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Structure and lithium transport phenomena in a new tripodand-grafted polysiloxane

Summary — New polymeric host for Li$^+$ cation-conducting polymer electrolytes has been described. Poly(methyl(2-(tris(2-(2-methoxyethoxy)ethoxy)silyl)ethyl)siloxane) trimethylsilyl terminated, average molecuar weight 19 100, has been synthesized by catalytic hydrosilylation reaction between a polysiloxane and appropriate vinyl-functionalized tripodand-type silane. On the basis of the obtained macromolecule a flexible polymer electrolyte membrane has been prepared by dissolving appropriate amount of lithium salt (LiPF$_6$) in the polymer matrix. Relation between the molecular structure and lithium cation conduction mechanism has been studied and discussed in terms of temperature dependence of specific conductivity and lithium cation transport number. The issue of decoupling of cationic mobility from polymer segmental motions has been addressed and discussed on the basis of solid state ^{7}Li NMR measurements.

Keywords: polymer electrolyte, Li-ion battery, podands, solid-state ^{7}Li NMR.

STRUKTURA I PRZEWODNICTWO KATIONÓW LITU W NOWEGO TYPU POLISILOKSANIE Z BOCZNYMI GRUPAMI TRÓJPODANOWYMI

Streszczenie — Zbadano właściwości zsyntetyzowanego nowego typu polimerowego elektrolitu z mechanizmem przewodzenia opartym na kationach litu. Na drodze katalitycznej hydrosililacji, przy użyciu polisiloksanu i trójpodandu krzemowego z grupą winylową otrzymano poli(2-tris(2-(2-metoksyetoksy)etyloksy)sililoetylo)metylosiloksan o średnim ciężarze cząsteczkowym 19 100. W wyniku rozpuszczenia w wytworzonej matrycy polimerowej soli litu (LiPF$_6$) uzyskano elastyczne membrany elektrolitowe. Określano zależność właściwości elektrochemicznych oraz mechanizmu przewodnictwa jonowego od struktury kompleksu polimer-sól litu. Na podstawie pomiarów ^{7}Li NMR rozważono problem braku sprzężenia dynamiki łańcucha polimerowego i dynamiki kationu litu. Struktura molekularna zsyntezowanego związku zawiera centra trójpodandowe przyłączone do polisiloksanowego łańcucha głównego (rys. 1). Polimer wykazuje strukturę amorficzną ze słabo zaznaczoną przemianą szklistą w temperaturze z zakresu 10—20 °C (rys. 2, 3). Zależność logarytmu przewodnictwa od odwrotności temperatury, wyznaczona dla kompleksu polimer-sól litu, ma przebieg prostoliniowy, co sugeruje nietypowy dla polieterowych elektrolitów polimerowych mechanizm przewodnictwa, oraz brak sprzężenia pomiędzy ruchami termicznymi segmentów polimerowych a transportem jonowym (rys. 4). Liczba przenoszenia kationu litu jest stosunkowo duża, co wskazuje na znaczną ruchliwość kationu Li$^+$ (rys. 5). W celu dokładniejszej oceny dynamiki kationu wykonano ^{7}Li NMR uzyskanego kompleksu w szerokim zakresie temperatury i określono zależność szerokości piku od temperatury (rys. 6). Zależność ta nie wykazuje charakterystycznego przegięcia w temperaturze przemiany szklistej, co potwierdza przypuszczenie o braku sprzężenia dynamiki polimeru z dynamiką kationu. Ponadto zaobserwowano rozszczepienie piku NMR poniżej temperatury ok. -30 °C, co przypisano dwóm odmiennym koordynacjom kationu przez eterowe atomy tlenu. Badania pozwoliły na zaproponowanie nowego typu mechanizmu transportu litu w polimerze, charakterystycznego dla obecności zorganizowanych centrów podandowych (rys. 7, schemat A). Otrzymany polimer jest interesującym przykładem przewodzącej matrycy dla kationów i może stanowić podstawę do wytwarzania wysokoprzewodzących elektrolitów polimerowych do akumulatorów litowych.

Słowa kluczowe: elektrolity polimerowe, akumulatory litowo-jonowe, podandy, ^{7}Li NMR.

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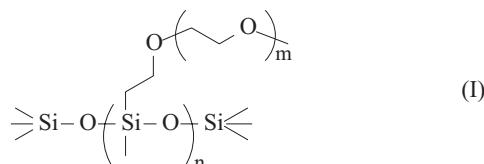[2)] Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland.

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Complexes of various polymers with lithium salts have been investigated for a long time as potential solid electrolytes for a new generation of liquid-free lithium-ion (Li-ion) batteries. In this respect, electrolytes based on poly(ethylene oxide) and its derivatives have attracted by far the greatest attention. In this type of materials lithium cations are coordinated by ether oxygen atoms in either the main chain or side chains of the polymer host [1—3].

Transport of lithium cations in most of these polymer architectures is coupled with random thermal motions of entangled polyether segments. The major drawback of this mode of ionic transport is that, in spite of great efforts, the measured room temperature conductivity still remains too low in most cases for any practical application. It thus seems clear that the idea of coupling of cationic transport with segmental movements has fundamental inherent limitations. Therefore is seems justified to search for new polymeric structures that would enable decoupling the two processes.

In our laboratory we have been considering a concept of arranging lithium coordination sites in polymeric materials in ordered structures. The idea is based upon a hypothesis that one-dimensional array of vicinal, relatively rigid lithium coordination sites would create pathways for favorable cation transport. One possible way of realizing this idea is grafting a polysiloxane chain with the so-called silicon tripodand centers. A tripodand center is formed by linking three polyether units to a common silicon atom [4—7]. This may be done by reaction of appropriate silane (silicon tripodand with vinyl functional groups) with a polysiloxane having Si-H bonds on one side of the chain. This simple concept has already proved to be promising in terms of synthesis and basic characteristics. Podands are non-cyclic structures in which several polyoxyethylene chains are linked to a common central atom (for example silicon) or to a larger structural arrangement. Number of oxygen atoms constituting the chains and their length determine the ability of the podand center to form complexes with alkali metal cations. Podands are sometimes called open-chain analogues of crown ethers and cryptands, however they are characterized by low cost, ease of synthesis and non-toxicity [7]. Certain liquid silicon tripodands have recently been proved to be a promising functional co-solvents/additives for Li-ion battery electrolytes [8, 9].

The idea of grafting a polysiloxane main chain with polyether units is not new and has been proposed by Khan *et al.* [10] as early as in 1988. More recently a similar approach has been described by Oh *et al.* [11]. Based on a similar general concept, various copolymers with comb, double comb, cyclic and cross-linked structures have been reported in the recent years [12—24]. In one of the most recent works, Rossi *at al.* [12] have reported, among others, a family of oligomeric structures analogous to the one shown (I).

Depending on the parameters n (1—2), m (2—7) and the number of carbon atoms in the spacer between the polyether chain and the siloxane backbone (0—3), conductivities ranging from 1.87 mS/cm up to 5.75 mS/cm have been measured at 25 °C. LiBOB or LiTFSI [lithium bis(trifluoromethanesulfonyl)] have been used as lithium salts.

In our previous work we have demonstrated that polymer electrolytes prepared by dissolving $LiPF_6$ in poly(methyl(2-(tris(2-methoxyethoxy)silyl)ethyl)siloxane) trimethylsilyl terminated, average molecular weight 13 800 [structure shown (II)], not only can be formed into flexible membranes but, more importantly, exhibit very high room temperature specific conductivities and anodic stability [25]. The most important feature of this type of structures, especially in comparison with those considered by Rossi and others, is a peculiar type of self-assembling. Three polyether chains linked by the central silicon atoms constituting silicon tripodand centers, will always have strong tendency to enclose around one Li^+ ion, thus creating an ordered array of "cages" (II).

(II)
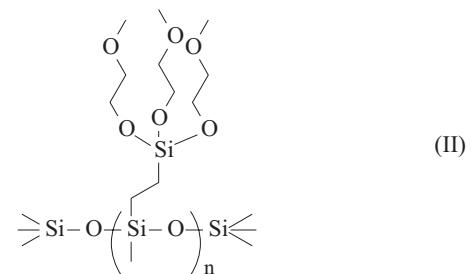
In the present work we further explore the relationship between molecular structure and cation transport properties of these "tripodand-type polymers". Synthesis of a new polymer from this family has been described. Apart from conventional physico-chemical and electrochemical characterization, a series of solid-state ^7Li NMR measurements in a wide range of temperatures has been performed in order to get closer insight into the cation transport mechanism.

EXPERIMENTAL

Materials

The following materials were used in this work:

— solution of poly(methylhydrosiloxane), trimethylsilyl terminated (Merck), average molecular weight 2550;

— anhydrous benzene (Merck);

— vinyl tris(2-(2-methoxyethoxy)ethoxy)silane (Merck);

— Karstedt catalysts, 3 % solution in xylene;

(I)

— polymer LiPF$_6$ (Aldrich, 99.99 %);
— acetonitrile (pure p.a., POCh).

Polymer synthesis

The polymer has been synthesized according to the equation (1):

$$(1)$$
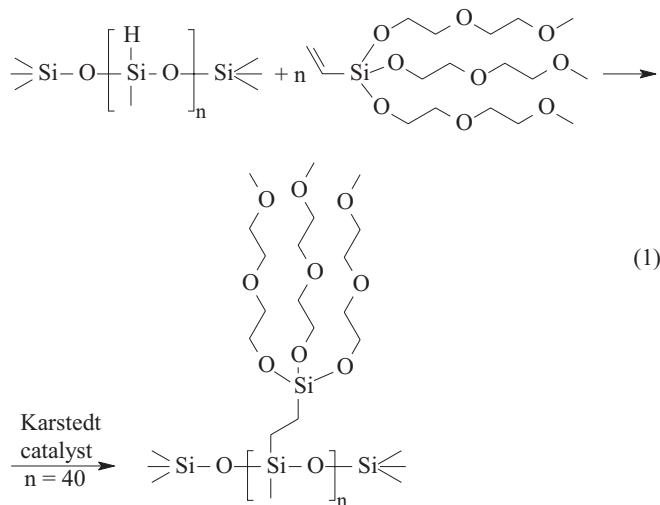
The procedure was similar to that described in the work [25]. To the solution of poly(methylhydrosiloxane) trimethylsilyl terminated (25 g, Gelest), in anhydrous benzene (25 cm^3), vinyl tris(2-(2-methoxy-ethoxy)ethoxy)silane (160 g) and Karstedt catalyst (0.01 cm^3) were added. The obtained mixture was stirred at 50 °C and the conversion was monitored by ^{1}H NMR. After about 150 h no SiH and vinyl hydrogen signals were observed. The NMR data are the following: ^{1}H NMR (C$_6$D$_6$): δ 3.78 (t, 6H, SiOC**H$_2$**); 3.51 (t, 6H, **CH$_2$**OCH$_3$), 3.45 (m, 12H, **CH$_2$**O); 3.22 (s, 9H, OC**H$_3$**); 0.44 (bs, 2H, CH$_3$SiC**H$_2$**); 0.34 [bs, 2H, C**H$_2$**Si(OR)$_3$]; 0,11 (s, 3H, C**H$_3$**SiCH$_2$); 0,02 [s, 0.4 H, (C**H$_3$**)$_3$SiO]. The solvent was evaporated in vacuum and the polymer was obtained as a colorless, transparent gum-like substance. All operations were carried out under inert atmosphere.

MM+ semi-empirical method was used for modeling and visualization of the molecular structure of the synthesized compound [26].

Polymer electrolyte preparation

Polymer electrolyte was prepared by solvent — casting technique. The polymer, LiPF$_6$ and acetonitrile were mixed together and left for 48 h under stirring. The solution was then poured onto PTFE dish and left for another several days for slow solvent evaporation. Molar ratio of ether oxygen atoms to lithium cations (O:Li) was 12.9:1 (explication later in the text). For electrochemical tests, the membranes were cut into round slices of 12.2 mm diameter, followed by placement in electrochemical cells. Typical thickness of the electrolyte membranes was

0.30—0.35 mm. All the operations were carried out in a glove-box filled with argon (water content <20 ppm).

Methods of testing

— DSC measurements have been carried out for pure polymer and polymer/salt complex using Netzsh DSC 200 differential scanning calorimeter. The samples were cooled down to -25 °C or -45 °C followed by heating up to 70 °C at the rate of 5 °C/min.

— Wide angle XRD patterns have been recorded for pure polymer and polymer/salt complex using Phillips PW-1710 diffractometer with CuKα radiation. XRD measurements have been performed at 25 °C.

— ^{7}Li NMR spectra have been recorded using the BRUKER DSX-300 AVANCE spectrometer. Chemical shift was defined as LiCl = 0 ppm, resonance frequency: 116.642 MHz, rotation speed: 6 kHz, spectral range: 100 kHz, number of scans: 40.

— Conductivity was measured in two-electrode symmetrical cells with stainless steel electrodes, using Voltalab PGZ-301 potentiostat/galvanostat with frequency response analyzer. The cells were thermostated using Votsch climatic chamber. The temperature was controlled with the accuracy of ±0.2 °C. Conductivity was calculated conventionally by fitting the corresponding Nyquist plots. Three measurements (cells) were done for each individual electrolyte and for the purpose of analysis and presentation the median values were taken.

— Lithium transport number has been calculated according to the procedure proposed by Bruce and Vincent [27—30].

— Direct current polarization and impedance spectroscopy measurements have been performed with the application of two-electrode Li/electrolyte/Li cells, using PARSTAT 2263 aparatus.

RESULTS AND DISCUSSION

As it might be expected on the basis of earlier experience, reaction of a polysiloxane reagent with a suitable double bond-functionalized silicon tripodand resulted in a desired polymer architecture [25]. This can be described as polysiloxane backbone grafted with Si-tripodand centers. The developed synthesis scheme may thus be regarded as versatile for obtaining such a particular polymer architectures. Fig. 1 shows the molecular model of the silane reagent — lithium cation complex, as well as visualization of the synthesized polymer host. The polymer has a wax-like consistency and is transparent and yellowish in color.

Due to the presence of polyether side elements the whole polymer is expected to form complexes with lithium salts, similarly to polyethylene oxide hosts. Indeed, polymer-LiPF$_6$ complex has been prepared in a conventional manner by dissolving both polymer and salt in acetonitrile and casting on a Teflon dish. After sol-
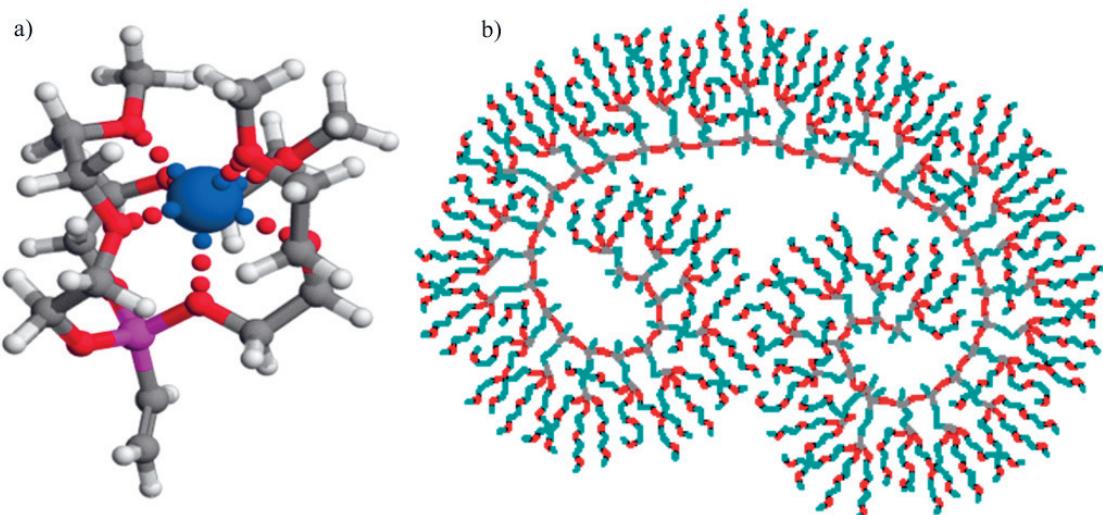
Fig. 1. Molecular model calculated for the complex of vinyl tris(2-(2-methoxyethoxy)ethoxy)silane with Li⁺ (a) and visualization of poly(methyl(2-(tris(2-(2-methoxyethoxy)ethoxy)silyl)ethyl)siloxane) trimethylsilyl terminated, average molecular weight 19 100 (b)

vent evaporation the resulting solid electrolyte membranes are robust enough to be cut into round slices. This feature is essential for further consideration of a new polymer matrix as viable solid electrolyte for lithium batteries. The apparent increase of mechanical stability of the polymer after the salt dissolution can be explained in terms of self-organization of short polyoxyethylene chains forming "tripodand cages" in the presence of

This does not, however, exclude the possibility of some two-dimensional ordering in the microstructure of the complex. It is also difficult to find a classical glass transition on the DSC curves (Fig. 3). However, certain phase (glass-like) transition can be observed on a cooling scans for both materials between 10 and 20 °C. This is in
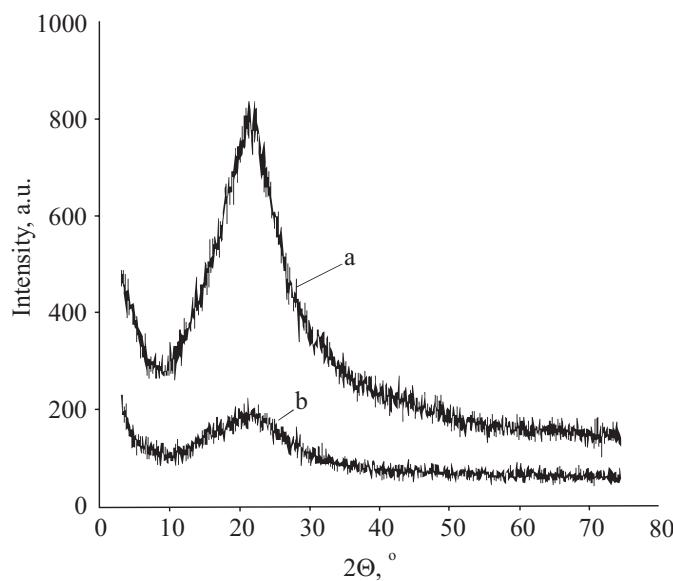

Fig. 3. DSC traces recorded for the pure polymer (solid lines) and for the polymer/salt complex (dashed lines)

Fig. 2. XRD patterns recorded for the pure polymer (a) and for the polymer/salt complex (b)

cation, leading to some kind of order in the microstructure. However, no signs of crystalline ordering can be detected by means of wide-angle XRD technique neither for pristine polymer nor for the complex with lithium salt (see Fig. 2).
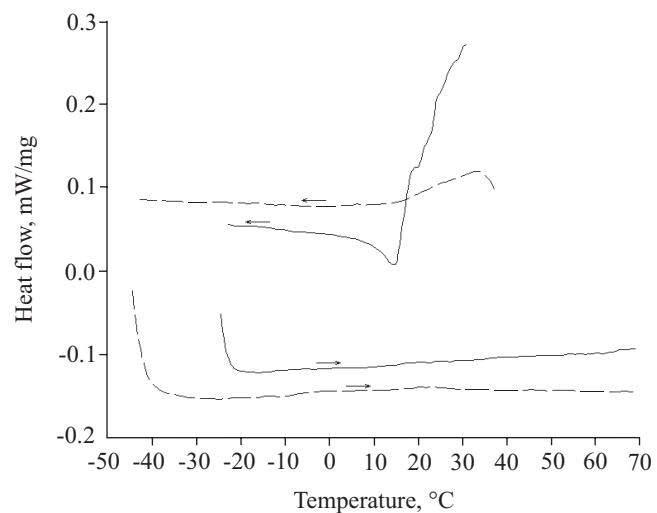
rough agreement with transitions observed earlier for a similar polymer structure [25]. One can assume, however with no certainty, that some suppression of segmental motions occurs at this temperature range. One can expect somewhat lower T_g for polysiloxane structure, however one should also keep in mind that the presence of lithium salt significantly modifies the physico-chemical properties, especially when polyether side chains are present, making the molecular structure more rigid.
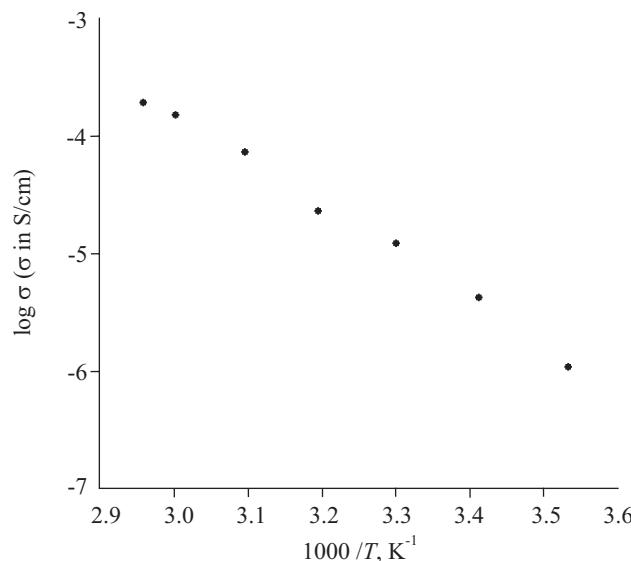
Fig. 4. Arhenius plot determined for the polymer/salt complex

Fig. 5. Summary of the determination of cationic transference number; the main frame — Nyquist plots, the inset — polarization curve

Fig. 4 shows the temperature dependence of specific conductivity measured for the polymer/salt complex in Arhenius coordinates. Specific conductivity at 25 °C was determined as $\sigma_{25} = 4.3 \cdot 10^{-6}$ S·cm^{-1}. Assuming that the presented dependency in the analyzed temperature range is linear, activation energy of cationic transport was determined as $E_a = 61.3$ kJ/mol.

Cationic transference number t^+ has been estimated according to the equation (2):

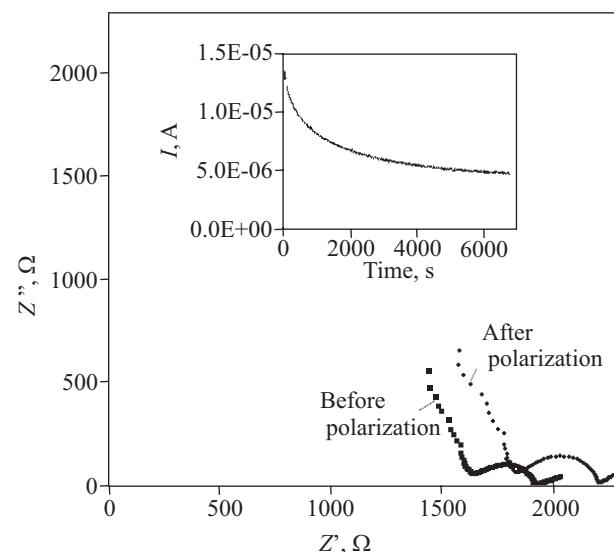$$t^+ = I_\infty(\Delta V - I_0 R_0) / I_0(\Delta V - I_\infty R_\infty) \qquad (2)$$

where: R_0 — *initial charge transfer resistance*, R_∞ — *steady state charge transfer resistance*, I_0 — *initial current*, I_∞ — *steady state current*, ΔV — *polarization potential*.

The values of I_0 and R_0 (before polarization) have been determined as $1.37 \cdot 10^{-5}$ A and $2.85 \cdot 10^2$ Ω respectively, whereas the values of I_∞ and R_∞ (after polarization at $V = 30$ mV) — as $1.80 \cdot 10^{-6}$ A and $3.50 \cdot 10^2$ Ω respectively. The value of lithium cation transference number has been cal-
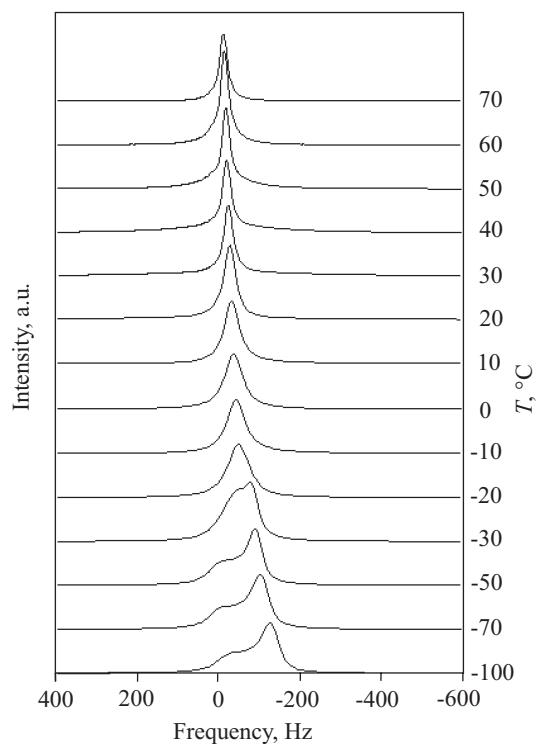

Fig. 6. ^{7}Li NMR spectra recorded for the polymer/salt complex at various temperatures (on the left) and the temperature dependency of the central peak's width (on the right)

culated as t^+ = 0.32. Corresponding polarization curve and impedance spectra are presented in the Fig. 5.

Solid state ^{7}Li NMR spectra have been recorded for the polymer/salt complex in several temperatures ranging from -100 °C up to 70 °C (see Fig. 6). Full widths at half maximum (*FWHM*) values measured for the central peaks have been plotted against temperature. With decreasing temperature the peak broadens gradually and finally splits into two signals at -30 °C. The splitting becomes more and more distinct as the temperature drops down to -100 °C. Interestingly, upon subsequent re-heating the two signals merge again into one. There are no clear signs of any abrupt change of the peak's width around 10—20 °C that could be ascribed to so-called motional narrowing.

As it has already been pointed out, self-organization of tripodand centers after doping with lithium salt leads to a structure in which polyether elements are highly ordered along the polysiloxane backbone (see Fig. 1). Such phenomenon has been described in the past for "free" Si-tripodands, but is also valid for Si-tripodand centers attached to a backbone. Semi-empirical studies reveal that such a Si-tripodand center comprising three oxygen atoms in each of the three polyoxyethylene chains {like for example EtSi[(OCH$_2$CH$_2$)$_2$OCH$_3$]$_3$} will form 1:1, 1:2 and 1:3 complexes with Li$^+$. Heats of formation (ΔHOF) of the respective complexes ware calculated as -104.28, -126.28 and -74.19 kcal·mol^{-1} [31]. Close vicinity of such cationic sites is likely to produce favorable conditions for Li$^+$ hopping (Fig. 7). Another advantage of such a concept is strong salt dissociation. Cation entrapped in a Si-tripodand cage will also be shielded from the environment, thus suppressing the formation of contact ion pairs.
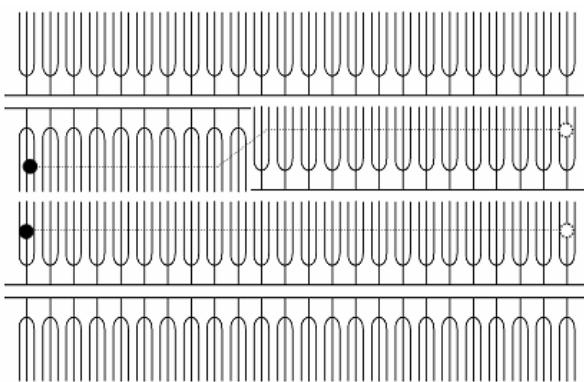

Fig. 7. Model representation of possible cation conduction pathways in a tripodand-type polymer electrolyte

Room temperature specific conductivity measured for the studied polymer electrolyte (4.3 · 10^{-6} S·cm^{-1} at 25 °C) is obviously too low for practical applications. Conductivity of the order of 10^{-3} S·cm^{-1} at 25 °C has been observed for analogous polymer with slightly shorter polyether segments forming tripodand centers [25]. Two remarks

should be made at this point. The salt concentration has arbitrarily been established for the present work in such a way that the theoretical occupation of "tripodand cages" would be 75 %, which corresponds to O:Li ratio of 12.9:1. This is most probably far from optimum and by increasing the concentration of charge carriers it should be possible to enhance the conductivity markedly. The second remark is more general. Rossi *et al.* [12] noticed that for polysiloxanes with polyether side chains studied by them conductivity was inversely dependent on the side chain length. This somewhat surprising result can be acknowledged on the basis of our experience with tripodand-type side chains. We suppose that shorter side chains behave more favorably in terms of self-organization, thus being more prone to form fast conduction pathways.

A question may be raised whether Li$^+$ are not trapped too firmly by the tripodand cages to ensure sufficiently high cation mobility. In such a case conductivity would be rather anionic. Our estimation of transference number gives the value of t^+ = 0.32, which seems relatively high, especially as compared to PEO-based electrolytes. Various t^+ values have been reported in the literature for PEO-based polymer electrolytes (without fillers and plasticizers), typically ranging from 0.1 to 0.2, depending on the method applied, salt concentration, temperature and other parameters [32, 33]. It should be kept in mind that reliability of the method used for the determination of transference number applied in this work (combination of AC and DC measurements) has a number of limitations and the result should be treated with caution. By adjusting the strength of complexation (different type Si-tripodand center) and anion size it should be possible to enhance lithium transference to some extent.

Solid state ^{7}Li NMR has been proved to be a valuable technique for getting insight into the lithium transport mechanism in polyether-based polymer electrolytes. In particular, the so-called motional narrowing of the central peak in the temperatures corresponding to glass transition has widely been treated as evidence for coupling of the cation dynamics with thermal chain segment motions [34, 35]. It is widely accepted that such coupling occurs in the vast majority of polymer-lithium complexes, being an important inherent limitation of fast cation transport. One of rare cases of decoupling is described by Every *et al.* [36] for poly(vinyl alkohol) based electrolytes. The motivation of our experiments was to search for the evidence for possible decoupling of cation and polymer dynamics. For the time being, the issue must remain without definite solution in light of the fact that no clear glass transition could be detected. If we assume that what can be observed on the DSC traces at around 10 and 20 °C is some glass-like phase transition, then indeed, in the corresponding temperature range there is no abrupt line narrowing. On this basis it may be claimed, however with caution, that in the described polymer/salt complex polymer and cationic movements are decoupled.
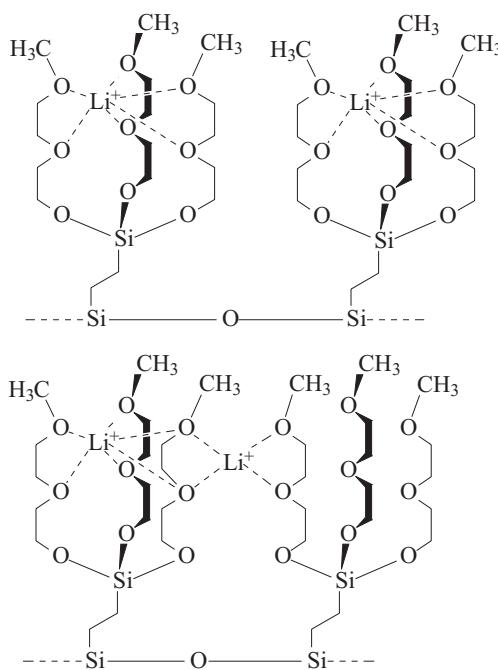
Scheme A. Two possible lithium co-ordination sites occurring when a cation moves along the main chain

A distinct splitting of the NMR signal starting from -30 °C deserves some attention, since to our best knowledge, it has not been reported in the literature. In our opinion the splitting reflects an intermediate state in the process of cation hopping from one tripodand center to another (this situation is showed in the Scheme A). Additional signal may correspond to different type of coordination experienced by Li⁺ when a cation is "shared" by two vicinal tripodand cages.

CONCLUSIONS

1. New polymer, poly(methyl(2-(tris(2-(2-methoxyethoxy)ethoxy)silyl)ethyl)siloxane) trimethylsilyl terminated, average molecular weight 19 100, has been synthesized as new polymeric host for lithium salts and potential solid solvent for Li-conducting polymer electrolytes.

2. Thin, flexible membranes prepared by dissolving LiPF6 in the synthesized polymer (O:Li ratio — 12.9:1) show satisfactory mechanical properties, appreciable ionic conductivity and relatively high cationic transference number, making it possible to consider the obtained polymer electrolyte as prospective solution for Li-ion cells. Further optimization of salt concentration is necessary. The proposed concept of polymer architecture can be a basis for further development.

3. The polymer/salt complex is amorphous. On the molecular level the complex consists of ordered lithium coordination sites (Si-tripodand centers) grafted onto a polysiloxane main chain. Although ^{7}Li NMR measurements failed to prove it unambiguously, it may be assumed that cation transport is principally realized by hopping (with the activation energy of 61.3 kJ/mol) of Li⁺

ions between the neighboring, rigid sites, independently of random thermal motions of polymer segments. ^{7}Li NMR experiments give valuable insight into the mechanism of cation transport through an unexpected splitting of the central ^{7}Li signal at low temperatures.

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