Synthesis And Ionic Conductivity of Siloxane Based Polymer Electrolytes with Propyl Butyrate Pendant Groups

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Abstract – Hydrosilylation reactions of 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane with allyl butyrate catalyzed by Karstedt's, H_2PtCl_6 and Pt/C catalyst were studied and 2.4.6.8-tetra (propyl butyrate)-2.4.6.8-tetramethylcyclotetrasiloxane was obtained. The reaction order, activation energies and rate constants were determined. Ring-opening polymerization of 2.4.6.8-tetra (propyl butyrate)-2.4.6.8-tetramethylcyclotetrasiloxane in the presence of CaF_2, LiF, KF and anhydrous potassium hydroxide in 60-70 ^{o}C temperature range was carried out and methylsiloxane oligomers with regular arrangement of propyl butyrate pendant groups were obtained. The synthesized products were studied by FTIR and NMR spectroscopy. The polysiloxanes were characterized by wide-angle X-ray, gel-permeation chromatography and DSC analyses. Via sol-gel processes of oligomers doped with lithium trifluoromethylsulfonate or lithium bis (trifluoromethylsulfonyl)imide, solid polymer electrolyte membranes were obtained. The dependences of ionic conductivity of obtained polyelectrolytes on temperature and salt concentration were investigated, and it was shown that electric conductivity of the polymer electrolyte membranes at room temperature changed in the range $3.5\times10^{-4}{\sim}6.4\times10^{-7}$ S/cm.

Key words: Polysiloxanes, Membranes, Cross-Linking, Polymer Electrolyte, Ionic Conductivity

1. Introduction

Hybrid organic-inorganic materials, where molecular organic and inorganic fragments are combined, have been considered potentially attractive for developing new materials with a broad spectrum of interesting properties. In comparison with organic and inorganic constituents and polymers separately, hybrid organic-inorganic materials have many advantages [1-4].

Polymer electrolytes (PE) play an important part in electrochemical devices such as batteries and fuel cells. To achieve optimal performance, the PE must maintain a high ionic conductivity and mechanical stability at both high and low relative humidity. The polymer electrolyte also needs to have excellent chemical stability for long product life and robustness.

According to the prevailing theory, ionic conduction in polymer electrolytes is facilitated by the large-scale segmental motion of the polymer backbone, and primarily occurs in the amorphous regions of the polymer electrolyte. Crystallinity restricts polymer backbone segmental motion and significantly reduces conductivity. Consequently, polymer electrolytes with high conductivity at room tem-

perature have been sought through polymers which have highly flexible backbones and have largely amorphous morphology.

The interest in polymer electrolytes was increased also by potential applications of solid polymer electrolytes in high energy density solid state batteries, gas sensors and electrochromic windows.

Conductivity of 10^{-3} S/cm is commonly regarded as a necessary minimum value for practical applications in batteries [4,5]. At present, polyethylene oxide (PEO)-based systems are most thoroughly investigated, reaching room temperature conductivities of 10^{-7} S/cm in some cross-linked salt in polymer systems based on amorphous PEO-polypropylene oxide copolymers. However, conductivity with such value unfortunately is low, resulting from the semicrystalline character of the polymer as well as from the increase on the glass transition temperature of the system. It is widely accepted that amorphous polymers with low glass transition temperatures T_g and a high segmental mobility are important prerequisites for high ionic conductivities. Another necessary condition for high ionic conductivity is a high salt solubility in the polymer, which is most often achieved by donors such as ether oxygen or imide groups on the main chain or on the side groups of the PE. It is well established also that lithium ion coordination takes place predominantly in the amorphous domain, and that the segmental mobility of the polymer is an important factor in determining the ionic mobility. Great attention was pointed to PEO-based amorphous electrolyte obtained by synthesis of comb-like polymers, by attaching short

ethylene oxide unit sequences to an existing amorphous polymer backbone.

Comb-like polysiloxanes solid PE systems incorporating different lithium salts nowadays attract much more attention because of relatively high conductivity of about 10^{-4} S/cm [5-7] and 5×10^{-4} S/cm for double comb polysiloxanes PE having two oligoether side groups per silicon and dissolved lithium bis(trifluoromethylsulphonyl)imide.

Synthesis and conductivity studies were published for another series of oligoether-substituted mono-comb polysiloxane PE, which was additionally cross-linked by α,ω-diallylpolyethyleneglycol [8,9]. Careful analysis of these and other results conducted in [10] confirms that there is no significant conductivity loss at transfer from double-comb to mono-comb polydisiloxanes.

It was observed that the dependence of materials conductivity s on the inverse temperature is described by one of the following types of regularities: 1) Vogel-Tammann-Fulcher (VTF) and 2) Arrhenius formula with two activation energies [11,12].

The aim of the present work was to obtain new solid polymer electrolyte membranes on the base of comb-like methylsiloxane matrix with regular arrangement of propyl butyrate pendant groups and to investigate their electric conducting properties.

2. Experimental

2-1. Materials

2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (D_4^H) (Aldrich), platinum hydrochloric acid (Aldrich), Karstedt's catalyst ($Pt_2[(Vin-SiMe_2)_2O]_3$) or platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (2% solution in xylene) (Aldrich), platinum hydrochloric acid (Aldrich), Pt/C (10%) (Aldrich) and allyl butyrate (Aldrich) were used as received. 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.

2-2. Characterization

FTIR spectra were recorded on a Nicolet Nexus 470 machine with MCTB detector. ^{1}H, ^{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. The temperatures of thermal transitions including glass transition temperatures T_g corresponded to the maxima of the peaks. The heating and cooling scanning rates were 10 K/min.

Gel-permeation chromatographic investigation involved the use of Waters Model 6000A chromatograph with an R 401 differential refractometer detector. The column set comprised 10^3 and 10^4 Å Ultrastyragel columns. Sample concentration was approximately 3% by weight in toluene and typical injection volume for the silox-

ane was 5 µL flow rate - 1.0 ml/min. The GPC was standardized 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. CuK$_\alpha$ radiation was used with graphitic monochromator; the angular velocity of the motor was $\omega \approx 2$ ^{o}/min.

The content of active $\equiv$Si-H groups in hydroorganosiloxanes was calculated according to the literature data [13].

2-3. Hydrosilylation reaction of D_4^H with allyl butyrate in the presence of Karstedt's catalyst

D_4^H (2.00 g, 8.316 mmol) 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 butyrate (4.4764 g, 0.03493 mol). The mixture was then dissolved in 3 ml of toluene, and 3 µL Karstedt's catalyst was syringed in to the flask. The homogeneous mixture was degassed and placed into an oil bath, which was previously set to 50 ^{o}C and reaction continued at 50 ^{o}C. The reaction was controlled by decrease of intensity of active $\equiv$Si-H groups.

Then 0.1% activated carbon was added and refluxed for 3 h for deactivation of catalysts.

All volatiles were removed by rotary evaporation, and the obtained product 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 colorless viscous product, 6.0 g (93%). FTIR (KBr, cm^{-1}): no -Si-H absorption at 2169; 1079, 1149, 1265, 1735 and 2800-3100. ^{1}H NMR (d-DMSO, CCl$_4$), δ (ppm): singlet signal δ=0.14 ($\equiv$Si-Me); multiplet signals with center of chemical shifts δ=0.6, 0.9, 1.65, 2.22 and 3.90 ppm characteristic for protons in $\equiv$Si-C$^1\underline{H}_2$-, $\underline{C}^7\underline{H}_3$, $\underline{C}^6\underline{H}_2$, $\underline{C}^2\underline{H}_2$ and $\underline{C}^3\underline{H}_2$ groups accordingly. ^{13}C NMR (d-DMSO, CCl$_4$), δ (ppm): Signals with chemical shifts δ=13.11, 17.53, 21.57, 35.3, 36.67, 65.16 and 171.53 ppm correspond to C^7,C^2, C^1, C^6, C^5, C^3 and C^4. ^{29}Si NMR δ (ppm): -22.0 ppm.

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

2-4. Ring-opening polymerization reaction of D_4^R

The 1.1470 g (1.5232 mmol) of compound D_4^R was 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 ^{o}C and was polymerized under nitrogen for 25 h. After that, 7 ml of toluene was added to the mixture and the product was washed by water at least four times, filtered, evaporated and the oligomer was precipitated at least three times into pentane to remove side products. Finally, all volatiles were removed under vacuum to isolate 1.06 g (93%) colorless viscous oligomer (II).

FTIR (KBr, cm^{-1}): absorption at 1095, 1033, 1188, 1265, 1735-1743,

2800-3100 and 3457. ^{1}H NMR (d-DMSO, CCl$_4$), δ (ppm): δ=0.14 (s - ≡Si-Me); δ=0.55 (m - ≡Si-C^{1}H$_2$-), 0.9 (m - C^{7}H$_3$), 1.65 (m - C^{6}H$_2$), 2.22 (m - C^{2}H$_2$) and 3.90 (m - C^{3}H$_2$) accordingly. ^{13}C NMR (d-DMSO, CCl$_4$), δ (ppm): 13.11, 17.53, 21.57, 35.3, 36.67, 65.16 and 171.53 for C^7, C^2, C^1, C^6, C^5, C^3 and C^4. ^{29}Si NMR δ (ppm): -19.8 ppm.

Ring-opening co-polymerization reaction of compound I with various amount of hexamethyldisiloxane as a terminating agent was carried out by the same manner.

2-5. General Procedure for Preparation of Cross-Linked Polymer Electrolytes

The 0.75 g of oligomer II was dissolved in 4 ml of dry THF and thoroughly mixed for half an hour before the addition of catalytic amount of acid (one drop of 0.1 N HCl solution in ethyl alcohol) and five drops tetraethoxysilane to initiate the cross-linking process. After stirring for another 3 h, the required amount of lithium triflate from the previously prepared stock solution in THF was added to the mixture and further stirred for 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 days 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.

2-6. AC Impedance Measurements

The total ionic conductivity of samples was determined by locating a membrane between two disk-like bronze electrodes with 10 mm diameter and a thickness of 2 mm. The electrode/electrolyte assembly was secured in a suitable constant volume support which allowed extremely reproducible measurements of conductivity to be obtained between repeated heating-cooling cycles. The cell support was placed in an oven and the change of sample temperature was measured by a thermocouple close to the electrolyte disk. The bulk conductivities of the electrolytes were obtained during a heating cycle using the impedance technique (Impedance meter BM 507-TESLA for frequencies 50 Hz-500 kHz) over a temperature range between 20 and 110 °C. Voltamograms measured at room temperatures were obtained by use of simple arrangement allowing the registration of the value of current passing true the electrolyte sample at gradual increase of the voltage.

3. Results and Discussion

It's known that hydrosilylation reaction of D$_4^H$ with allyl butyrate and vinyltriethoxysilane in melt condition proceeds vigorously, which changes the direction of hydride addition and with obtaining of partially substituted cyclotetrasiloxanes [14].

For obtaining of full addition product, hydrosilylation reactions of D$_4^H$ with allyl butyrate at molar ratio 1:4.1 of initial compounds in dilute solution of dry toluene at 50 °C have been carried out.
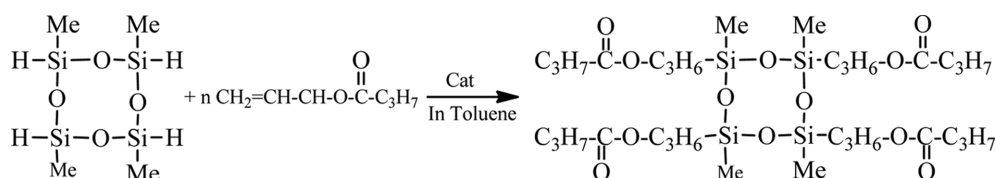
Separately, preliminary heating of initial compounds with catalysts at temperatures 50~60 °C showed that in these conditions polymerization of D$_4^H$, or allyl butyrate and destruction of siloxane backbone does not take place. No changes in the NMR and FTIR spectra of initial compounds were found. So, hydrosilylation reaction of D$_4^H$ with allyl butyrate proceeds according to the following Scheme 1.

The obtained organocyclotetrasiloxane I-D$_4^R$ is a transparent, viscous products well soluble in ordinary organic solvents.

The structure and composition of the obtained compounds were studied by determination of molecular masses, FTIR, ^{1}H, ^{13}C and ^{29}Si NMR spectra data. Some physical chemical properties of organocyclotetrasiloxanes are presented in Table 1.

The obtained organocyclotetrasiloxane I-D$_4^R$ is a transparent, viscous products well soluble in ordinary organic solvents. In ^{29}Si NMR spectra of compounds I, one can see resonance signal with chemical shift δ = -22 ppm corresponds to the presence of RR'SiO (D) units.

In ^{1}H NMR spectra of D$_4^R$ the multiplet signal with center of chemical shift δ = 1.2 ppm corresponds to methin protons in =CH-CH$_3$ group, which proves that hydrosilylation partially proceeds according to the Markovnikov rule. From these spectra it's evident that the hydosilylation reaction mainly proceeds accordingly to the anti-Markovnikov rule.

Scheme 1. Hydrosilylation reaction of D$_4^H$ with allyl butyrate. Where: n=4.1. 50 °C-I, 40 °C-I^1, 30 °C-I^2.

Table 1. Some physical chemical properties of organocyclotetrasiloxanes

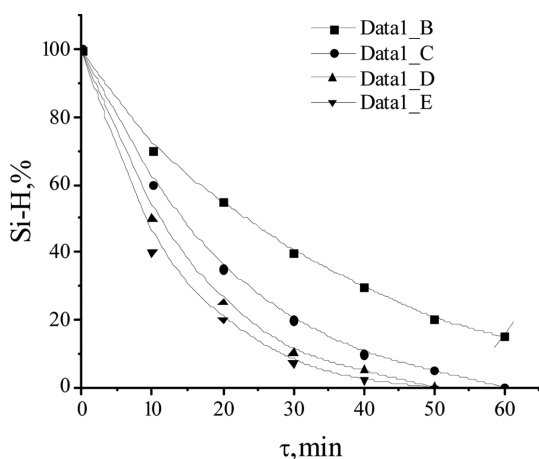| #	Reaction Temp-re, °C	Yield, %	n_D^{20}	d_4^{20}	M*$_{RD}$		M	
					Calcul.	Found	Calcul.	Found
I	50	93	1.441	1.0734	187.64	187.72	753	735
I^1	40	91	1.441	-	-	-	753	-
I^2	30	90	1.441	1.0734	-	-	-	-

*Molecular refraction.

Fig. 1. Dependence of changes of concentration of active ≡Si-H groups on the time, during hydrosilylation reactions of D_4^H with allyl butyrate, where curve B represents the values obtained at 50 °C (Pt/C Catalyst - the curve is presented partialy), curve C represents the values obtained at 30 °C, curve D - 40 °C and curve E - 50 °C (Karstedt's catalyst).

During the hydrosilylation reaction of D_4^H with allyl butyrate in dry toluene solution (C=0.1272 mol/l), a decrease of active ≡Si-H groups' concentration with the time was observed. As evident from Fig. 1, all active ≡Si-H groups participate in hydrosilylation reaction. With an increase of temperature the reaction rate increases.

The hydrosilylation reaction runs vigorously during the first 10 minutes and after is weakened. Hydrosilylation reaction in the presence of platinum hydrochloric acid proceeds with the same rate as in the presence of Karstedt's catalyst, but in case of Pt/C the hydrosilylation reaction proceeds less actively. So Fig. 1 allows concluding that the activity of catalysts for hydrosilylation reactions of D_4^H with allyl butyrate decreases in the next rank: Karstedt's catalyst $\approx H_2PtCl_6 >$ Pt/C.

One can see that at the initial stages the hydrosilylation reaction is of second order in case of stoichiometric relationships between initial compounds in view of ≡Si-H bonds.

The reaction rate constants of hydrosilylation reactions of D_4^H with allyl butyrate at various temperatures were determined with following values: $k_{50\,°C} \approx 0.9657$, $k_{40\,°C} \approx 0.6494$ and $k_{30\,°C} \approx 0.4663$ l/mol·s.

From the dependence of reaction rate constants' logarithm on the reciprocal temperature, the activation energy of hydrosilylation reaction was calculated, which is equal to $E_{act} \approx 29.96$ kJ/mol.

For obtaining linear methylsiloxane oligomers with propyl butyrate side groups the ring opening polymerization reactions of D_4^R were carried out. As a catalysts alkali fluorides, tetramethyl ammonium hydroxide and powder-like dry potassium hydroxides were used.

It is known that ionic fluorides show high catalytic activity, similar to typical nucleophils such as potassium hydroxide to catalysts in reactions of siliconorganic compounds: reduction [15], dehydrocondensation [16], hydrolysis [17] and polymerization reactions of organocyclosiloxanes [18]. In last case polymerization eighth cycle proceeds very slowly.

Polymerization reactions were carried out in inert atmosphere, in temperature range 50~120 °C and in toluene solution at 50~110 °C. By gas-liquid chromatography (GLC) it was established that alkali fluorides in this condition do not promote obtaining of polymers and only 25~30% of initial compounds take place in ring opening polymerization in case of KF. So the yield of polymers is very low.

It was shown that catalytic activity of various ionic fluorides in relation of polymerization of organocyclotetrasiloxanes decreases in as $CaF_2 <$ LiF < KF.
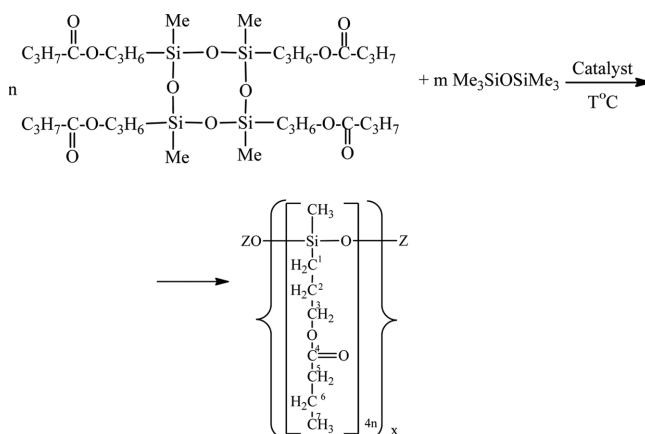
So this type of catalyst is not convenient for polymerization of these types of organocyclotetrasiloxanes with such substituted donor type side groups.

Ring-opening polymerization and co-polymerization reactions of D_4^R in the presence of terminated agent hexamethyldisiloxane and without it have been studied in inert atmosphere, in toluene solution in the temperature range 60~70 °C, in the presence of powder-like anhydrous potassium hydroxide (0.05~0.01% of total mass). It was established that ring-opening polymerization in the presence of potassium hydroxide proceeds during 48~64 h. The optimal condition of polymerization reaction was determined and it was established that it's better to carry out the polymerization reactions in solution in temperature range 50~60 °C in the presence of 0.01% (mass) dry potassium hydroxide. Polymerization reactions proceed according to the following Scheme 2.

The synthesized oligomers are vitreous viscous products, which are well soluble in organic solvents with the specific viscosity $\eta_{sp} \approx$ 0.062~0.2. Structures and compositions of the oligomers were determined by elemental and functional analyses, FTIR, ^{1}H, ^{13}C and ^{29}Si NMR spectral data.

In FTIR spectra of oligomer II and III one can observe absorption bands at 3457 cm^{-1} characteristic for ≡Si-OH groups. In oligomer III this absorption bond was not observed.

The resonance signals of $\underline{C}^6\underline{H}_2$ and $\underline{C}^2\underline{H}_2$ protons overlap. In the spectrum the multiplet signal with center of chemical shift δ=1.2 ppm is preserved, which corresponds to methine protons (product

Scheme 2. Ring-opening polymerization of D_4^R in the presence of potassium hydroxide. Where: m=0, Z=H-II (P) (50 °C), II^1 (60 °C). m>0, Z=SiMe₃, n : m: -4 : 0.8-III^1 (60 °C), 4 : 0.65-III^2 (60 °C), 4 : 0.5-III^3 (60 °C), 4 : 0.4-III^4 (50 °C).

Table 2. Some characterizations of oligomers obtained via polymerization and copolymerization reactions of D_4^R and hexamethyldisiloxane (HMDS)

#	Monomers		Molar ratio	Reaction	Degree of polymerization 4n		Molecular	η_{sp}	Yield, %
	Cyclic products	Terminated agent	Monomer: TA	Tem-re T^oC	Expect Value n	Found Value n	masses*		
II	D_4^R	-	1:0	50	-	-	1887**	0.082	93
II[1]	D_4^R	-	1:0	60	-	-	1800**	0.062	92
III[1]	D_4^R	HMDS	4:0.8	60	5	4.9	3922 3847	0.085	90
III[2]	D_4^R	HMDS	4:0.65	60	6.2	6.3	4901 4790	0.090	91
III[3]	D_4^R	HMDS	4:05	60	8	7.7	6178 5990	0.092	89
III[4]	D_4^R	HMDS	4:0.4	50	10	9.8	7682 7532	0.10	92

*In numerator there are calculated values, in denominator - found values.

**Molecular masses are obtained via ebullioscopy method.

of Markovnikov addition) in fragment $=C\underline{H}-CH_3$.

It was established that the ratio of initial cyclotetrasiloxane compound and TA in copolymerization reactions performs considerable influence on the molecular mass of obtained polymers. By changing of ratio of D_4^R and TA it is possible to regulate molecular masses of obtained oligomers. In Table 2 some characteristics of synthesized oligomers are presented.

In Table 2 molecular masses of oligomers are presented. By GPC method it was shown that the oligomer II has trimodal molecular weight distribution. The average number molecular mass is equal to $\overline{M}_n = 1.887 \times 10^3$ and the average weight molecular mass - $\overline{M}_\omega \approx 5.666 \times 10^4$. Thus, the polydispersity index is equal to D=4.08.

For obtained oligomers wide angle X-ray analyses were carried out, and it was shown that oligomers are represented as one-phase amorphous systems. On the diffractogram one can observe two diffraction maximums at $2\theta^0 \approx 11.7 \; 5 \sim 12.00^0$ and $2\theta^0 \approx 20.50 \div 20.75^0$.

The first maximum corresponds to interchain distances es d_1 which changes in the range $d_1 = 7.37 \sim 7.53$ Å. This value of d_1 is near to interchain distances of polymethylalkylsiloxanes [3] and second one at $d_2 = 4.28 \sim 4.33$ Å, which characterizes both intra- and interchain atomic interactions.
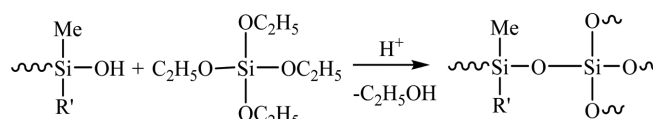
Synthesized oligomers were investigated by DSC analyses, and it was shown that they are characterized with only single endothermic peak, which corresponds to the glass transition temperature $T_g \approx -83$ °C for oligomer II and $T_g \approx -78$ °C for oligomer III[2].

The T_g values of the membranes each complexed with 20 and 15 wt% lithium triflate show that they slightly rise -62 °C (PS1-15%) with an increase of the amount of lithium triflate -58 °C (PS1-20%).

Preparation of polymer electrolyte membranes has been realized by the following way. The oligomer II (P) was dissolved in dry THF in glass-ware and certain amount of 0.1 M solution of lithium salts CF_3SO_3Li - S1 or $CF_3(SO_2)N^-(Li^+)(SO_2)CF_3$-S2 in THF was added and stirred for 30 minutes with a magnetic stirrer. Then five drops of tetraethoxysilane and one drop 0.1 M solution of HCl in methyl alcohol was added for initiation of sol-gel processes.

Obtaining of polymer electrolyte membranes from oligomer P proceeds according to the following Scheme 3.

It is known that electric conductivity of the polyelectrolytes is highly dependent on the content of different salts with slight decrease at relatively high temperatures, which may be due to formation of the
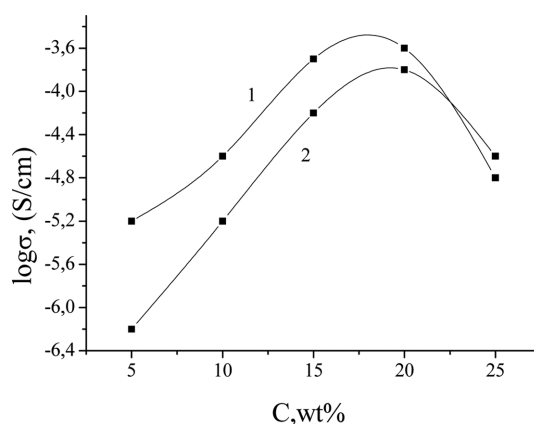
Scheme 3. Cross-linking reaction of oligomers.

ion-pairs [19].

The salts S1 and S2 were introduced to the polymers with concentrations of 5, 10, 15 20 and 25 mass % of each salt.

First, it was necessary to define the character of dependence of compounds' electric conductivity on the concentration of Li salts. The curve in Fig. 2 show that these dependences have extreme character, the conductivity rises with an increase of the salt concentration, reaches a maximum value and after declines. Obviously this fact may be described with increasing of charge carrier's number. The maximum of ionic conductivity can be described by two opposing processes, which are in accordance with conceptions noted in [9]: 1) increasing of the number of charge carriers (ions) in result of increasing of the salt concentration; and 2) increasing of possibility of the formation of ion pairs, thanks to which ion migration will be prevented in the electrolyte network.

In accordance with Fig. 2 data the above noted maximums on the curves for systems PS1 and PS2 appear at concentrations near 17~18 wt% of salt, respectively.

The quantitative difference between curves in Fig. 3 leads to the

Fig. 2. Ionic conductivity of the systems based on polymer P as a function of salt S1 (1) and S2 (2) concentrations at 25 °C temperature.

conclusion that in the electrolyte PS1 ions of the salt S1 having relatively small anions is characterized with more high mobility, than that for the salt S2. Therefore the maximum of conductivity for PS1 is higher to some extent than for PS2 having anions with less mobility. Decreasing of conductivity of both electrolytes at relatively high concentrations of both types of salts is due to above mentioned phenomenon - increasing of probability of formation of ion pairs at high ion concentrations.

On the basis of well known experimental results about the effect of the length of side groups on the value of conductivity of polyelectrolytes, it would be expected that the conducting complexes containing the molecules with long side groups would be more conductive than ones with relatively short side chains. However, the literature data obtained by other authors and by us shows that, as a rule, it is no direct correlation between side chains lengths and conductivity of polyelectrolytes [15-18]. For the main reason for these deviations, we can find not only in the side chain lengths. There are also other factors (e.g., molecular morphology, content of salts, distribution of salt molecules between polymer chains and the character of interactions between them), which influence simultaneously the electrical conductivity of polyelectrolytes and creates the difficulties in unique establishment of real nature of the polyelectrolytes conductivity. At establishment of the effect of microstructure of the polymer system on the mobility of Li ion, it must be taken into account the effect of the free volume between macromolecules and salt molecules. Therefore, it is very difficult to define the effect of the influence of the length of side chains on the free volume, because at increasing of side chain length on last apparently has non linear character. The exact estimation of the free volume with different methods would be introducing some definition to this problem.

Usually, coming from practical interests, the dependence of the conductivity on temperature of polyelectrolytes one defines mainly in the range of about 30~90 ℃ [6,7]. The conductivities of the investigated compounds defined on these limits are given in Table 3.

The dependence log s -1/T has nearly linear character and obeys the Arrhenius law (Figs. 3 and 4). These curves were designed after several measuring of this dependence and the data of conductivities were obtained after averaging of them.

As seen from Figs. 3 and 4, the conductivity of the investigated compounds rises with an increase of temperature. Main factor which defines such character of these dependences must be found in increasing of charge carriers (ions) mobility at increasing of temperature. This conclusion on the temperature dependence of conductivity of PE is in good agreement with experimental data presented on Fig. 3 and the Table 3.
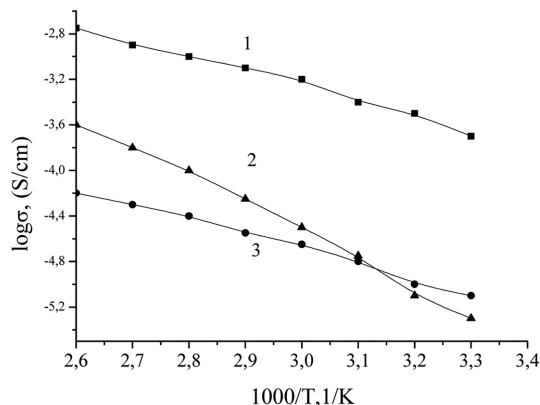

Fig. 3. Arrhenius plots of ionic conductivity for polymer electrolytes PS1 containing 20 (1), 5 (2) and 10 wt% (3) of salt S1.
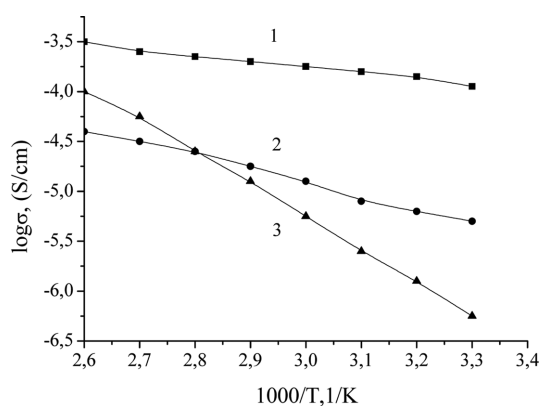

Fig. 4. Arrhenius plots of ionic conductivity for polymer electrolytes PS2 containing 20 (1), 10 (2) and 5 wt% (3) Li salt S2.

It was interesting to define the dependence of current - voltage for investigated PE. On Fig. 5 the curves of I-V functional dependences (so called the voltamograms) for some obtained membranes are presented.

The dependences I-U, i.e., voltamograms (Fig. 5), show that in the used interval of changes of constant voltage the value of the current increases with definite deviation from linearity. The behavior of the curves corresponds to character of dependence of carriers transport on the nature of salt ions. As noted above, the second salt ions differ from first ones with more high volume to some extent and relatively low mobility. Therefore, at increasing of the voltage accelerated ions after charge-phonons scattering are gradually slowed, which is reflected in the deviation from the linearity of V-A characteristics.

At this time appears the Joule heat, which is one of the reasons of destruction of the conducting channels due to heat scattering of charges leading to decreasing of the electrical current passing through

Table 3. The conductivities of investigated compounds PS1 and PS2, defined at 30 and 90 ℃

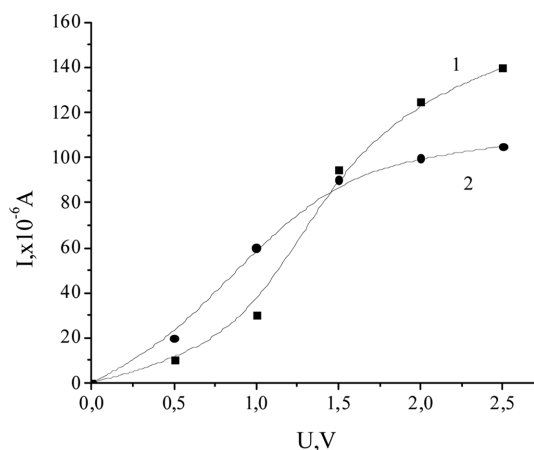| Salt	S₁					S₂				
Concentr. wt%	5	10	15	20	25	5	10	15	20	25
S(30 ℃), S/cm	6.3×10^{-6}	1.2×10^{-5}	3.2×10^{-4}	3.5×10^{-4}	1.6×10^{-5}	6.4×10^{-7}	6.6×10^{-6}	1.5×10^{-5}	1.3×10^{-4}	7.2×10^{-6}
S(90 ℃), S/cm	2.5×10^{-4}	5.2×10^{-5}	7.9×10^{-4}	1.1×10^{-3}	2.4×10^{-4}	3.3×10^{-5}	2.3×10^{-5}	6.2×10^{-5}	3.4×10^{-4}	2.6×10^{-5}

Fig. 5. Voltamograms for membranes containing 20% S1 (1) and same amount of S2 (2).

material. This deviation appears for the membrane PS2 earlier than for PS1 at containing one and same concentration of the salts because of difference in sizes and mobility of the compared ions.

For estimation of the effect of free volume in polyelectrolyte compounds on the ion conductivity, we provided experiments on investigation of the influence of external pressure on the conductivity for the investigated polyelectrolytes (Fig. 6).

The curves on Fig. 6 show that this dependence of resistance on the pressure has exponential character in relatively narrow interval of pressures. This result is unexpected to some extent, because, as it is well known, the free volume in the polymer matrix under increasing pressure decreases and, consequently, the transport of Li ions must be decreased. However, it may be suggested that at same time the segmental mobility of side chains of oligoesters significantly decreases, which in general presents a definite barrier on the way of Li ions thanks to interactions between charge carriers and phonons corresponding to side group vibrations.

Therefore, the noted barrier will be decreased at increasing of pressure. Probably from two effects (decreasing of free volume and
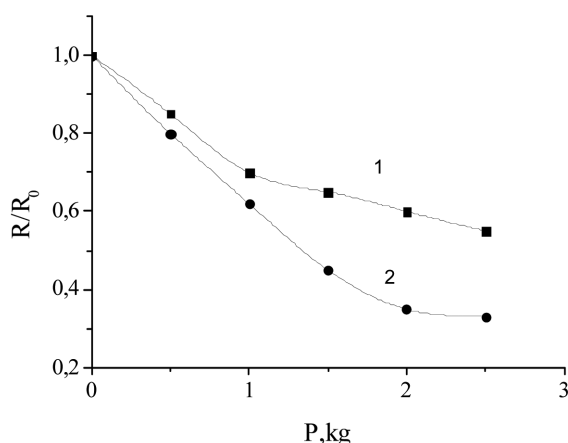

Fig. 6. Dependence of the resistance of electrolytes based on PS1 with 10 (1) and 20 (2) wt% S1 on the loading of the films with square 1 cm². R$_o$-resistance of the samples at normal pressure.

simultaneously the phonon- charge carrier's interaction), the second is more effective than the first one in the considered case. Generally, the conductivity of polyelectrolytes will depend significantly on the ratio of these factors.

4. Conclusions

By hydrosilylation reaction of D$_4^H$ with allyl butyrate in the presence of platinum catalyst, 2.4.6.8-tetra (propyl butyrate)-2.4.6.8-tetramethylcyclotetrasiloxane in a quantitative amount have been obtained. Via polymerization and co-polymerization reactions of 2.4.6.8-tetra (propyl butyrate)-2.4.6.8-tetramethylcyclotetrasiloxane with hexamethyldisiloxane or without it, comb-like methylsiloxane oligomers with regular arrangement of propyl butyrate in a side chain have been obtained.

The experiments on the establishment of dependences of conductivity of the comb-like polysiloxanes electrolytes on the Li salt concentration show that these dependences have an extreme character. Decreasing of conductivity at increasing of salt concentration after definite value of last is described by formation of ion pairs, which decreases the charge transfer through the molecular matrix. Conductivity of the noted materials increases at increasing of temperature because of increasing of charge carriers (ions) mobility. The conductivity of the obtained PE increases at increasing of pressure in dependence of salt types due to decreasing of mobility of molecular segments and decreasing of charge-phonon interactions.

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