

Research Article

Preparation and Characterization of Styrene Bearing Diethanolamine Side Group, Styrene Copolymer Systems, and Their Metal Complexes

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The two copolymer systems of styrene bearing diethanol amine side group and styrene were prepared by free radical polymerization method at 60°C in presence of 1,4-dioxane as solvent and AIBN as initiator. Their metal complexes were prepared by reaction of the copolymer used as ligand P(DEAMSt-co-St)L'' and Ni(II) and Co(II) metal ions, which was carried out in presence of ethanol and NaOH at 65°C for 48 h in pH = 7.5. The structures of the copolymers used as ligand and metal complexes were identified by FT-IR, ¹H-NMR spectra, and elemental analysis. The properties of the copolymers used as ligand and metal complexes were characterized by SEM-EDX, AAS, DSC, TGA, and DTA techniques. Then, the electrical properties of the copolymers and metal complexes were examined as a function of the temperature and frequency, and the activation energies (E_a) were estimated with conductivity measurements.

1. Introduction

Polymer-metal complexes are an important class of polymers formed by coordination of polymeric ligands with transition metal ions [1]. The structural perimeter of the ligand function is one of the key factors in the determination of the ability of polymeric ligands to form complexes with metal ions [2, 3].

The polymer-supported ligands are prepared as chemically modified with various monomers. This modified monomers are significant as ion changers because they can be prepared to desired selectivity with suitable ionophore reagents [4]. These ligands have high mechanical and chemical stability. The ligands are very important for metal ion complexation because of their hydrophilicity, accessibility, and high capacity [5]. Such ligands include iminodiacetates [4, 6], amides [7], hydroxylamines [8], Schiff bases [9], and phosphonates [10]. Usually, these ligands are prepared by the modification of crosslinked copolymers polystyrene, poly(vinyl benzyl) chloride, poly(glycidyl methacrylate), and polyacrylic acid [11]. These kinds of polymers have highly functional characteristic. Recently, many studies have been conducted on polymer-metal complexes and in the

literature there are polymer-metal complexes that were successfully prepared from polyacrylonitrile and its copolymers [12], poly(acrylonitrile-co-vinyl acetate) [13], polyacrylamide [14], polyethyleneimine [15], and the other polymers and monomers. In these reactions, Cu(II), Ni(II), Co(II), Zn(II), and Fe(II) are used as transition metal ions.

In this study, we synthesized monomer bearing diethanolamine (DEA), containing hydroxyl groups as ligand DEAMSt, and its combination with styrene in two different copolymers using free radical polymerization method. These copolymers were used as ligand. The metal complexes were prepared by reaction of the copolymers used as ligands with Ni(II) and Co(II) metal ions. The characterization of the prepared ligand and metal complexes was performed by infrared (FT-IR), ¹H-NMR, Elemental analyses, SEM-EDX, AAS, TGA, DTA, and DSC and dielectrical properties were investigated by impedance analyzer.

2. Materials and Methods

2.1. Materials. Diethanolamine (DEA), 4-(chloromethyl)styrene (CMS) (Aldrich), N,N-dimethylformamide (DMF),

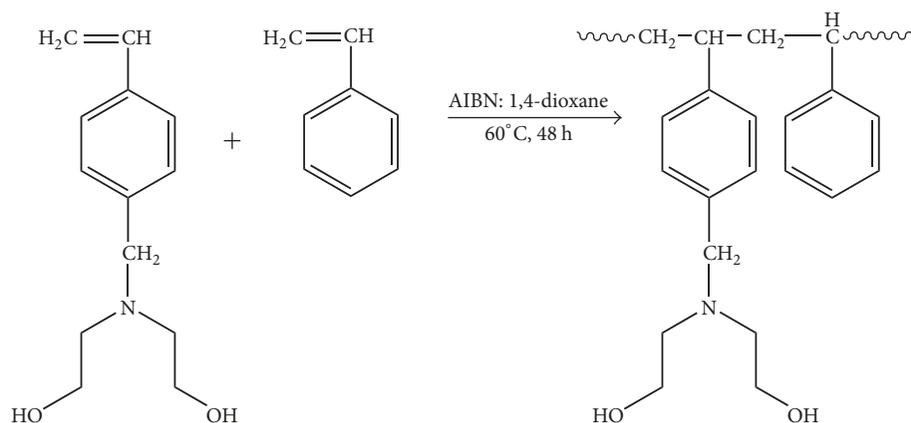


FIGURE 1: Synthesis reaction of $\text{P}(\text{DEAMSt-co-St})\text{L}''$ used as ligand.

tetrahydrofuran (THF), 2,2'-Azobisisobutyronitrile (AIBN), n-hexane, 1,4-dioxane, diethyl ether, dichloromethane, sodium hydroxide (NaOH), sodium bicarbonate (NaHCO_3), and ethanol (Fluka) were used without further purification. The metal ion salts were used in the form of nickel acetate ($\text{Ni}(\text{CH}_3\text{COOH})\cdot 4\text{H}_2\text{O}$) and cobalt acetate ($\text{Co}(\text{CH}_3\text{COOH})\cdot 4\text{H}_2\text{O}$) (Fluka).

2.2. Instrumentation. The instruments used in our study were as follows: Perkin-Elmer (FT-IR infrared spectrometer), $^1\text{H-NMR}$ nuclear magnetic resonance (400 MHz Bruker AVANCE III) spectrometer machine, using as solvent CDCl_3 , elementary analyses on a FLASH 2000 (organic) analyzer, SEM-EDX scanning electron microscope (on a EVOLS 10), AAS atomic absorption spectroscopy (Perkin-Elmer Analyst 800), melting point device (Stuart SMP 30), DSC differential scanning calorimeter (Shimadzu DSC-50), and thermal analyzer under N_2 atmosphere flow using a heating rate of $20^\circ\text{C}/\text{min}$ at 200°C . TGA thermal analyzer (Shimadzu DTG-60 AH TGA-60) and DTA differential thermal analyzer (Shimadzu DTG-60 AH DTA-60) under N_2 flow with a heating rate of $10^\circ\text{C}/\text{min}$ at 700°C and LRC metter analyzer (on a Quadtech 7600 precision) over the frequency range at 100 Hz–2 kHz.

2.3. Preparation of $\text{P}(\text{DEAMSt-co-St})\text{L}''$ Used as Ligand. In our previous study [16] the synthesis of styrene monomer with DEAM side group (DEAMSt) was done according to a method adapted from the literature [16, 17]. The copolymers in two different combinations were prepared from styrene monomer with diethanolamine side group. The synthesis of copolymers was carried out by free radical polymerization method. For this purpose, it was placed to two different polymerization tubes: first tube, 0.880 g (0.004 mol) DEAMSt and 3.740 g (0.036 mol) styrene and 0.036 g AIBN, and second tube, 2.650 g (0.012 mol) DEAMSt and 2.910 g (0.028 mol) styrene and 0.044 g AIBN, in which 1,4-dioxane was used as solvent and AIBN was used as initiator. The prepared mixtures were passed through argon gas for 10 min. The polymerization tubes were closed, and the content of polymerization tubes was polymerized within oil thermostat at 60°C for 48 h.

The obtained first product was precipitated in ethanol and second product in diethyl ether. Then, $\text{P}(\text{DEAMSt-co-St})\text{L}''$ used as ligand was dried at 40°C under vacuum for 24 h (Figure 1). The structure of ligands was characterized by FT-IR, $^1\text{H-NMR}$, elemental analysis, and SEM. The composition of copolymers was determined by $^1\text{H-NMR}$ spectra. The combinations (%) were found as $\text{P}(\text{DEAMSt}\%13\text{-co-St})$ and $\text{P}(\text{DEAMSt}\%38\text{-co-St})$.

2.4. The Preparation of Polymer–Metal Complexes $\text{P}(\text{DEAMSt-co-St})\text{L}''-M$ ($M: \text{Ni(II)}, \text{Co(II)}$). $\text{P}(\text{DEAMSt-co-St})\text{L}''$ -metal complexes were prepared in presence of solvent [18, 19]. The procedure of $\text{P}(\text{DEAMSt}13\%\text{-co-St})\text{L}''\text{-Ni}$ complex was as follows. For this purpose, a mixture of 0.3 g (0.00045 mol) $\text{P}(\text{DEAMSt}13\%\text{-co-St})\text{L}''$ ligand dissolved in 40 mL ethanol was stirred for 2 h at 65°C and the pH of the solution was calibrated by adding dilute 0.1M NaOH solutions in water. One hour after a dilute solution of nickel acetate 0.056 g (0.00025 mol) was added dropwise to the mixture and the polymer-metal solution was refluxed at 65°C for 48 h. The precipitated $\text{P}(\text{DEAMSt}13\%\text{-co-St})\text{L}''\text{-Ni}$ complex was filtered, washed with distilled water up to pH 6, and dried at 40°C under vacuum. The obtained $\text{P}(\text{DEAMSt}13\%\text{-co-St})\text{L}''\text{-Ni}$ complex was light green color (yield 71%). The same procedures were followed for the preparation of $\text{P}(\text{DEAMSt}13\%\text{-co-St})\text{L}''\text{-Co}$ (yield 57%), $\text{P}(\text{DEAMSt}38\%\text{-co-St})\text{L}''\text{-Ni}$ (yield 64%), and $\text{P}(\text{DEAMSt}38\%\text{-co-St})\text{L}''\text{-Co}$ (yield 50%) complexes.

Polymer-metal complexes prepared by metal ions of $\text{P}(\text{DEAMSt-co-St})\text{L}''$ ligand were obtained as light green for Ni(II) and black for Co(II). The resulting color metal complexes were insoluble in any organic solvents. The reason of the insoluble metal complexes in organic solvents is due to their crosslinked structure [12, 20]. Therefore, the characterization of polymer-metal complexes was carried out by FT-IR, DTA, TGA, SEM, AAS, and elemental analysis.

3. Results and Discussion

3.1. Characterization. In our study $\text{P}(\text{DEAMSt-co-St})\text{L}''$ used as ligand was synthesized by the copolymerization of styrene

TABLE 1: FT-IR spectra data of P(DEAMSt-co-St) and its metal complexes.

Copolymer	$\lambda = \text{cm}^{-1}$				
	OH	C=C	C-N	C-O	C-O-M
P(DEAMSt13%-co-St)L''	3436	1601 (s)	1371, (1120–1250) (s)	1029 (s)	
P(DEAMSt13%-co-St)L''-Ni	3443 (b)	1600 (b)	1383, (1100–1250) (b)	1028 (b)	1028
P(DEAMSt13%-co-St)L''-Co	3443 (b)	1600 (b)	1383, (1100–1250) (b)	1029 (b)	1029
P(DEAMSt38%-co-St)L''	3401	1601 (s)	1367, (1120–1250) (s)	1030 (s)	
P(DEAMSt38%-co-St)L''-Ni	3435 (b)	1603 (b)	1383, (1100–1250) (b)	1019 (b)	1019
P(DEAMSt38%-co-St)L''-Co	3435 (b)	1603 (b)	1383, (1100–1250) (b)	1018 (b)	1018

s: strong; b: broad; C=C: aromatic ring protons; M: metal ions.

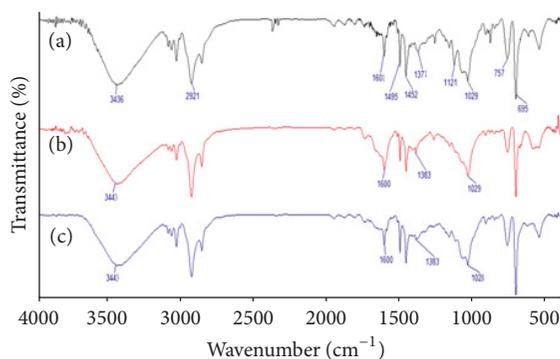


FIGURE 2: FT-IR spectrums of (a) P(DEAMSt13%-co-St)L'', (b) P(DEAMSt13%-co-St)L''-Co, and (c) P(DEAMSt13%-co-St)L''-Ni.

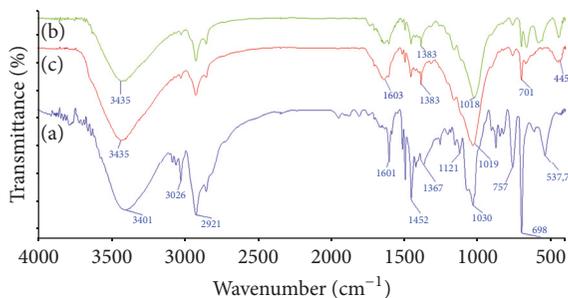


FIGURE 3: FT-IR spectra of (a) P(DEAMSt38%-co-St)L'', (b) P(DEAMSt38%-co-St)L''-Co, and (c) P(DEAMSt38%-co-St)L''-Ni.

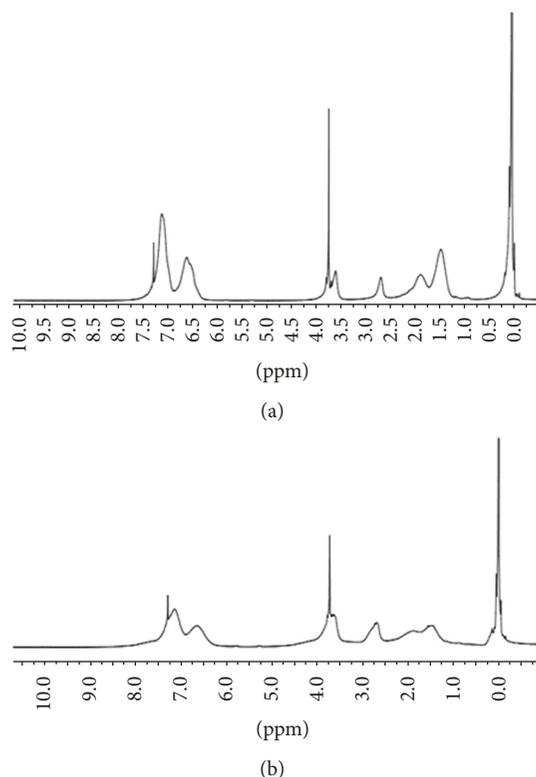
with diethanolamine side group and styrene monomers. The metal complexes were prepared by adding an aqueous solution of metal acetate in the ethanol solution including P(DEAMSt-co-St)L''. The metal complexes were not solved in any organic solvents. Therefore, the characterization of obtained ligands was carried out by FT-IR and the formation of P(DEAMSt-co-St)L'' ligands and their metal complexes were supported by elemental analysis (EA), atomic absorption spectroscopy (AAS), and scanning electron microscope (SEM).

The structure of ligands was determined by FT-IR, $^1\text{H-NMR}$ spectroscopies techniques (Figures 2-3). The FT-IR spectrum data of ligands and metal complexes are summarized in Table 1.

According to the data in Table 1, the bonds in the spectrum of ligands and metal complexes are characteristic adsorption bands. The FT-IR spectra of P(DEAMSt-co-St)L'' ligands have a characteristic adsorption band for (13% DEAMSt and 38% DEAMSt) at 3436, 3401 cm^{-1} (-OH) at stretching vibration. These bands at 3436 and 3401 cm^{-1} regions were assigned to -OH stretching vibration of the intramolecular hydrogen band. These bands are also observed in the spectra of metal complexes at 3443–3435 cm^{-1} respectively, but quite shallow and the wavenumber peak shifts from 3436–3401 to 3443–3435 cm^{-1} , showing for the formation of metal complexes. These, depending on the complexes formation have been decreased in peak intensity as a result of interactions between -OH and metal ions [21]. Consequently, the formation of water inside and outside coordination sphere of the metal complexes decreased the bending energy of the -OH band. This is the peak change of -OH band showing the coordination participation with metal ions. These broad peaks include not only the fraction of the moieties of the ligands but also complex formation [22]. The C=C stretching vibration on the aromatic ring was observed between 1600 and 1603 cm^{-1} and the sharp peaks at 1365 cm^{-1} and 1100–1250 cm^{-1} were referred to the -C-N stretching vibration [23]. The C-N bands of the metal complexes were observed to shift toward a high wavenumber at 1385 cm^{-1} and 1383 cm^{-1} and quite splayed, large, and broader peak at 1100–1250 cm^{-1} [23]. The ligands containing 13% DEAMSt and 38% DEAMSt appeared to be strong bands of C-O at 1029–1030 cm^{-1} , respectively. These bands in C-O bands of metal complexes were seen as quite broader at 1028, 1029, 1032, and 1018 cm^{-1} , which demonstrate that they were joined in the polymer matrix of the metal ions (C-O in -C-O-Ni, C-O- in -C-O-Co) [24]. When the ligands are complexed with the metal because of the electrical density on the nitrogen it shifts toward lower wavenumbers. In our study, bands in the metal complexes (M-O) were seen at 450 cm^{-1} , while M-O bands are appeared at 550–450 cm^{-1} in the literature [19, 24]. The change in color of the polymer-metal complexes is due to the orbital transition in which color changes are resulted from the change in the energy of orbitals, possibly caused by binding metal ions, because these new colors are not colors of neither the metal salt nor the ligand. The results obtained showed that metal complexes were formed.

TABLE 2: Elemental analysis and SEM-EDX data for ligands and their metal complexes.

Copolymer	Formula	Calculated% C:H:N	Found% C:H:N	SEM-EDX calculated (M)/found (M)%
P(DEAMSt13%-co-St)L''	(C ₂₁ H ₂₇ O ₂ N)	87.07 : 7.91 : 1.53	87.12 : 7.60 : 1.37	-----
P(DEAMSt13%-co-St)L'' -Ni	(C ₂₁ H ₂₅ O ₂ N) ₂ -Ni	71.00 : 6.39 : 1.24	73.14 : 7.60 : 1.50	19.88/18.27
P(DEAMSt13%-co-St)L'' -Co	(C ₂₁ H ₂₅ O ₂ N) ₂ -Co-2H ₂ O	62.65 : 5.69 : 1.09	64.6 : 6.37 : 1.44	17.78/15.25
P(DEAMSt38%-co-St)L''	(C ₂₁ H ₂₇ O ₂ N)	79.16 : 8.22 : 3.12	77.39 : 7.87 : 3.59	-----
P(DEAMSt38%-co-St)L'' -Ni	(C ₂₁ H ₂₅ O ₂ N) ₂ -Ni-2H ₂ O	55.82 : 5.73 : 2.50	56.86 : 5.99 : 2.45	13.79/11.74
P(DEAMSt38%-co-St)L'' -Co	[(C ₂₁ H ₂₅ O ₂ N) ₂ -Co-2H ₂ O]-4H ₂ O	51.44 : 5.28 : 2.30	49.89 : 5.28 : 1.90	12.76/12.85

FIGURE 4: ¹H-NMR spectrums of (a) P(DEAMSt13%-co-St)L'' and (b) P(DEAMSt38%-co-St)L'' copolymers as used ligands.

The ¹H-NMR spectra of P(DEAMSt13%-co-St)L'' and P(DEAMSt38%-co-St)L'' ligands are given in (Figure 4). The ¹H-NMR spectra show the characteristic signals at 6.3–7.6 ppm for aromatic ring protons, at 3.9 ppm phenyl CH₂-N protons signals, at 3.7 ppm CH₂-O protons signals, at 2.7 ppm -N-CH₂ protons signal, and at 1.2–2.3 ppm (-CH and -CH₂) protons signal in the polymer chain. These results indicate that the ligand occurred. The metal complexes were insoluble in any organic solvent. Therefore, ¹H-NMR spectra could be not recorded [12, 20].

3.2. Composition of Copolymers. The copolymers yielded combinations determined from the ¹H-NMR spectrums. To take into account integral heights of the aromatic ring protons (6.3–7.6 ppm) and N-CH₂ protons at 2.7 ppm, calculated

composition of % DEAMSt and % St for the first copolymer was found as 13% DEAMSt and 87% St and for the second copolymer was found as 38% DEAMSt and 62% St.

3.3. Elemental Analysis Results SEM Images of the P(DEAMSt-co-St)L'' and Metal Complexes. The empirical formula were determined from elemental analysis results (by using values of C, H, and N%) and SEM-EDX (for estimation of metal%). The results are summarized in Table 2. In addition, a certain amount of polymer-metal complex samples was taken and burned in the ash furnace at 400°C. The ash-formed samples were dissolved in HNO₃ to complete the specific volume. Ni and Co values were determined against the standards in the AAS of the samples. According to the results obtained, the metal values in the complex supported the SEM-EDX and elemental analysis results.

The results found via both methods are compatible with each other. Only some of them showed a difference of about two units, which is consistent with the literature [22]. The SEM images of the ligands and metal complexes are given in Figures 5-6. SEM images of the ligands and metal complexes show the morphological differences on the surface. The morphological differences of the surface of polystyrene chlorine ended (PS-Cl), polystyrene diethanolamine ended (PS-DEA), and polystyrene with diethanolamine ended for the every side of chain (PS(DEA)₂) resins [5] have been recorded in the literature.

Comparing with each of these three appearances, the amount of pores on the surface of PS-DEA and PS-(DEA)₂ resins was increased due to the introduction of the -N(CH₂CH₂OH) groups. It is implied that the macroporous structure of P(DEAMSt13%-co-St)L'' and P(DEAMSt38%-co-St)L'' ligands was not damaged and was quite smooth.

After the reaction of Co(II) and Ni(II) metal ions with P(DEAMSt-co-St)L'' ligands increased the number of pores were collapsed and wrapped and a damaged structure was formed. These pieces of information demonstrate that the polymer matrix is bonded with Co(II) and Ni(II) metal ions [23, 25].

3.4. Thermal Characterization. The curves determined by differential scanning calorimetry (DSC) for P(DEAMSt13%-co-St)L'' and P(DEAMSt38%-co-St)L'' used as ligand are shown in (Figure 7). The glass transition temperature (*T_g*) of ligands (L'') was found from DSC curves. Both ligands showed a single transition. The glass transition temperature

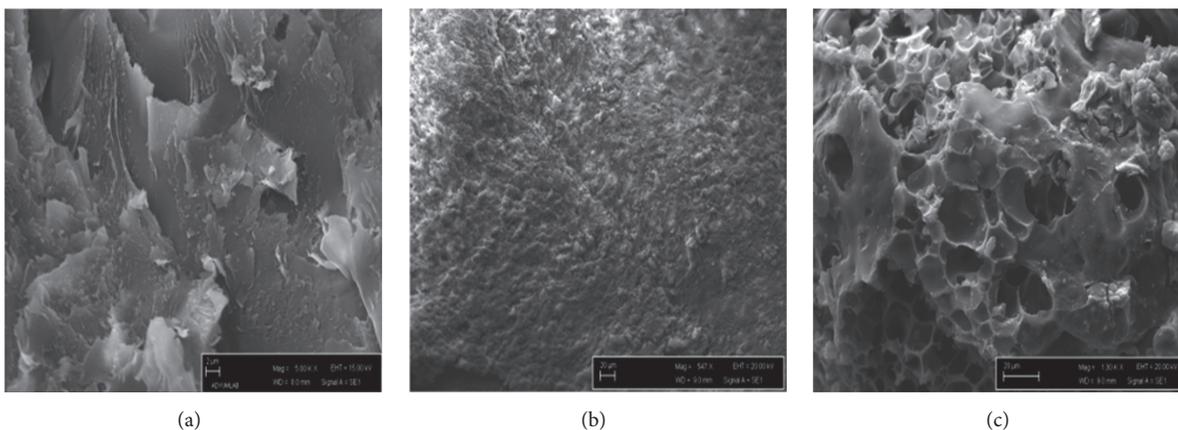


FIGURE 5: The SEM images of (a) P(DEAMSt13%-co-St)L'', (b) P(DEAMSt13%-co-St)L''-Ni, and (c) P(DEAMSt13%-co-St)L''-Co.

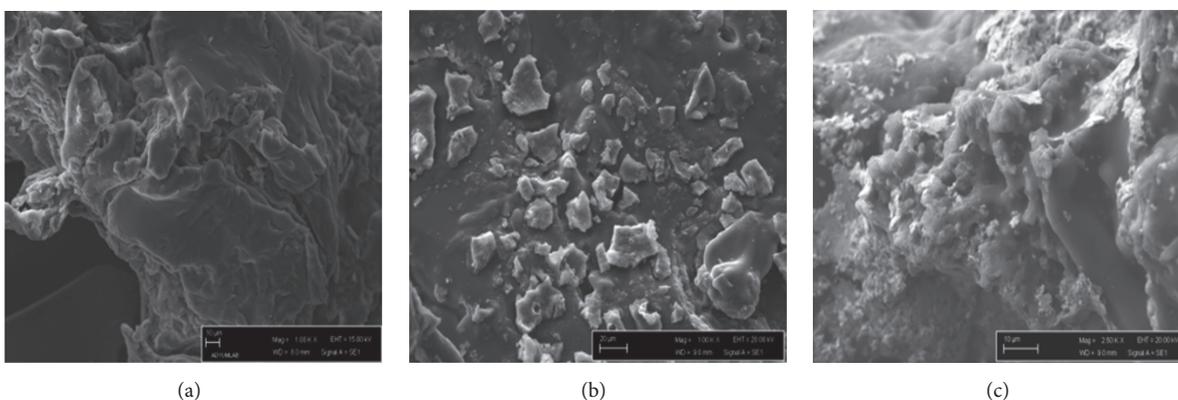


FIGURE 6: The SEM images of (a) P(DEAMSt38%-co-St)L'', (b) P(DEAMSt38%-co-St)L''-Ni, and (c) P(DEAMSt38%-co-St)L''-Co.

(T_g) for P(DEAMSt13%-co-St)L'' and P(DEAMSt38%-co-St)L'' was measured as 98 and 86°C respectively. The glass transition temperature (T_g) of the different combination copolymers was decreased with the increased amount (%) of the (DEAMSt) units in the ligand structure. In our previous study, the glass transition temperature (T_g) of P(DEAMSt)L' was found as 82°C [16]. It was found that the increased amount of DEAMSt in the copolymer composition was close to the glass transition temperature of P(DEAMSt)L'. The glass transition temperature (T_g) value of P(DEAMSt13%-co-St)L'' was higher than that of P(DEAMSt38%-co-St)L''. Decrease in the T_g values of copolymer systems depending on increasing DEAMSt units is probably due to increase in free volume and the chain flexibility.

The similar behavior has been shown in the literature [26–28]. The DSC curves of their metal complexes were recorded but no explanatory information was available. For this purpose, the melting point of polymer-metal complexes was measured, but the complexes did not show a definite melting point only decomposed to about 280°C.

A comparative work of the thermal behaviours of both copolymers and their metal complexes was carried out under N₂ flow using a heating rate of 10°C/min between

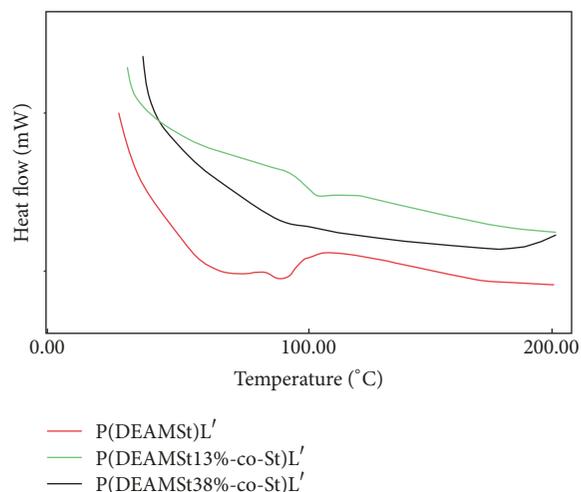


FIGURE 7: DSC curves of P(DEAMSt)L', P(DEAMSt13%-co-St)L'', and P(DEAMSt38%-co-St)L''.

room temperature and 700°C by thermogravimetric analyses (TGA). The TGA curves of ligands and metal complexes made by Co(II) metal ions showed a decomposition with two

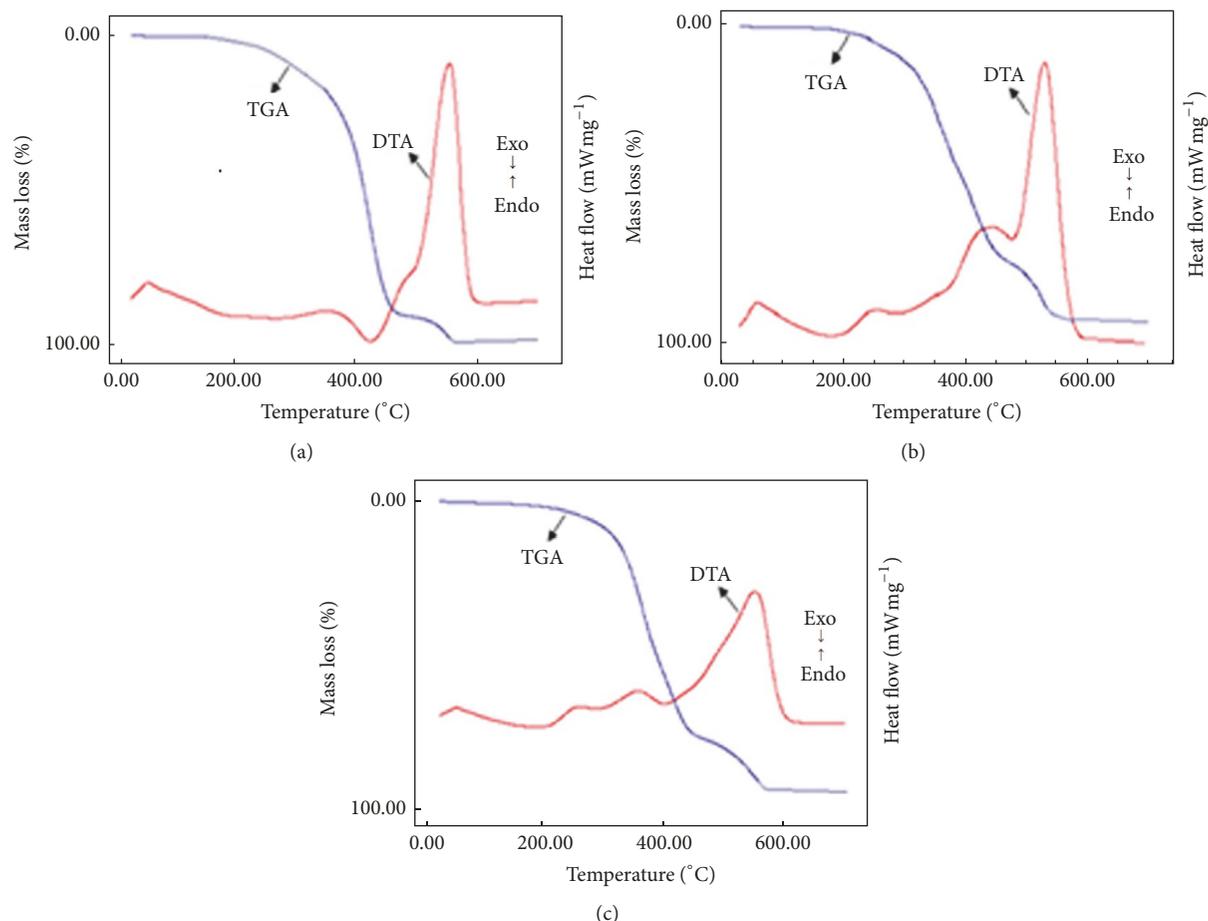


FIGURE 8: The TGA and DTA thermograms of (a) P(DEAMSt13%-co-St)L'', (b) P(DEAMSt13%-co-St)L''-Co, and (c) P(DEAMSt13%-co-St)L''-Ni.

stages and metal complexes made by Ni(II) decomposed at three stages (Figures 8-9).

According to their thermograms, the first stage was faster than the second stage. This may be resulted from the fact that the noncoordinating part of the polymers decomposed first and later coordinating part of the polymers decomposed. The weight loss observed on the TGA curves of metal complexes below 200°C is due to physisorbed water. As the molecular weight of the polymer supported complexes is very large, only some structures such as very small percentage of coordinated water and acetate are suggested that is about 3% in the complexes [29].

The weight loss between 100 and 200°C may impute the elimination of adsorbed moisture over dehydration [25]. Both ligands show decomposition with two stages. The initial and final decomposition temperatures of P(DEAMSt13%-co-St)L'' and P(DEAMSt38%-co-St)L'' ligands were observed between 300–580°C and 272–622°C, respectively. In the first stage, a maximum weight loss of 61.24% was observed between 300 and 426°C for P(DEAMSt13%-co-St)L'' ligand and a maximum weight loss of 60.61% was observed between 272 and 430°C for P(DEAMSt38%-co-St)L''. In the second stage, a maximum weight loss of 29.44% was observed

between 436 and 580°C for P(DEAMSt13%-co-St)L'' ligand and a maximum weight loss of 31.42% was observed between 446 and 622°C for P(DEAMSt38%-co-St)L''. Both ligands lost 91.92% of their original weight and the ligands left 9.8% reside at 600°C, respectively.

The TGA curve of P(DEAMSt13%-co-St)L''-Co complex also shows a decomposition with two stages. P(DEAMSt13%-co-St)L''-Co complex starts to decompose at 248°C. The complex is stable up to 248°C. The initial and final decomposition temperatures of P(DEAMSt13%-co-St)L''-Co complex were observed between 248 and 585°C and it shows a decomposition with two stages. In the first stage, a maximum weight loss of 45.34% was observed between 248 and 370°C for P(DEAMSt13%-co-St)L''-Co complex. In the second stage, a maximum weight loss of 25.33 was observed between 407 and 585°C for P(DEAMSt13%-co-St)L''-Co complex. The P(DEAMSt13%-co-St)L''-Co complex lost 70.67% of its original weight and left 29% reside at 600°C.

The TGA curve of P(DEAMSt13%-co-St)L''-Ni complex shows a decomposition with three stages. P(DEAMSt13%-co-St)L''-Ni complex starts to decompose at 256°C. The complex is stable up to 256°C. The initial and final decomposition temperatures of P(DEAMSt13%-co-St)L''-Ni complex were

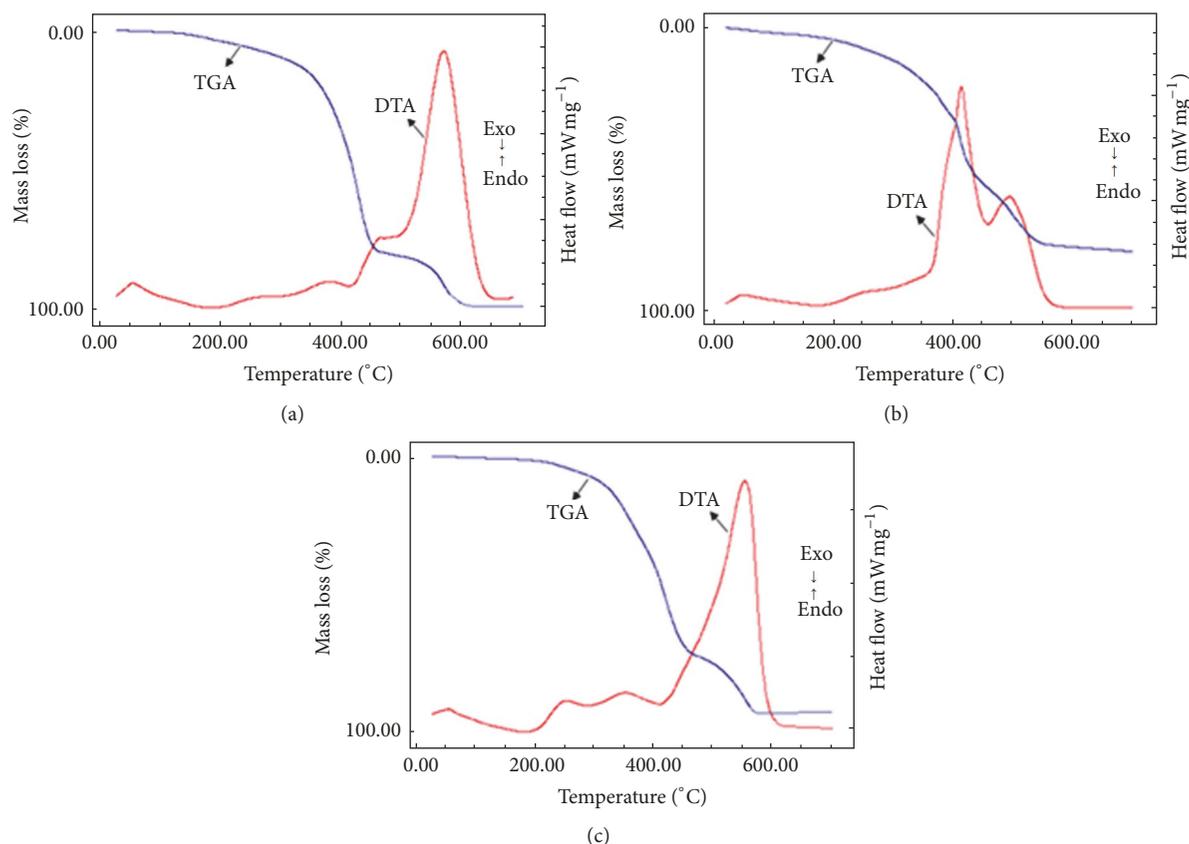


FIGURE 9: The TGA and DTA thermograms of (a) $P(\text{DEAMSt}38\%-\text{co-St})L''$, (b) $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Co}$, and (c) $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Ni}$.

observed between 256 and 590°C and it shows a three-stage decomposition. In the first stage, a maximum weight loss of 44.83% between 256 and 376°C, in the second stage a maximum weight loss of 23.73% between 408 and 427°C, and, in the third stage, a maximum weight loss of 20.81% between 518 and 590°C were observed for $P(\text{DEAMSt}13\%-\text{co-St})L''\text{-Ni}$ complex. The $P(\text{DEAMSt}13\%-\text{co-St})L''\text{-Ni}$ complex lost 89.37% of its original weight and left 11% residue at 600°C.

In DTA thermograms of $P(\text{DEAMSt}13\%-\text{co-St})L''$ ligand and polymer-metal complexes (Figure 8), for $P(\text{DEAMSt}13\%-\text{co-St})L''$ ligand, the first endothermic region was observed between 385 and 472°C and the second maximum exothermic region between 512 and 580°C. For the $P(\text{DEAMSt}13\%-\text{co-St})L''\text{-Co}$ complex, the first exothermic region was observed between 214 and 282°C, the second exothermic region between 381 and 475°C, and the third maximum exothermic region between 492 and 569°C. For the $P(\text{DEAMSt}13\%-\text{co-St})L''\text{-Ni}$ complex, the first exothermic region was observed between 216 and 285°C, the second exothermic region between 313 and 391°C, and the third maximum exothermic region between 474 and 591°C [30]. On the DTA thermograms of both $L''\text{-Ni}$ and $L''\text{-Co}$ metal complexes, the first exothermic region between 216 and 282°C was resulted from the water inside and outside of the coordination sphere.

On the other hand, the TGA curve of $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Co}$ complex also shows a decomposition with

two stages (Figure 9). $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Co}$ complex start to decompose at 200°C. The complex is stable up to 200°C. The initial and final decomposition temperatures of $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Co}$ complex were observed between 200 and 585°C and it shows a two-stage decomposition. In the first stage, a maximum weight loss of 45.57% was observed between 200 and 420°C and in the second stage a maximum weight loss of 15.86% between 422 and 585°C for $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Co}$ complex. The $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Co}$ complex lost 61.53% of its original weight and left 38% residue at 600°C.

The TGA curve of $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Ni}$ complex shows a decomposition with three stages. $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Ni}$ complex starts to decompose at 230°C. The complex is stable up to 230°C. The initial and final decomposition temperatures of $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Ni}$ complex were observed between 230 and 580°C and it shows a decomposition with three stages. In the first stage a maximum weight loss of 35.72% between 230 and 401°C, in the second stage a maximum weight loss of 11.93% between 410 and 446°C, and in the third stage a maximum weight loss of 22.32% between 450 and 580°C were observed for $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Ni}$ complex. The $P(\text{DEAMSt}38\%-\text{co-St})L''\text{-Ni}$ complex lost 69.99% of its original weight and left 30% residue at 600°C.

On the DTA thermograms of $P(\text{DEAMSt}38\%-\text{co-St})L''$ ligand and polymer-metal complexes (Figure 9),

for P(DEAMSt38%-co-St)L'' ligand, the first endothermic region was observed between 386 and 450°C and the second maximum exothermic region between 525 and 629°C. For the P(DEAMSt38%-co-St)L''-Co complex, the first exothermic region was observed between 200 and 250°C, the second exothermic region between 369 and 441°C, and the third maximum exothermic region between 465 and 553°C. For the P(DEAMSt38%-co-St)L''-Ni complex, the first exothermic region was observed between 219 and 279°C, the second exothermic region between 313 and 398°C, and the third maximum exothermic region between 490 and 587°C [30]. On the DTA thermograms of both L''-Ni and L''-Co metal complexes, the first exothermic region between 216 and 280°C showed elimination of the water inside and outside of the coordination sphere. This region was observed for both polymer-metal complexes.

According to the obtained results, it was found that the thermal stability of both ligands was better than that of the polymer-metal complexes, because the temperatures at which the ligands begin to decompose are higher than that of the temperatures at which the metal complexes begin to decompose. This is a result of interaction between the molecules due to the -OH in the molecular structure of the ligand. Another reason is the presence of water inside and outside the coordination sphere [19, 20]. At the same time, it is due to weight loss. When comparing the thermal stability of the metal complexes, it was seen that the thermal stability of Ni(II) metal complex was better than thermal stability of Co(II) metal complex. That is, the thermal stability was changed with the participated of metal ions into the coordination. The thermal stability of the prepared ligands and metal complexes was quite high. The literature records show that the weight loss is not formed at advanced temperatures as a result of the formation of metal oxides to 600°C [20]. In our work, the residue of metal complexes became stable at 600°C. Metal complexes with Co(II) of both ligands demonstrated the most residue (%). The DTA curve demonstrates maximum peak between 460 and 620°C for both polymer-metal complexes and ligands which are stable [31].

3.5. Dielectrical Properties. The dielectrics are materials having mobile charge which have either negative or positive charges. The dominant charge in their atoms and molecules is propped by atomic or molecular forces. If a material has an energy storage property, it is defined as dielectrical when it is applied with an electrical field. They are like insulators, so they do not conduct electricity, but they are influenced by electric field. The electrons and atoms are replaced with each other by the influence of electric field. As a result of this, their load center of electricity dislocates and electrical polarization occurs. Dipoles which occur after this event provide electric charge unit on the surface of the material [32].

The relative properties such as ϵ' (dielectric constant), ϵ'' (dielectric loss factor), σ (conductivity), and ω (angular frequency) determine the nature of the polymeric material, and also while σ is dominant in terms of conductive polymers ϵ' , ω is dominant in case of dielectrics.

Dielectric constant (ϵ') of ligands and metal complexes is calculated with the following [33]:

$$\epsilon' = C \frac{d}{\epsilon_0 A}, \quad (1)$$

where C is capacitance of the film; d is thickness of the film; A is effective area of the film; ϵ_0 is permittivity of free space ($\epsilon_0 = 8.854 \times 10^{-12}$ F/m) [34]. The dielectric loss factor is found by the formula, (ϵ'') = DF · ϵ'

The dielectrical measurements of the P(DEAMSt13%-co-St)L'', P(DEAMSt38%-co-St)L'', and their metal complexes were determined by using the LCR Meter Impedance Analyzer device. For this purpose, polymer (0.1 g) was pressed under the pressure at four tons and transformed to disk. Its thickness was measured and the disk surfaces were covered with silver paste. The measurements were carried out in the frequencies range (100 Hz–2 kHz) and at different temperatures (298 to 423 K). The dielectrical and conductivity properties of ligands and metal complexes were measured depending on frequency and temperature.

Figure 10 shows the frequency depending on dielectric constant (ϵ') and dielectric loss factor (ϵ'') of P(DEAMSt13%-co-St)L'' ligand and metal complexes. Figure 11 shows the frequency depending on dielectric constant (ϵ') and dielectric loss factor (ϵ'') of P(DEAMSt38%-co-St)L'' ligand and metal complexes. As seen in Figures 10-11 the dielectric constant (ϵ') and dielectric loss factor (ϵ'') were decreased with increasing frequency and reached a constant value at higher frequencies. The initial value of dielectric constant for polar materials is high, but as the frequency of the field is raised the value begins to fall which could be due to the dipoles not able to track the field variations at high frequencies [34, 35]. This is due to the effect of electrode polarization [36]. At high frequencies, the periodic reversal of the electric field occurs very fast so that there is no excessive ion diffusion in the direction of the field. The polarization because of the charge accumulation decreases, which leads to a reduction in the value of dielectric constant [37, 38]. Also, similar behavior is valid in the dielectrical loss factor.

Figure 12 shows the temperature depending on dielectric constant (ϵ') of P(DEAMSt13%-co-St)L'' ligand and metal complexes, P(DEAMSt38%-co-St)L'' ligand, and metal complexes. Generally, the rise of dielectric constant (ϵ') with temperature is related to decline in bond energies [39]. Increased temperature shows two types of effects on the dipolar polarization. It rises the positional vibration and gets weaker intermolecular forces. And also it rises the thermal tension and so violently disrupts the positional vibration [40]. Figure 12 shows that the dielectric constant (ϵ') increases with increasing temperature and at high temperatures increases more quickly. When the temperature rises, ionic and electronic polarizability sources start to rise or the dipoles comparatively occur free and they respond to the applied electric field. In this context, the polarization increases and also (ϵ') increases with temperature [41, 42]. In the literature, variation of the electric constant with temperature is different for polar and nonpolar polymers. Usually, for polar polymers the dielectric constant increases as temperature increases; but

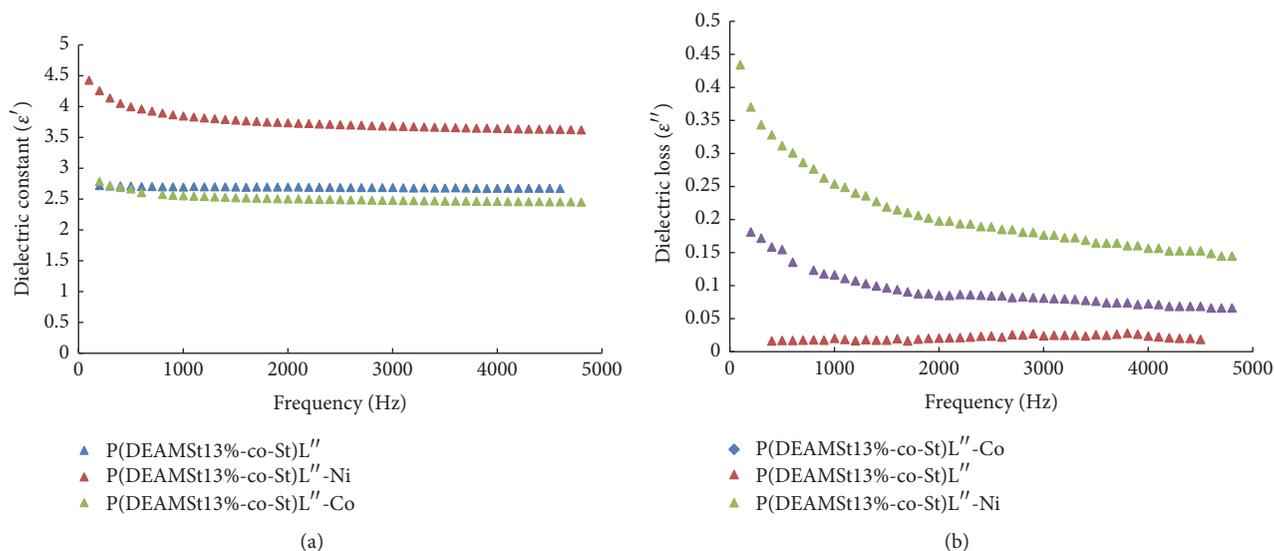


FIGURE 10: (a) The dielectric constant change. (b) The dielectric loses factor change of P(DEAMSt13%-co-St)L'' ligand and metal complexes with frequency (M: Ni, Co).

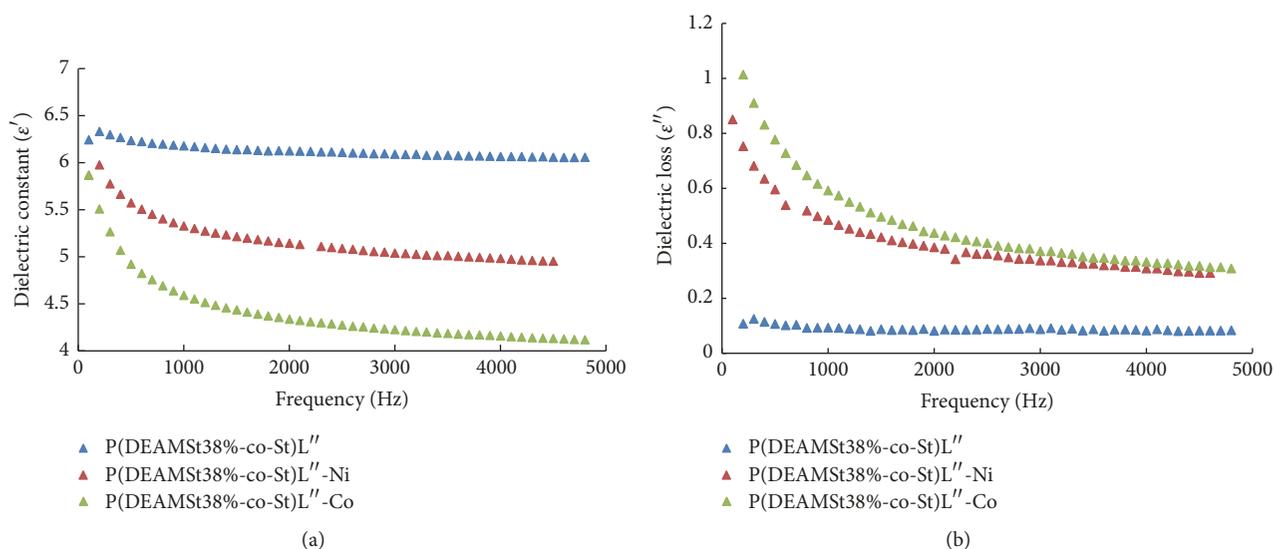


FIGURE 11: (a) The dielectric constant change. (b) The dielectric loses factor change of P(DEAMSt38%-co-St)L'' ligand and metal complexes with frequency (M: Ni, Co).

for nonpolar polymers the electric constant is independent from temperature [34]. In our study, the dielectric constant of both ligands and their metal complexes increased as temperature increased and decreased as frequency increased.

Additionally, the dielectric constant (ϵ'), the dielectric loss factor (ϵ''), and the conductivity (σ) values were calculated at 1 kHz and at the room temperature. Data on the dielectrical properties are given in Table 3.

In our previous study, the dielectric constant and dielectric loss factor values of P(DEAMSt)L' were found at room temperature and at 1 kHz [16]. As seen in Table 3 polarity is high due to the -OH groups present in the structure of P(DEAMSt)L' ligand, which leads to an increase in the dielectric constant ($\epsilon' = 13.58$). It was found that the

copolymers of this ligand with the styrene in two different compositions varied depending on the percent composition of the DEAMSt. The dielectric constant values were found for P(DEAMSt13%-co-St)L'' ligand ($\epsilon' = 2.69$) and for P(DEAMSt38%-co-St)L'' ligand ($\epsilon' = 6.18$). The dielectric constant of the ligand containing 38% DEAMSt was found to be higher than the dielectric constant of the ligand containing 13% DEAMSt. The value of the dielectric constant increased as the amount of DEAMSt in the structure of the copolymer increased and the P(DEAMSt)L' was seen closer to the dielectric constant value. In the copolymer containing 13% DEAMSt, the amount of styrene was too much so that the styrene reduced the polarity of the -OH groups by entering into the structure of the copolymer. These values were even

TABLE 3: P(DEAMSt)L', P(DEAMSt-co-St)L'', and P(DEAMSt-co-St)L''-M (M: Ni, Co) the dielectric constant (ϵ'), the dielectric loss factor (ϵ''), and the conductivity (σ) values at 1 kHz and at the room temperature and activation energy (E_a) values.

Polymer	Dielectric constant (ϵ')	Dielectric loss factor (ϵ'')	Conductivity (S/cm) (σ)	E_a/eV
P(DEAMSt)L'	13.58	10.21	$5,12 \times 10^{-7}$	0.62
P(DEAMSt13%-co-St)L''	2.69	0.020	1.16×10^{-6}	0.41
P(DEAMSt13%-co-St)L''-Ni	3.85	0.258	1.27×10^{-4}	0.10
P(DEAMSt13%-co-St)L''-Co	2.55	0.12	5.56×10^{-6}	0.16
P(DEAMSt38%-co-St)L''	6.18	0.093	4.71×10^{-6}	0.50
P(DEAMSt38%-co-St)L''-Ni	5.33	0.49	2.75×10^{-8}	0.11
P(DEAMSt38%-co-St)L''-Co	4.59	0.59	2.65×10^{-8}	0.26

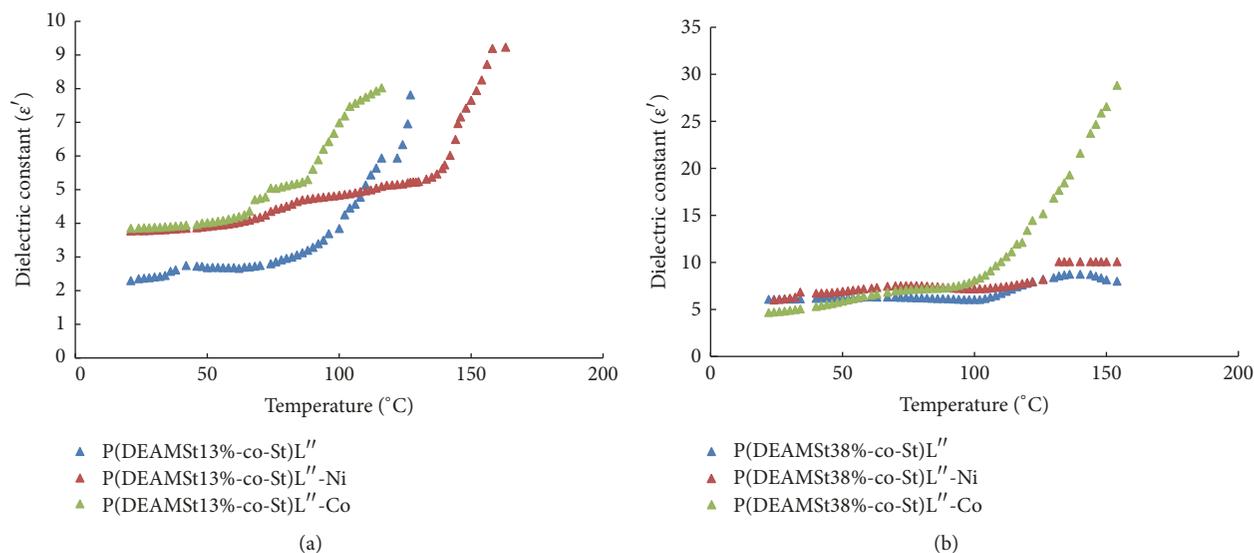


FIGURE 12: The dielectric constant change of (a) P(DEAMSt13%-co-St)L'' and (b) P(DEAMSt38%-co-St)L'' ligand and metal complexes with temperature. (M: Ni, Co).

lower when metal complexes of both ligands were compared. The dielectric constant of Ni(II) complex was found to be higher than dielectric constant of Co(II) complex. The value of the dielectric constant in the metal complex with the Ni(II) metal ion of the copolymer containing only 13% DEAMSt was found higher than dielectric constant of P(DEAMSt13%-co-St)L'' ligand. In this case, the participation of metal ions into the polymer matrix reduced the polarity of the -OH groups and thus increased their tendency to form complexes. As a result, both ligands tended to be more complex with the Ni(II) metal ion.

In the same way, when conductivity values were compared [16], the conductivity of P(DEAMSt)L' was lower than the conductivities of copolymers containing 13% DEAMSt and 38% DEAMSt. When the two copolymers are compared, the conductivity of the copolymer containing 38% DEAMSt was higher than the conductivity of the copolymer containing 13% DEAMSt. Conductivity decreased as the styrene units increased in the copolymers made with the styrene. The participation of styrene units in the structure of the polymer reduced the polarity of the -OH groups. When the conductivities of both ligands and their metal complexes are

compared, the conductivity of the metal complexes of both ligands with Ni(II) metal ion was seen that was higher than that of the conductivity of Co(II) metal complex. The value of the conductivity for the metal complex with the Ni(II) metal ion of the copolymer containing only 13% DEAMSt was found higher than conductivity of P(DEAMSt13%-co-St)L'' ligand. Similar behavior was also observed for the dielectric constant and dielectric loss factor values at room temperature for 1 kHz.

The conductivity measurements of both ligands and their metal complexes were determined as a function of frequency and temperature. The " σ_p " value of the conductance parameters was calculated using the following:

$$\sigma_p = G \cdot \frac{d}{A}, \quad (2)$$

where G is the conductance, d is thickness of the film, and A is the sample space.

The conductivity values of both ligands and their metal complexes are shown in Figures 13-14 depending on frequency and temperature. The conductivity of both ligands

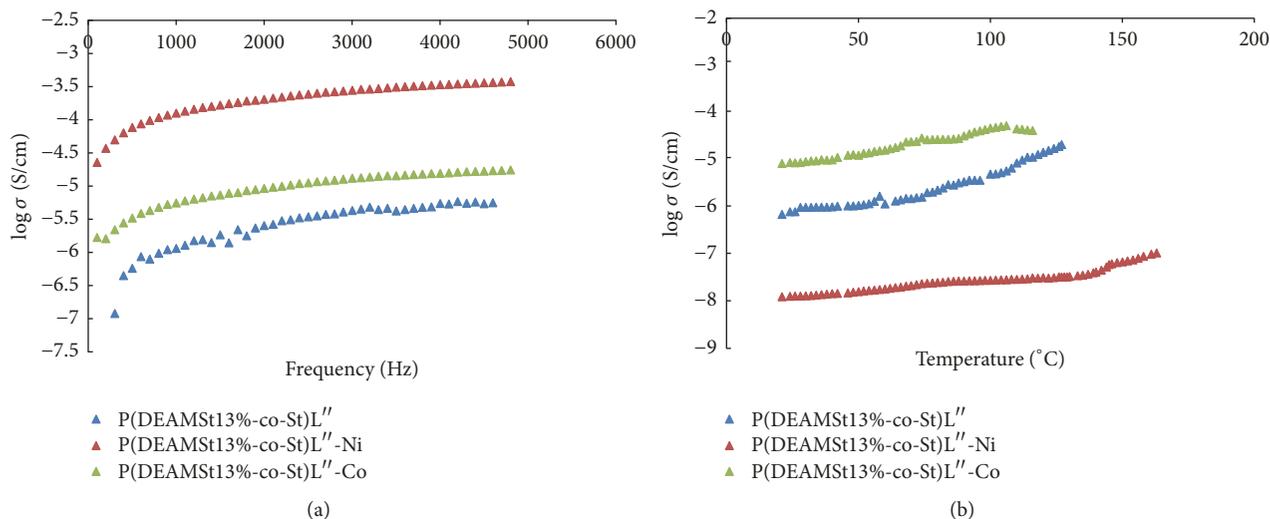


FIGURE 13: The conductivity change of P(DEAMSt13%-co-St) L'' ligand and metal complexes with (a) frequency and (b) temperature (M: Ni, Co).

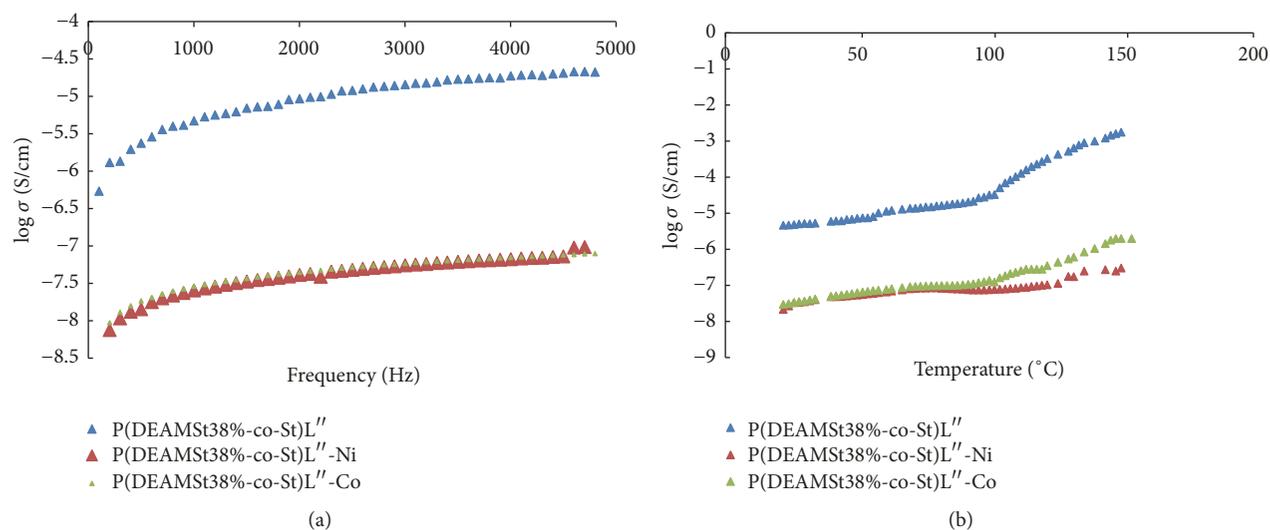


FIGURE 14: The conductivity change of P(DEAMSt38%-co-St) L'' ligand and metal complexes with (a) frequency and (b) temperature (M: Ni, Co).

and metal complexes increased proportionally with frequency and temperature [43]. Generally, conductivity is the free moving property of electrons. According to this, electrons move at a certain level energy. Usually, the electrical conductivity of the polymer relies on the presence of free ions chemically connected with macromolecule. The molecular chain does not participate in the transfer of electrical charge [38, 44]. At higher frequencies, an electron in the molecular orbital is stimulated to a higher energy level, in which the energy is spin connected and the electrons in the excited state either lead to a neighboring molecule or return to the base. But electrons prefer to be at the fundamental energy level, in which the conductivity increases with increasing frequency [45].

When the temperature increases, number of the load carriers increases, which increases polarity of the polymer and, in this case, the conductivity reaches a maximum value [46]. Consequently, the load carriers gain a basic activity with sufficient activation energy [42] which also increases the mobility and free volume of the polymer. Depending on the polarization, conductivity increases with increasing temperature [41]. In general, the hydrogen bonded polymers have higher conductivity. In particular, the conductivity values of the ligand containing 38% DEAMSt, as seen in Figure 14, were higher than that of the metal complexes. This is explained by the increase of the amount of DEAMSt moieties in the copolymer composition, in which the polarization of the ligand is higher. The conductivity decreased

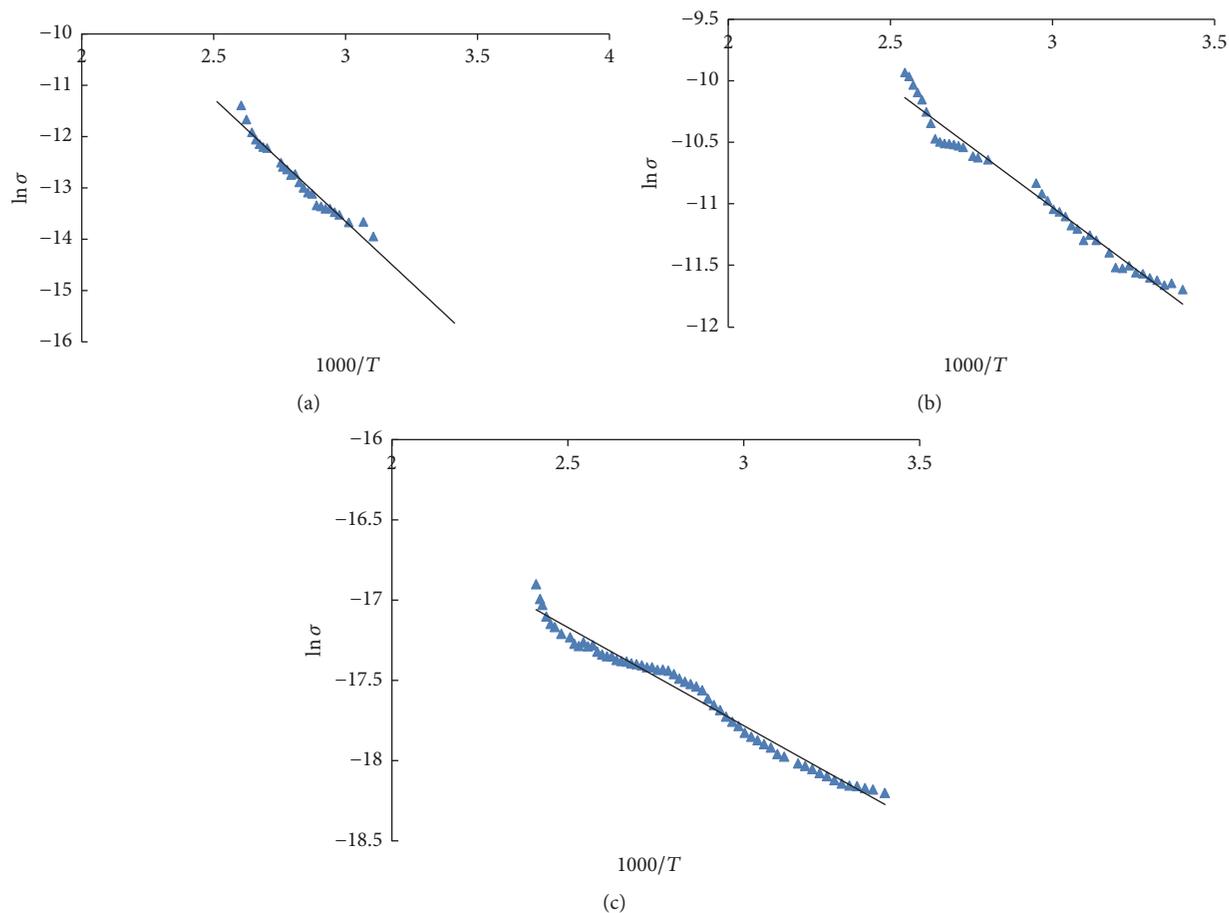


FIGURE 15: Temperature dependence of ionic conductivity for (a) P(DEAMSt13%-co-St) L'' ligand, (b) P(DEAMSt13%-co-St) L'' -Co, and (c) P(DEAMSt13%-co-St) L'' -Ni.

as amount of metal binding in complex structure increases. In similar studies, conductivity values are very low at room temperatures, but when the temperature rises above 100°C, the molecule also loses water and conductivity of the metal complexes increases in which the metal complexes behave as semiconductors [25, 47]. The conductivity values of the ligand containing 13% DEAMSt, as seen in Figure 13, were lower. The effect of the -OH groups in the structure is reduced since the amount of the styrene units in the copolymer composition is too much.

The activation energies of both ligands and their metal complexes were calculated by the Arrhenius equation:

$$\sigma = \sigma_o \cdot e^{-Ea/kT}, \quad (3)$$

where σ is conductivity (S/cm), σ_o is a constant that is proportional to the number of carrier ions, Ea is activation energy, k is the Boltzmann constant, and T is absolute temperature (K).

The activation energy (Ea) of electrical conduction was calculated from the slope of the plot depending on $\ln \sigma$ versus $1000/T$ (Figures 15-16). The activation energies of both ligands and their metal complexes calculated from the slopes of the lines were obtained from the graphs in Figures 15-16. The activation energy (Ea) is the barrier energy required

for the transport of ions and the activation energy of ionic conduction. When temperature increases, the energy barrier for ions transport decreases, which leads to an increase in ionic conductivity [48]. The temperature effect on electrical conductivity shows that the conductivity increases with temperature [49]. Data related to the activation energy are submitted in Table 3. The activation energies values were found for P(DEAMSt) L' ligand [16] ($Ea = 0.62$ eV), P(DEAMSt13%-co-St) L'' ligand ($Ea = 0.41$ eV), and P(DEAMSt38%-co-St) L'' ligand ($Ea = 0.50$ eV). The activation energy of the ligand containing 38% DEAMSt was found to be higher than the activation energy of the ligand containing 13% DEAMSt. The value of the activation energy increased as the amount of DEAMSt in the structure of the copolymer increased and the P(DEAMSt) L' was seen closer to the activation energy value. This is explained by the increase of the DEAMSt units in the polymer chain and the effect of polar groups. When the activation energy values available for ligands were compared with metal complexes, the activation energies in the polymer-metal complexes decreased by the participate of metals in the polymer matrix. In the metal complexes of both ligands with Ni (II) and Co (II) metal ions, lower activation energies were found in the metal complexes made with Ni (II) metal ion at high temperature. In this case, the ionic character

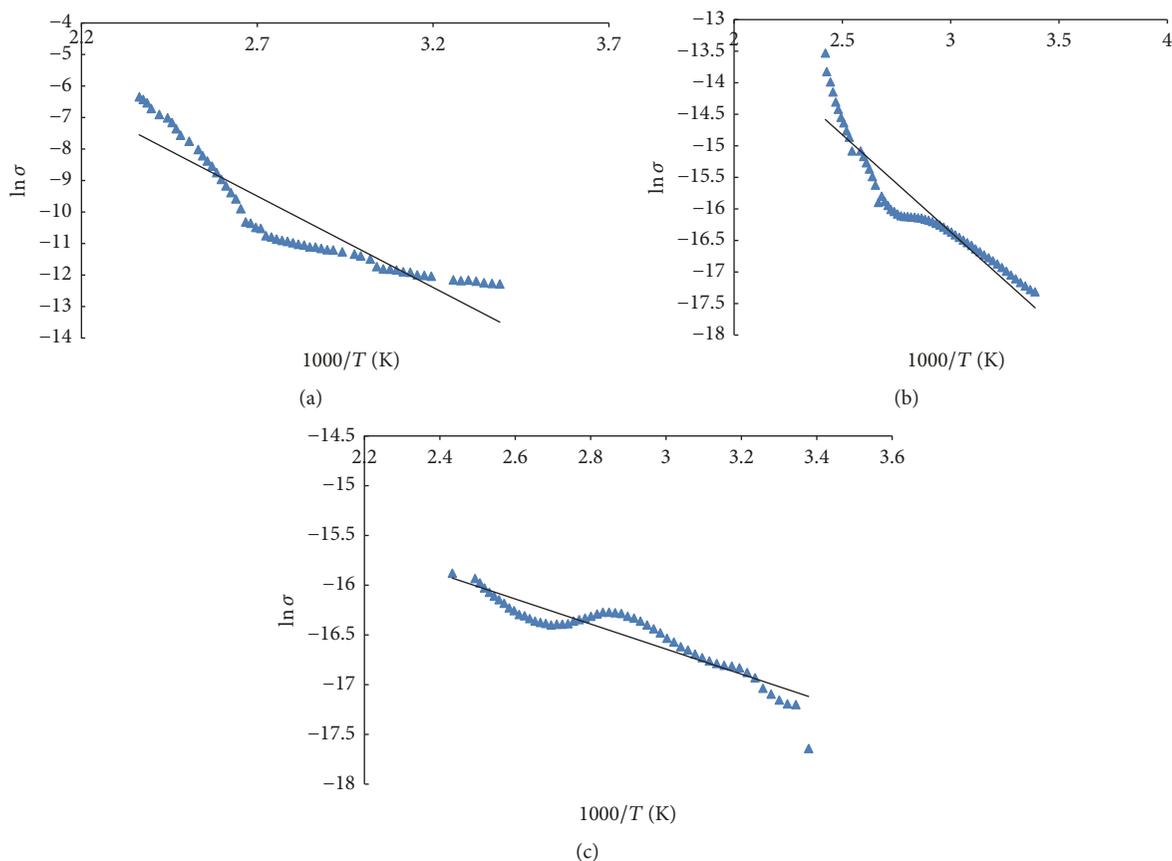


FIGURE 16: Temperature dependence of ionic conductivity for (a) P(DEAMSt38%-co-St) L'' ligand, (b) P(DEAMSt38%-co-St) L'' -Co, and (c) P(DEAMSt38%-co-St) L'' -Ni.

between the functional groups of ligands and metal ions is very high. In similar studies, when activation energies are decreased, ion transport number and conductivity increased, and the complexes at high temperature regions continue the superionic structure [47, 49].

4. Conclusion

The two copolymer systems at different combination from styrene with hydroxyl side groups and styrene monomers were prepared using free radical polymerization method. These copolymers were used as ligand. The metal complexes were prepared by reaction of copolymers used as ligand with Ni(II) and Co(II) metal ions. The characterization of the prepared ligand and metal complexes was studied by infrared (FT-IR), $^1\text{H-NMR}$, elemental analyses, SEM, TGA, DTA, and DSC, and dielectrical properties were measured as a function of frequency and temperature. The thermal stability of both ligands was better than that of the polymer-metal complexes. This is the result of the interaction between the molecules due to the $-\text{OH}$ in the molecular structure of the ligand. The dielectric constant and dielectric loss factor of both ligands increased with temperature and decreased in the applied frequency range. The dielectric constant, dielectric loss factor, and conductivity values of P(DEAMSt13%-co-St) L'' and P(DEAMSt38%-co-St) L'' ligands were found to

be much higher than those of the metal complexes. That is, the dielectric constant, dielectric loss factor, and conductivity values increased with rise of polar side groups in the polymer chain. This could provide contribution to raising the strength of the bonds with the interaction between $-\text{OH}$ groups of polymer. This is because of more hydrogen bonding due to $-\text{OH}$ group in P(DEAMSt-co-St) L'' . Again, the activation energy values of the ligands were higher than the activation energy values of the metal complexes. The reason for low activation energies of the metal complexes is that the complex formation tendencies are high and the ionic character between the metal ions and functional groups of the ligands are also high. In this case, the participation of metal ions into the polymer matrix reduced the polarity of the OH groups, and thus it increased their tendency to form complexes.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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