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Polyvinyl Chloride Modification with Sodium Salt of 2-Thiobenzimidazole

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Abstract—Polymer analogous reaction has been used to partially substitute chlorine atoms of polyvinyl chloride with 2-thiobenzimidazole fragments. ^{13}C NMR and IR spectroscopy studies have shown that the vinylene units are present in the modified polymer. The copolymer product has been used to prepare the membrane with proton conductivity of 1×10^{-2} to 0.04 S/cm at 25–195°C.

Keywords: poly(vinyl chloride), 2-thiobenzimidazole sodium salt, membrane, proton conductivity

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Polyvinyl chloride PVC is among the most important large-scale industrial polymers. The high content of chlorine in PVC, 56.8 wt %, causes its major advantages and drawbacks. In particular, PVC is 1.5 times cheaper than polyethylene, possess high durability and stability in contact with common acids, oxidizers, and solvents; furthermore, PVC is an excellent electric insulator. However, PVC melts are highly viscous and thermally unstable under the processing conditions. Hydrogen chloride evolving at heating PVC is known to catalyze further degradation of the polymer. The softening temperature of PVC is higher than the degradation temperature; hence, PVC cannot be melt-processed. PVC processing is generally performed after its plasticization with low-molecular compounds [1]. Another possible route of PVC properties modification is its polymer analogous reaction with nucleophiles [2, 3]. Polymers with new valuable properties have been prepared as a result of PVC chemical modification [4, 5]. As chlorine substitution in PVC is of undoubtful practical importance, the search for the new nucleophiles capable of the interaction with PVC and elaborating the optimal process conditions are of remarkable interest.

This work aimed at PVC modification via nucleophilic substitution of chlorine with benzimidazole fragments and the formation of proton-conductive membranes based on the reaction products.

Nucleophilic substitution of PVC chlorine with 2-thiobenzimidazole sodium salt was performed in the cyclohexanone medium at 80–120°C (Table 1). The presence of nitrogen and sulfur in the product confirmed that the substitution reaction occurred. The amounts of vinyl chloride in the copolymer product as calculated from the content of the residual chlorine and from the nitrogen content were different (Table 1), pointing at the side reaction of dehydrochlorination. The deviation between the two calculated values reflected the degree of the elimination reaction.

IR spectra of the modified PVC specimens contained the absorption bands of the polymer backbone methylene and methine groups (1420, 1320, and 960 cm^{-1}) as well as those assigned to 2-thiobenzimidazole fragments (a group of bands at 1520–1400 cm^{-1}); moreover, the band appeared at about 1640 cm^{-1} typical of vinylene units.

The presence of the ~CH=CH~ fragments in the copolymer products was confirmed by the ^{13}C NMR spectra that contained the signals of carbons of the unreacted vinyl chloride units [58.0–64.0 ppm (CHCl) and 46.0–48.4 ppm (CH$_2$)], the broadened signals of 2-thiobenzimidazole units[110–118 (C^{4,7}), 122 and 126 (C^{5,6}), ≈140 (C^{8,9}), and 142–150 (C^{2}) ppm], and the

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† Deceased.

Table 1. Conditions of PVC modification with 2-thiobenzimidazole sodium salt

Exp. no.	T, °C	Duration, h	Elemental analysis of the product, wt %		
			N	S	Cl
1	80	8	7.52	10.02	25.02
2	100	2	8.21	9.95	20.92
3	100	4	8.47	10.10	17.62
4	100	6	9.65	11.00	15.12
5	100	8	10.86	11.65	13.62
6	120	8	9.30	11.68	13.90

Table 2. Composition of the products of PVC modification with 2-thiobenzimidazol sodium salt

Exp. no.[a]	Units in the copolymer, mol %		
	unmodified units ~CH_2–CHCl~	units modified with 2-thiobenzimidazole	vinylene units ~CH=CH~
1	68.93	27.22	3.85
2	62.19	28.75	9.06
3	55.85	29.74	14.41
4	50.53	35.29	14.18
5	47.06	41.03	11.91
6	47.68	36.12	16.20

[a] The exp. numbers correspond to those in Table 1.

highly overlapped strong signals at 128–127 ppm assigned to the ~CH=CH~ groups.

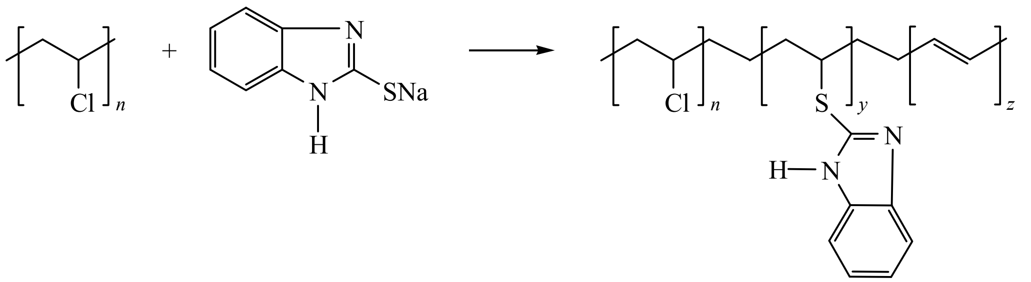
Content of the vinylene fragments (V) in the modified PVC was calculated as follows.

$$V = 100 - (VC + BI).$$

In the equation, VC stands for the amount of vinyl chloride units calculated from the chloride content and BI is the amount of 2-thiobenzimidazole fragments calculated from the nitrogen content.

Increase of the studied reaction temperature led to higher fraction of the vinylene units in the copolymer product (Table 2, Exp. 1, 2, and 6). The highest fraction of the ~CH=CH~ units was 16.20 mol %; however, the product was still soluble in the reaction mixture (Table 2, Exp. 6). Hence, no crosslinking via the double bonds of vinylene units occurred under the conditions of nucleophilic substitution.

Basing on the obtained data, we derived the following scheme of the PVC modification.



The presence of strongly basic nitrogen atoms in the product could afford significant proton conductivity of the produced modified PVC, when doped with acids. The model membrane was prepared from the product with the highest 2-thiobenzimidazole fragments fraction (Table 2, Exp. 5). The 0.3 mm thick membrane was obtained from the 10 wt % solution in DMF via the casting–evaporation procedure. The total exchange capacity of the membrane was of 1 mmol/g.

Proton conductivity of the membrane was measured by impedance spectroscopy (two-point method, $10^{-3} \times 10^{6}$ Hz) after doping with concentrated phosphoric acid during 24 h. The proton conductivity of the membrane as a function of temperature is shown in the figure.

The proton conductivity was 1.0×10^{-2} S/cm at 45°C. Upon further heating, the membrane proton conductivity was up to 3.8×10^{-2} S/cm, the effective activetion energy being of 26±1 kJ/mol. The membrane did not lose the mechanical integrity under the experimental conditions.

The low-temperature (20–50°C) proton conductivity of the membrane based on the modified PVC was lower than those of the membranes prepared from polybenzimidazole or Nafion. However, upon heating up to 200°C the conductivity of the membrane prepared in this work, about 0.04 S/cm, was close to that of polybenzimidazole-based membranes. The proton conductivity could be expected to further increase after modification of the membrane with certain inorganic and organic doping agents, similarly to [6, 7].

The major advantage of the reported PVC-based membrane is the simplicity of preparation. The membrane can be potentially used for fuel cells and separation devices involving ion-exchange membranes assemblies.

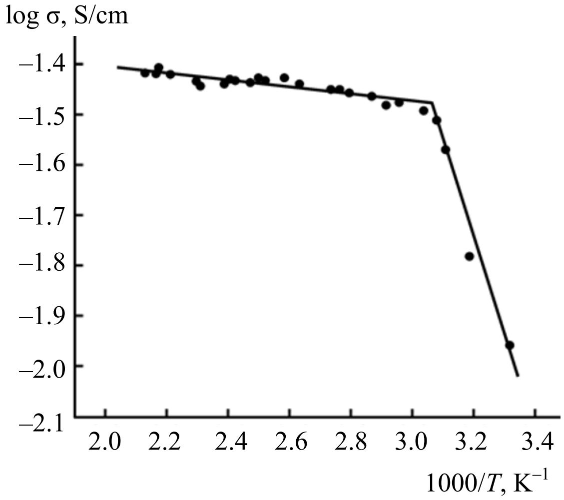
EXPERIMENTAL

We used the emulsion-polymerized PVC soluble in dimethylformamide, cyclohexanone, and (partially) in dimethylsulfoxide. The polymer parameters were as follows: the Fikentscher K-value 62–63, the decomposition temperature 120°C, and the specific surface area 1.81 cm^2/g. 2-Thiobenzimidazole (Fluka, "analytically pure" grade) was purified by recrystallization from the 1 : 1 aqueous ethanol; mp 304–305°C. Cyclohexanone and dimethylformamide were purified via the usual procedures [8].

Elemental analysis of the products was performed using the ThermoFinnigan gas analyzer. IR spectra (KBr pellets or mineral oil suspension) were recorded using the Specord IR-75 and Bruker IFS-25 spectrometers. ^{13}C NMR spectra of the copolymers solutions in DMSO-d_6 were recorded using the VXR-500S Varian spectrometer (125.5 MHz).

The membrane was prepared via solution casting and the solvent evaporation from the copolymer 10 wt % solution in dimethylformamide; the membrane thickness was measured using the Mitutoyo digital micrometer with the accuracy ±1 μm.

The membrane exchange capacity was measured by potentiometric titration of the copolymer specimens (0.0453 g) immersed into the NaCl (0.1 mol/L) solution with aqueous HCl (0.01 mol/L). pH of the solution was measured with the Ekoniks-Ekspert 001 voltmeter equipped with the Mettler Toledo combined pH electrodes. The pH value was automatically recorded each 3 s. The experiment was performed till the stationary state of the ion exchange was attained.



The Arrhenius plot of proton conductivity of the membrane based on the modified PVC.

Resistivity of the membrane was measured in contact with deionized water using the 2V-1 alternated current bridge at 10 Hz to 600 kHz and at 20–100°C. Ionic conductivity of the membrane at each temperature was determined by the impedance extrapolation onto the active resistance axis.

2-Thiobenzimidazole sodium salt. 0.1 mol of 2-thiobenzimidazole was dissolved in 100 mL of ethanol, and 0.1 mol of NaOH was added in the form of aqueous solution. The reaction mixture was left standing during 3 h at room temperature. After the solvents elimination, the salt formed was washed with ethanol and dried in a vacuum dessicator over P_2O_5. The salt purity was determined by potentiometric titration.

PVC modification. Equimolar amount of 2-thiobenzimidazole sodium salt was added by portions to the 4 wt % solution of PVC in cyclohexanone. In all cases, the modified PVC was soluble in the reaction mixture. The products were isolated via dialysis or precipitation into water followed by filtration. The so obtained copolymer was dried in a vacuum drying cabinet. Other preparation conditions are collected in Table 1.

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REFERENCES

1. *Poluchenie i svoistva polivinilkhlorida* (Preparation and Properties of Polyvinylchloride), Zil'berman, E.N., Ed., Moscow: Khimiya, 1968.
2. Kameda, T., Ono, M., Grause, G., Mizoguchi, T., and Yoshioka, T., *Polym. Degrad. Stab*., 2009, vol. 94, no. 1, p. 107. DOI: 10.1016/j.polymdeqradstab.2008.10.006.
3. Shaglaeva, N.S., Sultanrareev, R.G., Zabanova, E.A., Lebedeva, O.V., and Trofimova, K.S., *Russ. J. Appl. Chem*., 2008, vol. 81, no. 1, p. 131. DOI: 10.1007/s11167-008-1029-8.
4. Shaglaeva, N.S., Bayandin, B.B., Sultangareev, P.G., Vakul'skaya, T.I., Khutsishvili, S.S., and Orkhokova, E.A., *Russ. J. Appl. Chem*., 2013, vol. 86, no. 10, p. 1576. DOI: 10.1134/S1070427213100182.
5. Ermakova, T.G., Kuznetsova, N.P., Volkova, L.I., and Myachina, G.F., *Russ. J. Appl. Chem*., 2009, vol. 82, no. 3, p. 488. DOI: 10.1134/S10704277209030252.
6. Matsuda, A., Kanzaki, T., Kotani, Y., Tatsumisago, M., and Minami, T., *Solid State Ionics*, 2001, vol. 139, nos. 1–2, p. 113. DOI: 10.1016/S0167-2738(01)00692-0.
7. Safronova, E.Yu. and Yaroslavtsev, A.B., *Russ. J. Inorg. Chem*., 2010, vol. 55, no. 10, p. 1499. DOI: 10.1134/S0036023610100013.
8. Weisberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., *Organic Solvents*: *Physical Properties and Methods of Purification,* New York: Wiley, 1955.