continuing interest. The fabulous properties of polyimides [15], such as a low dielectric constant, considerable thermal and photo stability, notable chemical resistance, and

high optical transmittance, predetermine their widespread applications as casts and layers used as insulators, protective or capsulation layers, and mechanical or diffusion barriers, in opto- and microelectronics [16, 17]. Metal incorporated monomers are used to synthesize the electrically conductive polysulfone [18, 19] and have been extensively investigated for their potential applications in the field of fuel cells [20, 21].

Poly(ethersulfone)s are a family of high performance engineering thermoplastic materials with high glass transition temperature, high thermal stability, good mechanical properties, and excellent resistance to hydrolysis and oxidation which play an important role in fabricating optical waveguiding materials [22, 23]. Few reliable and operationally mild protocols have been reported for the preparation of fluorinated polyethersulfones [24] and HEPES {2-[4-(2-hydroxyethyl)1-piperazinyl]ethane sulphonic acid} modified new metallophthalocyanine complexes [25]. The need for thermally stable polymers has suggested the possibility of using polyethersulfones with appropriate ion-conducting sites.

In this present work, we made an attempt to synthesize the modified polyethersulfone, containing alternating flexible biphenyl sulfone and ether segments in addition to biphenyl valeric acid moieties. The reactive carboxylic acid functionality was exploited to hold the HEPES moiety via ester linkage. The physicochemical changes in the resulting polymers were investigated.

2. Experimental

2.1. Materials. 4,4'-Dichlorodiphenyl sulfone (DCDPS), 4,4'-bis(4-hydroxyphenyl) valeric acid, Dimethylformamide (DMF) and dicyclohexylcarbodiimide (DCC) were purchased from Aldrich, and 2-[4-(2-hydroxyethyl)1-piperazinyl]ethane sulphonic acid (HEPES) was purchased from Himedia Chemicals. All the chemicals were of reagent grade and used without further purification. Double distilled water was used throughout the study.

2.2. Instrumentation. Elemental analysis was performed with a Perkin Elmer PE 2400 CHN elemental analyzer. The Fourier transform infrared (FT-IR) spectra were recorded by a Thermo Nicolet -5700, USA spectrometer (diamond window method). The ^1H & ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard reference. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Diamond TGA/DTA thermogravimetric analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. The number and weight average molecular weights (M_n and M_w) of VALPSU valeric acid-based polyethersulfone were estimated by gel permeation chromatography (HP/GPC, Waters). Degassed tetrahydrofuran (THF) was used as eluent at a flow rate of $1.0\text{ mL}/\text{min}$. A set of monodisperse polystyrene standards covering the range of 10^3 – 10^7 was used for the molecular weight calibration. The dielectric measurements were carried out using impedance analyzer model HIOKI 3352-50 HiTESTER Version 2.3. Samples of powdered polymer

samples were pressed into tablets and sandwiched between two silver-plated stainless steel electrodes; 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 electrodes. The electrical contacts were checked to verify the ohmic connection. The measurements were carried out at room temperature in between the 50 Hz–5 MHz. The capacitance value (C) and ac conductance (G) were directly obtained from the instrument. The dielectric constant (ϵ') and ac conductivity (σ_{ac}) values are calculated using the relations $\epsilon' = C_p d / \epsilon_0 A$ and $\sigma_{ac} = G d / A$, respectively, where " d " is the thickness of the polymer tablet, " A " is the cross-section area, and ϵ_0 is the permittivity of the free space. All these measurements were made under dynamic vacuum.

2.3. Methods of Preparations

2.3.1. Synthesis of Valeric Acid-Based Polyethersulfone (VALPSU). VALPSU with active carboxylic acid pendant groups was prepared from the nucleophilic displacement reaction of 4,4'-dichlorodiphenyl sulfone (DCDPS) with 4,4'-dihydroxy biphenyl valeric acid. The method was adopted from the previously described synthetic protocols [26, 27].

A typical synthesis of this polyether sulfone VALPSU was conducted in a three-neck flask equipped with a nitrogen inlet, stirrer, Dean-Stark trap, and condenser. The flask was charged with 4,4'-dichlorodiphenyl sulfone (DCDPS), 1g (3.48 mmol), 0.997 g of 4,4'-dihydroxy biphenyl valeric acid (3.48 mmol), K_2CO_3 (1.06 g, 7.66 mmol), N-methyl pyrrolidine (10 mL), and toluene (10 mL), and the flask was purged with dry nitrogen, three times. The reaction mixture was then heated to 140°C for 2 h until the toluene was all condensed in the Dean-Stark trap. Upon dehydration, the polymerization was heated to 180°C for 22 h. The thick gelly crimson red reaction mixture was diluted with 5 mL of NMP and then plunged into 300 mL of demineralised water containing 10% hydrochloric acid. The precipitated polymer was repeatedly washed with excess of water and dried in vacuum at 60°C for 48 h.

Yield: 90%. FT-IR (diamond window, cm^{-1}): 1349 (C–N, sym), 1253 (S=O, sulfone). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): $\delta = 1.51$ – 1.57 (br s, 8H), 1.99 – 2.01 (br s, 5H), 2.34 (br s, 4H), 6.67 (d, 1H), 6.98 (m, 11H), 7.07 (d, 10H), 7.20 (m, 10H), 7.88 (d, 10H), 12.06 (br s, 3H). Anal. calcd. for $\text{C}_{29}\text{H}_{24}\text{O}_6\text{S}$: C, 69.58; H, 4.83; O, 19.18; S, 6.41; found: C, 69.72; H, 4.81; O, 19.02; S, 6.33%.

2.3.2. Synthesis of VALPSU-HEP-60 Polymer (P-60). A direct synthesis of a modified VALPSU polyether sulfones with 60 mass% HEPES (VALPSU-HEP-60) is discussed. In a 100-mL, three-neck flask equipped with a mechanical stirrer and a nitrogen inlet/outlet, 1.0 g (9.0 mmol) of VALPSU and 0.623 g (3.0 mmol) of DCC were added and stirred by adding 10 mL DMF to form the soluble and more reactive derivative. The solution was stirred at room temperature for 0.5 hours until complete dissolution of the polymer and DCC,

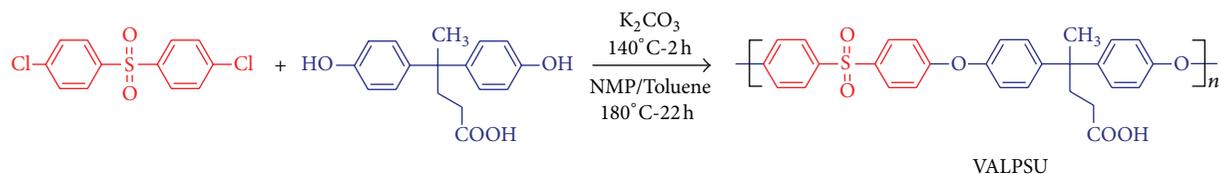


FIGURE 1: Synthesis of VALPSU polymer with pendant carboxylic acid groups.

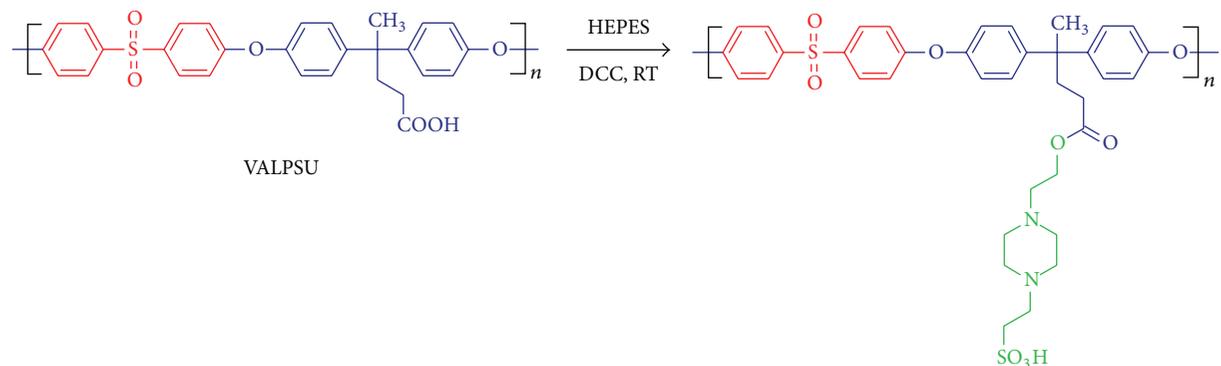


FIGURE 2: Synthesis of HEPES-modified VALPSU polymer.

and then 0.6 g (2.5 mmol) of HEPES was added along with 5 mL of DMF using syringe into the reaction mixture. The jelly reaction mixture was stirred at ambient temperature for 22 h with further addition of 3–5 mL DMF; the HEPES-modified polymer precipitated into an excess of 5% methanolic solution. The precipitated polymer was collected by filtration and pulverised and washed several times with 1 : 1 acetone and water mixture. The resulting white, polymer VALPSU-HEP-60 was dried under vacuum at 60°C for 24 h.

Yield: 90%; FT-IR (diamond window, cm^{-1}) 1736 (C=O, sym.), 1646 (C=O, asym.), 1385 (C–N, sym.), 1088 (S=O, asym.), 1011 (S=O, sym.), 1243 (S=O, sulfone). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 0.98–1.37 (m, 2H), 1.53–1.62 (m, 2H), 1.69–1.72 (d, 1H), 2.00 (br s, 1H), 2.33 (br s, 1H), 7.01–7.06 (d, 2H), 7.21 (br s, 1H), 7.86 (br s, 3H).

A similar procedure was followed for the synthesis of polymers VALPSU-HEP-20 and VALPSU-HEP-40. The spectral and analytical data are given below.

2.3.3. VALPSU-HEP-40 Polymer (P-40). Yield: 90%; FT-IR (diamond window, cm^{-1}) 1736 (C=O, sym.), 1646 (C=O, asym.), 1385 (C–N, sym.), 1088 (S=O, asym.), 1011 (S=O, sym.), 1243 (S=O, sulfone). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 0.98–1.36 (m, 2H), 1.53–1.61 (m, 2H), 1.69–1.71 (d, 1H), 2.00 (br s, 1H), 2.33 (br s, 1H), 7.01–7.05 (d, 2H), 7.21 (br s, 1H), 7.86 (br s, 3H).

2.3.4. VALPSU-HEP-20 Polymer (P-20). Yield: 90%; FT-IR (diamond window, cm^{-1}) 1736 (C=O, sym.), 1646 (C=O, asym.), 1385 (C–N, sym.), 1088 (S=O, asym.), 1011 (S=O, sym.), 1243 (S=O, sulfone). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 0.98–1.35 (m, 2H), 1.52–1.60 (m, 2H), 1.68–1.71 (d, 1H),

2.00 (br s, 1H), 2.33 (br s, 1H), 7.01–7.04 (d, 2H), 7.21 (br s, 1H), 7.86 (br s, 3H).

The synthetic routes are presented in Figures 1 and 2.

3. Results and Discussion

3.1. Synthesis and Characterization of Polymers. The synthesis of new polymer VALPSU with active carboxylic acid moiety was achieved via conventional aromatic nucleophilic substitution polymerization technique from 4,4'-Bis(4-hydroxyphenyl) valeric acid and 4,4'-Dichlorodiphenyl sulfone; the polycondensation was carried out at an elevated temperature in NMP/Toluene azeotrope in presence of anhydrous pulverised potassium carbonate. FTIR data and NMR chemical shifts obtained for the synthesized polymers are in reassuring agreement with the proposed structure. Several reports with pendant substitution of the polysulfones via various linkages are presented [28, 29]; the present one is the new synthetic approach particularly in designing the HEPES unit hanging to the VALPSU polymer backbone. The amount of HEPES with respect to the unmodified polymer VALPSU (P-00) varied as 20, 40, and 60 mass%, and the polymers, thus, obtained were designated as VALPSU-HEP-20 (P-20), VALPSU-HEP-40 (P-40), and VALPSU-HEP-60 (P-60), respectively. The incorporation of HEPES moiety in polymer was confirmed by FTIR spectroscopy (diamond window method) in the range of 400–4000 cm^{-1} , in each scan, and the amount of well-grounded sample was kept constant (1 mg) in order to estimate the changes in the intensities of the characteristic peaks with respect to the amount of HEPES modification. The FTIR and NMR (^1H & ^{13}C) spectra of VALPSU and HEPES-modified VALPSU were shown in

TABLE 1: Kinetic and thermodynamic parameters of polymers.

Samples	Decomposition range (°C)	E_a (kJ/mol)	$\ln A$	ΔH (kJ/mol)	ΔS (kJ/K)	ΔG (kJ/mol)
P-00	370–495	0.001536	-9.9834	-5.86626	-162.271	114.52
	535–665	0.007732	-7.6386	-7.25405	-159.918	139.67
P-20	160–265	0.000877	-10.6251	-4.03596	-164.389	79.81
	395–645	0.006444	-7.9999	-6.58874	-159.989	126.90
P-40	165–310	0.001159	-10.3160	-4.23135	-163.890	83.42
	405–635	0.004174	-8.6507	-6.59101	-159.981	126.90
P-60	170–315	0.001031	-10.4434	-4.2767	-163.885	84.31
	420–625	0.003529	-8.8928	-6.5989	-160.323	127.31

Supplementary Material (see Supplementary Material available online at <http://dx.doi.org/10.1155/2013/897034>). C–H (asymmetric and symmetric stretching) of $-\text{CH}_2$ -groups at 2932 and 2850 cm^{-1} , O–H stretching at 3326 cm^{-1} , and carbonyl frequency at 1704 cm^{-1} confirms the polymer VALPSU clutched the HEPES with (“ester bond”). Signal broadening of the spectrum is observed due to polymerization. The signals resonated at 12.06 ppm was assigned to carboxylic acid protons, and signals at the range of 2.01 and 2.34 ppm were assigned to methylene protons, indicating that the 4,4'-bis(4-hydroxyphenyl) valeric acid moiety was introduced successfully and indicating the formation of polysulfone (VALPSU) with carboxylic acid pendants. Further signal at $174.48\text{ }\delta$ in ^{13}C NMR spectra confirms the carbon of carboxylic acid and two methylene carbons at $29.77\text{ }\delta$ and $36.05\text{ }\delta$. The molecular weight of VALPSU polymer was determined by GPC with polystyrene as the standard and THF as the eluent and showed M_w of 12150 with polydispersity 4.83. The polysulfone with pendant carboxylic acid groups was soluble in THF, DMF, DMAc, DMSO, and NMP at ambient temperature. The thin solid films of polymers are made by pressing into tablets of minimum thickness for further characterization.

3.2. Thermal Analysis. Thermal properties of the polymers were examined by TGA measurements. Thermogravimetric analysis was carried out for all the polymers, and the patterns were presented in Figure 3. Poly(arylene ether sulfone)s with carboxylic acid (P-00) exhibited two steps of degradation, whereas polymers containing HEPES (P-20, P-40, and P-60), shows three degradation steps.

The initial weight loss step started at around $160\text{--}315^\circ\text{C}$ in case of HEPES-modified polymers and was attributed to the desulfonation of sulfonic groups, where $-\text{SO}_3\text{H}$ was easily exterminated by releasing H_2O , SO_2 and other sulfur oxides, which is not observed in starting poly(arylene ether sulfone). Another major weight loss in the range $250\text{--}410^\circ\text{C}$ were assigned to the decomposition of HEPES unit and the remaining carboxylic acid groups from polymer backbone. Third degradation step is in the range of $550\text{--}620^\circ\text{C}$ can be accounted for the main polymeric chain. While Polymer VALPSU shows two step degradations owing to the decarboxylation of $-\text{COOH}$ in $370\text{--}495^\circ\text{C}$ range and main polymer backbone observed at temperature range $535\text{--}665^\circ\text{C}$, no

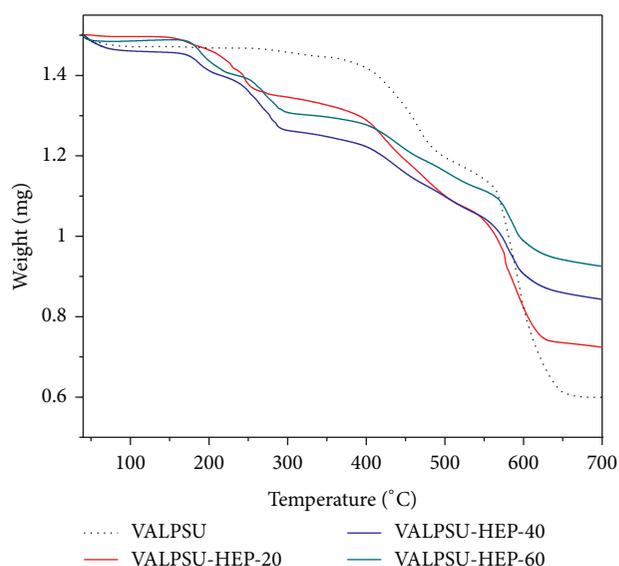


FIGURE 3: TGA thermograms of polysulfones at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

weight loss was observed before 150°C because the polymers were totally dried before analysis.

Kinetic and thermodynamic parameters were calculated using Broido's method [30]. Broido has developed a model, and the activation energy associated with each stage of decomposition was also evaluated by this method. The equation used for the calculation of activation energy (E_a) is

$$-\ln\left(\ln\left(-\frac{1}{Y}\right)\right) = \left(\frac{E_a}{R}\right)\frac{1}{T} + \text{Constant}, \quad (1)$$

where $Y = (W_t - W_\infty)/(W_o - W_\infty)$.

“Y” is the fraction of the number of initial molecules not yet decomposed; W_t —the weight at time t ; W_∞ —the weight at infinite time (i.e., zero), and W_o —the initial weight. A plot of $-\ln(\ln(-1/Y))$ versus $1/T$ gives an excellent approximation to a straight line. The slope is related to the activation energy. Plots of $-\ln(\ln(-1/Y))$ versus $1/T$ (Figures 4(a) and 4(b)) were developed for the decomposition segments. From the plots, the activation energy (E_a) and frequency factor ($\ln A$) were evaluated. The enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) have been calculated using standard

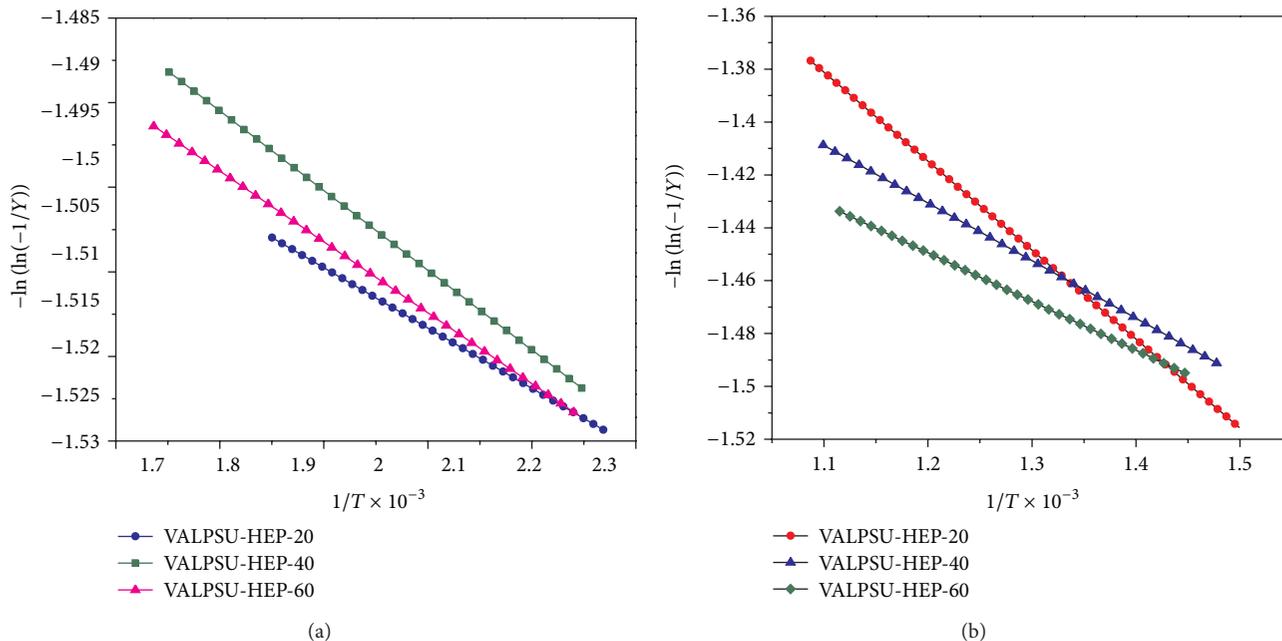


FIGURE 4: (a) Plots of $-\ln(\ln(-1/Y))$ versus $1/T \times 10^{-3}$ for the first step decomposition of sulfonic acid groups in P-20, P-40, and P-60 samples. (b) Plots of $-\ln(\ln(-1/Y))$ versus $1/T \times 10^{-3}$ for the third step decomposition of polysulfone chain in P-20, P-40, and P-60 samples.

equations and are summarized in Table 1. The results indicate that in the case of HEPES-modified VALPSU, the activation energy is the lowest in the temperature range of 160° – 315° C indicating that this is the fastest step. The back bone of polymer has (ether and sulfone) linkages, and the stability of the polyethersulfones depend upon the breaking temperature of these bonds which lies in the temperature range 395° – 645° C of the degradation reaction; it could be predicted that the final steps are slow compared to the initial step where the breaking up of ether and sulfone linkages take place.

3.3. AC Electrical Measurements

3.3.1. Frequency Dependence AC Conductivity (σ_{ac}), Dielectric Constant (ϵ') and Dielectric Loss ($\tan \delta$). Frequency dependence variation of dielectric constant at room temperature was presented in Figure 5. It is observed from the plot that, in general, it follows inverse, as followed by almost all the dielectric and ferroelectric materials, dispersion with relatively high dielectric constant can be observed in ϵ' -Log (frequency) plot, the dielectric constant values (measured at 10^6 Hz at room temperature) were found in the range of 488–278 and decreased with the increasing of the HEPES content, and the dielectric constant drops at high frequencies, due to the fact that the dipoles can no longer follow the high frequencies. Increase in the ϵ' is witnessed by VALPSU-HEP-20 than the basic VALPSU polymer may due to the freely exchangeable sulfonic acid ionic moieties in addition to the carboxylic acid groups. Further modification of VALPSU above 60 mass% of HEPES results not much appreciable variation to ϵ' , so HEPES incorporated to VALPSU in maximum percentage (60 mass%) to achieve ϵ' of 278. Higher HEPES content in

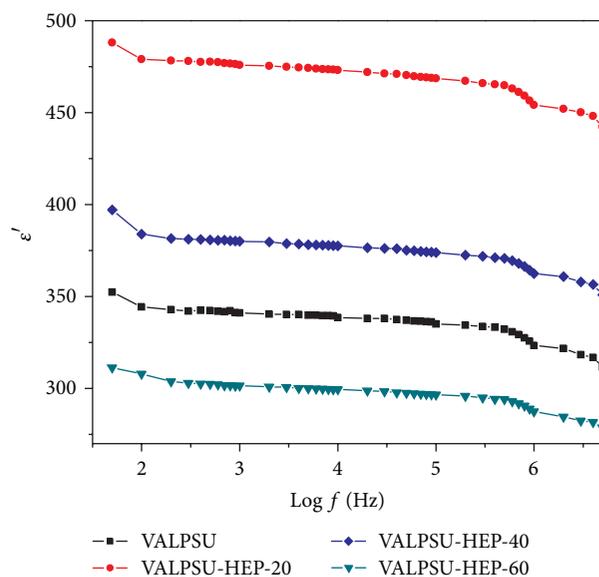


FIGURE 5: Room temperature variation of dielectric constant (ϵ') with \log (frequency) of VALPSU and HEPES-modified VALPSU.

the polymer upshots the inter- and intra-molecular hydrogen bonding, so it attributed low dielectric constant values.

Dielectric loss ($\tan \delta$) as a function of \log (frequency) is shown in Figure 6. As per the plot, $\tan \delta$ decreases with increase of frequency and attains the constant value, and higher HEPES content in the polymers experiences much higher dielectric loss. The dielectric losses of all the HEPES-modified poly(arylene ether sulfone)s are lower than 0.18.

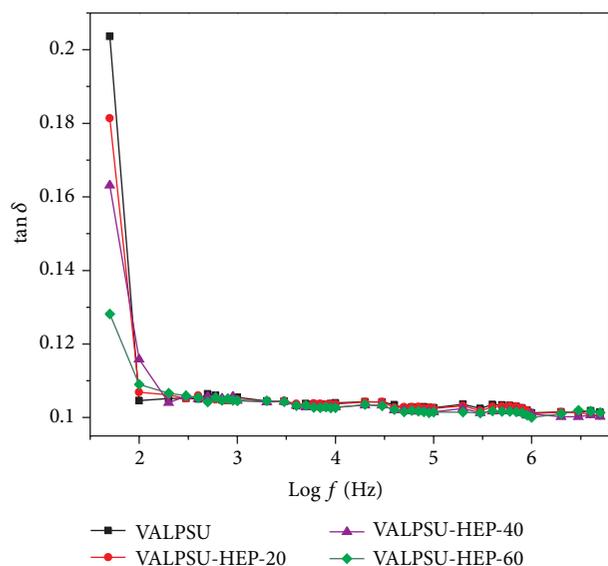


FIGURE 6: Room temperature variation of loss tangent on log (frequency) for VALPSU and HEPES-modified polymers.

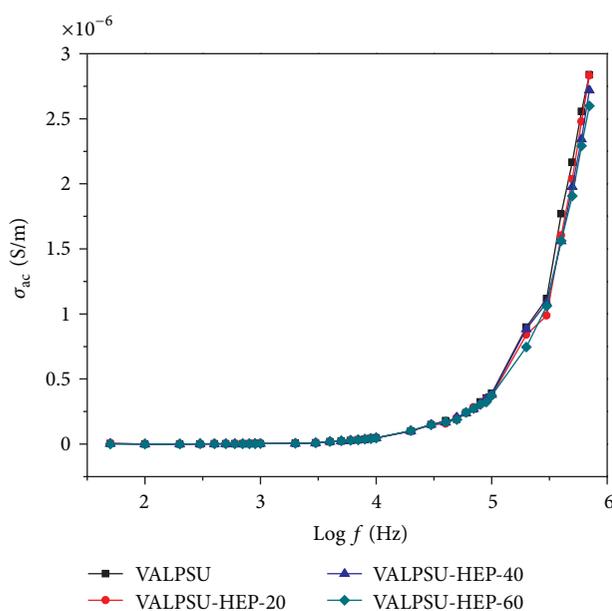


FIGURE 7: Room temperature variation of AC conductivity with log (frequency) for VALPSU and HEPES-modified polymers.

This decrease in dielectric loss with the increasing frequency and HEPES content is usually associated with low ion drifting and restriction in dipole polarisation or interfacial polarisation due to hydrogen bonding interactions of the polar groups. Peak resonance could not be noticed in our case since they might be beyond our ac measurement range [31, 32].

The variation of conductivity as a function of frequency at ambient temperature is shown in Figure 7. The ac conductivity of the sample depends on its dielectric nature, at low frequencies; σ_{ac} varies linearly and increases steeply above the frequency 5 MHz. At room temperature, frequency

independent ac conductivity is observed in low frequency region, and the model is based on the classical hopping of electrons over the barrier [32]. The mechanisms of dipole polarization were more complex, since HEPES units are covalently bonded to the backbone of the VALPSU macromolecule, which is an insulating material. The difference in the ac conductivities of HEPES-modified VALPSU was found to be almost negligible. An additional factor affecting the molecular mobility in HEPES-modified poly(arylene ether sulfone)s may be related to the formation of intra- and intermolecular hydrogen bonds resulting from incorporation of HEPES functional group into poly(arylene ether sulfone)s.

4. Conclusion

Protic ionomers with pendant heterocyclic HEPES unit were synthesized and characterized via nucleophilic aromatic substitution reaction; it was demonstrated that good thermally stable polymeric materials can be prepared from the pendant carboxylic acid functional poly(arylene ether sulfone)s (VALPSU); polymer modification is done at room temperature by mild DCC coupling condition. Dielectric behaviour of the synthesized polymers was examined, which illustrates that the higher the HEPES content in the polymer, the lower will be the dielectric constant which is due to inter- and intra-molecular hydrogen bonding. Also low dielectric loss is experienced by the polymers because of low ion drifting. The ac conductivity of the polymers varies linearly and increases sharply above the frequency 5 MHz. Low dielectric constant materials with high thermal stability with adequate mechanical properties are prime candidates for opto- and microelectronics. Further, incorporation of suitable ceramic and nanocomposites into these polymer matrix results in high dielectric constant materials and can applicable in high operating frequencies devices.

Conflict of Interests

It is to state that neither authors nor their institution has a financial or other relationship with any organization or people that may influence the author's work. The authors are not being paid by any organization or agency related to the product. There is no conflict of interests to be declared.

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