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Synthesis of cross-linked comb-type polysiloxane for polymer electrolyte membranes

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Abstract: Hydrosilylation reaction of 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane with allyl acetoacetate and vinyltriethoxysilane at 1:3:1 ratio of initial compounds in the presence of Karstedt's catalyst ($\text{Pt}_2[(\text{VinSiMe}_2)_2\text{O}]_3$), platinum hydrochloric acid (0.1 M solution in THF) and platinum on the carbon have been studied and $\text{D}_4^{\text{R,R'}}$ type methylorganocyclotetrasiloxane has been obtained.

Ring-opening co-polymerization reactions of methylorganocyclotetrasiloxane and hexamethyldisiloxane, in the presence of catalytic amount of powder-like potassium hydroxide, have been carried out and linear methylsiloxane oligomer with regular arrangement of propyl acetoacetate and triethoxysilane groups in the side chain has been obtained. The synthesized methylorganocyclotetrasiloxane and oligomers were studied by FTIR, ^1H , ^{13}C , ^{29}Si NMR spectroscopy. Comb-type oligomers were characterized by gel-permeation chromatography, wide-angle X-ray and differential scanning calorimetric methods.

Via sol-gel processes of doped with lithium trifluoromethylsulfonate (triflate) or lithium bis-(trifluoromethylsulfonyl)imide oligomer systems solid polymer electrolyte membranes have been obtained. The dependence of ionic conductivity as a function of temperature and salt concentration has been studied. The electrical conductivity of these materials at room temperature belongs to the range of 7×10^{-8} to $4 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ and depends on the structures of grafted anion receptors and the polymer backbones.

Key words: polysiloxanes, cross-linking, kinetics, polyelectrolyte, membranes.

Introduction

Over the past decade, there has been interest in generating solid polymer electrolytes for high energy density lithium batteries [1, 2]. Polysiloxanes attract the widest interest among the inorganic backbone polymers. The reason lies in properties of polysiloxanes such as strong heat resistance, elastomeric behavior, biocompatibility, thermal-, UV- and oxidative stabilities, low surface energy, good weather ability, low

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melting points and glass transition temperatures, convenient rheological properties and outstanding electrical properties [3].

The properties of organosilicon polymers depend on the structure of macromolecular chains and on the nature of organic groups surrounding the silicon atom [4]. In comb-type copolymers there are different size and nature organic substituent groups bonded to the methylsiloxane hydrophobic matrix. A wide range of variation of these substituent groups is possible. Some organosilicon copolymers contain donor groups and exhibit complexing properties [5-7].

The polysiloxanes with very low glass transition temperatures, $T_g = -123^\circ\text{C}$ for poly(dimethylsiloxane) and extremely high free volumes and thermo-oxidative stability [8, 9] are expected to be good hosts for Li^+ transport when polar units are introduced onto the polymer backbone. Oligo(ethylene glycol)-substituted polysiloxanes as ionically conductive polymer hosts have been previously investigated by Smid [10, 11], Shriver [12-14], Acosta [15] and West and co-workers [16, 17]. The more recent synthesis and conductivity studies of a bis-substituted polysiloxane with pendant oligo(ethylene glycol) chains have been reported by Hooper et al [18]. A six-oxygen side-chain polymer host when doped with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) showed the highest room temperature conductivity ($4.0 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$) yet observed for a polymer electrolyte. However, the dimensional stability of these polymer electrolytes is poor. It is not possible to use the complexes as separators in all solid-state lithium polymer batteries since the glutinous materials flow even under mild pressure at ambient temperature.

Usually for obtaining solid polymer electrolytes on the base of organosilicon polymers as starting materials are used polymethylhydrosiloxane (PMHS) matrix. Via hydrosilylation or dehydrocondensation reactions of this matrix with allyl-, vinyl- or hydroxyl-containing compounds methylorganosiloxane with different donor groups in the side chain are obtained. Such proposed method of obtaining comb-type methylsiloxane oligomers is not reasonable because reaction requires a large time, replacement of all $\equiv\text{Si-H}$ does not proceed completely and various linking systems are obtained. Furthermore during reaction often branching and cross linking processes take place.

We now report about synthesis of methylorganocyclotetrasiloxane $\text{D}_4^{\text{RR}'}$ with propyl acetoacetate and triethoxysilane groups (as cross-linking moieties) at silicon; co-polymerization reaction of $\text{D}_4^{\text{RR}'}$ with hexamethyldisiloxane (HMDS) as a terminating agent (TA) and obtaining comb-type methylsiloxane oligomers with regular arrangement of pendant groups; creation of new solid polymer electrolyte membranes on the base of lithium salts and investigation of their properties.

Results and discussion

The main aim of our work was the synthesis of methylorganocyclotetrasiloxane containing propyl acetoacetate and triethoxysilane pendant groups at silicon. From literature [19] it's known that hydrosilylation reaction 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (D_4^{H}) with allyl acetoacetate and vinyltriethoxysilane in melt condition proceeds vigorously, which changes the direction of hydride addition and partially substituted hydroxyl containing methylcyclotetrasiloxanes are obtained.

For obtaining of fully addition products hydrosilylation reactions of D_4^{H} with allyl acetoacetate and vinyltriethoxysilane at ratio 1:3:1 of initial compounds have been carried out in dilute solution of dry toluene or THF (50%) at 50°C in the presence of platinum catalysts.

$$\begin{array}{c}
 \text{Me} \quad \text{Me} \\
 | \quad | \\
 \text{H}-\text{Si}-\text{O}-\text{Si}-\text{H} \\
 | \quad | \\
 \text{O} \quad \text{O} \\
 | \quad | \\
 \text{H}-\text{Si}-\text{O}-\text{Si}-\text{H} \\
 | \quad | \\
 \text{Me} \quad \text{Me}
 \end{array}
 + 3 \text{H}_2\text{C}=\text{C}(\text{H})-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3
 + \text{CH}_2=\text{CH}-\text{Si}(\text{OC}_2\text{H}_5)_3
 \xrightarrow{\text{Cat}}$$

$$\begin{array}{c}
 \text{O} \quad \text{O} \quad \text{Me} \quad \text{Me} \quad \text{O} \quad \text{O} \\
 || \quad || \quad | \quad | \quad || \quad || \\
 \text{H}_3\text{C}-\text{C}-\text{H}_2\text{C}-\text{C}-\text{O}-\text{C}_3\text{H}_6-\text{Si}-\text{O}-\text{Si}-\text{C}_3\text{H}_6-\text{O}-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\
 | \quad | \quad | \quad | \\
 \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
 | \quad | \\
 \text{H}_3\text{C}-\text{C}-\text{H}_2\text{C}-\text{C}-\text{O}-\text{C}_3\text{H}_6-\text{Si}-\text{O}-\text{Si}-\text{C}_2\text{H}_4\text{Si}(\text{OC}_2\text{H}_5)_3 \\
 || \quad || \quad | \quad | \\
 \text{O} \quad \text{O} \quad \text{Me} \quad \text{Me}
 \end{array}$$

In spite of the fact that the hydrosilylation reaction was carried out in a dry solution of toluene or tetrahydrofuran the reaction is heterogeneous. As a result the viscous transparent liquid product soluble in organic solvents is obtained. The structure and composition of obtained compound I was studied by determination of molecular masses, FTIR, ^1H , ^{13}C and ^{29}Si NMR spectra data.

²⁹Si NMR spectra of compound I (Figure 1) showed resonance signal with chemical shift $\delta = -20.0$ ppm which corresponds to the presence of RR'SiO (D), as well as resonance signal with chemical shift $\delta = -66.0$ ppm can be assigned to T moieties in triethoxysilyl group [20].

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Fig. 1 ^{29}Si NMR spectra of compound I.

Fig. 2 ^1H NMR spectra of compound I.

For obtaining cross-linked product sol-gel processes of compound I has been carried out. To solution of compound I in THF the catalytic amount of acid (one drop of 0.1 N HCl solution in ethyl alcohol) to initiate the cross-linking process was added. After stirring for another 3 h the solvent was allowed to evaporate slowly overnight. Cross-linked product was dried in an oven at 70°C for 3 h and at 100°C for 1 h. The obtained product is rigid, homogeneous and transparent film. Sol-gel reaction proceeds according to the following scheme 2:

Scheme 2. Sol-gel reaction of compound I.

Solid polymer electrolyte membranes on the base of P_1 were obtained as it is stated above.

Polymerization and copolymerization reaction of compound I and hexamethyldisiloxane (TA) have been studied in inert atmosphere in dry toluene solution in temperature range 50-60°C in the presence of powder-like unhydrous potassium hydroxide (0.01% of total mass).

It was established that during polymerization reaction without terminating agent ring-opening polymerization in the presence of potassium hydroxide proceeds during 40-48 h, but the reaction product during synthesis or after some time undergo to cross-linking processes. It's possible that cross-linking reaction takes place between terminal hydroxyl and pendant ethoxy groups according to the scheme 3:

Scheme 3. Possible cross-linking reaction.

Therefore for obtaining of soluble polymers ring-opening co-polymerization reactions of compound I and TA at various ratios of initial compounds in inert medium in temperature range 50-60°C has been studied. Preliminary heating of initial compounds in the temperature range of 50-60°C showed that in these conditions polymerization of D_4^{H} , allyl acetoacetate or vinyltriethoxysilane and destruction of siloxane backbone does not take place. So, a ring-opening co-polymerization reaction of compound I with TA proceeds according to the scheme 4:

Fig. 3 ^1H NMR spectra of oligomer III^1 .

GPC investigation of oligomers has been carried out and it was shown that oligomers III^1 and III^2 has monomodal molecular weight distribution. The oligomer III^1 are characterized with low value of polydispersity. The polydispersity of oligomers is about $P=1.1$ and molecular weight $\bar{M}_n = 3.775 \times 10^3$ and $\bar{M}_w = 4.147 \times 10^3$. Number-average molecular weight of oligomer III^1 is near with expected values. The polydispersity of III^2 is about $P=2.18$, and $\bar{M}_n = 5.772 \times 10^3$ and $\bar{M}_w = 12.64 \times 10^3$. The found values of number average molecular weights slightly lower compared with expected molecular weight.

Via DSC investigation of oligomer III^1 it was shown that oligomer is characterized only with one transition temperature, which characterized glass transition temperature $T_g = -82^\circ\text{C}$.

Wide angle X-ray investigations for synthesized oligomers have been carried out and it was shown that oligomers are characterized with two diffraction maximums $d_1=7.23 \text{ \AA}$ and $d_2=4.23 \text{ \AA}$, characteristic for amorphous systems. First diffraction maximum d_1 characterized interchain distance while the second one characterized both intra-molecular and interchain interactions [5].

On the basis of obtained oligomers the electrolytes containing the lithium triflate and lithium bis(trifluoromethylsulphonyl)imide with different concentrations were prepared.

Solid polymer electrolyte (PE) membranes from linear oligomers may be obtained by sol-gel processes according to the following scheme:

Scheme 5. Possible cross-linking reaction of linear oligomers.

For simplicity we introduced to the text the following abbreviations: polymer P_1 instead of II and polymer P_2 instead of III¹. Lithium salts: triflate - S_1 and bis(trifluoromethylsulfonyl)imide - S_2 . So the electrolytes abbreviations will be as P_1S_1 , P_1S_2 , P_2S_1 and P_2S_2 , respectively. There were prepared the samples as disc like membranes with thickness in the range 200 μm . The samples were placed to the cage with two cylindrical electrodes made from brass, which was connected to standard impedance device, working at the frequencies up to 20 kHz. This cage was placed to the thermostat allowing the change of the samples temperature in the range from room temperature up to 150°C.

On the Figure 4 the electrical conductivity on the temperature of P_1S_1 and P_1S_2 electrolytes are presented. The curves of these dependences show that the values of the electrical conductivity of polymer membranes and the range of their change, significantly depends on both, polymer type and salt concentration. In case of PE - P_1S_1 containing 10 wt. % of S_1 the conductivity of the PE is rather low in all the temperature range. However the conductivity of the same PE with relatively high concentration (20 wt. %) gets the significances on two order higher than for P_1S_1 containing 10 wt. % of this salt. Difference between conductivities of P_1S_1 and P_1S_2 may be described by difference in the electrical states of the PEs. Probably in the first PE possibility of creation of donor-acceptor complex is lower than in second one and consequently the corresponding conductivity for second PE is higher (but at low concentrations of the salts) besides of relatively high mobility of the anions of the first salt. However the picture is changed at more high content of the salts. In accordance with the conception expressed in [18] at increasing of the concentration of salts with relatively big anions the probability of creation of so called pairs of the ions increases and consequently the current density decreases more intensively than in case of little anions.

Fig. 4 Dependence of electrical conductivity on the temperature for membranes P_1S_1 , salt concentration in wt. % - 10 (1) and 20 (2); P_1S_2 : 10 (3) and 20 (4).

It is interesting the behaviour of the conductivity of PE - P_1S_2 with 20 wt. % of the salt. In this case, low conductivity of this PE at low temperatures increases with the rise of temperature, because of damage of charge pairs and increasing of mobility of corresponding ions. The wide interval of changes of conductivity of PE - P_1S_2 must be due to gradual structural changes of this material (gradual increasing of the segmental mobility of the polymer side groups).

Fig. 5 Dependence of electrical conductivity on the temperature for membranes P_2S_1 , salt concentration in wt. % - 20 (1) and 10 (2); P_2S_2 : 10 (3) and 20 (4).

The dependence of conductivity of PE based on polymer P_2 on salt concentration is presented on the Figure 5. The curves shown on this figure differ one from another with relatively narrow interval of values. The low electrical conductivity of these compounds shows, that the microstructure is less suitable for the charge transfer in these polymer matrixes. In general the conductivity values at the edge temperatures are shown in the Table 2.

Tab. 2 Dependence of conductivities for compounds based on polymers P_1 and P_2 at initial and last measuring temperatures

Membrane	Polymer	Salt	Salt Concentration wt. %	σ , (20°C), S/cm	σ , (115°C), S/cm
P_1S_1	P_1	S_1	10	9.0×10^{-8}	2.5×10^{-6}
P_1S_1	P_1	S_1	20	2.2×10^{-6}	5.2×10^{-5}
P_1S_2	P_1	S_2	10	6.1×10^{-7}	2.3×10^{-5}
P_1S_2	P_1	S_2	20	2.5×10^{-7}	5.9×10^{-5}
P_2S_1	P_2	S_1	10	5.4×10^{-7}	7.2×10^{-5}
P_2S_1	P_2	S_1	20	6.5×10^{-7}	9.1×10^{-5}
P_2S_2	P_2	S_2	10	6.2×10^{-7}	4.1×10^{-5}
P_2S_2	P_2	S_2	20	8.2×10^{-8}	2.5×10^{-5}

The voltamograms of the compounds P_1S_1 , P_1S_2 , P_2S_1 and P_2S_2 are presented on the Figures 6 and 7.

Fig. 6 Voltamograms of compounds on the basis of polymer P₁, 1-10 wt.% S₁, 2-20 wt. % S₁, 3-20 wt.% S₂ and 4-10 wt.% S₂.

Fig. 7 Voltamograms of compounds on the basis of polymer P₂ - 1-10 wt. % S₁, 2-20 wt. % S₁, 3-20 wt. % S₂ and 4 -10 wt. % S₂.

These dependences show that in the used interval of the changes of voltage the currents are changed linearly, which is due to no significant formation of the heat effect after charge transfer in the polymer matrix.

Experimental part

Materials

2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (Aldrich), platinum hydrochloric acid (Aldrich), Karstedt's catalyst - $(\text{Pt}_2[(\text{VinSiMe}_2)_2\text{O}]_3)$ complex (2% solution in xylene) (Aldrich), Pt/C (10%) (Aldrich), allyl acetoacetate (Aldrich) and vinyltriethoxysilane were used as received. Lithium trifluoromethylsulfonate (triflate) and lithium bis(trifluoromethylsulfonyl)imide were purchased from (Aldrich). Toluene was dried over and distilled from sodium under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. 0.1 M solution of platinum hydrochloric acid in THF was prepared and kept under nitrogen at low temperature.

Characterization

FTIR spectra were recorded on a Nicolet Nexus 470 machine with MCTB detector. ^1H , ^{13}C NMR and ^{29}Si NMR spectra were recorded on a Varian Mercury 300VX NMR spectrometer, using DMSO and CCl_4 as the solvent and an internal standard. Differential scanning calorimetric investigation (DSC) was performed on a Netzsch DSC 200 F3 Maia apparatus. Thermal transitions including glass transition temperatures T_g were taken as the maxima of the peaks. The heating and cooling scanning rates were 10 K/min.

Gel-permeation chromatographic investigation was carried out with the use of Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å Ultrastaygel columns. Sample concentration was approximately 3% by weight in toluene and typical injection volume for the siloxane was 5 μL flow rate – 1.0 ml/min. standardization of the GPC was accomplished by the use of styrene or polydimethylsiloxane standards with the known molecular weight.

Wide-angle X-ray analyses were performed on a Dron-2 (Burevestnik, Saint Petersburg, Russia) instrument. A-CuK_α was measured without a filter; the angular velocity of the motor was $\omega \approx 2^\circ/\text{min}$.

Determination of $\equiv\text{Si-H}$ content was calculated according to the method [21].

Hydrosilylation reaction of 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane with allyl acetoacetate and vinyltriethoxy silane in the presence of Karstedt's catalyst

2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (2.0000 g, 0.00832 mole) were transferred into a 100 mL flask under nitrogen using standard Schlenk techniques. High vacuum was applied to the flask for half an hour before the addition of allyl acetoacetate (3.5465 g, 0.0249 mole) and vinyltriethoxysilane (1.5825 g, 0.00832 mole). The mixture was then dissolved in 3 mL of toluene, and 0.1 M solution of platinum hydrochloric acid in tetrahydrofuran ($5 \div 9 \cdot 10^{-5}$ g per 1.0 g of starting substance) was introduced. The homogeneous mixture was degassed and placed into an oil bath, which was previously set to 50°C and reaction continued at 50°C . The reaction was controlled by decrease of intensity of active $\equiv\text{Si-H}$ groups. Than 0.1% activated carbon was added and refluxed for 12 h for deactivation of catalysts.

All volatile products were removed by rotary evaporation and the compound was precipitated at least three times into pentane to remove side products. Finally, all

volatiles were removed under vacuum and further evacuated under high vacuum for 24 h to isolate the colourless viscous polymer, 6.77 g (95%). FTIR (KBr, cm^{-1}): no –Si-H absorption at 2169; 1079, 1149, 1265, 1735 and 2800-3100. ^1H NMR (d-DMSO, CCl_4), δ (ppm): 0.14 ($\equiv\text{Si-Me}$), 0.95 (m, $-\text{OCH}_2\text{CH}_3$), 1.10 ($=\text{CH-CH}_3$); 0.5, 1.60, 3.45, 3.75 and 4.1 (m in OSiCH_2 , $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{COCH}_2\text{CO-}$, OCH_2CH_3 and $-\text{OCH}_2-$). ^{13}C NMR (d-DMSO, CCl_4), δ (ppm): -3.7, -1.4, 7.5, 12.5, 17.8, 29.0, 49.0, 57.5, 66.0 and 166.2. ^{29}Si NMR δ (ppm): -20.0, -46.0 - -57.0, -66.0 [20, 21].

The hydrosilylation reactions in the presence of other catalysts were carried out according to the above-mentioned method.

Hydrolytic polycondensation of 2.4.6-tris(propyl acetoacetate)-8-ethyltriethoxysilane-2.4.6.8-tetramethylcyclotetrasiloxane (I)

To the solution 1.4202 g (1.7418 mmole) of compound I in 3 ml dry THF in inert area a few drops of 0.1 N hydrochloric acid solutions in ethanol were added for initiation of sol-gel reaction. After stirring during 3 h the solvent was evaporated and solid product was dried at 80°C and during 3 h and at 100°C in vacuum. As a result the homogeneous transparent film (P_1) was obtained.

Ring-opening polymerization reaction of 2.4.6-tris(propyl acetoacetate)-8-ethyltriethoxysilane-2.4.6.8-tetramethylcyclotetrasiloxane with hexamethyldisiloxane

The 1.6325 g (2.0022 mmole) of compound I were transferred into 50 mL flask under nitrogen. High vacuum was applied to the flask for half an hour. Then the compound was dissolved in 1.8 ml dry toluene and 0.01 % of total mass powder-like potassium hydroxide was added. The mixture was degassed and placed in an oil bath which was previously set to 60°C was polymerized under nitrogen for 48 h. After to the reaction mixture 7 ml of toluene was added and the product is washed by water. The crude product was stirred with MgSO_4 for 6 hours, filtered, evaporated and the polymer was precipitated at least three times into pentane to remove side products. Finally, all volatiles were removed under vacuum to isolate colourless viscous polymer. FTIR (KBr, cm^{-1}): no –Si-H absorption at 2169; 1079, 1149, 1265, 1735 and 2800-3100. ^1H NMR (d-DMSO, CCl_4), δ (ppm): 0.14 ($\equiv\text{Si-Me}$), 0.5 (m OSiCH_2), 0.95 (m, $-\text{OCH}_2\text{CH}_3$), 1.15 ($=\text{CH-CH}_3$), 1.65 (m, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 3.50 ($-\text{COCH}_2\text{CO-}$), 3.75 (m, OCH_2CH_3) and 4.1 (m, $-\text{OCH}_2\text{-CH}_2-$). ^{29}Si NMR δ (ppm): -20.0, -34.81, -46.0, -57.0, -66.0 [21].

Ring-opening copolymerization reaction of compound I with various amount of hexamethyldisiloxane as a terminating agent has been carried out by the same manner.

General procedure for preparation of cross-linked polymer electrolytes from compound I

To the solution of 0.75 g compound I in 4 mL of dry THF the catalytic amount of acid (one drop of 0.1 N HCl solution in ethyl alcohol) to initiate the cross-linking process was added. After stirring for another 3 h required amount of lithium triflate from the previously prepared stock solution in THF was added to the mixture and stirring continued for further 1 h. The mixture was then poured onto a Teflon mould with a diameter of 4 cm and solvent was allowed to evaporate slowly overnight. Finally, the membrane was dried in an oven at 70°C for 3 d and at 100°C for 1 h. Homogeneous and transparent film (P_1) with average thickness of 200 μm were obtained in this way. These film were insoluble in all solvents, only swollen in THF.

Preparation of cross-linked polymer electrolytes from compound III¹

0.75 g of oligomer III¹ was dissolved in 4 mL of dry THF and thoroughly mixed for half an hour, then catalytic amount of acid (one drop of 0.1 N HCl solution in ethyl alcohol) was added to initiate the cross-linking process. After stirring for another 3 h required amount of lithium triflate from the previously prepared stock solution in THF was added to the mixture and stirring continued for further 1 h. The mixture was then poured onto a Teflon mould with a diameter of 4 cm and solvent was allowed to evaporate slowly overnight. Finally, the membrane was dried in an oven at 70°C for 3 d and at 100°C for 1 h. Homogeneous and transparent films with average thickness of 200 µm were obtained in this way. These films were insoluble in all solvents, only swollen in THF.

The polymer electrolyte membranes with various amount of lithium bis(trifluoromethylsulfonyl)imide have been prepared with the same manner.

Conclusion

Via hydrosilylation reaction of D₄^H with allyl acetoacetate and vinyltriethoxysilane in the presence of platinum catalyst D₄^{R,R'} type compound has been obtained. By ring-opening polymerization reaction the cross-linkable polymers with both propyl acetoacetate and triethoxysilane pendants were synthesized. The polymers were linked via sol-gel processes and lithium salts containing solid polymer electrolyte membranes have been obtained.

Electrical conductivity of membranes and the range of their change significantly depend on both polymer type and salt concentration. Difference between conductivities of P₁S₁ and P₁S₂ (also for P₂S₁ and P₂S₂) may be described by distinction in the type of salts and their anions. At low concentrations of the salts it may be assumed that in the first PE possibility of creation of donor-acceptor complex is lower than in second one and consequently the corresponding conductivity for second PE is higher, besides of relatively high mobility of the anions of the first salt. However the character of the electrolytes conductivity at high concentrations of the salts changes essentially: the conductivity of electrolytes with S₂ at increasing of temperature rises lower than for electrolytes with S₁ because of increasing of probability of formation of the anion pairs in the PEs with S₂ (big anions) leading to decreasing of conductivity of the PE in comparison with one containing S₁ (small anions).

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