FLUORINE CONTAINING SILOXANE BASED POLYMER ELECTROLYTE MEMBRANES

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Since Wright discovered ionic conductivity in a PEO/Na$^+$ complex, the research and development effort have become quite active on solid polymer electrolytes (SPE), in particular, on the improvement of the ionic conductivity. The principal requirements for high conductivity of a SPE are the ability to solvate ions and a low glass transition temperature to afford facile ion transport.

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, 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, chemical stability, thermal stability, and low toxicity.

The polysiloxanes, with very low glass transition temperatures, Tg = - 123^0 C for poly(dimethylsiloxane), and extremely high free volumes, are expected to be good hosts for Li$^+$ transport, when polar units are introduced into the polymer backbone. 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 give us possibility to change ion-conducting properties of polymer electrolyte membranes.

The main aim of our work was the synthesis methylcyclotetrasiloxane ($D_4^{R,R'}$) with propyl 2,2,3,3-tetrafluoropropyl acrylate groups and ethyltriethoxysilyl groups at silicon via hydrosilylation reaction of 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (D_4^H) with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxy in the presence of platinum catalysts (platinum hydrochloric acid, Karstedt's catalysts and Pt/C (10%) at 50^{0}C have been caried out in melt condition and in toluene solution. It was established that hydrosilylation reaction of D_4^H with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane proceeds vigorously at the begening stages first 3-7 minutes. From literature [15] it's known that hydrosilylation reaction 2.4.6.8-tetrahydro-2.4.6.8-tetramethylcyclotetrasiloxane (D_4^H) with allyl butyrate and vinyltriethoxysilane in melt condition proceeds vigorously, which changes the direction of hydride addition and partially substituted hydroxyl containing methylcyclotetrasiloxanes are obtained.

For decreasing of 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 we continue to study reations in dry diluted toluene solution at various temperatures: 30, 40 and 50^{0}C. During the hydride addition reactions, the changes of active $\equiv$Si-H bonds' concentrations in time were observed. During hydrosilylation reaction of D_4^H with 2,2,3,3-tetrafluoropropyl acrylate the decrease of active Si-H bond in 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 rank: Karstedt's catalyst≈ H_2PtCl_6 > Pt/C.

The optimal condition of hydrosilylation reaction of D_4^H to 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane have been determined it is 50^0C temperature and dilute solution in dry solvent (toluene) and Karstedt's catalysts.

The reaction proceeds according to the following scheme 1:
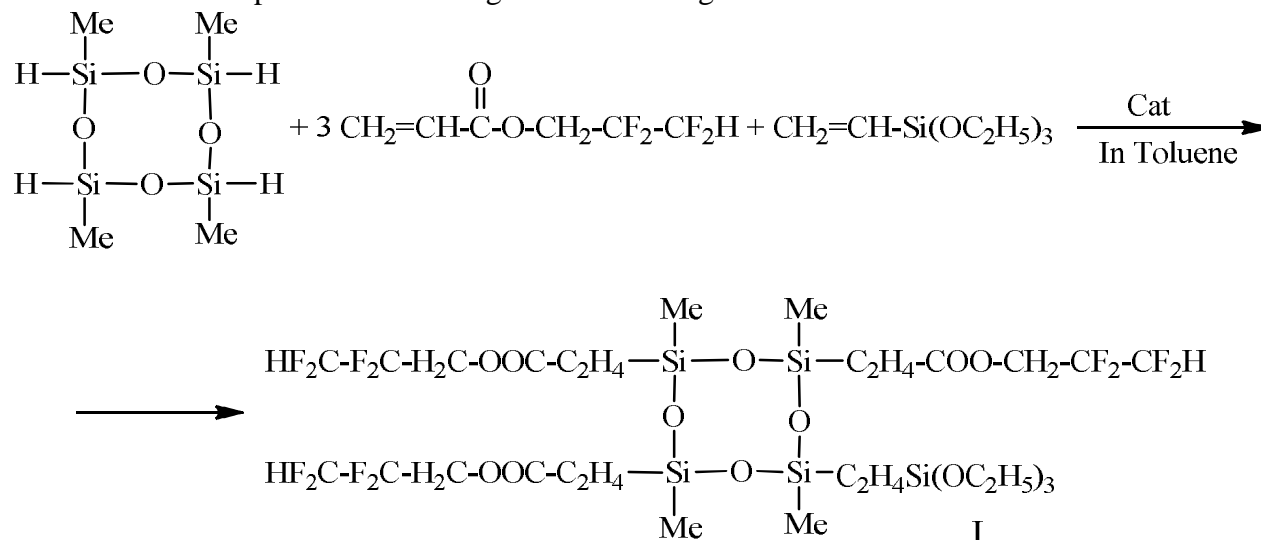
Scheme 1. Hydrosilylation reaction of D_4^H with 2,2,3,3-tetrafluoropropyl acrylate and vinyltriethoxysilane

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

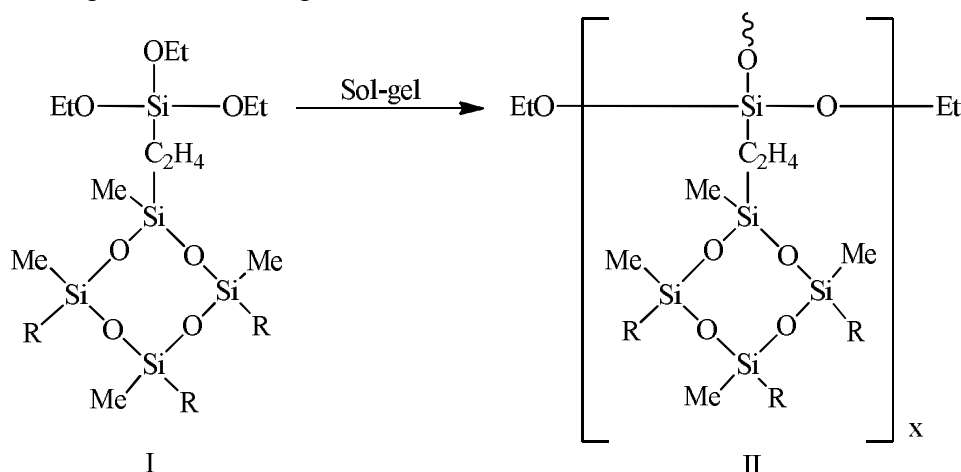In the FTIR spectra of compounds I (Figure 1 and 2) one can observe absorption bands characteristic for asymmetric valence oscillation of linear ≡Si-O-Si≡ bonds at 1080 cm^{-1}. One can observe absorption bands at 786, 1171, 1270, 1762 and 2800–3100 cm^{-1}, characteristic for valence oscillation of ≡Si-CH$_3$, CO-O, ≡Si-C≡, C=O and ≡C-H bonds accordingly. The absorption bands characteristic of Si-H bonds disappears.

In the ^1H NMR spectra of compound I (Figure 2) one can see singlet signals for Si-Me protons with chemical shift δ=0.12 ppm, signal with center of chemical shift at δ=0.56 and 1.2 ppm for methylene protons in the fragment ≡Si-CH$_2$ (anti Markovnikov addition to vinyltriethoxy silane and 2,2,3,3-tetrafluoropropyl acrylate); The triplet signal with center of chemical shift at δ=0.9 and 1.6 ppm corresponds to methyl protons in in the fragment =CH-CH$_3$ (in case of Markovnikov addition); The signal with center of chemical shift δ=1,64 and 2.4 ppm corresponds to methine protons during Marcovnikov addition to to vinyltriethoxy silane and 2,2,3,3-tetrafluoropropyl acrylate. The multiple signal with center of chemical shifts at δ=2.4 ppm is characterized for the methylene protons in -CH$_2$-CO- fragment. The multiple signal at 3.8 ppm characterize the methylene protons in the CH$_3$-CH$_2$-O groups. Multiple signal with center of chemical shifts at δ= 4.56 ppm is characterized for methylene protons in -CO-CH$_2$-CF$_2$- fragment. triple signals in the range 5.95 – 5.61 ppm is characteristic for protons in CF$_2$H fragment.

In ^{13}C NMR spectra of compound I one can observe signal characteristic for ≡Si-CH$_3$ groups with chemical shift at δ≈ -3.4 ppm and signals, for carbon atoms with chemical shifts at δ≈ -1.9, 1.49, 7.9, 8.8, 18.2, 26.6, 27.1, 58.4, 107, 107.8 and 173 ppm corresponds 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**-CH$_2$-CF$_2$-, -O$\underline{CH_2}$CH$_3$, -$\underline{CF_2}$-, -$\underline{CHF_2}$ and $\underline{C}$=O groups accordingly. ^{13}C NMR spectra of compound I completely is in conformity with ^{1}H NMR spectra of compound I.

Via sol-gel reaction of compound I - 2.4.6-tri(propyltrifluoroacacetate)-8-ethyl-triethoxysilane-2.4.6.8-tetramethylcyclotetrasiloxane doped with 1-2 drop of hydrogen chloride solution in ethanol at room temperature thin transparent film have been obtained. Sol-gel reaction proceeds according to the following scheme 2:

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

Where: R=-C$_2$H$_4$-C(O)O-CH$_2$-CF$_2$-CF$_2$H.

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 investigation have been carried out. On the cooling and heating curves the obtained membrane has only one temperature characteristic which belongs to glass transition temperature $T_g \approx 39.1.$ ^{o}C.

By us firstly have been suggested preparation solid polymer electrolyte membranes from monomer type $D_4^{R,R'}$ cyclosiloxane (I) using sol-gel reaction via, doping with lithium trifluoro-methylsulfonate (triflate) salt and hydrogen chloride solution in ethanol, crosslinking processes take place with formation thin films.

Investigations of electric conducting properties of obtained electrolytic membranes were fulfilled with use AC impedance spectroscopy. The measurements were conducted at temperatures in the range 25 – 90^{0}C.

Table 1

Specific volumetric electric conductivity of membranes on the basis of compound I containing 5wt% (1), 10wt% (2), 15wt% (3), and 20wt%(4) the salt CF$_3$SO$_3$Li at 25^{0}C and 90^{0}C

Membrane	Salt	Salt concentration. wt%	Ion conductivity, S/cm	
			at 25°C	at 90^{0}C
1	CF$_3$SO$_3$Li	5	4.2×10^{-7}	8.3×10^{-4}
2	CF$_3$SO$_3$Li	10	8.1×10^{-4}	$9,2 \times 10^{-3}$
3	CF$_3$SO$_3$Li	15	7.7×10^{-5}	2.1×10^{-3}
4	CF$_3$SO$_3$Li	20	6.4×10^{-5}	1.1×10^{-3}

In accordance with the Table 1 and Figure 1, on which the temperature dependence of electrical conductivity in Arrhenius coordinates are presented, an essential effect on the membranes conductivity creates the level of concentration of the salt CF$_3$SO$_3$Li. One can see that the membrane containing 10 wt% of the salt is characterized with maximal conductivity

(8.1x10^{-4} S/cm), when this parameter for analogue membrane containing 5wt% of this salt even on three order is lower (4.2x10^{-7} S/cm). Value of Conductivity of membranes containing more high concentrations of the salt occupied the significances between noted above. Such character of the filler concentration dependence of the conductivity of the polymer membranes are in good agreement with known experimental data and reason of it arising (decreasing of charge transfer phenomenon because of formation of ion pairs with relatively low mobility at high concentrations of the salts [1]. The experiments show that the temperature dependence of electrolyte conductivity more exactly is described by known as Vogel-Tammann-Fulcher (VTF) formula [2]. In this case the curves obtain a straight line form, which is more available for calculation of the activation energy.

From the Figure 1 one can see that the intervals of change of membranes conductivity in the selected range of temperature differ one from another. One of the possible interpretations of this result may be founded on the difference between current densities corresponding to each electrolyte. Namely, the charges density in the polymer matrix the higher the higher is a salt concentration and correspondingly the ions concentration in it. Consequently, in this case the temperature more effectively influences on the charge mobility in the electrolytes with lower concentration of charges in more wide temperature interval, or, by other words, (number of scattering of them after their interactions is low, then in electrolytes with higher concentrations, although in the same time electrolytes with low concentration of ions has lower conductivity in comparison with electrolytes containing more high concentrations of the same ions.
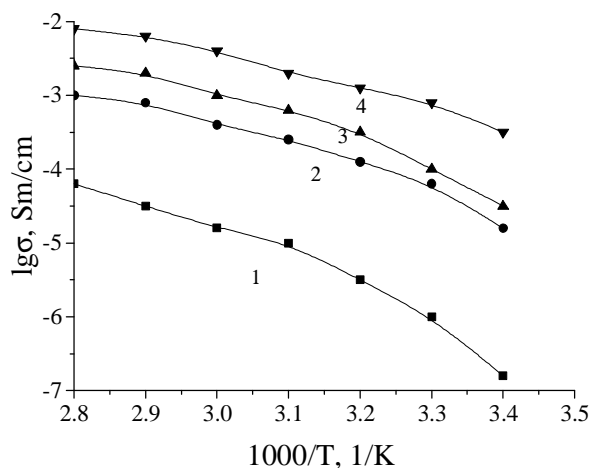

Figure 1. Temperature dependence of the specific volumetric electric conductivity of membranes on the basis of compound II containing 5 wt% (1), 10 wt% (4), 15 wt% (3), and 20 wt%(2) the salt CF$_3$SO$_3$Li

There are calculated the significations of the calculated from experimental curves activation energies of obtained electrolyte membranes conductivity. These values are in accordance with known rulethe higher is conductivity the lower is activation energy. The conductivity of electrolytes containing this salt with amount 15 and 20wt% is lower than for analogue with 10wt% salt because of formation of the ion-pairs with mobility lower than for mono-ions.

References:
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