

# Ionic interactions and transport characteristics of a new polymer electrolyte system containing poly(propylene glycol) 4000 complexed with $\text{AgCF}_3\text{SO}_3$

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**Abstract** The effect of concentration of  $\text{AgCF}_3\text{SO}_3$  salt on the behavior of ionic transport within the polymer electrolyte system containing the polymer host poly(propylene glycol) of molecular weight 4000 (PPG4000) has been investigated in terms of spectroscopic and electrochemical properties. It is evident that the presence of well-defined interactions between the ether oxygens and silver cations arising due to the complexation of the silver salt with the polymer matrix has enabled the chosen polymer electrolyte system to possess the maximum room temperature (298 K) electrical conductivity of  $9.4 \times 10^{-5} \text{ S cm}^{-1}$  in the case of the typical composition having the ether oxygen-to-metal ratio (O:M) of 4:1 and the lowest activation energy  $E_a$  of 0.46 eV for  $\text{Ag}^+$  ionic conduction.

**Keywords** Polymer electrolyte · Poly(propylene glycol) · Silver ion · Conductivity

## 1 Introduction

Polymer electrolytes have acquired special interest in recent years owing to the feasibility of their technological applications in various electrochemical devices operating at around sub-ambient and moderate temperatures [1–3]. For instance, electrochemical sensors having an electrode component based on polymer electrolytes would enable detection of substances in poorly conductive liquids as well as in gases in view of their interesting features. Some of the

most promising polymeric hosts for such application areas include poly(dimethyldiallylammonium chloride) [4], plasticized poly(vinyl chloride) containing tetrabutylammonium hexafluorophosphate and a poly(ethylene oxide) complex with silver trifluoromethane sulfonate [5]. Interestingly, several attempts at replacing hydrophilic Nafion by a hydrophobic polymer electrolyte were also reported in the past [6].

Ion-conducting polymer systems, formed by the dissociation of salts in suitable ion-coordinating polymers are generally known to offer many promising features [7–9]. Whereas an understanding of the macroscopic properties associated with an efficient lithium ionic transport in polymer electrolytes has well-advanced and specific demands on salt and host structures that give rise to appreciably high ionic conductivity values are rather well established, silver trifluoromethane sulfonate ( $\text{AgCF}_3\text{SO}_3$ )-based systems appear to offer certain specific advantages in terms of ionic conductivity and electrochemical stability [10, 11]. The most significant aspect, in this context, may be the fact that the above silver salt undergoes little ion association due to the charge delocalization. It is also important to note that the silver ionic transference number is generally higher than that of other reported cations thus leading to an appreciably low concentration polarization too [12].

In this study, an experimental attempt to examine the effect of silver salt concentration on the spectroscopic and electrochemical characteristics of a poly(propylene glycol) (PPG)-based polymer electrolyte system for electrochemical gas sensors has been made. Earlier reports on the polymer host namely, PPG of molecular weight 4000 revealed its importance as a model system for high molecular weight solid polymer electrolytes [13–19]. Our previous work dealt with the detailed concentration

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dependence of ionic interactions in PPG–AgCF<sub>3</sub>SO<sub>3</sub> complexes and enabled us to demonstrate the behavior of symmetric  $\nu_s$  (SO<sub>3</sub>) stretching and C–O–C stretching vibrations [20].

## 2 Experimental

### 2.1 Preparation of polymer electrolyte samples

Specimens of silver polymer electrolytes were prepared by complexing appropriate quantities of PPG (4000) (Polysciences Inc., USA) with varying concentrations of the silver salt, AgCF<sub>3</sub>SO<sub>3</sub> (Purity 99%, Aldrich) in order to obtain five different compositions having ether oxygen-to-cation ratios (O:M) of 2:1, 3:1, 4:1, 5:1, and 6:1, respectively. Prior to the complex formation, AgCF<sub>3</sub>SO<sub>3</sub> was dried in a vacuum oven at 393 K for 1 h, whereas the host polymer was dried at 353 K for 1 h. Subsequently, the salt was added directly without any solvent into the PPG polymer liquid at 343–353 K followed by constant stirring for a duration of 1 h. The polymer–salt complexes corresponding to two specific O:M ratios of 2:1 and 3:1 were also prepared by the same method, however, by using acetonitrile as the solvent in order to dissolve the relatively large amounts of the salt. The solvent was evaporated completely from the specimens by the process of vacuum drying at 333 K for 24 h. The polymer electrolyte samples thus synthesized were all transparent and of high optical quality. Such samples were stored in a dry desiccator for further analyses during the course of this study.

### 2.2 Fourier transform infrared studies

The Fourier transform infrared (FT-IR) spectra were recorded for all the synthesized specimens of PPG–AgCF<sub>3</sub>SO<sub>3</sub> complexes at room temperature using a Perkin–Elmer RX1 spectrophotometer. The samples were sandwiched between a pair of KBr plates for the purpose of recording the FT-IR spectra with a wave number resolution of 2 cm<sup>-1</sup> over the wave number range 4000–400 cm<sup>-1</sup>.

### 2.3 Differential scanning calorimetric studies

The glass transition temperature ( $T_g$ ) data for pure PPG and a PPG–AgCF<sub>3</sub>SO<sub>3</sub> complex having an O:M ratio of 4:1 were obtained by employing differential scanning calorimetric (DSC) analysis. The DSC curves were recorded over the temperature domain 163–523 K using a NET-ZSCH DSC 204 instrument at a heating rate of 10 K min<sup>-1</sup> under dry nitrogen atmosphere.

### 2.4 Transport number measurements

The transport number data for silver cation ( $t_{Ag^+}$ ) in all the PPG–AgCF<sub>3</sub>SO<sub>3</sub> polymer electrolyte samples were determined by employing the combination of dc polarization and ac impedance techniques as proposed by Bruce and Vincent [21]. The measurements were carried out with the aid of a pair of symmetrical and reversible silver electrodes by mounting the specimens between the pair of electrodes. Experimentally, the time dependence of the dc current was measured by means of a Keithley model 6517A Electrometer at room temperature employing an applied dc voltage of 50 mV. The values of resistance of the specimen before and after polarization were evaluated by means of complex impedance data collected using a computer-controlled Hewlett-Packard Model HP 4284A Precision LCR Meter in the frequency range 1 MHz–20 Hz.

### 2.5 Electrical conductivity studies

The values of bulk electrical resistance ( $R_b$ ) of all the synthesized samples were estimated from the complex impedance data collected in the temperature range 298–363 K using a computer-controlled Hewlett-Packard Model HP 4284A Precision LCR Meter over the frequency range 1 MHz–20 Hz and at an applied potential difference of 500 mV. The complex impedance data were obtained for pure PPG and five different compositions of the system PPG–AgCF<sub>3</sub>SO<sub>3</sub> corresponding to O:M ratios of 2:1, 3:1, 4:1, 5:1, and 6:1, respectively, by employing a specially designed conductivity cell having a fixed sample thickness of 2 mm. The samples were effectively held between a pair of cylindrical silver non-blocking electrodes in conjunction with a teflon spacer and suitably placed in a temperature-controlled oven during the present electrical conductivity studies. The electrical conductivity ( $\sigma$ ) values of individual polymer-based specimens were evaluated using the equation

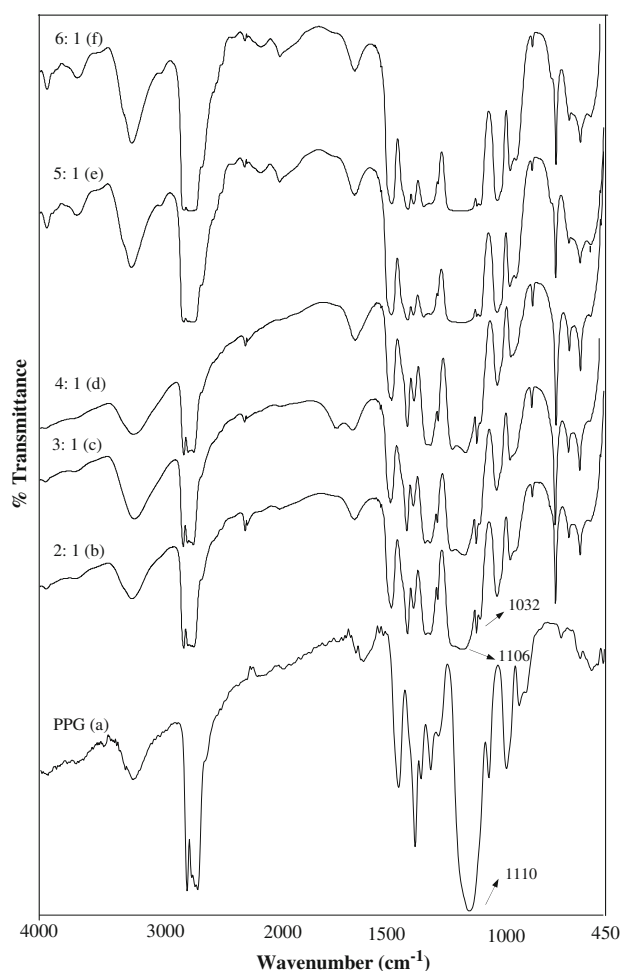
$$\sigma = 1/R_b(t/A) \quad (1)$$

where  $A$  is the area of cross section and  $t$  is the thickness of the sample.

## 3 Results and discussion

### 3.1 FT-IR spectral data

Figure 1a depicts the FT-IR spectrum observed at room temperature (298 K) for pure PPG whereas Fig. 1b–f represents the FT-IR data obtained for five different compositions of the PPG–AgCF<sub>3</sub>SO<sub>3</sub> polymer complex corresponding to O:M ratios of 2:1, 3:1, 4:1, 5:1, and 6:1



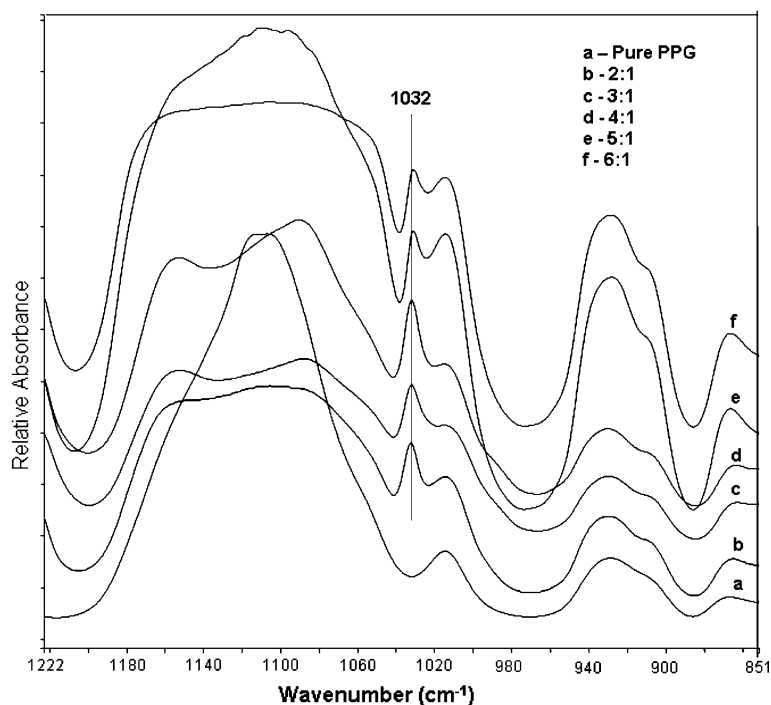
**Fig. 1** FT-IR spectra of pure PPG and PPG- $\text{AgCF}_3\text{SO}_3$  complexes having five different O:M ratios of 2:1, 3:1, 4:1, 5:1, and 6:1, respectively

respectively. A careful examination of Fig. 1a tends to reveal that the characteristic C–O–C stretching mode of vibration associated with pure PPG would correspond to the absorption band appearing at  $\sim 1110\text{ cm}^{-1}$ . Interestingly, it is also evident from a comparison of all the above FT-IR spectra that the observed changes in intensity, shape, and position of the C–O–C stretching mode may be due to the possible oxygen–cation interactions whereas that of  $\text{SO}_3$  symmetric stretching may be attributed to ion–ion interactions occurring within the polymer–salt complexes of PPG- $\text{AgCF}_3\text{SO}_3$  system [20]. It is quite apparent from Fig. 1a–f that the typical absorption band of C–O–C stretching mode appearing at  $\sim 1110\text{ cm}^{-1}$  for pure PPG would shift toward  $1106\text{ cm}^{-1}$  in the case of specimens having O:M ratios of 2:1, 3:1, 4:1, and 5:1 and saturate at  $\sim 1111\text{ cm}^{-1}$  for an O:M ratio of 6:1 corresponding to the lowest  $\text{AgCF}_3\text{SO}_3$  content. In other words, it is interesting to note that when the concentration of the silver salt namely,  $\text{AgCF}_3\text{SO}_3$  is suitably increased in such a manner

as to vary the O:M ratio from 6:1 to 2:1 the main band pertaining to the C–O–C stretching mode of vibration would shift toward the low frequency region apart from becoming an asymmetric type of vibration. The fact that the intensity of the C–O–C stretching mode decreases coupled with band broadening of the peak with increase of O:M ratio tends to suggest the presence of more interactions. These features may be assigned to the various ion–polymer interactions occurring within the polymer matrix as a result of the complexation between the silver salt, namely,  $\text{AgCF}_3\text{SO}_3$  and the chosen polymer.

Furthermore, it is obvious from Fig. 1d that the maximum shift of the C–O–C stretching occurs in the case of the complexation having an O:M ratio of 4:1, thus implying the optimum extent of salt–polymer complexation corresponding to the release of mobile ions as is also evidenced from the appearance of an intense absorption band at  $\sim 1032\text{ cm}^{-1}$  corresponding to the  $\text{SO}_3$  stretching vibration mode. Similarly, the asymmetric shape of those absorption bands appearing at  $\sim 1032$  and  $1038\text{ cm}^{-1}$  may be attributed to the existence of both free ions and ion–ion pairs, respectively, within the system. Interestingly, Fig. 2 indicates certain salient features of the  $\text{SO}_3$  stretching mode of vibration observed in the case of five different compositions of the PPG- $\text{AgCF}_3\text{SO}_3$  complex having O:M ratios of 2:1, 3:1, 4:1, 5:1, and 6:1, respectively, in comparison with the relevant part of the absorption spectra obtained for pure PPG during the course of analysis of the present FT-IR measurements. It may be clearly seen from Fig. 2 that the shoulder peak appearing at  $\sim 1032\text{ cm}^{-1}$  exhibits the maximum intensity in the case of the composition corresponding to an intermediate O:M ratio of 4:1, while showing reduced intensities in the remaining compositions. This aspect implies that as the content of  $\text{AgCF}_3\text{SO}_3$  is increased such that the O:M ratio varies from 6:1 to 4:1 the strength of silver cation–polymer interactions would increase further and reach an optimum level at an O:M ratio of 4:1, thereby releasing the maximum number of free anions within the polymer matrix. Beyond this optimum concentration of the silver salt namely,  $\text{AgCF}_3\text{SO}_3$ , further addition of  $\text{AgCF}_3\text{SO}_3$  toward an O:M ratio of 2:1 is found to result in weak interactions between the silver cation and polymer as is evident from the reduced intensity of the  $\text{SO}_3$  stretching band at  $\sim 1032\text{ cm}^{-1}$  in the case of  $\text{AgCF}_3\text{SO}_3$ -rich compositions corresponding to O:M ratios of 3:1 and 2:1 respectively. Therefore, it is reasonable to infer that the proximity of ions in all the chosen compositions of the PPG- $\text{AgCF}_3\text{SO}_3$  polymer complex having O:M ratios from 2:1 to 6:1 has been clearly revealed by the present FT-IR results. Figure 1 also suggests that those absorption bands corresponding to the symmetric  $\text{CF}_3$  which appear at  $\sim 1225$  and  $\sim 756\text{ cm}^{-1}$  in addition to the presence of the band at  $\sim 1156\text{ cm}^{-1}$  owing

**Fig. 2** Features of the  $\text{SO}_3$  stretching mode with varying O:M ratios

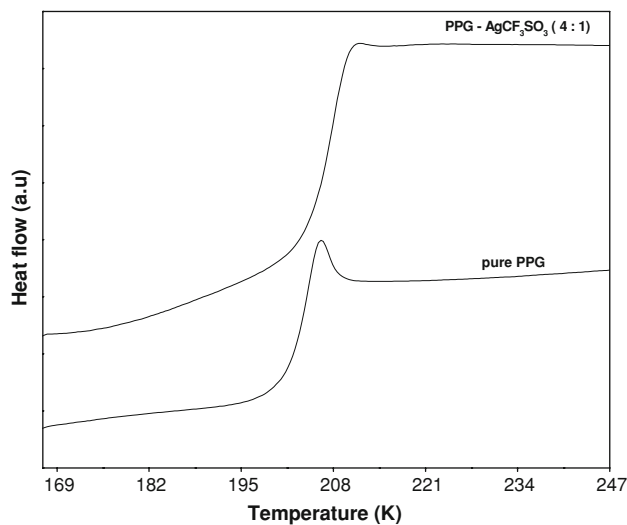


to the asymmetric  $\text{CF}_3$  mode of vibration are highly sensitive to their environmental changes and appear to serve as a means of yielding complementary information regarding the trend of the typical  $\text{SO}_3$  stretching mode as well as in establishing the coordination of  $\text{CF}_3\text{SO}_3^-$  ions within the PPG- $\text{AgCF}_3\text{SO}_3$  matrix itself [20].

In addition to the above observations, the present thermal analytical data to be discussed in the following section are also expected to throw more light on the polymer-salt complexation phenomenon occurring between PPG and  $\text{AgCF}_3\text{SO}_3$ .

### 3.2 DSC data

Figure 3 represents the experimentally observed DSC traces for the pure polymer host material namely, PPG and a typical PPG- $\text{AgCF}_3\text{SO}_3$  complex corresponding to an O:M ratio of 4:1, highlighting the appearance of the glass transition temperature ( $T_g$ ). It is interesting to note from Fig. 3 that the glass transition temperature of pure PPG is 203 K whereas the corresponding value for the PPG- $\text{AgCF}_3\text{SO}_3$  complex having an O:M ratio of 4:1 is found to appear at 208 K. Therefore, it is reasonable to argue that the observed increase in the glass transition temperature as a result of incorporation of the silver salt namely,  $\text{AgCF}_3\text{SO}_3$  into the polymer host (PPG) may be attributed to the complexation phenomenon occurring between PPG and  $\text{AgCF}_3\text{SO}_3$ . In other words, the addition of the silver salt into the polymer matrix would facilitate the formation of ion-polymer interactions thus involving the probable ion-



**Fig. 3** Thermal analysis of pure PPG and PPG- $\text{AgCF}_3\text{SO}_3$  complex having an O:M ratio of 4:1

dipole interactions between silver cation and the polyether oxygen within the structural matrix of the system. The fact that the present FT-IR results have already revealed the existence of complexation between PPG and  $\text{AgCF}_3\text{SO}_3$  tends to suggest that the DSC analytical data and FT-IR results are in good agreement with each other.

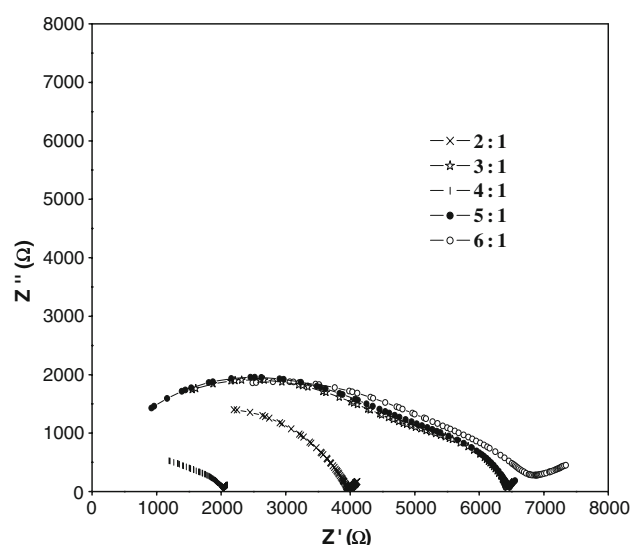
### 3.3 Transport number studies

The variation of the transport number of  $\text{Ag}^+$  ions ( $t_{\text{Ag}^+}$ ) as a function of composition obtained for the PPG- $\text{AgCF}_3\text{SO}_3$

system by means of the combined analysis of dc polarization and ac impedance data at room temperature (298 K) is presented in Table 1. Table 1 suggests that the value of  $t_{\text{Ag}^+}$  increases from 0.41 to 0.42 with increasing concentration of the silver triflate salt from an O:M ratio of 6:1 to 4:1, and decreases to 0.4 for compositions containing O:M ratios of 3:1 and 2:1. In general, the trend of increasing value of  $t_{\text{Ag}^+}$  with increasing concentration of the silver salt ( $\text{AgCF}_3\text{SO}_3$ ) may be an evidence of well-defined dissociation of  $\text{AgCF}_3\text{SO}_3$  within the polymer host PPG thus limiting the formation of ion-pairs. In the case of  $\text{AgCF}_3\text{SO}_3$ -rich compositions having O:M ratios of 3:1 and 2:1, the observed decrease in  $t_{\text{Ag}^+}$  may be attributed to the presence of dominating ion-pair products as confirmed by the present FT-IR results.

### 3.4 Electrical conductivity data

The complex impedance plots obtained for five different compositions of the polymer electrolyte system PPG- $\text{AgCF}_3\text{SO}_3$  having O:M ratios of 2:1, 3:1, 4:1, 5:1, and 6:1, respectively, at room temperature (298 K) are shown in Fig. 4. It is obvious from Fig. 4 that the value of intercept of these plots on the real axis ( $Z'$ ) decreases as the O:M ratio is varied from 2:1 to 4:1 and increases for the remaining two compositions corresponding to O:M ratios of 5:1 and 6:1. This means that the bulk resistance exhibits the lowest value for the typical composition having an O:M ratio of 4:1 thus implying that this particular composition would possess the maximum electrical conductivity at room temperature. In the case of silver salt-based polymer electrolytes, the transport of cations is mainly governed by the segmental motion of the polymer chains and percolation mechanism. In particular, silver cations are known to be either strongly coordinated to -OH end groups (cation to the oxygen and anion to hydrogen) or ether oxygens of the polymer chains [20]. It was reported that those cations coordinated to the -OH end groups are more stable than their counterparts coordinated to the ether oxygen within the polymer chain. In the case of the particular intermediate composition corresponding to an O:M ratio of 4:1, an exact coordination of the ether oxygen to the silver cations may



**Fig. 4** Complex impedance plots of PPG- $\text{AgCF}_3\text{SO}_3$  system having five different O:M ratios of 2:1, 3:1, 4:1, 5:1, and 6:1, respectively, at room temperature (298 K)

be apparently present [20]. The solvation effects are expected to influence the concentration dependence and in turn the ion transport is likely to be influenced by various ion pairs apart from  $\text{Ag}^+$ -O interactions. Therefore, the strength of such interactions is crucial for the ionic transport to occur within the electrolyte matrix wherein the interaction between cations and anions is very weak accompanied by the presence of free ions probably formed during the dissociation of the salt within the amorphous phase of the polymer (PPG). The complexation of four ether oxygens with a silver cation and the terminal hydroxyl groups may also be influenced by the solvation of the cation. Such free anions would tend to provide additional sites and increase the mobility of the cations while being closely associated with the relaxation modes of the polymer host and enhancement of the polymer segmental motions. However, the ionic mobility is expected to increase with the formation of free ions in conformity with the present FT-IR, DSC, and transport number studies. The feasibility of reduced segmental motion may be expected to occur in the case of typical compositions corresponding to O:M ratios of 2:1 and 3:1 as a result of either an incomplete dissociation of the salt or the formation of ion pairs. On the other hand, a drop in segmental motion may be interpreted to occur as a result of the effect of an increase in inter and intramolecular coordinations between the coordinating sites on the same or different polymer chains caused by those ions acting as transient cross-links thereby restricting the mobility of ions. On the other hand, at very low salt concentrations corresponding to O:M ratios of 5:1 and 6:1, the electrical conductivity is expected to fall sharply from its value at an infinite dilution wherein the formation of

**Table 1** Silver ionic transport number ( $t_{\text{Ag}^+}$ ) data for the PPG- $\text{AgCF}_3\text{SO}_3$  system at 298 K

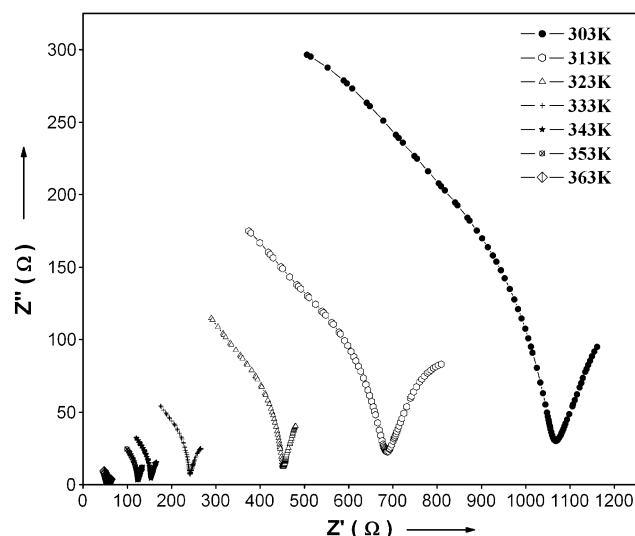
O:M ratio	Silver ionic transport number ( $t_{\text{Ag}^+}$ )
2:1	0.4
3:1	0.4
4:1	0.42
5:1	0.41
6:1	0.41



non-conducting ion pairs would limit the segmental motion of the ions.

The measured room temperature electrical conductivity ( $\sigma_{298\text{ K}}$ ) values of pure PPG and PPG–AgCF<sub>3</sub>SO<sub>3</sub> complexes having O:M ratios of 2:1, 3:1, 4:1, 5:1, and 6:1 have been found to be  $1.68 \times 10^{-8}$ ,  $2.8 \times 10^{-5}$ ,  $4.8 \times 10^{-5}$ ,  $9.4 \times 10^{-5}$ ,  $2.9 \times 10^{-5}$ , and  $2.8 \times 10^{-5}$  S cm<sup>-1</sup>, respectively. These data suggest that the conductivity enhancement observed in the chosen system may be attributed to the percolation effect resulting in a rapid increase in the segmental motion of the polymer chain thus leading to the occurrence of the most favorable segmental motion in the case of the composition having an O:M ratio of 4:1, which is found to exhibit the best conductivity value of  $9.4 \times 10^{-5}$  S cm<sup>-1</sup> at 298 K.

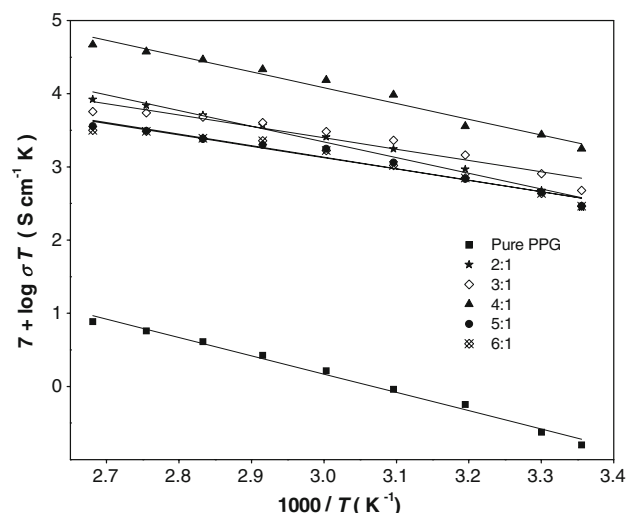
Figure 5 shows the complex impedance plots obtained for the best conducting composition of the polymer electrolyte system PPG–AgCF<sub>3</sub>SO<sub>3</sub> having an O:M ratio of 4:1 over the temperature range 303–363 K. It is also interesting to observe from Fig. 5 that the point of intercept on the real axis ( $Z'$ ) is shifted toward origin and hence the value of bulk resistance ( $R_b$ ) decreases with increasing temperature. These aspects tend to suggest the most probable enhancement of ionic mobility with temperature that could be explained on the basis of the ionic transport mechanism involving coordinating sites, local structural relaxation, and segmental motion of the polymer chain. At an elevated temperature, the mobility of the polymer chain may be thought of as being considerably promoted thereby resulting in an increased fraction of free volume within the polymer electrolyte and hence an enhanced electrical conductivity value as in the case of similar polymer–salt complexes [15].



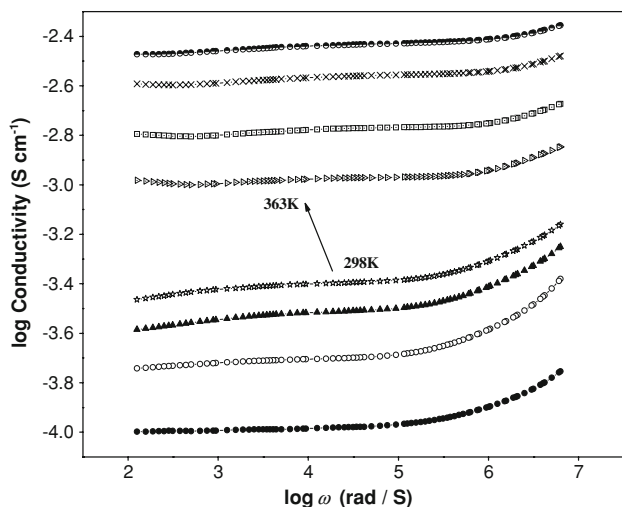
**Fig. 5** Complex impedance plots obtained for the PPG–AgCF<sub>3</sub>SO<sub>3</sub> complex having an O:M ratio of 4:1 at various temperatures

The observed trends of temperature dependence of electrical conductivity of pure PPG and PPG–AgCF<sub>3</sub>SO<sub>3</sub> polymer–salt system having O:M ratios of 2:1, 3:1, 4:1, 5:1, and 6:1 are shown in Fig. 6. The fact that the electrical conductivity ( $\sigma$ ) increases when the temperature ( $T$ ) is raised from 298 to 363 K may be ascribed to the most probable increase in the free volume of the polymer electrolyte. It is evident from the values of slopes of these  $\log \sigma T$  plots evaluated through linear fitting technique that the activation energies ( $E_a$ ) for electrical transport mechanisms in the various specimens of pure PPG and PPG–AgCF<sub>3</sub>SO<sub>3</sub> complexes having O:M ratios of 2:1, 3:1, 4:1, 5:1, and 6:1 are 0.51, 0.51, 0.5, 0.46, 0.49, and 0.5 eV, respectively. The maximum ionic conductivity of  $9.4 \times 10^{-5}$  S cm<sup>-1</sup> obtained for an O:M ratio of 4:1 is thus found to be associated with the minimum activation energy of 0.46 eV exhibited by the same composition. These results tend to confirm that electrical conductivity data are in good agreement with the present FT–IR results.

Figure 7 represents the variation of electrical conductivity of the best conducting composition of the polymer electrolyte system PPG–AgCF<sub>3</sub>SO<sub>3</sub> namely, an O:M ratio of 4:1 as a function of frequency obtained at eight different temperatures 298, 303, 313, 323, 333, 343, 353, and 363 K, respectively. It is obvious from all these conductivity spectra that each isotherm is characterized by the appearance of a frequency-independent component in the lower frequency region which may be attributed to the electrode polarization effects. In the higher frequency region, the observed conductivity is much less temperature-dependent owing to the possibility of coupled forward and backward displacements of ions. In order to understand the correlation between the observed electrical conductivity ( $\sigma$ ), activation energy ( $E_a$ ), and complexation within the typical

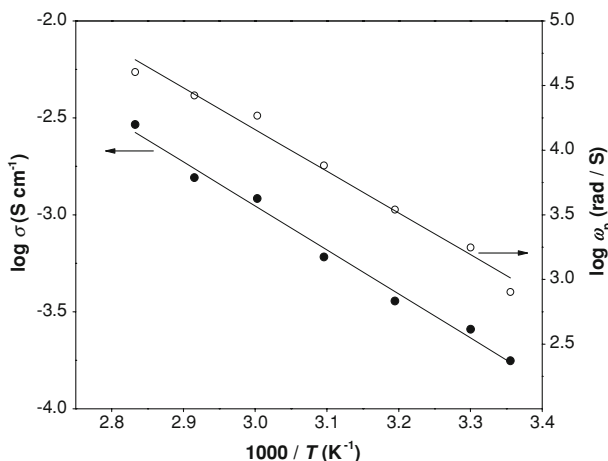


**Fig. 6** Plots of  $\log \sigma T$  versus  $1/T$  obtained for pure PPG and PPG–AgCF<sub>3</sub>SO<sub>3</sub> complexes



**Fig. 7** Electrical conductivity spectra obtained for the best conducting composition of the PPG–AgCF<sub>3</sub>SO<sub>3</sub> system at different temperatures

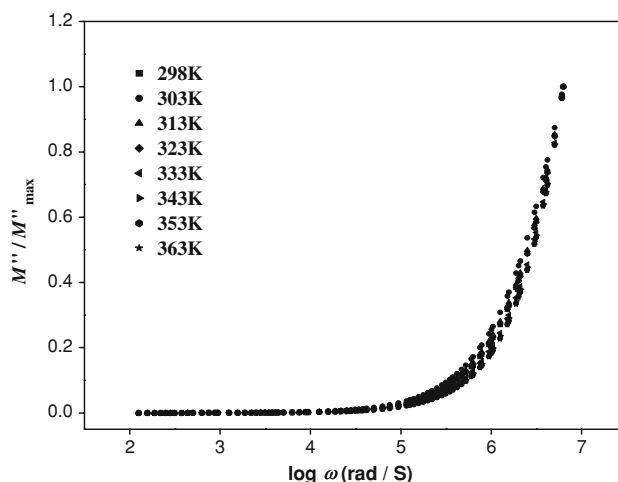
sample having an O:M ratio of 4:1, a comparison of the dependence of the maximum angular frequency,  $\omega_p$  for the mobile ion in the chosen polymer electrolyte obtained from the conductivity spectra and that of the electrical conductivity ( $\sigma$ ) as a function of temperature was carried out as shown in Fig. 8. The fact that the slope of the plot of  $\log \sigma$  versus  $1/T$  represents the activation energy for ionic migration whereas that of  $\log \omega_p$  versus  $1/T$  denotes the migration energy for the mobile ions has enabled the comparative analysis to infer that the conduction mechanism within the PPG–AgCF<sub>3</sub>SO<sub>3</sub> complex remains the same and that those charge carriers responsible for both ionic conduction as well as conductivity relaxation phenomena would involve Ag<sup>+</sup> ions facilitated by segmental motion of polymer chains within the structural network of the PPG–AgCF<sub>3</sub>SO<sub>3</sub> complex.



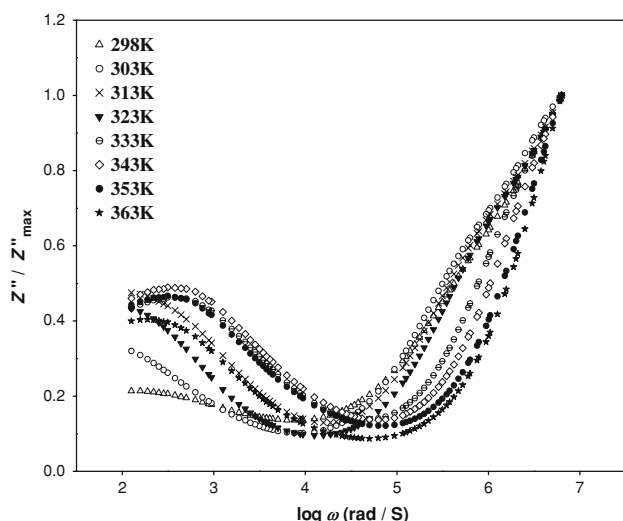
**Fig. 8** Variation of electrical conductivity and maximum angular frequency ( $\omega_p$ ) of the best conducting composition having an O:M ratio of 4:1 as a function of temperature

### 3.5 Modulus analysis

The normalized modulus spectra obtained in the form of plots of  $M''/M''_{max}$  versus  $\log \omega$  where  $M''$  denotes the imaginary part of modulus and  $\omega$  is the angular frequency at eight different temperatures 298, 303, 313, 323, 333, 343, 353, and 363 K for the best conducting PPG–AgCF<sub>3</sub>SO<sub>3</sub> complex having an O:M ratio of 4:1 are shown in Fig. 9. It is clear from Fig. 9 that the observed electric modulus spectra exhibit a broad asymmetric nature at elevated temperatures. This trend appears to suggest that those dynamical processes occurring within the sample at different frequencies may exhibit a type of relaxation which is essentially a thermally activated one in accordance with the present electrical conductivity analysis. The superimposability of these modulus spectra noticed during the present investigation may be ascribed to the occurrence of a distribution of relaxation times which is almost temperature-independent, as in the case of polymer electrolyte systems in general [1, 2]. On the other hand, Fig. 10 depicts the set of normalized impedance spectra obtained for the above composition at eight different temperatures, 298, 303, 313, 323, 333, 343, 353, and 363 K, respectively. It is interesting to note from Fig. 10 that the low frequency peaks may be attributed to the electrode polarization effects whereas the bulk relaxation phenomena of the systems are highlighted in the high frequency region. It is therefore, reasonable to argue that the segmental motion of the polymer chain along with cation or the displacement of cation from one site to another within the polymer electrolyte would result in a very low relaxation time, thus implying a fast ionic transport of the cation. At higher frequencies, the displacement of ions may tend to be coupled with simultaneous backward and forward hopping processes thereby resulting in a relaxation of ions which is



**Fig. 9** Normalized modulus spectra for the composition having an O:M ratio of 4:1 at different temperatures



**Fig. 10** Normalized impedance spectra for the composition having an O:M ratio of 4:1 at different temperatures

expected to be less temperature-dependent. The fact that all the present modulus spectra are superimposable also suggests the feasibility of an enhancement of localized segmental motion or mobile charge carriers at higher frequencies as revealed by the presence of the conductivity relaxation mechanism which is found to be independent of temperature. Furthermore, a careful analysis of the modulus and impedance spectra appears to reveal the characteristic feature that both the modulus and impedance peaks occur at the same frequency thus confirming the presence of a bulk relaxation process within the chosen system. The present investigation has thus demonstrated the feasibility of realization of an appropriate polymer electrolyte for electrochemical device applications.

#### 4 Conclusions

The impact of polymer–salt complexation on ionic conductivity, ionic interactions, and ionic mobility has been examined in the case of a typical polymer electrolyte system involving PPG 4000 complexed with  $\text{AgCF}_3\text{SO}_3$ . The evidence of strong interactions among the cations, anions, and ether oxygen, and hydroxyl groups has also been demonstrated. The appreciably high room temperature ionic conductivity of the order of  $10^{-5} \text{ S cm}^{-1}$

realized in the chosen polymer electrolyte at an intermediate salt concentration could be attributed to the enhanced segmental mobility of the polymer chain. The combined analysis of the segmental and structural relaxations with varying polymer–salt concentrations has suggested that the coupling of these relaxations would contribute significantly to the overall ionic mobility of the system. Such features appear to offer a suitable polymer electrolyte for the development of advanced electrochemical devices.

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