Materials Science-Poland, Vol. 24, No. 1, 2006

Ionic conductivity of polymer electrolytes comprising acrylonitrile–butyl acrylate copolymer and a lithium salt

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New polymer electrolytes were prepared by mixing random copolymers of acrylonitrile and butyl acrylate (poly(AN-*co*-BuA)) with lithium bis(trifluoromethanesulfone) imide (LiTFSI). Electrical properties were studied by the impedance spectroscopy. The glass transition temperature was studied by DSC. Presented results concern a broad range of compositions, from a pristine copolymer to the system with 98 wt. % of salt. Correlation was established between the glass transition temperature, ionic conductivity, and salt content in the system. Mixtures of poly(AN-*co*-BuA) and LiTFSI exhibit much lower glass transition temperatures than the parent copolymer. Effects of ageing were observed for electrolytes with high salt content.

Key words: *polymer electrolyte; acrylonitrile–butyl acrylate copolymer; lithium bis(trifluoromethane-sulfone)imide; polymer-in-salt electrolyte*

1. Introduction

Polymer electrolytes have received much attention in the past two decades. There has been a persistent interest in the development of highly efficient energy sources for applications such as cellular phones, mobile computers, and vehicles with electrical propulsion. Polymer electrolytes with high salt content are investigated in search for obtaining electrolytes characterised by effective anion immobilisation, which combine good mechanical properties of the polymer and high ionic conductivity of solid electrolytes. Such systems, named “polymer-in-salt” electrolytes, were first described by

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Angell et al. [1]. After this pioneering work, many papers were published concerning mainly polyacrylonitrile (PAN)-based systems [2–4]. For these systems it was proposed that ion mobility is not directly connected to the segmental relaxation of the polymer matrix but that it results from the high degree of ion aggregation. PAN is, however, soluble only in a small number of aprotic solvents, such as DMSO, which are very difficult to remove during membrane preparation.

We propose the use of random copolymers of acrylonitrile (AN) and butyl acrylate (BuA) as the polymeric matrix. These copolymers are well soluble in acetonitrile, a volatile solvent that can easily be removed. In this work, we describe electrical properties of rubbery solids obtained by mixing lithium bis(trifluoromethanesulfone)imide (LiTFSI) and random copolymers poly(AN-*co*-BuA). Compositions ranging from a pure copolymer, through low salt content systems (corresponding to traditional "salt-in-polymer" electrolyte), to "polymer-in-salt" electrolytes with high salt content up to 98 wt. %, were investigated by DSC and impedance spectroscopy.

2. Experimental

2.1. Sample preparation

Lithium bis(trifluoromethanesulfone)imide $LiN(CF_3SO_2)_2$ (Aldrich) was dried under vacuum at 120 °C. Acetonitrile (Aldrich) was dried and distilled under an argon atmosphere prior to use. The copolymers of butyl acrylate (BuA) (Aldrich, reagent grade) and acrylonitrile (AN) (Aldrich, reagent grade) were obtained by radical polymerisation in the presence of azo-bis-isobutyronitrile (AIBN) as an initiator. Copolymerisation was carried out from 3 to 5 hours in the temperature range 60–70 ºC in an oil bath. For this study, a copolymer with an average molar ratio of AN m.u. (monomeric units) to BuA m.u. equal to 2:1 was prepared (67 mol % of acrylonitrile).

$LiN(CF_3SO_2)_2$ was combined with the copolymer in an acetonitrile solution in the appropriate ratio. Electrolyte membranes were obtained by casting the solution on Teflon dishes and drying in two stages under vacuum. Acetonitrile was first removed under 2500 Pa for 50 h, and then drying was carried out at 0.1 Pa for about 140 h. The salt was added in the amount of 10–98 wt. % of the electrolyte, thus in a molar ratio between 0.045:1 and 20:1 with respect to AN m.u. of the copolymer.

2.2. Differential scanning calorimetry

DSC experiments were performed on a Perkin-Elmer Pyris 1 scanning calorimeter equipped with a low-temperature measuring head. The samples were placed in hermetically closed aluminium pans. DSC traces were recorded with a heating rate of 20 °C/min after rapid cooling from 120 °C to –100 °C. The glass transition temperature was determined from the second heating run.

2.3. Impedance spectroscopy

The cells for impedance measurements were prepared in a glove box under an argon atmosphere. Circular samples (16 mm in diameter) were cut from films of thicknesses between 0.3 and 0.6 mm and mounted between gold-plated stainless steel electrodes in a gas tight holder. The holder was placed in a thermostat, and heated or cooled by Peltier elements between –60 °C and 145 °C. Temperature was controlled by an Eurotherm 2408. Impedance spectra were recorded at a constant temperature during heating and cooling runs. A computer-controlled set-up based on a Novocontrol Alpha-N dielectric analyser or a Solartron 1260 impedance analyser and a Keithley 428 current amplifier [5] was used in the frequency range 10^7–10^{-2} Hz. The amplitude of the AC signal was 20 or 100 mV rms. The stability of impedance, measured for a selected set of frequencies, was tested over the period of acquisition of an impedance spectrum. Measurements at a given temperature were automatically repeated until the drift of impedance was below a specified limit (e.g., 1% of the relative change per hour) [6].

3. Results and discussion

3.1. DSC studies

The physical properties of the obtained polymer electrolytes depend on the share of the lithium salt and the matrix used. Systems comprising poly(AN-*co*-BuA) and about 20 wt. % of the salt are a stiff rubber. With increasing salt content, the films become more flexible. At 74 wt. % of the salt, the membranes are flexible. At salt contents above 90 wt. %, the membranes exhibit the properties of a metastable, very viscous liquid.

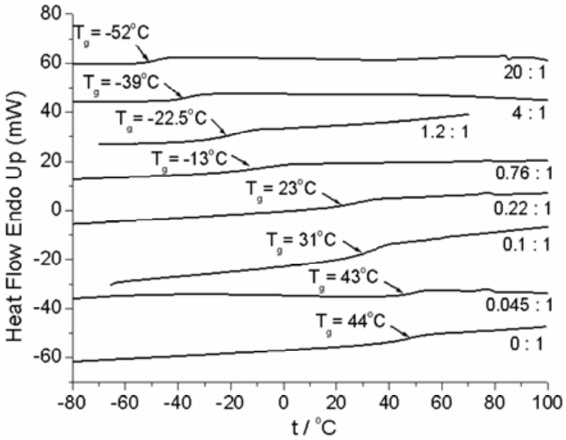

Fig. 1. DSC traces recorded during heating at a rate of 20 °C /min, after a rapid cooling from 120 °C. The glass transition is seen on the plot as a deviation in the endothermic direction. The value of T_g for each sample was taken at the centre of the slope

Table 1. Results of DSC and the electrical characterisation of the system poly(AN-*co*-BuA) with LiTFSI [*]

Molar ratio Li:AN	Weight % of LiTFSI	σ at 50 °C [S·cm^{-1}]	T_g [°C]	T_0 [°C]	$T_g - T_0$ [°C]	log(R_τ)
0:1	0	1.2×10^{-11}	44	–40	84	2.5
0.045:1	10	1.28×10^{-10}	43	–23	66	3.5
0.1:1	19.7	1.2×10^{-10}	31	–38	69	1.5
0.22:1	35	2.1×10^{-8}	23	–90	113	4.2
0.76:1	65	9.4×10^{-6}	–13	–100	87	5.5
1.2:1	74.6	7.3×10^{-6}	–22	–95	73	3.3
4:1	91	5.2×10^{-6}	–39	–94	55	1.2
20:1	98	1.2×10^{-4}	–52	–102	50	3.9

[*] Composition is given as a molar ratio of LiTFSI to AN m.u. The content of the salt is also given in weight percent. The glass transition temperature, T_g, measured by DSC, is compared with the ideal glass transition temperature, T_0, obtained by fitting the VTF function to the temperature dependence of conductivity. The logarithm of the de-coupling index, log(R_τ), is based on Eq.(3)

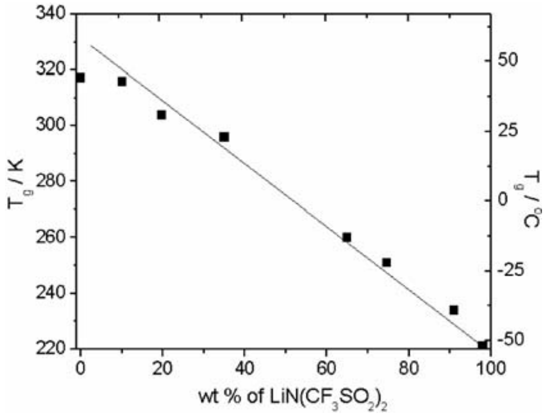

Fig. 2. Dependence of the glass transition temperature, T_g, measured by DSC, on the content of $LiN(CF_3SO_2)_2$ in the systems with poly(AN-*co*-BuA) comprising 67 mol % of acrylonitrile m.u.

The dependence of the mechanical properties of the systems on salt content is correlated with the glass transition temperature. Figure 1 shows the DSC traces for all samples with glass transition temperatures, T_g, marked. The values of the glass transition temperatures are given in Table 1. The main observation is that the salt operates like a plasticiser and that T_g for composites is lower than that of the parent copolymers. In addition, the dependence of the glass transition temperature T_g on the content of salt appears to be linear (Fig. 2). By extrapolating the dependence of T_g on salt content, the value of T_g for pure LiTFSI was estimated to be about –52 °C. The plasticising effect of lithium salts was already observed in other polymer-in-salt electrolytes comprising polyacrylonitrile or its copolymers [7, 8], but the mechanism of this phenomenon is not fully understood yet.

3.2. Ionic conductivity

Figure 3 shows the temperature dependences of the conductivity of poly(AN-*co*-BuA) with LiTFSI for the compositions listed in Table 1. The presented conductivity data were collected during cooling after first heating the cast film to about 100 °C.

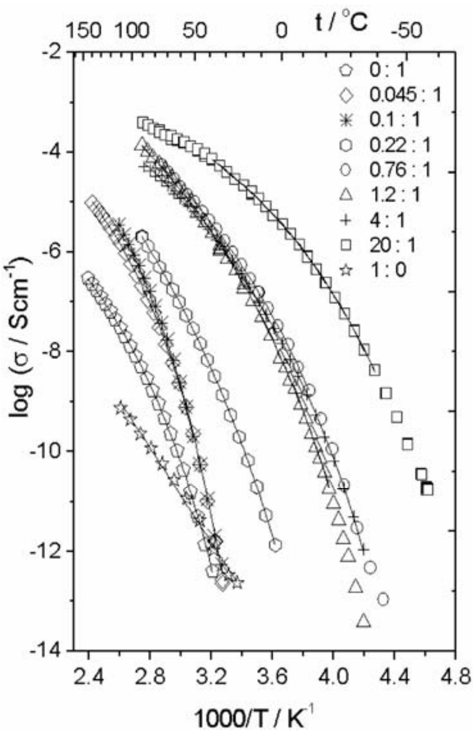

Fig. 3. Temperature dependence of the ionic conductivity of the electrolytes composed of LiTFSI and poly(AN-*co*-BuA) copolymer containing 67 mol % AN m.u. The composition of each sample is given by its respective molar ratio LiTFSI:AN m.u. The continuous lines represent the VTF function, fitted for temperatures above the glass transition temperature. The conductivity of the pristine LiTFSI salt (marked as 1:0) is fitted with a straight line representing the Arrhenius dependence

Figure 3 shows also the variation of ionic conductivity with temperature for the pristine LiTFSI salt placed between blocking electrodes, which after heating to 120 °C gives a reproducible Arrhenius-type dependence:

$$\sigma(T) = A\exp[\,-E_A/(k_BT)\,] \tag{1}$$

The conductivity of the crystalline salt at 50 °C was measured to be about 3×10^{-12} S/cm, and the activation energy in the temperature range 30–90 °C was about 1 eV.

The temperature dependence of ionic conductivity for amorphous electrolytes composed of LiTFSI and AN-*co*-BuA copolymers (Fig. 3) is well fitted by the Vogel–Tamman–Fulcher function:

$$\sigma(T) = A\exp[-B/(T - T_0)] \tag{2}$$

In this equation, A is the pre-exponential factor, proportional to the concentration of charge carriers, B is the pseudo-activation energy for conduction, and T_0 is the ideal glass transition temperature. The electrical conductivity of the studied electrolytes depends on the content of lithium salt in the system. Conductivity at 50 °C ranged from 10^{-11} to 10^{-4} S/cm, showing an increase with increasing lithium salt content. Figure 4 shows the dependence of conductivity on the content of $LiN(CF_3SO_2)_2$. The ideal glass transition temperature, T_0, obtained from the fit of the VTF function is considerably lower than the T_g obtained from DSC. The difference between T_g and T_0 is also included in Table 1. The value of $T_g - T_0$ ranges from 50 °C to 113 °C.

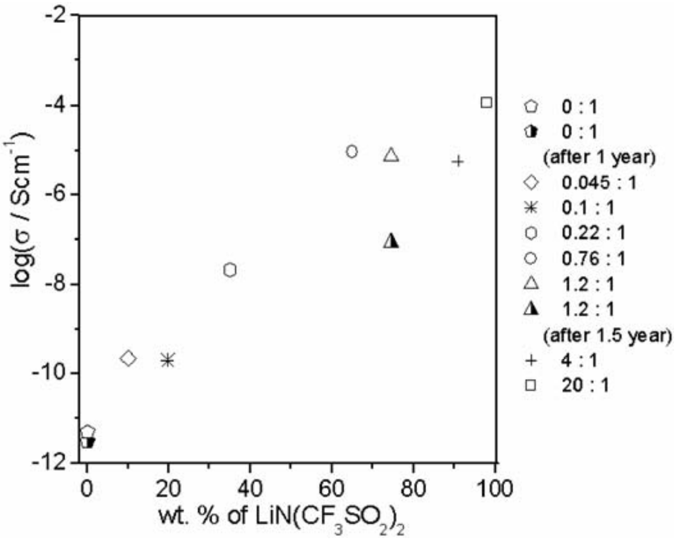

Fig. 4. Dependence of conductivity measured at 50 °C on the content of $LiN(CF_3SO_2)_2$ in the system with poly(AN-*co*-BuA) copolymer containing 67 mol % m.u. of AN. A decrease in electrical conductivity for LiTFSI:AN (1.2:1) was observed over a period of several months

The conductivity measured at the glass transition temperature, σ_{Tg}, allows the estimation of the de-coupling index R_τ, which is defined as the ratio of the shear relaxation time to the conductivity relaxation time [9]. The de-coupling index reflects the level of freedom of mobile ions from the interference by the immobile elements. At the glass transition temperature, T_g, the decimal logarithm of the de-coupling index can be obtained from an approximate relation [9]:

$$\log(R_\tau) = 14.3 + \log(\sigma_{Tg}) \tag{3}$$

For the LiTFSI/AN-*co*-BuA system, the logarithm of de-coupling index is between 1.2 and 5.5 (Table 1), generally higher than that for the poly(ethylene oxide)–LiTFSI system, in which $\log(R_\tau)$ is usually between 1 and 2 [10]. The values obtained for the studied system, however, are much lower than $\log(R_\tau)$ equal to 9.8 reported for poly(vinylsulfonic) acid lithium salt, in which the backbone oxygen is absent [11]. For comparison, typical values of $\log(R_\tau)$ for highly conducting inorganic glasses are close to 12 [9, 12–13].

For prospective applications, it is important to test the long-term stability of the obtained polymer electrolytes. The cast films were examined after over one year of storage at room temperature in a dry box with circulating argon. Changes in the physical properties were noticed. Films with a high content of the salt became less flexible or even brittle, and opaque instead of transparent. Impedance measurements on samples cut from the aged films were made under the same conditions as previously made on samples cut from freshly cast films. A comparison of the effect of ageing on the temperature dependence of ionic conductivity in the pure copolymer and polymer-in-salt system with the molar ratio of 1.2:1 LiTFSI to AN m.u. is presented in Figure 5.

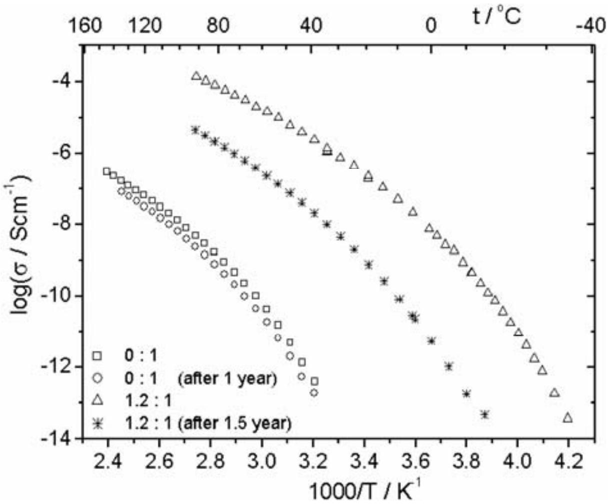

Fig. 5. The effect of ageing on the ionic conductivity of pristine poly(AN-*co*-BuA) and a polymer-in-salt electrolyte of molar ratio 1.2:1 LiTFSI to AN m.u. in poly(AN-*co*-BuA). Temperature dependence of conductivity, measured for samples from freshly cast film and for the same films after 1 or 1.5 years of storage at room temperature in an argon atmosphere

Conductivity in the polymer-in-salt system decreased by about two orders of magnitude after 1.5 years of storage, whereas the conductivity of the pristine copolymer decreased by only about 4 times after 1 year. The glass transition temperature of the pristine copolymer did not change, whereas in the case of the 1.2:1 Li:AN m.u. electrolyte it increased significantly. The nature of the changes is not clear yet. Possible phase segregation in systems with high salt content should be taken into account. A loss of volatile remnants, left from the technological process, may cause a decrease in the conductivity of the pristine copolymer.

4. Conclusions

AN-*co*-BuA copolymers with LiTFSI form flexible membranes exhibiting a glass transition temperature significantly lower than that of the parent copolymer. The glass transition temperature, T_g, decreases with increasing lithium salt content. The conductivities of these systems increase with increasing salt content. The temperature dependence of conductivity in these systems may be described by a VTF equation. Values of the de-coupling index are considerably lower in comparison to typical values for highly conducting inorganic glasses, but higher than values for PEO-LiTFSI systems. After long-lasting storage at the room temperature in an argon atmosphere, a considerable decrease in conductivity was observed for some systems. The nature of this lack of stability is not understood yet and is presently subject to further investigations.

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Received 10 December 2004
Revised 10 January 2005