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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Modification of Polyvinyl Chloride with Na(K) Salts of 1,2,4-Triazole and 1,2,3-Benzotriazole

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Abstract—The possibility of polyvinyl chloride modification by nucleophilic substitution of chlorine with sodium and potassium salts of 1,2,4-triazole and 1,2,3-benzotriazole in dimethylformamide at 40–80°C was examined.

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Polyvinyl chloride (PVC) is one of the most important, readily available, and cheap large-tonnage polymers. It exhibits a set of valuable properties [1–3]. The growth of the PVC production is due to steady expansion of its application fields [4]. Owing to limited solubility and low heat resistance of PVC, processing and production of materials based on it is impossible without effective additives (stabilizers and plasticizers). The presence of the C–Cl bond allows modification of PVC to obtain a wide range of polymeric materials and articles with a new set of valuable service properties.

PVC can be modified by nucleophilic substitution of chlorine atoms using salts of various azoles [5, 6]. Compounds containing a triazole ring are used in industry, agriculture, and medicine [7–9], in particular, 1,2,4-triazole is used as plasticizer [7].

The goal of this study was modification of commercial PVC with sodium and potassium salts of 1,2,4-triazole and 1,2,3-benzotriazole in DMF, examination of the structure and physicochemical properties of the copolymers, and development on their basis of proton-conducting composites promising as membranes for fuel cells.

EXPERIMENTAL

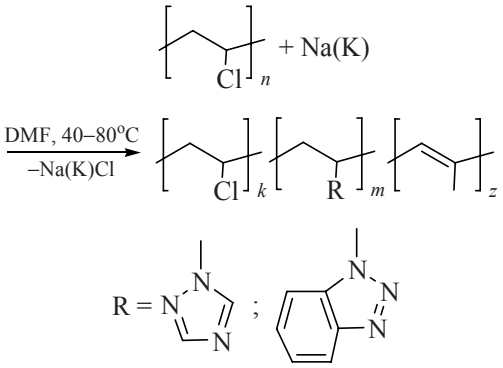
We used commercial PVC, MM 70 000, synthesized by the suspension procedure at the Sayanskkhimplast Joint-Stock Company. Sodium and potassium salts of 1,2,4-triazole and 1,2,3-benzotriazole were prepared by reactions of triazoles preliminarily purified by recrystallization with alkali metal hydroxides in absolute ethanol at 24°C. The alcohol from the reaction mixture was removed, and the salts were dried by azeotropic distillation of water with benzene using a Dean–Stark trap. The purity of the salts was evaluated by potentiometric titration. Pure grade dimethylformamide was purified by the known procedure [10].

Modification of PVC with Na(K) salt of triazoles was performed in a four-necked flask equipped with a stirrer, a reflux condenser, a capillary for feeding argon, and a thermometer. The reactants in a DMF solution were heated to 40–80°C. The molar ratio of PVC and azole salts was 1 : 1 or 1 : 2 (Table 1). After the process completion, the insoluble black precipitate was separated by centrifugation, washed with water, alcohol, and diethyl ether, and dried in a vacuum. The reaction solution of the copolymer in DMF was poured into water. The precipitated dark brown precipitate of the copolymer was filtered off, washed with water to disappearance of chloride ions, and dried in a vacuum at 40°C to constant weight.

The IR spectra of the copolymers were recorded on a Bruker IFS-25 spectrometer. Samples were prepared as KBr pellets and mulls in mineral oil. The ^{13}C NMR spectra of samples with noise proton decoupling were

recorded on a Varian VXR-500S spectrometer (operating frequency 125.5 MHz), with 2.5 s relaxation delay and 90° pulse, in DMF-d_7. Chromium tris-(acetylacetonate) (0.02 M) was used as relaxant. The ESR spectra of powders were recorded at room temperature on an SE/X-2547 spectrometer (Radiopan, Poland). The concentration of paramagnetic centers was calculated by the standard procedure [11]. Thermogravimetric analysis of the copolymers was performed on an MOM derivatograph (Hungary) (sample weight 50 mg, heating rate 5 deg min^{-1}, DTG sensitivity 1/10. The specific conductivity was measured by the van der Pauw four-probe method at a frequency of 500 Hz at 25°C.

PVC was modified by treatment with sodium and potassium salts of 1,2,4-triazole and 1,2,3-benzotriazole, with nucleophilic substitution of chlorine by triazole fragments. The reaction was performed in DMF at various molar ratios of reactants (1 : 1, 1 : 2) in the temperature interval 40–80°C. Two fractions were obtained: soluble in polar organic solvents and insoluble. According to the IR, ^{13}C NMR, and analytical data, nucleophilic substitution of chlorine in polyvinyl chloride by the azole fragment, accompanied by dehydrochlorination as a side reaction, leads to the formation of copolymers containing in macromolecules not only vinyl(benzo)triazole (VT) and vinyl chloride (VC) units, but also polyvinylene (PV) fragments:



In the insoluble fraction, along with polyvinylenes, cross-linked structures are formed as a result of PVC dehydrochlorination [1]. The reaction conditions and compositions of the soluble copolymers synthesized are given in Table 1.

Table 1. Conditions of PVC modification with sodium and potassium salts of triazoles and composition of soluble copolymer fractions

PVC : azole salt, mol : mol	*T*, °C	*t*, h	*t*, h	Elemental analysis, %		Copolymer composition, mole fraction			Degree of substitution (by N) α, %
				N	Cl	VC	VT	PV	
1,2,4-Triazole Na salt									
1:1	40	15	17	7.35	24.03	0.677	0.175	0.148	11.3
1:1	60	6	30	8.70	18.80	0.530	0.207	0.263	13.4
1:1	80	6	85	12.4	12.65	0.356	0.295	0.349	19.0
1:2	40	15	12	5.16	25.16	0.709	0.123	0.168	7.92
1:2	60	6	64	9.38	16.14	0.455	0.223	0.322	14.4
1:2	80	6	76	21.20	4.04	0.114	0.505	0.381	32.5
1,2,4-Triazole K salt									
1:1	40	15	8	4.97	25.78	0.726	0.118	0.156	8.42
1:1	60	6	20	6.31	21.37	0.602	0.150	0.248	10.70
1:1	80	6	51	7.59	16.96	0.478	0.181	0.341	12.87
1:2	80	6	69	19.00	5.71	0.161	0.452	0.387	32.21

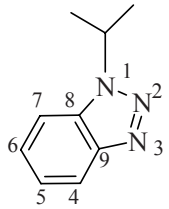
Table 1. (Contd.)

PVC : azole salt, mol : mol	*T*, °C	*t*, h	*t*, h	Elemental analysis, %		Copolymer composition, mole fraction			Degree of substitution (by N) α, %
				N	Cl	VC	VT	PV	
1,2,4-Benzotriazole Na salt									
1:1	60	6	32	10.71	23.07	0.650	0.255	0.095	21.81
1:1	80	6	43	13.80	15.47	0.436	0.328	0.236	28.10
1:2	40	15	22	5.01	24.64	0.758	0.119	0.123	10.20
1:2	60	6	23	11.10	15.74	0.443	0.264	0.293	22.60
1:2	80	6	54	18.16	8.32	0.234	0.433	0.333	36.98
1,2,4-Benzotriazole K salt									
1:1	40	15	21	9.27	25.14	0.708	0.221	0.071	20.36
1:1	60	7	35	11.64	22.52	0.634	0.277	0.089	25.48
1:1	80	7	47	15.17	19.47	0.547	0.361	0.092	33.32
1:2	40	6	25	6.86	23.11	0.651	0.163	0.186	16.07
1:2	80	6	37	22.9	4.36	0.123	0.545	0.332	50.29

With increasing temperature, the copolymer yield and degree of substitution increase. The highest degree of substitution of chlorine by the (benzo)triazole ring (α = 32–50%) is attained when the reaction is performed at 80°C for 6 h at 1 : 2 molar ratio of PVC units to the salt. The mole fraction of vinyl(benzo)-triazole units in the macromolecules of the copolymers obtained is 0.43–0.55.

The IR spectra of the copolymers contain stretching vibration bands of the triazole ring at 1055–1061, 1220, 1420–1570, and 3140 cm^{-1} or of the benzotriazole ring at 1180, 1450, 1560, 1614, 3020, and 3070 cm^{-1}. The formation of polyene fragments in the copolymer structure is confirmed by appearance of bands at 1630–1650 cm^{-1}, belonging to C=C stretching vibrations. The C–Cl stretching vibrations are manifested at 600 and 680 cm^{-1}.

Table 2. ^{13}C NMR data for the soluble fraction of the copolymer prepared by PVC modification with benzotriazole sodium salt (1 : 1)

Structural unit of copolymer	Chemical shift, ppm
–CHCl–CH_2–	56.6–59.4 (C^1), 43.8–46.4 (C^2)
	144 ($C^{4,9}$), 118.2–119.5 ($C^{5,8}$), 126.7–127.5 ($C^{6,7}$), 59.0–62.5 (CH)
–CH=CH–	$C_{1,2}$ (127.5–133.8)

The ^{13}C NMR spectra confirm the structure of the copolymers obtained. They contain signals characteristic of carbon atoms of the vinylbenzothiazole, vinyl chloride, and vinylene units (Table 2).

We studied the thermal oxidative degradation of the starting PVC and of the soluble and insoluble copolymers obtained by its modification. We found that PVC is thermally stable up to 210°C, and above this temperature accelerated degradation is observed, with 48% weight loss at 250°C and an exothermic effect. This is due to dehydrochlorination of PVC. With further heating, the PVC residue slowly degrades, with complete burnout at 550°C. The synthesized copolymers are thermally stable up to 160 (soluble fraction) and 210°C (insoluble fraction). At 250°C, the weight loss of the soluble copolymers is 15%, and that of insoluble copolymers, 3%. At 550°C, soluble copolymers degrade virtually completely, whereas insoluble copolymers lose only 20% of their weight. The degradation of insoluble copolymers is

characterized by an exothermic maximum at 490°C. This fact suggests the bond cleavage in the backbone, with the formation of a cross-linked carbonized polyene product.

Along with high resistance to thermal oxidative degradation, the insoluble fractions of the copolymers are characterized by room-temperature electrical conductivity of 10^{-9}–10^{-7} Ω^{-1} cm^{-1} and paramagnetism, with the concentration of paramagnetic centers of 2.5×10^{17}–6.0×10^{20} spin g^{-1}.

The soluble copolymers form high-quality elastic films from solutions in DMF, DMSO, and some commercial solvents (R-4, R-219, etc.). Films based on copolymers and their composites with polyvinyl butyral exhibit ionic conductivity of 10^{-5}–10^{-7} Ω^{-1} cm^{-1}, which increases to 10^{-3}–10^{-4} Ω^{-1} cm^{-1} after doping the films with orthophosphoric acid. As for mechanical properties, the films are characterized by tensile strength of $(3–39) \times 10^6$ N m^{-2} and elongation at break of 5–34% [12]. The results obtained show that the copolymers are promising for the development of membranes for fuel cells.

CONCLUSIONS

(1) New soluble and insoluble copolymers containing vinyl chloride, vinylazole, and vinylene units in macromolecules were prepared by nucleophilic substitution of chlorine in polyvinyl chloride using sodium and potassium salts of 1,2,4-triazole and 1,2,3-benzotriazole.

(2) The insoluble copolymers exhibit enhanced heat resistance, electrical conductivity, and high paramagnetism.

(3) Soluble copolymers and composites based on them are characterized by the capability to form high-quality films exhibiting mechanical strength and ionic conductivity and showing promise for the development of membranes for fuel cells.

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