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Chemistry

FLUORINE CONTAINING SILOXANE BASED POLYMER ELECTROLYTE MEMBRANES

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Abstract. The hydrosilylation reaction of 2,4,6,8-tetrahydro-2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane in the presence of platinum catalysts (platinum hydrochloric acid, Karstedt's catalysts and Pt/C (10%) at 323 K) has been carried out and corresponding addition adduct ($D_4^{R,R`}$) has been obtained. The synthesized product $D_4^{R,R}$ was analyzed by FT-IR, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. Sol-gel reactions of $D_4^{R,R}$ doped with lithium trifluoromethylsulfonate (triflate) have been studied and solid polymer electrolyte membranes have been obtained. Electric conductivity of solid polymer electrolyte membranes has been determined *via* electrical impedance spectroscopy.

Keywords: hydrosilylation, sol-gel reactions, spectroscopy, polymer electrolyte membrane, electric conductivity.

1. Introduction

The wide application of organosilicon polymers in many fields of techniques pushed the development of organosilicon chemistry and increased application-oriented researches in above mentioned field. Nowadays, development of new and more efficient methods of energy storage and conversion is one of the major problems facing scientists. This includes the efficient storage of electricity. Therefore, development of batteries and other energy storage devices with high energy density, low energy losses during operation, low cost and long lifetime is one of the most important challenges [1-3].

The promotion of the anion–cation dissociation is desirable, because it leads to enhancement of ionic conductivity *via* an increase in the free ion concentration. Recognizing that the ionic conductivity of polymer electrolytes is enhanced in the elastomeric amorphous phase by the segmental motion of the polymer chains, a significant research has been undertaken to develop a polymer structure having a highly flexible backbone and amorphous character. Among the polyphosphazenes, polyacrylate and inorganic polymers, polysiloxanes are particularly promising because they can have a wide variety of substituents bound to silicones in the backbone of the alternating silicon and oxygen atoms. Polysiloxanes are superior to polyphosphazenes because of their backbone flexibility, high chemical and thermal oxidation stability, easy processing, low cost and low toxicity [2, 4-6].

It is well known that polysiloxanes are characterized by very low glass temperature T_g = 150 K for polydimethylsiloxane, extremely high free volume, high segmental mobility and the present best matrix for Li-ion transportation. The high solubility of the corresponding salt in the polymer is another factor for achievement of high ion-conductivity. This condition is created by introduction to the polymer-electrolyte main chain or side group of such "host" donor group, as ester oxygen imide group, halogen, especially fluorine groups. Formation of the grid like structures increases the mechanical properties of polymer-electrolytes [4, 7-9].

Among organosilicon compounds, the comb-type polymers with donor fragments at silicon atoms are very interesting because by the change of nature and structure of side donor groups it is possible to change the properties of obtained polymers in a wide range.

Comb-type polymers with donor side groups are mainly obtained *via* hydrolytic polycondensation reactions donor groups containing diorganodichlorosilanes. The second way is modification reactions of industrial product polymethylhydrosiloxane (PMHS), *via* hydrosilylation reaction of polymethylhydrosiloxane with allyl-, vinyl- or unsaturated bonds containing compounds in the presence of platinum catalysts (Pt/C, platinum hydrochloric acid, Karstedt's catalyst) [10], or using dehydrocoupling

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reactions of polymethylhydrosiloxane with hydroxyl- and donor groups containing compounds in the presence of catalysts.

The third way of synthesis of comb-type polyorganosiloxanes is the hydrosilylation reactions of 2,4,6,8-tetramethyl-2,4,6,8-tetrahydro-cyclotetrasiloxane (methylcyclotri-, -pentasiloxanes) to allyl or vinyl containing compounds in the presence of platinum catalysts and then polymerization or copolymerization reactions of obtained organocyclosiloxanes in the presence of terminating (regulating) agent hexamethyldisiloxane or without it, in the presence of nucleophilic catalysts. In this case, polyorganosiloxanes with regular arrangement of side donor groups are obtained [11].

The properties of organosilicon polymers depend on the structure of macromolecular chains and on the nature of organic groups surrounding the silicon atom [6]. 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 [8, 9].

A variety of organic donor groups can be bound to the silicon that includes fluorine host groups in the side chain of siloxane matrix, which gives us possibility to change ion-conducting properties of polymer electrolyte membranes.

The aims of our work are the synthesis of $D_4^{R,R'}$ type methylorganocyclotetrasiloxane with 2,2,3,3-tetrafluoropropyl propionate side group and ethylsilyltriethoxy groups (as cross-linking moieties) at silicon; determination of their structure by FT-IR and NMR spectroscopy; investigation of sol-gel reaction of this compound for obtaining new solid polymer electrolyte membranes on the base of lithium salts (CF_3SO_3Li) and study of their electro-physical properties.

2. Experimental

2.1. Materials

All synthetic manipulations were carried out under an atmosphere of dry nitrogen gas using standard vacuum line Schlenk techniques. All solvents were de-gassed and purified prior to use according to standard literature methods: toluene, hexane, and tetrahydrofuran were distilled from sodium/benzophenone ketyl. All other reagents (Aldrich) were used as received or distilled prior to use.

2,4,6,8-tetrahydro-2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H), propyl 2.2.3.3-tetrafluoropropyl acrylate and vinyltriethoxysilane, Karstedt's catalyst ($Pt_2[(VinSiMe_2)_2O]_3$)-platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (2% solution in xylene), platinum hydrochloric acid (Aldrich), Pt/C (10%) and lithium trifluoromethyl sulfonate (triflate) were purchased from Aldrich and used as received. Toluene was dried and distilled from sodium under atmosphere of dry nitrogen. Tetrahydrofuran (THF) was dried and distilled from K–Na alloy under an atmosphere of dry nitrogen.

2.2. Characterization

FT-IR spectra were recorded on a Nicolet Nexus 470 machine with MCTB detector. ^1H, ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker ARX400 NMR spectrometer at 400 MHz operating frequency with $CDCl_3$ as the solvent and an internal standard. Differential scanning calorimetric investigation (DSC) was performed on a Nietzsche DSC 200 F3 Maia apparatus. Thermal transitions including glass transition temperatures T_g were taken as the maxima of the DSC peaks. The heating and cooling scanning rates were 10 K/min.

2.3. Hydrosilylation Reaction of D_4^H with 2,2,3,3-Tetrafluoropropyl acrylate and Vinyltriethoxysilane

0.6000 g (0.00249 mol) of 2,4,6,8-tetrahydro-2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) was 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 2,2,3,3-tetrafluoropropyl acrylate 1.3920 g, (0.0312 mol) in 5 ml dry toluene and Karstedt's precatalyst solution (20 μl). The homogeneous mixture was degassed and placed into an oil bath, which was previously set to 323 K and the reaction continued at 323 K. Then 0.4748 g (0.00249 mol) of vinyltriethoxysilane in 3 ml of dry toluene was added. The reaction was controlled by decreasing the intensity of active ≡Si–H groups [12]. After finishing reaction 0.1 wt % of activated carbon was added and refluxed for 2 h for deactivation of catalysts. All volatiles were removed by rotary evaporation at 323–333 K and further evacuated under high vacuum for 10 h to isolate the colourless viscous compound (2.3 g, 93 %).

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

2.4. General Procedure for Preparation of Cross-Linked Polymer Electrolytes

1.0 g of the base compound I was dissolved in 4 ml of dry THF and thoroughly mixed for half an hour. Then the required amount of lithium triflate from the previously prepared stock solution in THF was added to the mixture

and the stirring continued for 1 h. The mixture was then poured onto a Teflon mould with a diameter of 4 cm, and the catalytic amount of acid (one drop of 0.1N HCl solution in ethyl alcohol) was added to initiate the cross-linking process. The solvent was allowed to evaporate slowly overnight. Finally, the membrane was dried in an oven at 343 K for 3 h and at 373 K 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.

2.5. Ac Impedance Measurements

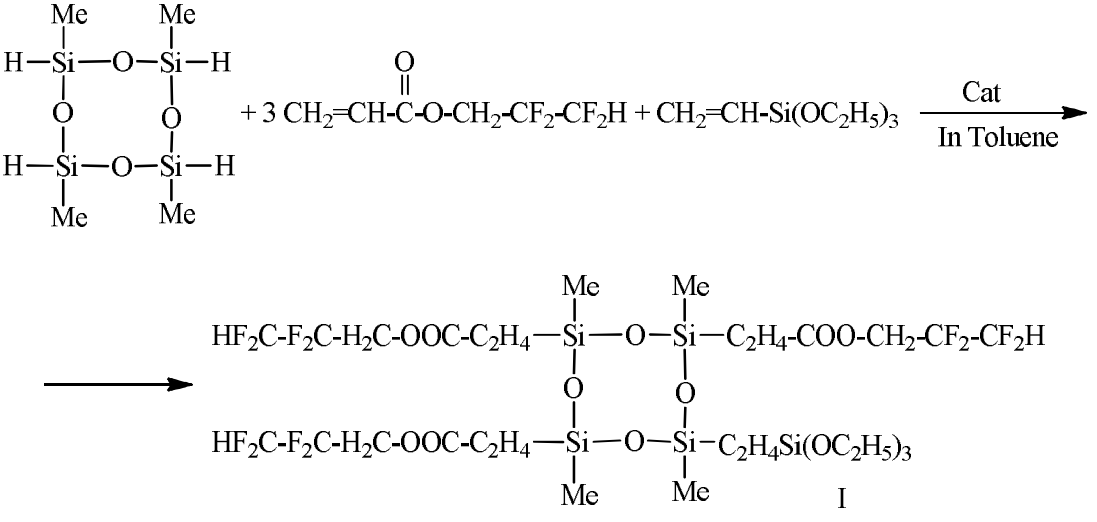
The total ionic conductivity of samples was determined by locating an electrolyte disk between two 10 mm diameter brass electrodes. The electrode/ electrolyte assembly was secured in a suitable constant volume support which allowed extremely reproducible measurements of conductivity to be obtained between repeated heating–cooling cycles. The cell support was located in an oven and the sample temperature was measured by a thermocouple positioned close to the electrolyte disk. The bulk conductivities of electrolytes were obtained during a heating cycle using the impedance technique (impedance meter BM 507–TESLA for frequencies of 50 Hz–500 kHz) within a temperature range of 303–363 K.

3. Results and Discussion

For the synthesis of methylcyclotetrasiloxane ($D_4^{R,R'}$) with propyl 2,2,3,3-tetrafluoropropyl acrylate groups and ethylsilyltriethoxy groups at silicon the hydrosilylation reaction of 2,4,6,8-tetrahydro-2,4,6,8-tetramythylcyclotetrasiloxane (D_4^H) with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane in the presence of platinum catalysts (platinum hydrochloric acid, Karstedt's catalysts and Pt/C (10%) at 323 K have been carried out in melt condition and in toluene solution. It was established that the hydrosilylation reaction of D_4^H with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane proceeds vigorously at the beginning stages first 3–7 min. From literature [7] it is known that the hydrosilylation reaction in melt condition proceeds vigorously, which changes the direction of hydride addition.

For decreasing the side reactions and for obtaining fully substituted cyclotetrasiloxane ($D_4^{R,R'}$) we have investigated hydrosilylation reactions of D_4^H with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane and we continue to study reactions in dry diluted toluene solution at various temperatures: 303, 313 and 323 K. During the hydride addition reactions, the changes of active ≡Si–H bonds concentrations on time have been studied. From this investigation it was clear that the activity of catalysts for hydrosilylation reactions of D_4^H with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane decreases in the next row: Karstedt's catalyst≈ H_2PtCl_6 > Pt/C.

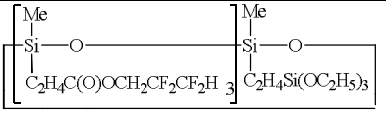
From the character of the concentration decreasing of active ≡Si–H bonds at the same temperature and various catalysts, as well as at the same catalysts and various temperatures and from the reaction duration the optimal conditions of hydrosilylation reaction of D_4^H to 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane have been determined: 323 K, dilute solution in dry solvent (toluene) and Karstedt's catalysts. The reaction proceeds according to the following scheme:



Scheme 1. Hydrosilylation reaction of D_4^H with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane

Table 1

Some physical chemical properties of organocyclotetrasiloxane

	Compound	Yield, %	n_D^{20}	d_4^{20}	M_{RD}*	M**
I		93	1.3977	1.3772	183.3 183.0	988 950

Notes: *molecular refraction – calculated values in numerator, found values in denominator; **molecular masses were determined *via* ebullioscopy method

The obtained organocyclotetrasiloxane I is transparent, viscous product well soluble in ordinary organic solvents. The structure and composition of obtained compound were determined by an elemental analysis, molecular mass, molecular refraction, FT-IR, ^{1}H, ^{13}C and ^{29}Si NMR spectra data.

In the FT-IR spectra of compound I one can observe absorption bands characteristic for asymmetric valence oscillation of linear ≡Si–O–Si≡ bonds at 1080 cm^{-1}. One can observe absorption bands at 786, 1171, 1270, 1762 and 2800–3100 cm^{-1}, characteristic for valence oscillation of ≡Si–CH_3, CO–O, ≡Si–C≡, C=O and ≡C–H bonds, respectively. The absorption bands characteristic of ≡Si–H bonds disappears.

The ^{29}Si NMR spectra of compound I showed a resonance signal with a chemical shift δ of -19 ppm and -27 ppm characteristic for RR'SiO (D) units in the cyclic fragment, signals with δ = -57.0 ppm can be assigned to the D^{OR} moieties. The resonance signal with the chemical shift δ = -65 ppm can be assigned to T moieties in a triethoxysilyl group [13].

In the ^{1}H NMR spectra of compound I (Fig. 1) one can see singlet signals for Si-Me protons with the chemical shift δ = 0.12 ppm, the signal with the centre of chemical shift at 0.56 and 1.2 ppm for methylene protons in the fragment ≡Si–$\underline{CH_2}$ (anti-Markovnikov addition to vinyltriethoxysilane silane and 2,2,3,3-tetrafluoropropyl acrylate).

The triplet signal with the centre of chemical shift at 0.9 and 1.6 ppm corresponds to methyl protons in the fragment =CH–$\underline{CH_3}$ (in case of Markovnikov addition). The signal with the centre of chemical shift at 1.64 and 2.4 ppm corresponds to methine protons during Markovnikov addition to a vinyltriethoxysilane silane and 2,2,3,3-tetrafluoropropyl acrylate. The multiple signals with the centre of chemical shift at 2.4 ppm is characterized for the methylene protons in –$\underline{CH_2}$–CO– fragment. The multiple signals at 3.8 ppm characterize the methylene protons in the CH_3–$C\underline{H_2}$–O groups. Multiple signals with the centre of chemical shift at 4.56 ppm is characteristic for methylene protons in –CO–$C\underline{H_2}$–CF_2– fragment. Triple signals in the range of 5.95–5.61 ppm is characteristic for protons in –$CF_2\underline{H}$ fragment.

In the ^{13}C NMR spectra of compound I (Fig. 2) one can observe a signal characteristic for ≡Si–CH_3 groups with the chemical shift $\delta \approx$ -3.4 ppm and signals for carbon atoms with chemical shifts $\delta \approx$ -1.9, 1.49, 7.9, 8.8, 18.2, 26.6, 27.1, 58.4, 107, 107.8 and 173 ppm corresponding to carbon atoms in the groups =CH–$\underline{CH_3}$, –OCH_2–$\underline{CH_3}$, =$\underline{CH}$–CH_3, ≡Si$\underline{CH_2}CH_2$–, –$\underline{CH_2}$CO–, –CO–$C\underline{H_2}$–CF_2–, –$O\underline{CH_2}CH_3$, –CF_2–, –$\underline{C}HF_2$ and $\underline{C}$=O groups, respectively. ^{13}C NMR spectra of compound I are completely agreed with its ^{1}H NMR spectra.

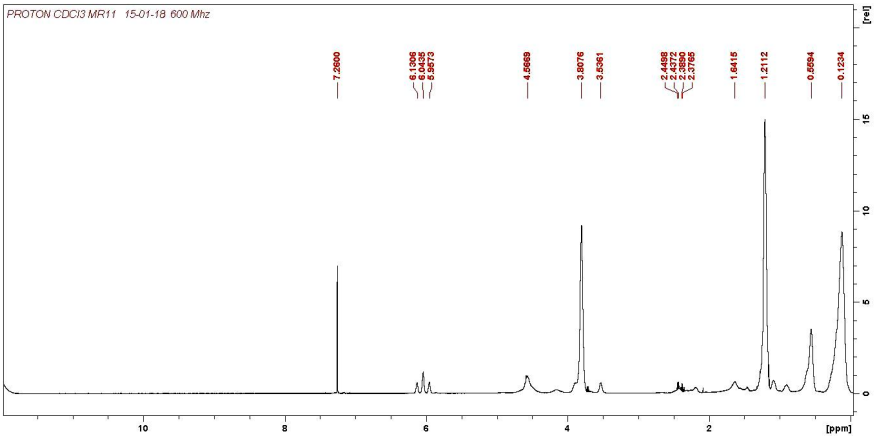


Fig. 1. ^{1}H NMR spectra of compound I

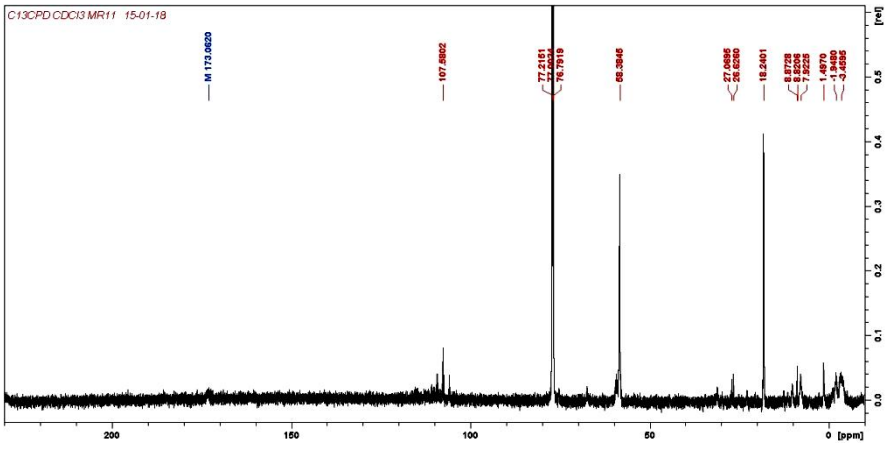
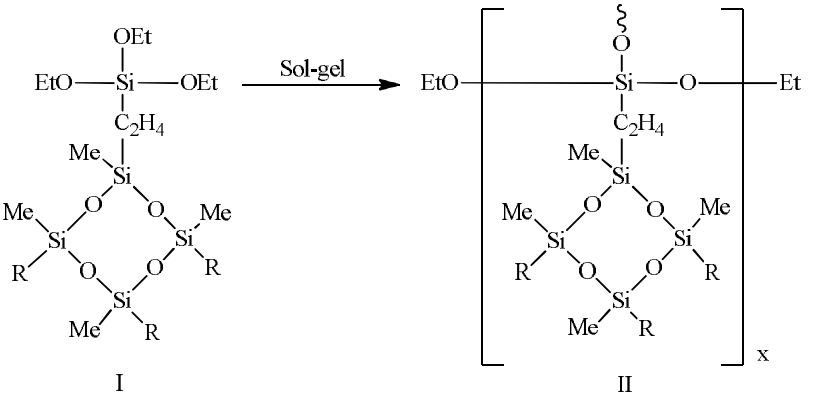


Fig. 2. ^{13}C NMR spectra of compound I

Solid polymer electrolyte membranes from monomer type D4R,R' cyclosiloxane was firstly prepared by us [14]. Using sol-gel reaction of compound (I), doped with lithium trifluorome-thylsulfonate (triflate) salt and hydrogen chloride solution in ethanol, cross-linking processes in the reaction mixture take place with thin films formation.

To obtain a cross-linked product the sol-gel process of compound I has been carried out. The catalytic amount of acid (one drop of 0.1N HCl solution in ethyl alcohol) was added to the solution of compound I in THF to initiate the cross linking process. After stirring for another 3 h the solvent was allowed to evaporate slowly overnight. The cross-linked product was dried in an oven at 343 K for 3 h and at 373 K for 1 h. The obtained product is a rigid, homogeneous and transparent film. Sol-gel reaction proceeds according to the following scheme:



where R = $–C_2H_4–C(O)O–CH_2–CF_2–CF_2H$

Scheme 2. Sol-gel processes of ethoxyl group containing organocyclotetrasiloxane I

Table 2

Specific volumetric electric conductivity of membranes II(1)–II(4) containing 5 wt % (1), 10 wt % (2), 15 wt % (3), and 20 wt %(4) of CF_3SO_3Li salt at 298 and 363 K

Membrane	Salt	Salt concentration, wt %	Ion conductivity, S/cm	
			at 298 K	at 363 K
II (1)	CF_3SO_3Li	5	$4.2\cdot10^{-7}$	$8.3\cdot10^{-4}$
II (2)	CF_3SO_3Li	10	$8.1\cdot10^{-4}$	$9.2\cdot10^{-3}$
II (3)	CF_3SO_3Li	15	$7.7\cdot10^{-5}$	$2.1\cdot10^{-3}$
II (4)	CF_3SO_3Li	20	$6.4\cdot10^{-5}$	$1.1\cdot10^{-3}$

In the FT-IR spectra of compound II one can observe the same signals which are observed for the compound I. For salt-complexed polymer electrolyte membranes II(3) and II(4) DSC investigations have been carried out. On the cooling and heating curves the obtained membrane has only one temperature characteristic which belongs to glass transition temperature $T_g \approx 231$–224 K.

Investigations of electric conducting properties of obtained electrolytic membranes were fulfilled using AC impedance spectroscopy. The measurements were conducted in the temperature range of 298–363 K.

In accordance with Table 2 and Fig. 3, in which the temperature dependences of electrical conductivity in Arrhenius coordinates are presented, an essential effect on the membranes conductivity creates the level of concentration of CF_3SO_3Li salt. One can see that the membrane containing 10 wt % of the salt is characterized by a maximal conductivity ($8.1 \cdot 10^{-4}$ S/cm), when this parameter for analogue membrane containing 5 wt % of this salt is lower by three order ($4.2 \cdot 10^{-7}$ S/cm). The experimental data on the temperature dependences of the electrical conductivity of membranes show that they also depend on the salt concentration for their part. The concentration dependence of electrical conductivity in general has an extreme character – at relatively low concentrations an increase in conductivity is observed, and then, as the conductivity increases, the salt concentration values are reduced by passing the maximum. In our case, the maximum conductivity is observed for a membrane containing near 10 wt % of the salt. The reason for this paradox can be explained as follows: it is clear that the membranes conductivity increases at the beginning with the increase in salt concentration (the number of the charge carriers increases), but at more high concentrations the second process – the decrease of the membranes conductivity – is observed and consequently the dependence of conductivity on salt concentration has a maximum. Decreasing of the membrane conductivity to some extent at relatively high concentrations of the salt is due to the formation of the so-called ion pairs, mobility of which is lower than for mono-ions [15] and, consequently, the membranes conductivity decreases. The experiments show that the temperature dependence of electrolyte conductivity is more exactly described by known as Vogel-Tammann-Fulcher (VTF) formula [16]. In this case the curves obtain a straight line form, which is more available for calculation of the activation energy.

From Fig. 3 one can see that the intervals of change of membranes conductivity in the selected range of temperature differ from one another. One of the possible interpretations of this result may be founded on the difference between current densities corresponding to each electrolyte. Namely, if the charges density in the polymer matrix is higher, the higher is a salt concentration and, correspondingly, the ions concentration in it. Consequently, in this case the temperature more effectively influences the charge mobility in the electrolytes with lower concentration than charges in more wide temperature interval, or, by other words, the number of their scattering after interactions is lower than in electrolytes with higher concentrations, although at the same time electrolytes with low concentration of ions have lower conductivity in comparison with electrolytes containing higher concentrations of the same ions.

Table 3 presents the activation energies of obtained electrolyte membranes conductivity calculated from experimental curves. These values are in accordance with the known rule – the higher is conductivity, the lower is activation energy. The conductivity of electrolytes containing the salt in amount of 15 and 20 wt% is lower than that of electrolytes with 10 wt % of salt due to the formation of the ion pairs with lower mobility than the mobility of mono-ions.

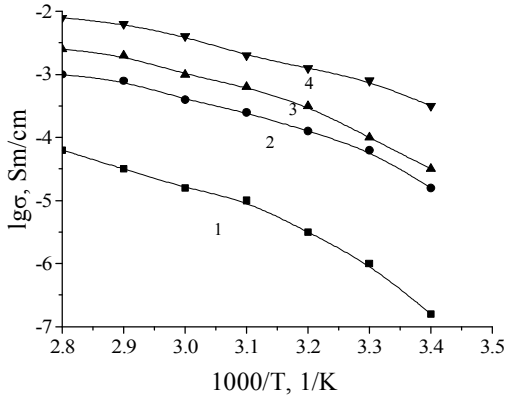


Fig. 3. Temperature dependence of the specific volumetric electric conductivity of membranes on the basis of compound II containing 5 (1), 10 (4), 15 (3), and 20 wt % (2) of CF_3SO_3Li salt

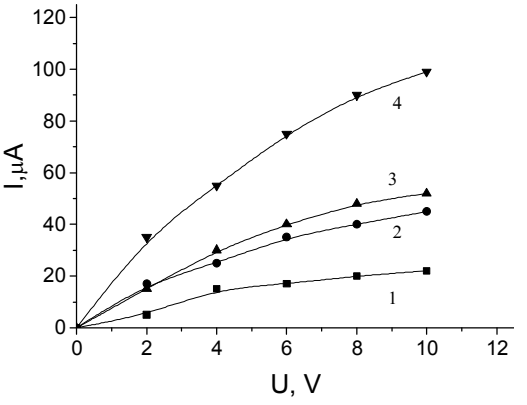


Fig. 4. Voltammograms of the polyelectrolyte membranes II(1)–II(4) containing 5 (1), 10 (4), 15 (3), and 20 wt % (2) of CF_3SO_3Li salt

Table 3

Activation energies of ion conductivity of membranes on the basis of compound II containing 5 wt % (1), 10 wt % (2), 15 wt % (3), and 20 wt %(4) of CF_3SO_3Li salt

Polyelectrolyte	1	2	3	4
$E_a \cdot 10^{-3}$, eV	97	69	77	85

In accordance with Fig. 4 the saturation of the electrical current significantly depends on the composition of the electrolytes. The longer the length of the initial linear part (up to bend) of the electrical current, the higher a conductivity. Deviations from the linear increase of intensity with voltage are partially related to charge-phonon interactions which are increased with increasing ion energy giving rise to a decrease of the electrolytes conductivity [17].

4. Conclusions

The corresponding addition adduct ($D_4^{R,R'}$) have been obtained *via* hydrosilylation reaction of tetrahydro tetramethylcyclotetrasiloxane (D_4^H) with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane in the presence of platinum catalysts at 323 K. Sol-gel reactions of $D_4^{R,R'}$ doped with lithium trifluoromethylsulfonate (triflate) have been studied and solid polymer electrolyte membranes have been obtained.

The membranes conductivity increases at the beginning with the increase in salt concentration (the number of the charge carriers increases), but at more high concentrations the second process – the decrease of the membranes conductivity – is observed and consequently the dependence of conductivity on salt concentration has a maximum. Decreasing of the membrane conductivity to some extent at relatively high concentrations of the salt is due to the formation of the so-called ion pairs, mobility of which is lower than for mono-ions and, consequently, the membranes conductivity decreases. Character of these electrolytes voltamograms corresponds to the value of electrolytes conductivity – the higher the conductivity, the higher a specific electric current in these materials.

Acknowledgments

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ФЛУОРОВМІСНІ ТВЕРДІ ПОЛІМЕР-ЕЛЕКТРОЛІТНІ МЕМБРАНИ НА ОСНОВІ СИЛОКСАНУ

Анотація. *Проведено реакції гідросилілування 2,4,6,8-тетрагідро-2,4,6,8-тетраметилциклотетра-силоксану (D_4^H) з 2,2,3,3-тетрафлуорпропіл акрилатом та вінілтриетоксисиланом у присутності платинових каталізаторів (платино хлориста воднева кислота, каталізатор Карстеда і каталізатора Pt/C (10%) за температури 323 К) та одержано відповідний адукт ($D_4^{R,R'}$). За допомогою Фур'є-спектроскопії, ^1H, ^{13}C, та ^{29}Si ЯМР спектроскопії проведено аналіз синтезованого продукту $D_4^{R,R'}$. Вивчено золь-гель реакції $D_4^{R,R'}$, допованого трифлуорметилсульфонатом літію (трифлат) та одержано тверді полімер-електролітні мембрани. Із застосуванням електроімпендасної спектроскопії визначено електропровідність твердих полімерних електролітних мембран.*

Ключові слова: *гідросилілування, золь-гель реакції, спектроскопія, полімерна електролітна мембрана, електропровідність.*