

INTERPENETRATING NETWORK ON THE BASIS
OF METHYLCYCLOTETRASILOXANE MATRIX*Omari Mukbaniani*^{1, 2, *}, *Jimsher Aneli*², *Marta Plonska-Brzezinska*³,
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Abstract. Hydrosilylation reaction of 2,4,6,8-tetrahydro-2,4,6,8-tetramethylcyclotetra siloxane (D_4^H) allyl trifluoroacetate and vinyltriethoxysilane catalysed by platinum catalysts has been studied. The synthesized $D_4^{R,R'}$ was analyzed with FTIR, 1H , ^{13}C , and ^{29}Si NMR spectroscopy. *Via* sol-gel reactions of $D_4^{R,R'}$ systems doped with lithium trifluoromethylsulfonate (triflate) solid polymer electrolyte membranes have been obtained. It has been found that the electric conductivity of the polymer electrolyte membranes at room temperature changes in the range of $(4 \cdot 10^{-5})$ – $(6 \cdot 10^{-7})$ S/cm.

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

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

The polysiloxanes with very low glass transition temperatures, $T_g = 150$ K for poly(dimethylsiloxane) and extremely high free volumes and thermo-oxidative stability [4, 5] 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 [6, 7], Shriver [8-10], Acosta [11] and West *et al.* [12, 13]. 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.* [5]. Six-oxygen side-chain polymer host when doped with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) showed the highest room temperature conductivity ($4.0 \cdot 10^{-4}$ S·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.

The polysiloxanes with very low glass transition temperatures $T_g = 150$ K for poly(dimethylsiloxane), extremely high free volumes and a high segmental mobility are expected to be good hosts for Li^+ transport. Another necessary condition for high ionic conductivity is a high salt solubility in the polymer, which is most often achieved by donors such as etheric oxygen, ester carbonyl groups or fluorine substituted groups on the main chain or on the side groups. Polysiloxanes are the excellent candidates for usage in solid polymer electrolytes because of their high chain flexibility, chemical stability, high thermal/oxidative stability, low toxicity, easy process ability and low cost.

Usually for obtaining solid polymer electrolytes on the base of organosilicon polymers as starting materials polymethylhydrosiloxane (PMHS) matrix is used. *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 the reaction requires long time, replacement of all $\equiv Si-H$ does not proceed completely and various linking systems are obtained. Furthermore during the reaction branching and cross linking processes often take place.

The second way of obtaining comb-type methylsiloxane oligomers is a polymerization reaction in advanced organocyclisiloxanes [14-16].

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We now report about synthesis of D_4^{RR} type methylorganocyclotetrasiloxane with propyl trifluoroacetate and ethyltriethoxysilane groups (as cross-linking moieties) at silicon. This compound is an interesting product because besides esteric groups also contains flouraine host donor groups and *via* sol-gel reactions directly gives us thin films.

2. Experimental

2.1. Materials

2,4,6,8-tetrahydro-2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H), and vinyltriethoxysilane (Aldrich), platinum hydrochloric acid (Aldrich), Karstedt's catalyst ($Pt_2[(VinSiMe_2)_2O]_3$) – platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (2% solution in xylene) (Aldrich), platinum hydrochloric acid (Aldrich), Pt/C (10 %) (Aldrich), allyl trifluoroacetate (Aldrich) and vinyltriethoxysilane (Aldrich) were used as received. Lithium trifluoromethylsulfonate (triflate) was purchased from (Aldrich). Toluene was dried and distilled from sodium under atmosphere of dry nitrogen. Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. 0.1M solution of platinum hydrochloric acid in THF was prepared and kept under nitrogen at low temperature.

2.2. Methods of Analysis

FTIR spectra were recorded on a Nicolet Nexus 470 spectrometer with MCTB detector. 1H , ^{13}C and ^{29}Si NMR spectra were recorded on a Varian Mercury 300VX NMR spectrometer, using dimethylsulphoxide 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.

2.3. Hydrosilylation Reaction of 2,4,6,8-Tetrahydro-2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) Allyl Trifluoroacetate and Vinyltriethoxysilane in the Presence of a Catalyst

2,4,6,8-tetrahydro-2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) 2.5000 g, (0.01039 mol) were transferred into 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 trifluoroacetate (4.8051 g, 0.0312 mol) in 5 ml of dry toluene and Karstedt's precatalyst solution (20 μ l). The homogeneous mixture was degassed and placed into an oil bath, which was previously set to 323 K and the reaction continued at this temperature. Then 1.9781 g (0.01039 mol) of vinyltriethoxysilane in 3 ml dry toluene was added. The reaction was controlled by the decrease of active $\equiv Si-H$ groups intensity. After finishing reaction 0.1 wt % 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 colorless viscous compound **I** (8.63 g, 93 %).

Other hydrosilylation reactions D_4^H with allyl trifluoroacetate and vinyltriethoxysilane in the presence of other catalysts were carried out according to the above mentioned method.

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

0.75 g of the base compound **I** was dissolved in 4 ml of dry THF and thoroughly mixed for half an hour. After stirring the 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, than a catalytic amount of acid (one drop of 0.1N HCl solution in ethyl alcohol) was added to initiate the cross-linking process and the solvent was allowed to evaporate slowly overnight. Finally, the membrane was dried in an oven at 343 K for 3 h and at 473 K for 1 h. Homogeneous and transparent films with average thickness of 200 μ m were obtained in this way. These films were insoluble in all solvents, only swollen in THF.

2.5. AC Impedance Measurements

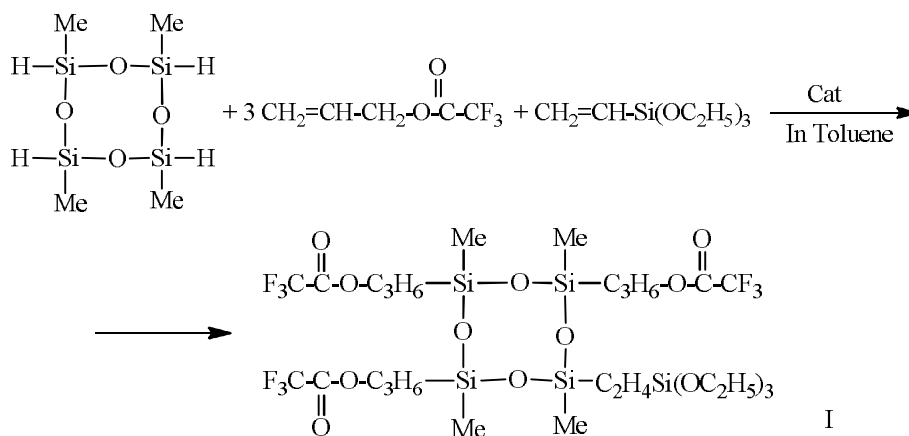
The total ionic conductivity of samples was determined by locating an electrolyte disk between two 10 mm diameter brass electrodes. The electrode/ electrolyte assembly was secured in a suitable constant volume support which allowed extremely reproducible measurements of conductivity to be obtained between repeated heating–cooling cycles. The cell support was located in the oven and the sample temperature was measured by the 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 50 Hz–500 kHz) within a temperature range of 303–363 K.

3. Results and Discussion

The main aim of our work was the methylcyclotetrasiloxane synthesis with propyl trifluoroacetate and ethyltriethoxy groups at silicon the hydrosilylation reaction of 2,4,6,8-tetrahydro-2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) with allyl trifluoroacetate and vinyltriethoxy in the presence of platinum catalysts (platinum hydrochloric acid, Karstedt's catalysts and Pt/C (10 %) at 323 K have been carried out in a melt condition and in a toluene solution. It was established that hydrosilylation reaction of D_4^H with allyl trifluoroacetate and vinyltriethoxysilane proceeds vigorously at the beginning stages first 3–7 min. From literature [14] it is known that hydrosilylation reaction of 2,4,6,8-tetrahydro-2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) with allyl butyrate and vinyltriethoxysilane in the melt condition proceeds vigorously, which changes the direction of hydride addition and partially substituted hydroxyl containing methylcyclotetrasiloxanes are obtained.

For decreasing side reactions and for obtaining fully substituted cyclotetrasiloxane ($D_4^{R,R}$) we have investigated hydrosilylation reactions of D_4^H with allyl trifluoroacetate and vinyltriethoxysilane. We continue to study reactions in the dry toluene solution (50–60 %) at various temperatures: 303, 313 and 323 K. During the hydride addition reactions, the changes of active $\equiv\text{Si-H}$ bonds concentrations in time were observed. During hydrosilylation reaction of D_4^H with allyl trifluoroacetate the decrease of active Si-H bond in a hydrosilylation reaction have been studied. It was shown that the activity of catalysts for hydrosilylation reactions of D_4^H with allyl trifluoroacetate decreases in the next row: Karstedt's catalyst $\approx \text{H}_2\text{PtCl}_6 > \text{Pt/C}$. The optimal condition of hydrosilylation reaction of D_4^H to allyl trifluoroacetate and vinyltriethoxysilane has been determined, it is 323 K temperature and dilute solution in dry solvent (toluene) and Karstedt's catalysts.

The reaction proceeds according to the Scheme 1:



Scheme 1. Hydrosilylation reaction of D_4^H with allyl trifluoroacetate and vinyltriethoxysilane

Table 1

Some physical chemical properties of organocyclotetrasiloxane

Compound I	Yield, %	n_D^{20}	d_4^{20}	M_{RD}^*	M^*
	93	1.3957	1.2804	$\frac{167.40}{166.99}$	$\frac{920}{893}$

Note: *numerator – calculated values, denominator – found values

The obtained organocyclotetrasiloxane **I** is a transparent, viscous product well soluble in ordinary organic solvents. The structure and composition of obtained compound were determined by elemental analysis, molecular mass, molecular refraction, FTIR, ^1H , ^{13}C and

^{29}Si NMR spectra data. Some physical chemical properties of organocyclotetrasiloxane are presented in Table 1.

In the FTIR spectra of compounds **I** and **II** (Figs. 1 and 2) one can observe absorption bands characteristic for asymmetric valence oscillation of linear $\equiv\text{Si-O-Si}\equiv$ bonds

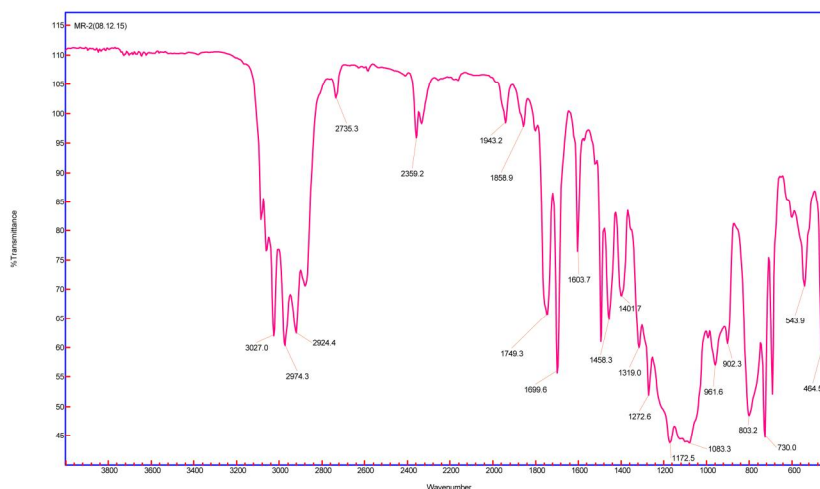
at 1051 cm^{-1} . One can observe absorption bands at $795\text{--}800$, 1188 , 1265 , $1735\text{--}1743$ and $2800\text{--}3100\text{ cm}^{-1}$, characteristic for valence oscillation of Si-CH_3 , CO-O , $\equiv\text{Si-C}\equiv$, C=O and $\equiv\text{C-H}$ bonds, respectively. The absorption bands characteristic of Si-H bonds disappear.

^{29}Si NMR spectra of compound **I** showed a resonance signal with a chemical shift $\delta = -19$ ppm and -27 ppm characteristic for $\text{RR}'\text{SiO}$ (D) units in a cyclic fragment, signals $\delta = -57.0$ ppm can be assigned to the D^{OR} moieties. The resonance signal with the chemical shift $\delta = -65$ ppm can be assigned to T moieties in a triethoxysilyl group [8].

In the ^1H NMR spectra of compound **I** (Fig. 2) one can see singlet signals for Si-Me protons with the chemical shift $\delta = 0.14$ ppm, δ signal with the center at

0.6 ppm for methyl protons in the fragment $=\text{CH-CH}_3$ (in case of Markovnikov addition); triplet signal in the fragment C^1H_2 with center of chemical shift $\delta = 0.97$ ppm (anti Markovnikov addition); multiple signals with the center of the chemical shifts at $\delta = 1.4$ and 1.8 ppm characteristic for protons in C^2H_2 and $=\text{CH-CH}_3$ (Markovnikov addition) groups. Also, the triple signal with the center of the chemical shift at $\delta = 4.4$ ppm corresponds to protons in the $\text{C}^3\text{H}_2\text{-O}$ group. In ^1H NMR spectra of compound **I** additionally one can observe m -signals with the center of the chemical shift at $\delta = 3.5$ ppm for methylene protons in the fragment $\text{O-CH}_2\text{-CH}_3$. The signals at 0.6 , 1.6 ppm for $=\text{CH-CH}_3$ and $=\text{CH-CH}_3$ (Markovnikov addition of vinyltriethoxysilane) overlap with the chemical shift of α -addition of allyl groups.

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Fig. 1. FTIR spectra of compound **I**

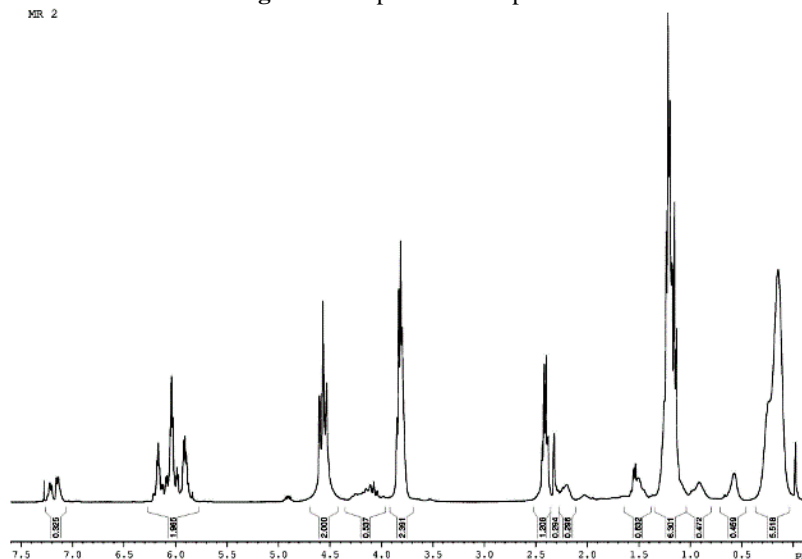


Fig. 2. ^1H NMR spectra of compound **I**

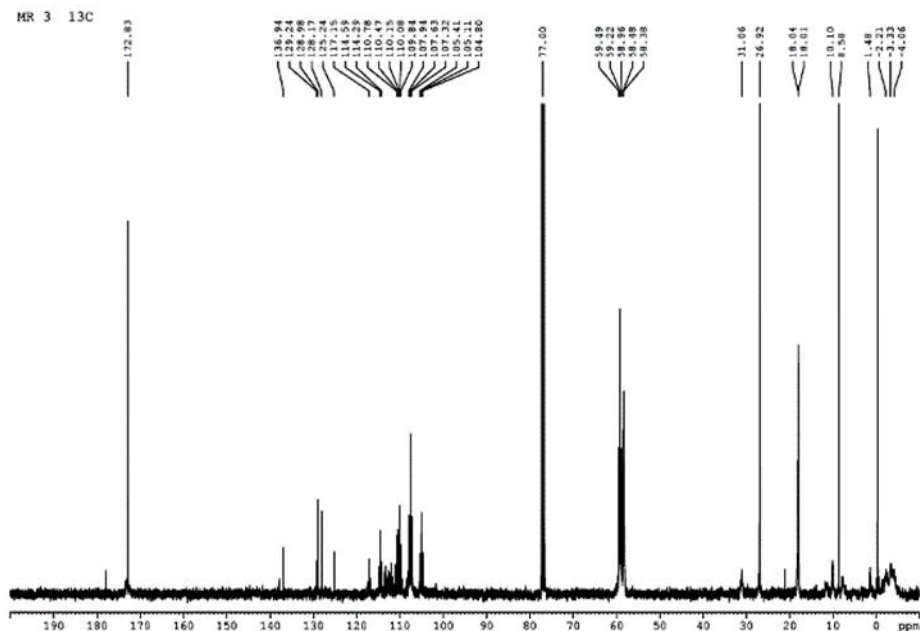
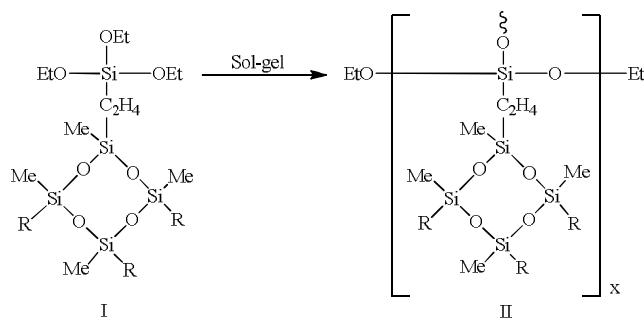


Fig. 3. ^{13}C NMR spectra of compound I

In the ^{13}C NMR spectra of compound **I** (Fig. 3) one can observe signals characteristic for $\equiv\text{Si}-\text{CH}_3$ groups with the chemical shift at $d \approx -0.2$ ppm and signals, for carbon atoms with the chemical shifts at $d \approx 12.5, 16.1, 17.2, 68.1, 112.5, 157$ ppm corresponding to carbon atoms in the groups $=\text{CH}-\text{CH}_3$, SiCH_2 , SiCH_2CH_2 , $=\text{CH}-\text{CH}_3$, $\text{SiCH}_2\text{CH}_2\text{CH}_2$, CF_3 and $\text{C}=\text{O}$ groups, respectively. Additionally one can observe chemical shifts for carbon atoms at 18.5 and 57.2 ppm characteristics for carbon in the fragments OCH_2CH_3 and OCH_2CH_3 , respectively.

Via sol-gel reaction of compound **I** – 2,4,6-tri(propyltrifluoroacetate)-8-ethyltriethoxysilane-2,4,6,8-tetramethylcyclotetrasiloxane doped with 1-2 drop of hydrogen chloride solution in ethanol at room temperature, thin transparent films have been obtained. Sol-gel reaction proceeds according to the Scheme 2:



Scheme 2. Sol-gel processes of ethoxyl group containing organocyclotetrasiloxane **I** where $\text{R} = -\text{C}_3\text{H}_6-\text{O}-\text{C}(\text{O})-\text{CF}_3$

In the FTIR spectra of compound **II** one can observe the same signals which are observed in compound **I**. For insoluble crosslinking system **II** DSC investigations have been carried out. On the cooling and heating curves the obtained membrane has only one temperature characteristic which belongs to a glass transition temperature $T_g \approx 231.3$ K.

Preparation of solid polymer electrolyte membranes from monomer type $\text{D}_4^{\text{R,R}'}$ cyclosiloxane (**I**) via sol-gel reaction, doping with lithium trifluoromethylsulfonate (triflate) salt and hydrogen chloride solution in ethanol have been suggested by us. Crosslinking processes take place with thin films formation.

In the polymer electrolyte membranes the lithium salts concentration has been varied from 5, 10, 15 and up to 20 %. In Table 2 ion conductivity of PE membranes on the base of **II** is presented.

AC impedance measurements were employed to investigate the variation of conductivity with temperature and salt concentration for all the obtained electrolytes. Fig. 4 illustrates the Arrhenius plots of the dependence of electrical conductivity of PE based on **II** with salts S_1 at different contents.

The dependences presented in Fig. 4 have a typical for analogical electrolytes character. Among them the membrane **II**(3) containing 15 wt % of the salt is characterized with a relatively high conductivity, when its analogs have a rather low conductivity at room temperature. The reason of this phenomenon may be described in terms of structural peculiarities of these membranes.

Table 2

Ion conductivity of PE membranes II(1)–II(4)

Membrane number	Salt	Salt concentration, %	Ion conductivity at 298 K, S/cm
II(1)	CF ₃ SO ₃ Li	5	2.4·10 ⁻⁶
II(2)	CF ₃ SO ₃ Li	10	3.7·10 ⁻⁶
II(3)	CF ₃ SO ₃ Li	15	4.7·10 ⁻⁶
II(4)	CF ₃ SO ₃ Li	20	3.4·10 ⁻⁶

Table 3

Activation energies of ion conductivity for PE membranes II(1)–II(4)

PE	II(1)	II(2)	II(3)	II(4)
$E_a \cdot 10^{-3}$, eV	94	91	75	82

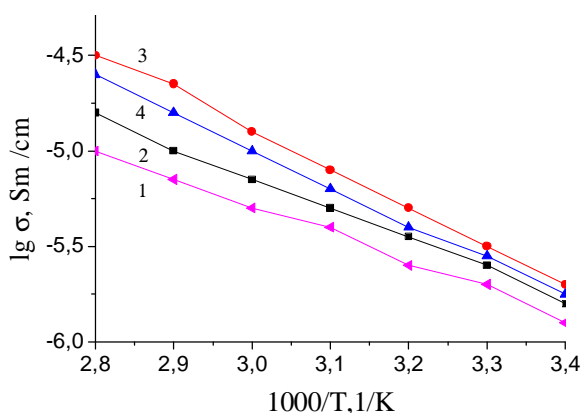


Fig. 4. Temperature dependence of the polyelectrolytes II(1-4). Numeration on the curves corresponds to those in Table 2

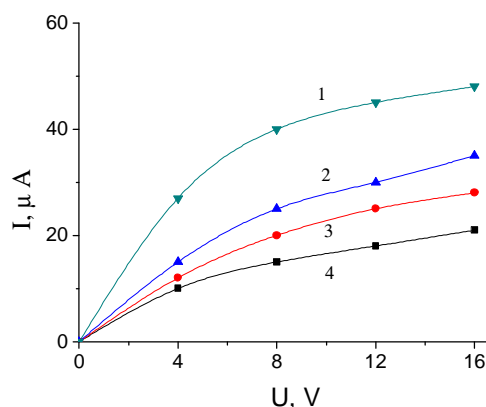


Fig. 5. Voltammograms of the polyelectrolyte membranes. The curve 1 corresponds to II(1); 2 – II(2); 3 – II(4) and 4 – II(3)

The activation energies of the conductivity of the investigated membranes obtained from temperature dependences of their conductance are presented in Table 3. In accordance with Table 3 the higher is electrical conductivity of the membrane, the lower is its activation energy, which is in agreement with the known property of electric conducting materials. In this case the membrane II(3) with such magnitude is characterized.

One of the electrical physical characteristic – the voltammograms of considered membranes is presented in Fig. 5. The curves of this dependence reflect the fact that membranes with more high specific electric volumetric conductivity are able to pass more electric current – the higher is its specific conductivity in general, the higher is the electrical current.

4. Conclusions

Via hydrosilylation reaction of D₄^H with allyl trifluoroacetate and vinyltriethoxy in the presence of platinum catalysts, corresponding D₄^{R,R'} with electro

donor propyl fluorine and triethoxysilyl fragments in the side chain have been obtained. The structure and composition of obtained compound were determined by elemental analysis, molecular mass, molecular refraction, FTIR, ¹H, ¹³C and ²⁹Si NMR spectra data. The D₄^{R,R'} linked *via* sol-gel reaction and lithium trifluoromethylsulfonate (triflate) containing solid polymer electrolyte membranes have been obtained.

The character of temperature dependence of the membrane conductivity in the range of 303–363 K coincides with known analogues. Numerical difference between values of electrical conductivity is described by peculiarities of the microstructure of membranes, on the one hand, and by the value of mobility of the ions, on the other one. Namely, the higher is the volume of the empties in a macromolecular system, the higher is electrical conductivity of the membranes. The dependence of electrical current on the external alternative voltage (so called voltammogram) in the membranes corresponds to the level of the initial conductivities of them – the higher is the conductivity of membranes, the higher is the level of electrical current through them.

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ВЗАЄМОПРОНИКНА СІТКА НА ОСНОВІ МЕТИЛЦИКЛОТЕТРАСИЛОКСАНОВОЇ МАТРИЦІ

Анотація. Вивчено реакцію гідросилування 2,4,6,8-тетрагідро-2,4,6,8-тетраметилциклотетрасилоксану (D_4^H) алілтрифлуороацетату та вінілтриетоксисилану, у присутності платинових каталізаторів. З використанням Фур'є, 1H , ^{13}C , та ^{29}Si ЯМР спектроскопії проведено аналіз синтезованого продукту $D_4^{R,R'}$. За допомогою соль-гелевих реакції систем $D_4^{R,R'}$, промотованих трифлуорометилсульфонатом літію (трифлат) одержано тверді полімерні електролітні мембрани. Встановлено, що електропровідність полімерних електролітних мембран за кімнатної температури змінюється в діапазоні $(4 \cdot 10^{-5}) - (6 \cdot 10^{-7})$ См/см.

Ключові слова: гідросилування, соль-гелеві реакції, спектроскопія, полімерна електролітна мембрана, електропровідність.