Copolymerization of the poly(*N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride) macromonomer with acrylamide

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Copolymers of the poly(*N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride) macromonomer (**1´**) with acrylamide (**2**) with a high content of cationic groups (up to 50%) were synthesized. The relative activities $r_{1'}$ and r_2 were calculated. The relative activities calculated by the Kelen—Tudos ($r_{1'}$ = 0.057±0.009, r_2 = 1.57±0.12) and Feynman—Ross ($r_{1'}$ = 0.055±0.011, r_2 = 1.58±0.14) methods are in accordance. The intrinsic viscosity and the yield of copolymers were found to decrease with an increase in the molar fraction of macromonomer **1´** in the monomer mixture.

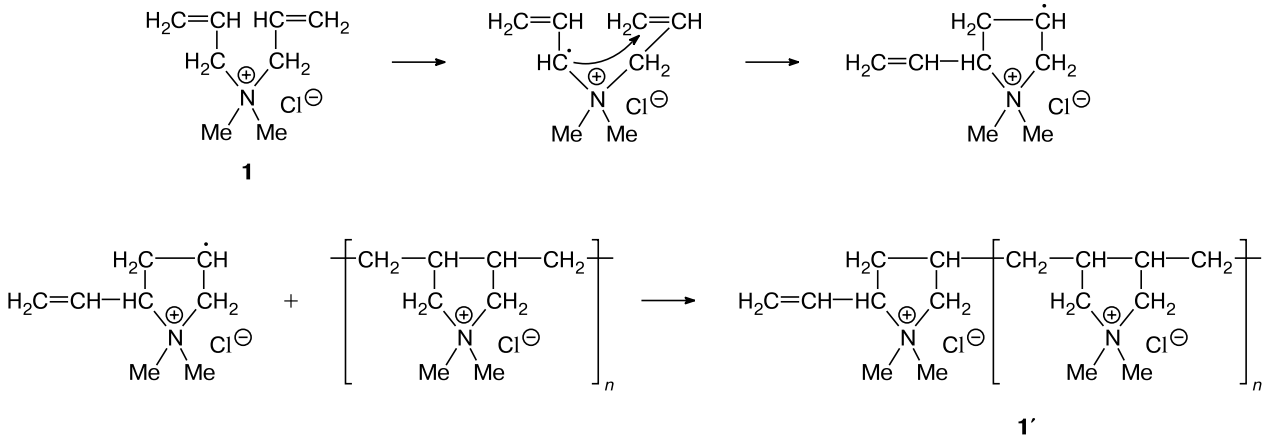
Key words: cationic polyelectrolytes, copolymerization, water-soluble polymers.

In a series of materials used presently in the petroleum, paper, and textile industries and in processes of sewage and water treatment, copolymers based on acrylamides are most popular.[1—9] Among them, a special role belongs to copolymers containing units of diallylic quaternary ammonium compounds and bearing a positive charge directly in the main chain of the copolymer. This provides a high charge density and favorably distinguishes these substances from other copolymers of cationic nature, whose charge is located on branches of the main chain.

Different reactivities of the vinylic monomer of acrylamide and diallylic quaternary ammonium salts do not allow one to prepare copolymers with a high content of the latter.

At the same time, it was found[10] that the homopolymerization of a representative diallylic ammonium compound, *N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride (**1**), gives a polymer containing the terminal vinylic double bond (Scheme 1) due to efficient chain transfer to the monomer. These bonds were detected by the radiochemical[11] and ^{13}C NMR techniques.[10]

Scheme 1



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Taking into account these data, we assumed that the terminal double bond of poly(*N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride) (**1´**) can be involved in copolymerization with monomers of different nature. In particular, hydrogels were obtained[12] directly from compound **1´** by radical cross-linking with the bifunctional cross-linking agent *N*,*N´*-methylenebisacrylamide at the terminal double bonds of the macromolecules. This seems promising for the development of new polymers containing positively charged groups and possessing unique properties. In the present work, we check this assumption.

Experimental

Poly(*N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride) (**1´**) was prepared according to a procedure[13] from compound **1** synthesized from dimethylamine (33% aqueous solution, high-purity grade) and allyl chloride (dried with calcium chloride and distilled over $CaCl_2$), b.p. 45 °C, n_D^{20} = 1.4100. Found (%): C, 59.35; H, 10.0; Cl, 22.04; N, 8.61. $C_8H_{16}ClN$. Calculated (%): C, 59.43; H, 9.98; Cl, 21.93; N, 8.66. Acrylamide (**2**, technical product) was twice recrystallized from acetone and dried *in vacuo* above P_2O_5 to a constant weight (m.p. 84 °C). The initiators were hydrogen peroxide (50% aqueous solution, analytical purity grade) and ammonium persulfate $(NH_4)_2S_2O_8$ (analytical purity grade, recrystallized from bidistilled water and dried *in vacuo* to a constant weight). The solvents were acetone and methanol (analytical purity grade). Sodium chloride (reagent grade) was used to prepare solutions for determination of intrinsic viscosity.

Polymer **1´** was synthesized by the radical polymerization of compound **1** in an aqueous solution under anaerobic conditions (2 mol L^{-1}, T = 60 °C, ammonium persulfate as the initiator ($1 \cdot 10^{-3}$ mol L^{-1}), polymerization duration 7 h). The intrinsic viscosity of synthesized polymer **1´** was 0.3 dL g^{-1}.

Copolymerization of **1´** with acrylamide (**2**) was carried out in an aqueous medium at different ratios of the comonomers (10 : 90, 15 : 85, 40 : 60, 60 : 40, 80 : 20, and 90 : 10). The total concentration of the comonomers was 0.7 mol L^{-1}, the initiator (H_2O_2) concentration was 0.5% (0.147 mol L^{-1}), T = 40 °C, and the duration of the reaction was 20 h for experiments on determination of the yields and intrinsic viscosities of the copolymers formed and 1.5 h for experiments on determination of the copolymer composition. Sealed ampules were placed in a thermostat. After the end of the reaction, the contents of the ampules were transferred into water-free cooled acetone, and the copolymer was isolated as a white precipitate. The product was twice washed with anhydrous acetone and treated with methanol to dissolve unreacted compound **1´**. Then the product was twice washed with methanol again and dried to a constant weight in a vacuum drying oven.

The intrinsic viscosity of solutions of polymers was measured at 30 °C on an Ubellohde viscosimeter using a 1 *M* solution of NaCl as the solvent.

The ^1H and ^{13}C NMR spectra of solutions of the polymers in deuterated water were recorded at room temperature on a Bruker MSL-300 spectrometer with working frequencies of 300 and 75.15 MHz, respectively. ^{13}C NMR spectra were obtained with spin-spin $^{13}C—^1H$ decoupling. For recording the ^1H and ^{13}C NMR spectra, the delay time between two pulse sequences was 3 and 5 s, respectively; the scan number was 64 and 20 000, respectively.

Chemical shifts were measured relative to the external standard Me_4Si, and the accuracy of measurements of chemical shifts was 0.05 ppm. The spectra were processed using the Bruker 1D WINNMR program.

The copolymer composition was determined by the direct titration of dilute solutions of the copolymers with a 0.001 *N* titrated solution of sodium polyethylenesulfonate. A 1% alcoholic solution of Toluidine Blue was used as the indicator. Titration was carried out until the color changed from blue to red-violet. Each solution was titrated at least 3 times.

The content of the cationic comonomer (wt.%) was calculated by the formula

$$x = M_1 C_1 V_1 / g.$$

Here M_1 is the molecular weight of the cationic comonomer; C_1 is the molar concentration of the titrant (mol L^{-1}); V_1 is the titrant volume in the point of equivalence (L); g is the weight of the copolymer in the volume of the solution taken for titration (g)

$$g = mV_2/V_3,$$

where m is the weight of the copolymer weighed sample (g); V_2 is the volume of the copolymer solution (mL); V_3 is the volume of the volumetric flask (mL).

The copolymer composition was recalculated from wt.% to mol.% by the equations

$$m_1 = \frac{x_1/M_1}{x_1/M_1 + x_2/M_2} \cdot 100\%,$$

$$m_2 = \frac{x_2/M_2}{x_1/M_1 + x_2/M_2} \cdot 100\%,$$

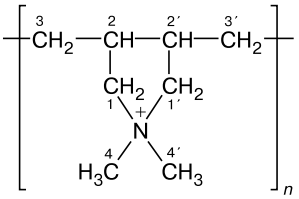
where x_1 and x_2 are the weight concentrations of the comonomers (wt.%); m_1 and m_2 are the molar concentrations of the comonomers (mol.%); M_1 and M_2 are the molecular weights of the monomers M_1 and M_2.

The copolymer composition was determined at the conversion of the comonomers at most 5%.

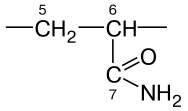
Results and Discussion

The initial monomer **1** and the corresponding polymer **1´** were preliminarily synthesized. The structures and compositions of the monomer and polymer were confirmed by ^1H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of sample **1´** contains low-intensity signals with δ 126.40 and 129.90 (H_2C=CH). The ^1H NMR spectrum also exhibits signals of the terminal H_2C=CH groups at δ 5.65—6.25. This indicates that macromolecules **1´**, which are introduced in copolymerization with acrylamide **2**, contain the terminal double bond.

The synthesized copolymers were studied by ^{13}C NMR spectroscopy. The chemical shifts in the ^{13}C NMR spectra of the copolymers of **1´** with **2** are given below.



1´



2

Atom	1, 1´	2, 2´	3, 3´	4, 4´	5	6	7
δ	70.35	38.25	26.45	52.45, 54.15	49.05	43.20	177.90

No signals indicating the terminal double bond in macromolecules **1´** were observed in the ^{13}C NMR spectra of the copolymers, whereas these signals were observed in the spectra of homopolymer **1´**. The ^{1}H NMR spectra of the copolymer samples also indicate the absence of terminal double bonds (no signals in the region of δ 5.65—6.25). Thus, we can conclude that copolymerization involves the terminal double bonds. A special series of experiments performed under the same conditions as the copolymerization of macromonomer **1´** with compound **2** showed no homopolymerization of macromolecules **1´** to occur under these conditions. Therefore, the spectral data confirm the formation of copolymers of macromonomer **1´** with compound **2**.

To reveal the dependence of the composition of the copolymers on the molar ratio of the comonomers and to calculate the copolymerization constants, we carried out the copolymerization of macromonomer **1´** with compound **2** at different ratios of the comonomers in the initial reaction mixture (Table 1).

The copolymerization constants of macromonomer **1´** with compound **2** were calculated by the Kelen—Tudos[14] and Feynman—Ross[15] methods. The $r_{1'}$ and r_2 values were 0.057±0.009 and 1.57±0.12 (Kelen—Tudos method) and 0.055±0.011 and 1.58±0.14 (Feynman—Ross method). Thus, the $r_{1'}$ and r_2 values obtained by the Kelen—Tudos and Feynman—Ross methods are in accordance.

The following conclusion is a result of comparison of these results with the data on the copolymerization of monomer **1** with compound **2** (r_1 = 0.06±0.03, r_2 = 6.4±0.4).[16] Although the copolymerization of macromonomer **1´** with compound **2** involves two vinylic comonomers, unlike that between monomer **1** and compound **2** involving the diallylic and vinylic comonomers, macromonomer **1´** (as well as **1**) is much less reactive than **2**. This is also caused, most likely, by steric hindrance, because macromolecules **1´** are bulky. The ratios of reactivities $r_2/r_{1'}$ = 27.5 (according to the Kellen—Tudos method) and r_2/r_1 = 106.7 indicate that macromonomer **1´** is more reactive than **1** in the copolymerization with **2**.

In addition, according to the obtained data, both compound **2** and macromonomer **1´** are considerably easier added to monomeric molecules **2** than to **1´**. In this case, the polymer contains excess units of **2** even at a higher content of macromonomer **1´** in the initial mixture. Nevertheless, since the macromonomer itself is a ready block of the cationic monomeric unit, copolymers with a high content of cationic groups can be obtained (see Table 1), which is confirmed by the data on titration of solutions of the synthesized copolymers.

Returning to the important role of the structure of macromolecules **1´** introduced into the copolymerization reaction, it should be mentioned that macromolecules **1´** contain groups with the tertiary N atom due to partial dequaternization. The presence of an insignificant amount of these groups in **1´** has been proved earlier[14] by NMR spectroscopy. Therefore, under our conditions, hydrogen peroxide decomposition is caused, most likely, by the redox reaction between its molecules and the groups in molecules **1´** containing the tertiary N atom.

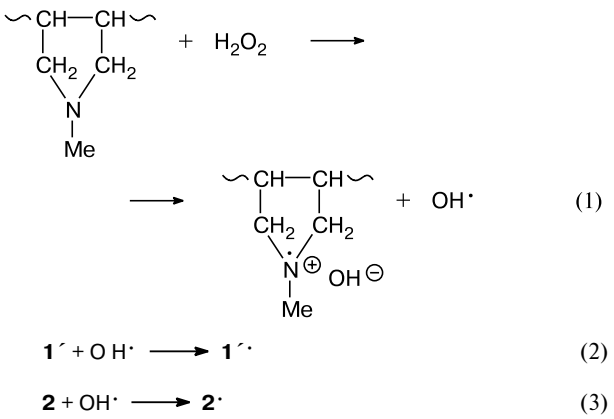
Thus, free radicals are formed in the reaction mixture and react with the double bonds of polymer **1´** and monomer **2** to form radicals **1´•** and **2•**, respectively. The initiation process can be presented as Scheme 2.

At high concentration of **1´** (and, hence, at low concentration of **2**) step (3) determines the formation of active centers to a less extent. With an increase in the molar

Table 1. Dependence of the copolymer composition on the molar ratio of **1´** and **2** in the reaction solution

$M_{1'}$	M_2	Yield of copolymers (%)	Composition of copolymers (%)		[η] /dL g^{-1}	Elemental composition (%)			
			$m_{1'}$	m_2		C	H	Cl	N
5	95	86	3.1	96.9	1.7	51.30	7.24	1.49	0.59
10	90	78	6.3	93.7	1.5	51.86	7.42	2.92	1.15
15	85	71	9.0	91.0	1.2	52.31	7.57	4.04	1.59
20	80	69	11.9	88.1	1.0	52.76	7.72	5.17	2.04
40	60	65	24.3	75.7	0.8	54.39	8.25	9.28	3.66
60	40	53	36.7	63.3	0.7	55.67	8.67	12.50	4.93
80	20	49	46.4	53.6	0.6	56.50	8.97	14.60	5.77
90	10	47	51.7	48.3	0.5	56.90	9.07	15.60	6.14

Scheme 2



fraction of **1´** in a monomeric mixture, step (2) becomes rate-determining to an increasing extent. At the same time, an increase in the concentration of macromonomer **1´** (which is inevitable with an increase in its molar fraction in a monomeric mixture) increases the viscosity of the initial monomeric mixture, decreasing the probability of collisions of the terminal double bonds of the macromolecules with the active radicals. As a result, the efficiency of reaction (2) decreases and, as a consequence, the yield and viscosity of the product decrease (see Table 1). This is confirmed by the above mentioned experiments, which showed that in the absence of compound **2** macromonomer **1´** does not react in post-polymerization, perhaps because of too low concentration of active centers localized at the ends of the polymeric molecules at high viscosity of the solution and steric hindrance caused by large sizes of macromolecules **1´**.

Thus, the formation of copolymers with a high content of cationic groups is due to the fact that one elementary act of the interaction of **1´** introduces several charged groups (instead of one group as in the case of copolymerization with monomeric compound **1**) to the copolymer composition rather than by the high reactivity of the macromonomer. The number of these groups is determined by the degree of polymerization of **1**, which was characteristic of macromonomer **1´** introduced into copolymerization with compound **2**. In other words, as already mentioned above, the formation of copolymers with a high content of the cationic groups is due to the fact that the macromonomer itself represents a ready block of the cationic monomeric unit. In addition, the copolymer composition is also determined by a decrease in the probability of collisions of the acrylamide molecules and radicals under the conditions of high viscosity of the solution with an increase in the content of macromonomer **1´** and, hence, the yield and intrinsic viscosity of the formed copolymers decrease in this case (see Table 1). This is caused by a decrease in the conversion of compound **2**, which results in the decrease in the extent of its incorporation into the copolymer composition. As a result, the copolymers with a high content of the cationic groups are formed.

Thus, the radical copolymerization of macromonomer **1´** with compound **2** makes it possible to prepare high-molecular-weight copolymers in good yield and with a high content of the cationic groups (up to ~50%), which was impossible for the copolymerization of monomeric **1** with compound **2**. The specific features of the copolymerization are caused by the nature of the comonomers and also by the viscosity of the reaction medium, which is higher for the copolymerization of the macromonomer and the second comonomer than that for the copolymerization of two comonomers. Varying the initial ratio of **1´** and **2** and controlling the viscosity of the reaction solution, one can synthesize copolymers with different contents of the cationic groups. The cyclolinear structure of the cationic blocks provides the high charge density due to which the synthesized copolymers become additionally valuable and the boundaries of their possible use are extended.

It has previously been shown[10,11,17] that during the homopolymerization of monomer **1** the chain transfer to the monomer results in the formation of radicals capable of continuing the kinetic chain upon the cleavage of the material chain, *i.e.*, the efficient chain transfer to the monomer occurs to form the terminal double bonds. The copolymerization of macromonomer **1´** with compound **2** was carried out at these double bonds, and the corresponding copolymers of different composition were synthesized and identified for the first time. It is found that the radical copolymerization with the vinylic monomers can be performed at the terminal double bonds in macromolecules **1´**, resulting in the formation of high-cation copolymers. The copolymerization constants of macromonomer **1´** with compound **2** were determined.

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