Star-branched poly(ethylene oxide) LiN(CF$_3$SO$_2$)$_2$: A promising polymer electrolyte

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ABSTRACT

Polymer electrolytes composed of star-branched poly(ethylene oxide) PEO with addition of LiN(CF$_3$SO$_2$)$_2$ salt (LiTFSI) of molar ratios EO:Li ranging from 1:1 to pure polymer were prepared by casting from solution. The electrolytes are studied by impedance spectroscopy and impedance spectroscopy performed simultaneously with optical microscope observation. Star-branched structure does not prevent the polymer without salt from crystallizing. A decrease of conductivity caused by crystallization is of similar order of magnitude as in linear PEO. Surprisingly, in electrolytes formed by addition of LiTFSI salt to the branched PEO is inhibited. In electrolytes with molar ratio EO:Li equal 10:1 and 6:1 subjected to subsequent cooling and heating runs, no traces of crystalline phase are detected by either polarizing microscope observation or differential scanning calorimetry. The ionic conductivity of studied electrolytes in amorphous state is comparable to that of electrolytes based on linear PEO. At temperatures below the melting temperature of electrolytes with linear PEO matrix, the conductivity of electrolytes based on branched PEO is much higher. As prepared, electrolyte with molar ratio of EO:Li equal 1:1 is also amorphous. Weak phase segregation effect is recorded in subsequent cooling and heating runs. This behaviour is different than observed for electrolytes based on linear PEO with similar molar ratio, which are strongly inhomogeneous and contain a large fraction of crystalline salt precipitates.

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1. Introduction

In the recent years, a steadily growing interest in issues related to energy storage and conservation has been observed, accompanied by dynamic growth of rechargeable batteries industry. Polymers seem to be a very promising electrolyte material, as they offer low cost, safety and flexibility of application. A great variety of different polymeric systems has been studied to perform the role of solid solvent for the ions. Poly(ethylene oxide) PEO seems to be a good choice for electrolyte matrix, as its polymeric chain is capable to wrap around lithium cations, creating coordination bonds [1]. However, PEO has also some serious drawbacks. The performance of electrolyte is strongly limited by crystallization of either pure polymer, or complexes of PEO with salt [2]. Usually, the crystalline phase has much lower ionic conductivity than the amorphous phase. The folded chains incorporated in crystalline lamellae are stiff and incapable of supporting ion transport with their segmental movements. Only a few rare cases are known, for which specific structure of

crystalline phase creates tunnels convenient for Li-ion conduction [3]. Therefore, in semicrystalline electrolyte the transport of ions relays mainly on continuity of amorphous pathways between the electrodes [4]. If those amorphous domains become separated by crystalline phase, a significant decrease of conductivity is recorded. Therefore the electrical properties of semicrystalline electrolyte strongly depend on its thermal history as well as morphology and composition of crystalline phases [5–6]. Such behaviour of electrolyte is not acceptable for practical usage in lithium-ion battery.

Several ways of overcoming the above mentioned limitations have been proposed. A significant improvement of ionic conductivity of polymer electrolyte can be achieved by addition of a solvent, thus creating a gel-type electrolyte [7]. However, in this case practical application seems to be limited by lack of mechanical stability and occurrence of passivation phenomena at the electrode/electrolyte interface. The crystallinity of electrolyte can be decreased by introduction of ceramic fillers, which are believed to additionally improve the ionic conductivity of electrolyte by interaction of surface groups with both polymer chains and charge carriers [8]. Sedimentation of the ceramic filler, leading to inhomogeneity of the electrolyte and nucleation of crystalline phase on the filler grains are the main disadvantages of such systems. Another

way to decrease the fraction of crystalline phase in the electrolyte is selection of an appropriate type of anion, which would disturb regular alignment of polymer chains during crystallization and act like a plasticizer of the polymer matrix. A widely known example is the bis(trifluoromethanesulfone) imide (TFSI$^-$) anion which significantly slows down crystallization kinetics of PEO [9]. An additional advantage of TFSI anion in respect to other anions is its highly delocalized charge, which improves solubility and allows for achieving high values of ionic conductivity [10], minimizing the ion–ion interactions [11]. The glass transition temperature T_g of electrolytes with LiTFSI salt is usually lower than that of electrolytes with other types of salts like LiClO$_4$ or LiCF$_3$SO$_3$, which is due to the flexible S–N–S bonds in LiTFSI. However, those plasticizing properties of LiTFSI seem to be limited only to electrolytes with low amount of salt. In electrolytes with higher concentration of LiTFSI, formation of crystalline complexes with PEO with stoichiometries of 6:1, 3:1 and 2:1 EO:Li was evidenced [12]. In our recent study we have shown, that in case of all of these crystalline phases, their presence in the electrolyte generally leads to a decrease of ionic conductivity [13].

The application of branched or hyper-branched polymer as the electrolyte matrix provides another effective method for improvement of electrolyte properties. Usually, the observed increase of conductivity in respect to the electrolyte based on unmodified polymer is attributed to lower crystallinity of the branched matrix [14]. The side chains are believed to prevent regular alignment of the polymeric chains into lamellae during crystallization. This effect seems to be more pronounced in electrolytes which additionally contain anions of plasticizing properties. Inhibition of crystallization has been reported for example for star-branched polymer prepared from reaction of polyethylene glycol monomethyl ethers with acid chlorides of hexakis(3,5-dicarboxyphenoxy)- and hexakis(4-carboxyphenoxy)cyclotriphosphazenes [15]. Although salt-free samples were partially crystalline, the electrolytes with dissolved LiClO$_4$ salt were found to be completely amorphous. Despite the lack of crystalline phase, rather low ionic conductivity value of 4×10^{-5} Scm^{-1} at 30 °C has been obtained, which can be attributed to higher glass transition temperature in respect to linear PEO. Higher values of conductivity were observed for example for branched electrolytes synthesized using boron compounds [16]. Ionic conductivity of 8×10^{-5} Scm^{-1} at 30 °C has been obtained in case of electrolyte based on branched poly(ethylene glycol) synthesized using boron trioxide. This value is still slightly lower than that of similar electrolytes based on linear PEO in the amorphous state, which has been attributed partially to interactions of ClO$_4^-$ anion with boron causing reduction of its mobility. Enhancement of ionic conductivity in respect to linear PEO has been reported in another work, in which PEG–borate ester was used as plasticizer of electrolyte composed of poly(ethyleneglycol) methacrylate (PEGMA) and LiTFSI salt [17]. In this case, amorphous system with ionic conductivity of 3×10^{-4} Scm^{-1} at 30 °C was obtained. A significant disadvantage of this electrolyte is however its low transference number for lithium cations ($t^+ = 0.11$) [18]. For electrolytes comprising branched polymer and LiClO$_4$ or LiCF$_3$SO$_3$ salts, more promising results were obtained, which has been attributed to stronger interaction of borate esters with those salts. Another interesting example in which branched structure prevents electrolyte from crystallizing are polymer blends. In this case, branched polymer is only an additive to poly(ethylene oxide). Such electrolyte, in which hyper-branched poly[bis(triethylene glycol)] benzoate capped with an acetyl group (HBP) was introduced to PEO-based electrolyte with LiClO$_4$ salt and BaTiO$_3$ filler, has been presented by Itoh et al. [19]. Ionic conductivity values of the order of 3×10^{-4} Scm^{-1} at 30 °C were reported.

In branched electrolytes the side chains play also another important role besides inhibition of crystallization. Their movements, faster than motions of polymer backbone, can enhance ion trans-

port through the matrix, as well as charge transfer reaction rate at the lithium electrode interface. In comb-shaped polyether electrolytes based on matrix of PEO and 2-(2-methoxyethoxy)ethyl glycydil (MEEGE), mixed with LiTFSI salt the ionic conductivity reached a maximum value of 3.3×10^{-4} Scm^{-1} at 30 °C [20,21]. The ionic conductivity was found to depend on the structure of the polymer matrix, especially the length of the side chains and proportions between PEO and MEEGE.

In this paper new polymer electrolytes based on star-branched PEO are presented and their properties are compared to those of electrolytes based on high molecular weight linear PEO.

2. Experimental

Star-branched polymer matrix of poly(ethylene oxide) arms with diepoxide core has been prepared according to procedure described in detail in previous publication [22]. So called first generation star has been synthesized (Scheme 1). The characterization of structure has been carried out by size exclusion chromatography (SEC) with triple detection: Knauer K-501 high-pressure liquid chromatography pump with an LDC refractive-index detector and Viscotek T60A dual detector (right-angle laser light scattering at $\lambda = 670$ nm (RALLS) and differential viscosimeter) [22]. Basing on data obtained from these methods, the average number of poly(ethylene oxide) arms in a typical star was estimated, which is between 20 (according to molecular weight measurement) and 26 (according to viscosity measurement). Each arm had a molecular weight of about 2000. The reactive sites on the diepoxide core have been partially phosphorylated – the degree of substitution by –OP(O)(ONa)$_2$ groups was estimated as 55%.

Lithium imide salt LiN(CF$_3$SO$_2$)$_2$ (Aldrich) was dried under vacuum and added to the star-branched matrix in acetonitrile solution. The obtained solution was poured onto a teflon dish and thin foil was formed after vacuum drying. Four different compositions of electrolyte were prepared, corresponding to molar ratio EO:Li of 10:1, 6:1, 2:1 and 1:1. Additionally, thin foil of branched PEO without salt was prepared by pouring molten polymer onto a teflon dish.

For characterization of the obtained films by differential scanning calorimetry (DSC) small fragments of the samples were encapsulated in pans for volatile samples and investigated using Thermal Analysis Q 2000 calorimeter.

The impedance spectra were measured in the frequency range from 10^7 to 10^{-2} or 10^{-3} Hz. Two types of measurement holder were used: with gold-plated stainless steel electrodes and with trans-
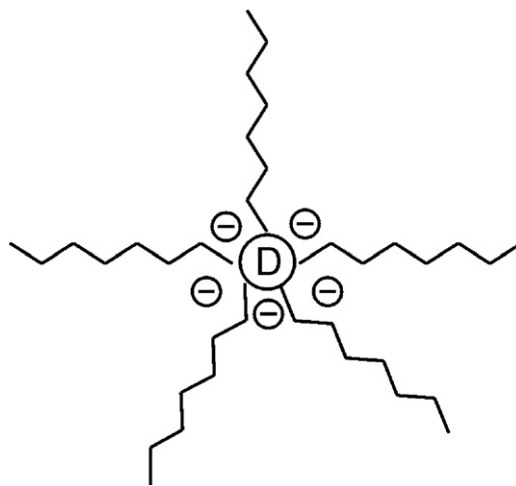
Scheme 1. Schematic representation of star-branched structure with first generation of arms: D – diepoxide core; Θ – reactive sites on the core (OP(O)(ONa)$_2$ or OH groups). Lines represent PEO chains.
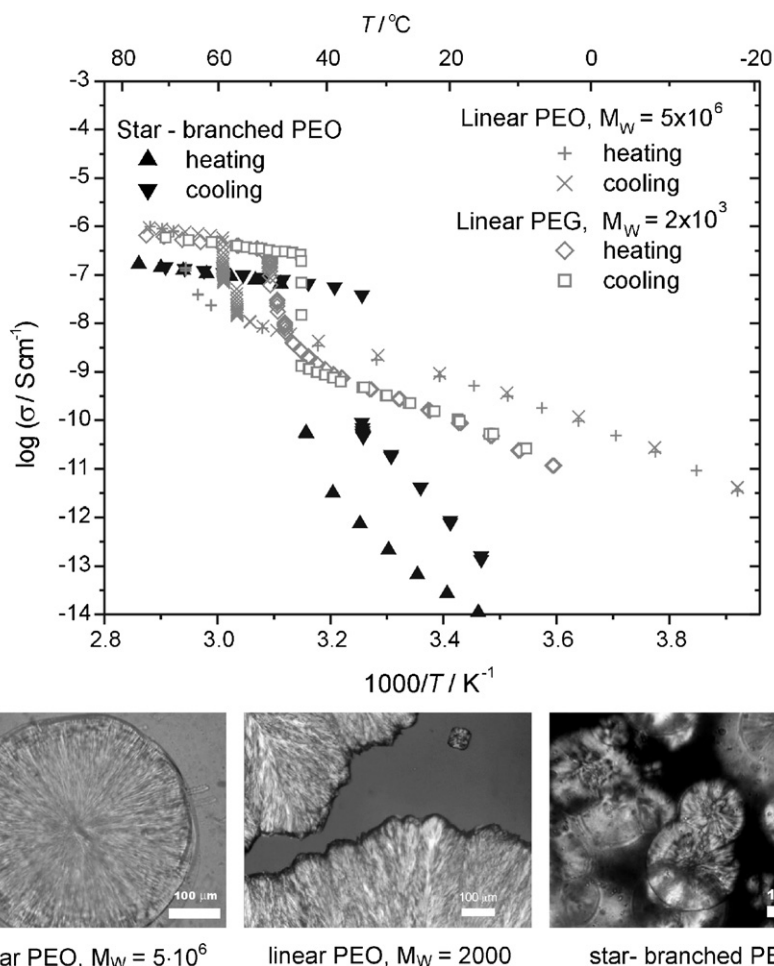
Fig. 1. Temperature dependence of conductivity for commercial PEO of different molecular weight (grey symbols) and for the star-branched PEO (filled black symbols). Polarizing microscope pictures (below) show typical morphology of crystallites, captured during early stage of crystallization.

parent electrodes. The second type of holder enabled impedance measurements simultaneous with polarizing microscope observation and was used for investigation of crystallization and melting phenomena. Glass plates covered with conductive ITO (indium tin oxide) layer formed a measurement cell, which was placed in a gas-tight holder sealed with an O-ring. The electrolyte sample, in the form of thin discs was placed in the holder under argon atmosphere. A small piece of metallic lithium was also placed inside the holder as an indicator of contamination. The holder was mounted on a microscope stage heated or cooled by Peltier elements. To prevent moisture condensation on the holder and the microscope objective, the microscope was placed in a dry box. The technical details regarding the experimental setup have been previously described [23].

Before and after the acquisition of the whole impedance spectrum, a short test scan was executed, with a wide frequency range from 10^7 to 3.16 Hz and only two frequencies per decade. Basing on the root-mean-square relative difference of the impedance (drift) calculated for these two test scans, the custom written measurement program modified the temperature ramps. A constant temperature was held as long as the impedance drift was larger than a preset drift limit. This way the mode of experiment was automatically switched between the study of the temperature dependence to the recording of the time dependence at constant temperature of both the microscopic picture and the impedance spectrum. Thus crystallization and melting of polymer electrolytes could be investigated in semi-isothermal conditions until the system reached steady state [24].

3. Results and discussion

3.1. PEO without salt

The temperature dependence of conductivity for the star-branched PEO without salt is presented in Fig. 1. For comparison, we have plotted conductivity measured under similar conditions for high molecular weight PEO ($M_W = 5 \times 10^6$, Aldrich), and low molecular weight PEG ($M_W = 2000$, Merck). For all polymers studied, the temperature dependence of conductivity follows a similar scheme: on cooling of molten (amorphous) sample, the conductivity decreases gradually. Then a steep decrease of conductivity (by more than one order of magnitude) takes place at constant temperature. According to the polarizing microscope pictures taken simultaneously with impedance measurement, this event is related to crystallization. On further cooling, the conductivity continues to decrease gradually. For linear high molecular weight PEO, the data in this temperature range were fitted well with Vogel–Tamman–Fulcher (VTF) function. For other samples, the measurement range was too narrow to determine the character of temperature dependence of conductivity.

A comparison of the data obtained for different polymers above melting temperature (about 70 °C for high molecular PEO, 50 °C for low molecular weight PEG and 47 °C for branched polymer) reveals that the conductivity of the branched polymer is 8 times lower than that of linear polymer. This difference can be understood if one takes into account the preparation method. The branched polymer

has been purified according to procedure described above, which resulted in removal of most low-molecular weight impurities. The two samples of linear PEO were cast from commercially available PEO, and they probably contain stabilizers, and remnants of the synthesis process. Therefore, the number of charge carriers in those samples is much greater.

Upon crystallization, the conductivity of branched PEO exhibits a very significant decrease by a factor of about 300. This is more than in the case of linear PEO, for which the conductivity of semicrystalline polymer was 100 times lower than that of amorphous polymer before crystallization. Such result seem to contradict the assumption that the branched structure decreases crystallinity of the electrolyte. The polarizing microscope pictures taken during crystallization process of branched and linear PEO reveal differences between morphology of crystallites in each case. For high molecular weight PEO, the spherulites are circular in shape and have usually a large diameter (of about 2 mm). The observed morphology can be classified as II or II/I regime of growth according to the Hoffmann classification [25]. For low molecular weight PEG, development of densely packed stacks of lamellae was observed, which formed polygonal growth front. As a consequence, the crystallites were axially oriented; such morphology indicates a stronger tendency towards regime I of growth. For the branched polymer a large number of small, circular crystallites with faint maltese cross pattern was observed with crossed polarizers. Their appearance can be classified as belonging to regime II.

The difference between crystallization regimes of different samples can be understood in terms of a greater number of polymer chain entanglements in the branched polymer. As a consequence, a greater number of defects constrains the lamellae width. This can also account for slightly lower melting temperature, and significantly lower crystallization temperature of the branched polymer (with similar drift detection criteria applied). Therefore, from the microscope observations it seems that the morphology of semicrystalline star-branched polymer should create better conditions for the ion transport than morphology of linear polymer. However, the conductivity is directly determined not only by the content of crystalline and amorphous phase, but relays on a number of other factors. The most important is continuity of amorphous pathways between the electrodes. These pathways can be blocked by crystalline phase within the electrolyte, but also at the electrolyte/electrode interface [26]. Analysis of impedance spectra revealed a significant decrease of value of the double layer capacitance related to crystallization. Such decrease is related to partial loss of contact of polymer electrolyte with the electrodes. Upon cooling after crystallization, a number of large cracks within the electrolyte was observed in the microscope pictures. This confirms that the electrolyte is stiff and detaches from the electrode surface, which can be partially responsible for the observed decrease of conductivity.

3.2. Electrolyte with molar ratio EO:Li equal 10:1

The electrolyte of this molar ratio was chosen as it corresponds to the eutectics between pure PEO and PEO$_6$:LiTFSI complex [12]. For low molecular weight linear PEO, a so called "crystallization gap" was observed in this eutectic range. In our recent publication, we have revealed that for the high molecular weight linear PEO, the crystallization can proceed quite effectively even for the eutectic composition, due to cooperative growth of spherulites of the two crystalline phases, PEO$_6$:LiTFSI complex and pure PEO [27]. The decrease of conductivity related to this crystallization process is visible in Fig. 2 at about 0 °C. It should be noted, that for electrolyte based on the linear PEO it was possible to overcool amorphous sample to a temperature at which crystallization was not possible due to proximity of the glass transition temperature.
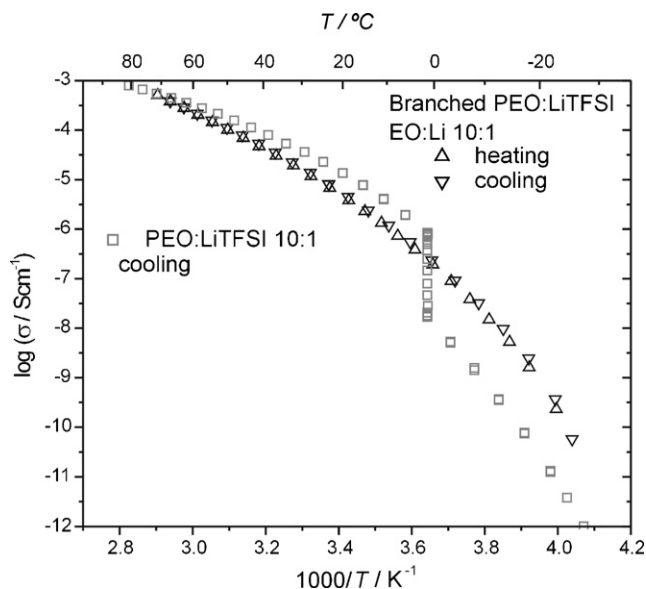

Fig. 2. Temperature dependence of conductivity for electrolyte with molar ratio EO:Li of 10:1 comprising star-branched PEO and LiTFSI. Cooling run for the electrolyte based on the high molecular weight linear PEO is shown for comparison.

In such case, the crystallization took place on following gradual heating.

In the case of electrolyte based on the branched PEO, there was no indication for any decrease of conductivity caused by crystallization. The temperature dependence of conductivity (Fig. 2) was fitted well with VTF function in the whole measured temperature range. Polarizing microscope pictures have also confirmed that the electrolyte was fully amorphous. In the temperature range in which electrolytes with linear and branched matrix are amorphous, the values of conductivity of electrolyte based on branched PEO are comparable to, or slightly lower than conductivity of electrolyte based on linear PEO. A more pronounced decrease of conductivity with decreasing temperature for electrolyte based on branched PEO can be related to higher glass transition temperature (−26 °C in comparison to −39 °C for electrolyte with linear PEO—Table 1). However, in the range of temperature in which electrolyte based on linear PEO is semicrystalline, the difference in conductivity values is about 50 times in favour of the electrolyte with branched matrix.

3.3. Electrolyte with molar ratio EO:Li equal 6:1

The molar ratio of this electrolyte corresponds to the stoichiometry of PEO$_6$:LiTFSI crystalline complex. On a phase diagram of the linear PEO–LiTFSI salt system, the crystalline phase of this complex has melting temperature lower than that of pure PEO [12]. Our study of electrolytes based on high molecular weight linear PEO has revealed that for electrolyte of this composition, the decrease of conductivity related to crystallization is particularly large [5]. This process can be observed in Fig. 3 as an isothermal drop of conductiv-

Table 1
Selected properties electrolytes of different molar ratio EO:Li based on linear or star-branched PEO and LiTFSI salt, estimated for samples in amorphous state (where possible). T_g, the glass transition temperature estimated by DSC; $R_\tau{}^*$, the decoupling index calculated at T_g. L, linear PEO, $M_W = 5 \times 10^6$, Aldrich; B, star-branched PEO.

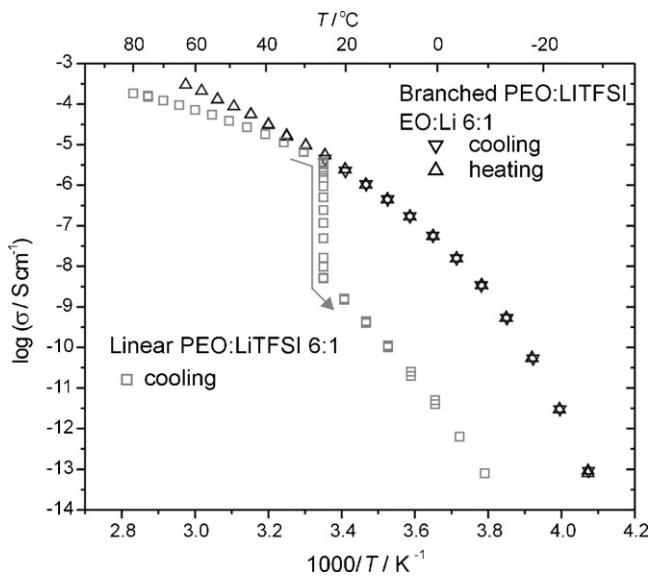| Molar ratio EO:Li	10:1		6:1		2:1		1:1	
	L	B	L	B	L	B	L	B
T_g (°C)	−39	−26	−27	−22	5	6	23	13
$\log R_\tau{}^*$	2	4	2.5	3	3	5	4.5[a]	6.5

[a] Semicrystalline.

Fig. 3. Temperature dependence of conductivity for electrolyte with molar ratio EO:Li of 6:1 comprising star-branched PEO and LiTFSI. Cooling run for the electrolyte based on the high molecular weight linear PEO is shown for comparison.

Fig. 4. Temperature dependence of conductivity for electrolyte with molar ratio EO:Li of 2:1 comprising star-branched PEO and LiTFSI. Cooling run for the electrolyte based on the high molecular weight linear PEO is shown for comparison.

ity at a temperature of 25 °C. The conductivity of the semicrystalline electrolyte was over 500 times lower than that of the amorphous one, which can be attributed to dense-packed crystalline phase, observed in polarizing microscope pictures [5].

The conductivity of electrolyte based on the branched PEO was comparable, or slightly higher, than that of electrolyte with the linear PEO in the amorphous state (above 25 °C; Fig. 3). A much more pronounced difference between the two systems is observed below that temperature. Despite cooling to temperature much below the expected temperature of crystallization of PEO_6:LiTFSI complex, the electrolyte based on branched PEO did not crystallize, which was evidenced by polarizing microscope pictures. Therefore, it retained relatively high ionic conductivity. It is remarkable, that no traces of crystalline phase were detected also on subsequent heating run, and results obtained in following temperature cycles were highly repeatable. The sample did not change its appearance even after a few months of storage in argon atmosphere, which indicates that the observed behaviour does not represent a metastable state. Glass transition temperature estimated from the DSC measurements was −22 °C, which is 5 degrees higher than in the case of electrolyte based on linear PEO (Table 1).

3.4. Electrolyte with molar ratio EO:Li equal 2:1

This composition of the electrolyte corresponds to stoichiometry of crystalline complex PEO_2:LiTFSI. The melting temperature of this crystalline phase is much higher than that of pure PEO. In electrolytes based on high molecular weight PEO, melting of PEO_2:LiTFSI complex took place at about 115 °C, according to polarizing microscope observations and DSC results [13]. On cooling of molten sample, a decrease of conductivity corresponding to crystallization was observed at about 100 °C (Fig. 4). The crystalline phase observed in the polarizing microscope was less regular than in the case of PEO:LiTFSI 6:1 electrolyte, hence the decrease of conductivity was not as big, but still significant. It is worth to notice, that although the temperature dependence of conductivity plotted in Fig. 4 can be considered as representative, we have evidenced possibility of obtaining electrolytes in various metastable states [13]. The electrolyte based on linear PEO can be easily overcooled in amorphous state. Unexpectedly high value of ionic conductivity was obtained by rapid cooling of electrolyte to temperature below the
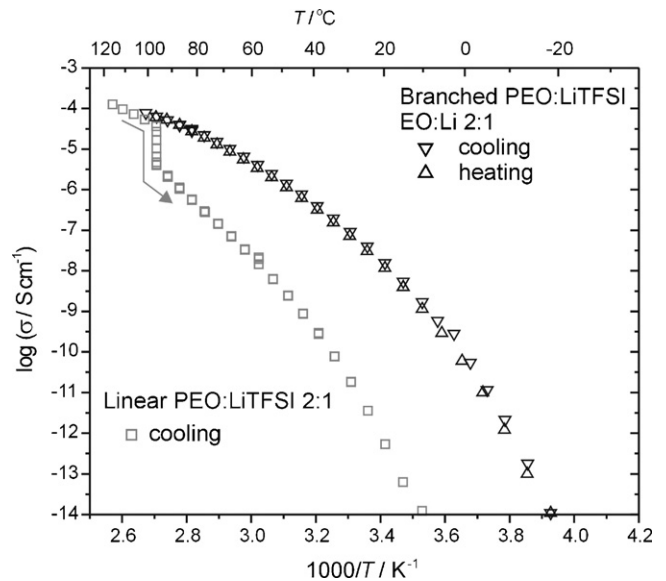
glass transition temperature. However, on gradual heating above room temperature the conductivity slowly decreased. Probably, the origin for such behaviour is related to the very high concentration of salt (77 weight percent of LiTFSI), which reaches solubility limit of the system at low temperature.

In the case of electrolyte based on the star-branched PEO, the effects described above were not detected. A very repeatable temperature dependence of conductivity was obtained for subsequent cooling and heating runs, as well as for heating after rapid cooling of the electrolyte. Similarly as in the case of electrolytes with molar ratios of 6:1 and 10:1 EO:Li, the 2:1 EO:Li electrolyte remained amorphous in the whole investigated temperature range, which was confirmed by the polarizing microscope observations. The glass transition temperature T_g = 6 °C obtained by DSC is in this case about the same as that of electrolyte based on linear PEO (T_g = 5 °C for rapidly cooled amorphous sample—Table 1). However, the decrease of conductivity with decreasing temperature (Fig. 4) is less pronounced. In the DSC traces obtained for sample of electrolyte based on star-branched PEO subjected to a few months storage time, a melting peak has been observed at 75 °C, followed by a much weaker second endothermic event at 134 °C.

3.5. Electrolyte with molar ratio EO:Li equal 1:1

In the temperature range available in our experimental equipment, the concentration of LiTFSI salt corresponding to the molar ratio of EO:Li 1:1 surpasses the solubility limit in the linear PEO. Therefore, presence of salt precipitates is expected. In electrolyte based on linear PEO, such effect has been evidenced [6]. Crystallization of pure salt resulted in a highly inhomogeneous structure of electrolyte, which was stiff, fragile and had a granular pattern. In the SEM pictures a crystalline "skeleton" with large pores was observed. This crystalline structure did not melt in the range of temperature available for microscope and impedance measurements (up to 130 °C). Such structure of electrolyte resulted in poor electrical contact with electrodes, which had a significant impact on the measured value of conductivity (Fig. 5). For cooling run, two subsequent events leading to a steep decrease of conductivity can be observed, one at 100 °C and second one at 55 °C. Both processes correspond to crystallization of the amorphous phase remaining in the electrolyte. Analysis of impedance results leads to conclusion
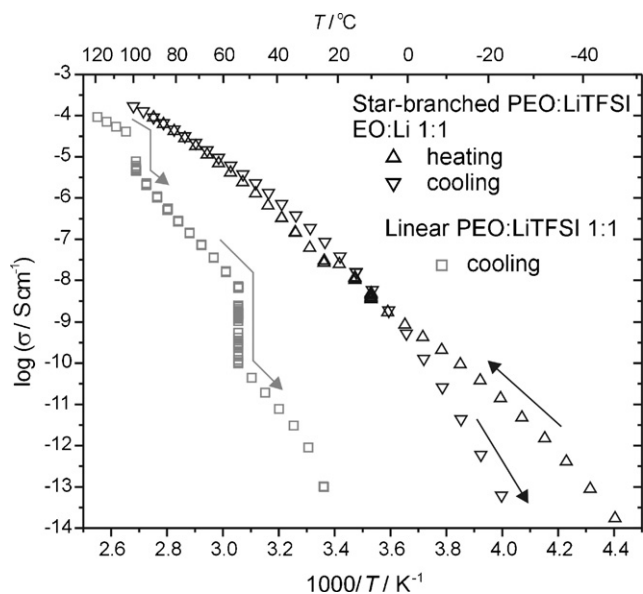
Fig. 5. Temperature dependence of conductivity for electrolyte with molar ratio EO:Li of 1:1 comprising star-branched PEO and LiTFSI. Cooling run for the electrolyte based on the high molecular weight linear PEO is shown for comparison.

that in this case, the magnitude of the decrease can be attributed mainly to a loss of the electrical contact at the electrode/electrolyte interface, which becomes the "weakest link" in the ion transport.

In the case of electrolyte based on the branched PEO, the phase segregation effect mentioned above was much less pronounced. The samples were obtained as a liquid of high viscosity. For a sample kept at room temperature under argon, first salt precipitates started to occur only after a few weeks storage time. The temperature dependence of conductivity of the electrolyte, measured between gold-plated electrodes is depicted in Fig. 5 for two subsequent runs: heating of electrolyte which has been previously gradually cooled to −50 °C, and subsequent cooling. In the temperature range between −50 °C and 0 °C, unexpectedly high values of ionic conductivity have been obtained. This temperature range is below the glass transition temperature of the studied system (T_g = 13 °C as estimated from DSC for rapidly cooled amorphous sample—Table 1), which indicates that the ion transport is strongly decoupled from the polymer matrix. This effect can be quantitatively characterized by value of the decoupling index R_τ^*, calculated at T_g [28]:

$$\log R_\tau^* = 14.3 + \log \sigma_{T_g} \qquad (1)$$

where the conductivity measured at the glass transition temperature is expressed in units S cm^{-1}. For the studied electrolyte with molar ratio of EO:Li equal 1:1 the obtained value of $\log R_\tau^*$ was about 6.5, whereas for PEO:LITFSI 10:1 electrolyte based on the same branched matrix a lower value of $\log R_\tau^*$ equal 4 has been obtained. For electrolytes based on linear PEO, a similar estimation gave values of about 2 for PEO:LiTFSI 10:1 electrolyte and 4.5 for PEO:LiTFSI 1:1—Table 1.

The amorphous state of polymer electrolyte with molar ratio EO:Li equal 1:1 based on branched PEO, observed in the initial cooling and heating run was metastable. On heating above 0 °C, a drift of impedance has been detected. In simultaneous impedance and polarizing microscope measurements performed in this temperature range in a similar temperature cycle (the measurements could not be extended below −20 °C due to the equipment limitations), an occurrence of inhomogeneity of electrolyte has been detected. It was not possible to unambiguously identify the crystalline phase—however, precipitation of crystalline LITFSI salt is probable. This event caused a slight decrease of con-

ductivity. On heating, the observed crystallites did not melt and electrolyte remained inhomogeneous. In the following cooling run, the decrease of conductivity related to temperature was more pronounced, which can be explained by weaker decoupling in a semicrystalline electrolyte. In the DSC trace of semicrystalline electrolyte, an endothermic step related to glass transition was observed at T_g = −3 °C. This is much lower than for rapidly cooled amorphous sample (T_g = 13 °C). Two subsequent melting events, one at 75 °C and second at 135 °C indicated that the sample contained two different crystalline phases. The significant difference between values of T_g obtained for semicrystalline and amorphous sample can be partially explained by difference of the content of salt in the amorphous phase [29]. In semicrystalline system the amount of salt in amorphous phase seems to be lower than the average concentration in the electrolyte. In our recent publication we have shown that crystallization of pure LiTFSI drains salt from the surrounding amorphous regions [6]. Therefore, the melting peak at 135 °C can be associated with LiTFSI.

It should be noted that, despite the crystallization processes described above, in general the ionic conductivity of the EO:Li 1:1 electrolyte based on branched PEO is significantly higher than that of the electrolyte based on high molecular weight linear PEO. Even after long crystallization time, the share of amorphous phase in electrolyte with star-branched PEO is still significant, and the electrolyte retains good mechanical properties. Much weaker phase segregation effect may indicate higher solubility of LiTFSI salt in the studied matrix.

4. Conclusions

Electrolytes based on the star-branched PEO seem to provide an interesting alternative for electrolytes based on the linear PEO. In the range of composition between EO:Li 10:1 and 2:1 the electrolytes remain amorphous, giving highly repeatable values of ionic conductivity in subsequent heating and cooling runs. At temperature range below the melting temperature of electrolytes with linear PEO matrix, the conductivity of electrolytes based on branched PEO is much higher, as the movement of ions is not disturbed by the presence of insulating crystalline phase. The investigated electrolytes exhibit also higher solubility of LiTFSI salt in the polymer matrix in comparison to the high molecular weight linear PEO. Amorphous state of the electrolyte can be obtained up to the molar ratio of EO:Li equal 1:1. Although weak effects of phase segregation (probably related to precipitation of salt) were recorded upon subsequent heating and cooling runs of this electrolyte, it appears to be much more homogeneous than electrolyte of identical molar ratio based on linear PEO. Moreover, the plot of the temperature dependence of conductivity indicates high degree of decoupling of ion transport from polymer matrix, which makes the studied system well suited for development of "polymer in salt" electrolytes.

The study, however, has revealed two main disadvantages of PEO:LiTFSI electrolytes based on branched PEO. One issue is related to higher values of the glass transition temperature in comparison to electrolytes based on linear PEO, which has been observed in the DSC curves and, to some extend, in the temperature dependence of conductivity. This effect occurred only for the electrolytes with low and medium concentration of salt; in electrolytes with high concentration of salt, an opposite trend has been observed. A second problem, that needs to be solved if the studied electrolytes are intended for practical application, is improvement of their mechanical properties. All of the investigated electrolytes with LITFSI salt were obtained in the form of a viscous liquid, which does not provide enough self-support to be a good membrane for the rechargeable battery. Introduction of a filler into the branched polymer matrix is planned to provide such support.

Presented results show that conductivity of electrolyte with branched polymer is similar to that of electrolytes based on linear PEO in the amorphous state. To meet the requirements of application in a battery, further study on improvement of conductivity will be carried. The studied system allows introduction of various functional groups into the polymer structure, either at the diepoxide core or at the chain ends, which can be used to promote dissolution of the salt and enhance transport of charge carriers. Once the limitations mentioned above are overcome, the studied branched PEO can become an attractive material for design of novel polymer electrolytes.

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