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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis and Absorption Power of New Polyelectrolyte Tetrazole-Containing Acrylic Hydrogels

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Abstract—The kinetic features of formation and equilibrium swelling in water and aqueous solutions of metals were considered for new hydrogels based on acrylic acid and methylenebisacrylamide modified with 2-methyl-5-vinyltetrazole in the polymerization stage. The influence of the concentration of the reactants on the gelation rate and the degree of equilibrium swelling was studied, as well as the influence of 2-methyl-5-vinyltetrazole on the properties of the copolymers prepared. Possible application fields for the new hydrogels were proposed.

Polyacrylate hydrogels find wide application owing to their unique water-absorbing and immobilizing power with respect to various media. These properties are of special value in the context of the present-day problems of biological medicine and ecology [1, 2]. Incorporation into the polymer structure of complexones, in particular, nitrogen-containing heterocyclic moieties, intensifies the absorption of aqueous solutions of electrolytes [3]. High complexing power of the tetrazole ring with respect to heavy and noble metal ions makes these gels suitable for water treatment application. The immunobiological activity of polyvinyltetrazoles and copolymers of vinyltetrazoles with acrylic acid (AA) makes these hydrogels promising for application in living bodies [4, 5].

The aim of this work is to study the kinetic features of gelation and the behavior of the gels in electrolyte solutions, as well as to analyze the mechanism of formation and interaction of the gel prepared with solutions of salts of copper, cobalt, nickel, and other metals.

EXPERIMENTAL

Network copolymers were prepared by radical polymerization of AA partially neutralized with sodium hydroxide (degree of neutralization $\alpha = 0.8–0.9$), 2-methyl-5-vinyltetrazole (MVT), and methylenebisacrylamide (MBAA) as cross-linking agents in an aqueous solution at 40–60°C. The initiator was the ammonium persulfate–tetramethylethylenediamine (TMED) redox system. The initial concentrations of the reactants in polymerization were as follows: monomer 30, MVT 0–70 wt % of the AA mass, and MBAA 0–0.9 wt % of the monomer mass. Prior to polymerization, 2-methyl-5-vinyltetrazole[1] was purified by vacuum distillation (bp 80°C at 20 mm Hg). The other reactants, as well as their purification and copolymerization procedures, were characterized in [6]. Polymerization was carried out in ampules; the reaction mixture was deoxygenated prior to adding the initiator by passing argon through the solution for 2–3 min. A specific feature of the experiment was freezing of AA in a refrigerator at 3–5°C prior to the reaction.

The kinetic parameter to be measured was the gelation time as estimated from the time of the onset of the fluidity loss by the reaction mixture.

The gel structure was investigated by ^{13}C NMR spectroscopy and differential thermal analysis (DTA). The presence of the tetrazole moiety in the polymer was judged from the peaks in the IR spectrum at ν 1100, 1208, and 1635 cm^{-1} (tetrazole ring vibrations). The resulting copolymers are thermally stable, as evidenced by the thermal oxidation analysis data as processed by the Freeman and Carrol's method (E_a = 420 kJ mol^{-1}).

The copolymers synthesized were kept in distilled water to remove the sol fraction. The equilibrium swelling of the gels and the swelling kinetics were studied by the standard gravimetric method. The degree of equilibrium swelling was calculated by the equation $Q = (m_s - m_d)/m_d$, where m_s, g, is the mass

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[1] Synthesized at the St. Petersburg State Technological Institute.

of the swollen sample, and m_d, g, is the mass of the dried sample [6].

The macrokinetics of the three-dimensional copolymerization of AA, MVT, and MBAA have a number of specific features. As seen from Fig. 1, the plot of the gelation time (induction period) vs. the MVT concentration has a maxumim at the MVT concentration of 10–20 wt % with respect to AA. The cross-linking agent, MBAA, exerts the expected effect: the induction period tends to increase, and the gelation rate, to decrease with decreasing MBAA concentration from 0.5 to 0.05 wt %. This is consistent with the mass action law in the gelation macrokinetics. The fact that at the MBAA concentrations over 0.5 wt % the gelation point is observed at a later time is due to the specific features of the gelation mechanism. The gel based on AA and MBAA, most likely, was formed by the colloidal-chemical mechanism, as indirectly noted in a number of works [7]. Dissimilar reactivities of AA and MBAA are responsible for the formation at high MBAA concentrations of blocks from the MBAA units with a low activity of side double bonds and of intramolecular rings, divinyl loops, and network of engagements [7]. Thus, at the MBAA concentration of 0.9 wt % the hydrogel has a heterogeneous structure.

The nonlinear dependence of the induction period on the MVT concentrtation in the reaction mixture can be explained by the difference in the relative copolymerization activity constants: $r_{AA} = 0.67$ and $r_{VT} = 0.29$ in the AA–5-vinyltetrazole system [8], $r_{AA} < r_{MBAA}$ [9], as well as by the influence of complexing with TMED [10, 11], formation of an interpolymeric complex in AA and MVT polymerization [12], and formation of ion pairs [8, 12]. It was found [8] that the carboxy groups from AA participate in hydrogen bonding with the proton from the tetrazole ring of unsubstituted 5-vinyltetrazole. As a result, the initial polymerization rate and the degree of conversion of the monomers tend to decrease with increasing content of vinyltetrazole in the monomer mixture. In our case, MVT can also induce polarization of the COO^-H^+ (Na^+) group of AA. A greater reactivity of the AA–MVT–MBAA system compared to the system without MVT is indicated by the calculated activation energies of the reaction, namely, E_{app} of 120 and 140 kJ mol^{-1} in the former and latter cases, respectively [these parameters were calculated form the plots of the gelation time t_g, min, vs. the synthesis temperature T (K)]. This fact can be explained by formation of the redox complex MVT–ammonium persulfate [13] initiating AA copymerization. Formation of a complex with the charge transfer between the persulfate ions and the "pyridinium type" nitrogen atom of MVT, i.e., of the tetrazole–ammonium persulfate redox system, was observed earlier [12]. Gel formation was observed in the system without ammonium persulfate. In that case, weakly cross-linked networks of predominantly physical nature were formed, as judged from a large amount of the sol fraction. The mechanism of such initiation is, evidently, due to formation of the MVT–TMED complex [10]. A high reactivity of MVT in gelation is supported by the ^{13}C NMR data: the sol fraction contains no MVT. At MVT concentrations over 30%, a strong gel is formed which retains its elasticity and the shape in the equilibrium swollen state. The analysis of the gelation mechanism should, probably, take into account the gel effect, which is indicated by the dependence of the gelation time on the MBAA concentration.

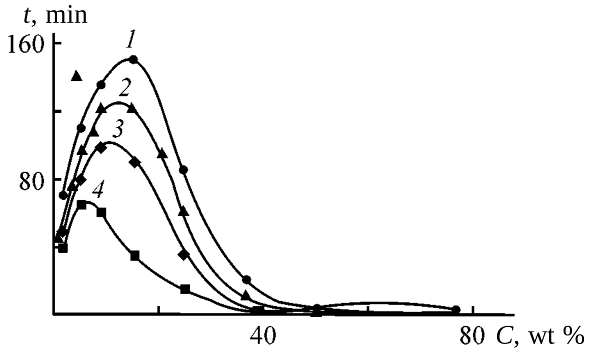

Fig. 1. Gelation time t as a function of the MVT concentration C at different proportions of the cross-linking agent (MBAA). Initiator (ammonium persulfate) concentration 0.4 wt %. MBAA concentration, wt %: (*1*) 0.1, (*2*) 0.2, (*3*) 0.9, and (*4*) 0.5.

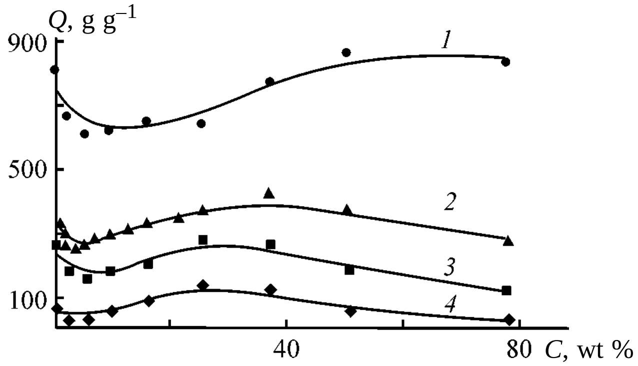

Fig. 2. Equilibrium degree of swelling Q of hydrogels in distilled water as a function of the MVT concentration C in the reaction mixture at different concentrations of MBAA. MBAA concentration, wt %: (*1*) 0.1, (*2*) 0.2, (*3*) 0.5, and (*4*) 0.9.

The influence of the MVT concentration on the

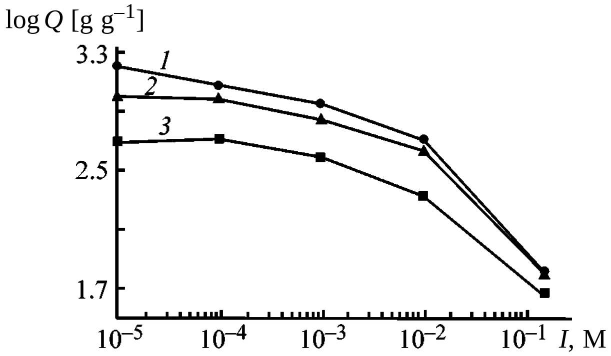

Fig. 3. Equilibrium degree of swelling Q of hydrogels based on AA and MVT as a function of the ionic strength of the external electrolyte I. MVT concentration in the reaction mixture 36 wt %. MBAA concentration, wt %: (*1*) 0.05, (*2*) 0.1, and (*3*) 0.2.

equilibrium degree of swelling of the hydrogel at different proportions of the cross-linking agent MBAA at 20°C is shown in Fig. 2. Based on data in Figs. 1 and 2, it is possible to prepare gels with desired properties within a certain period. This is essential for solving specific technical problems. e.g., fabrication of hollow fibers filled with a water-swelling absorbent. This problem can be solved, e.g., by selecting appropriate concentrations of the reactants.

Figure 2 shows that with decreasing proportion of the cross-linking agent the equilibrium degree of swelling tends to increase. The influence of the MVT concentration is ambiguous. In loosely cross-linked polymers the equilibrium degree of swelling tends to increase with increasing MVT concentraiton (to 80 wt %). With MBAA concentrations over 0.1 wt % the plot of the degree of swelling vs. the MVT concentration passes through a maximum, which shifts to lower MVT concentrations with increasing network density. The decrease in the equilibrium degree of swelling is due to increase in the proportion of the gel fraction.

In electrolyte solutions, the hydrogels of interest behave as three-dimensional membranes. The ion distribution pattern for the hydrogel–solution system varies with the composition of the surrounding solution (e.g., concentration and the nature of salt of polyvalent metal) [14]. Figure 3 presents a typical plot of the equilibrium degree of swelling vs. the ionic strength of the surrounding solution for polyelectrolyte hydrogels differing in the cross-linking density. It is seen that at the salt (sodium chloride) concentrations over 10^{-4} M the degree of swelling tends to decrease. The increased concentration of the ions outside the hydrogel was observed at salt concentrations under 1×10^{-4} M. Budtova *et al.* [2] theoretically interpreted these phenomena in terms of the Donnan theory and the diffusion approach. Those authors treated the gel as an ionic sorbent, and the thermodynamic basis of the phenomenon was considered in [15, 16]. The equilibrium degree of swelling for the gel with the metal salt concentrations of 1×10^{-4} M increases relative to that in distilled water. This can be explained by the structurization of the solution surrounding the gel, owing to participation of the MVT units in the system of intermolecular and ionic bonds [10, 17]. The gels under study collapse with the salt concentration increasing to 1×10^{-1} M.

Equilibrium degree of swelling Q of the hydrogels based on AA and MVT at different concentrations of $NiCl_2$, $CoCl_2$, and $CuCl_2$. MVT concentration 36.6, and MBAA concentration 0.2 wt %

Salt concentration, M	Q, g g^{-1}, in salt solution		
	$NiCl_2$	$CoCl_2$	$CuCl_2$
1×10^{-5}	544	556	546
1×10^{-4}	604	521	466
1×10^{-3}	110	212	238
1×10^{-2}	17	11	26

The table shows how the equilibrium degree of swelling varies with the concentrations of selected salts for hydrogels based on AA and MVT at 16°C.

It is seen that with increasing salt concentration the equilibrium degree of swelling tends to decrease. The hydrogels based on AA and MVT have high degrees of equilibrium swelling in salts compared to those based on AA. This is due to formation of chelate complexes with the Co^{2+}, Ni^{2+}, and Cu^{2+} ions involving both the tetrazole ring [18] and the acrylate groups [19]. It was found that the tetrazole-containing gels decolorize the salt solutions, and the hydrogels based on AA only partly sorb metals ion.

The swelling of the gels based on AA, MBAA, and MVT in salt solutions exhibit the following characteristic features that can be explained basing on the Donnan principle and the diffusion approach. In the initial stage the hydrogel swells faster in a more concentrated solution, and in salt solutions equilibrium is attained faster than in distilled water.

The swelling of the synthesized hydrogels can be described by an S-shaped curve (Fig. 4). It is seen that with increasing MVT proportion in the copolymer the degree of equilibrium swelling in distilled water tends to increase. The swelling rate of the copolymers in the initial stage of the process tends to increase with increasing MVT proportion in the monomer mixture.

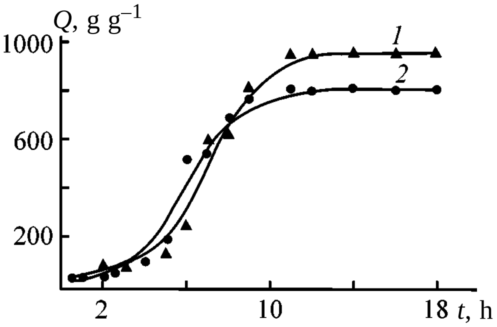

Fig. 4. Degree of swelling Q of hydrogels as a function of the time t at the cross-linking agent (MBAA) concentration of 0.1 wt %. MVT concentration in the reaction mixture, wt %: (*1*) 77 and (*2*) 36.

Our experiments suggest that the synthesis conditions ensuring the maximal absorption capacity of hydrogels based on AA, MVT, and MBAA as cross-linking agent are as follows: ammonium persulfate concentration 0.8 wt %, and synthesis temperature 60°C.

CONCLUSIONS

(1) Tetrazole-containing hydrogels based on acrylic acid, methylenebisacrylamide, and 2-methyl-5-vinyltetrazole were synthesized for the first time by radical copolymerization of monomers in aqueous solution.

(2) The kinetic features of gelation and the properties of the forming products were studied as influnced by the monomer ratio and the initiator concentration. The optimal conditions of preparing hydrogels with the maximal degree of equilibrium swelling and the shortest gelation time were determined.

(3) The equilibrium swelling of the gels in distilled water and solutions of copper, nickel, cobalt, and sodium salts at room temperature was studied. The gels exhibit high water-absorbing power in solutions with the salt concentration under 1×10^{-3} M, namely, up to 600 g g^{-1} for the gels synthesized at the methylenebisacrylamide concentration in the monomer mixture of 0.2 wt %. The high absorbing power of the gels in salt solutions is due to formation of chelate complexes.

(4) High immobilizing power of the gels prepared makes them promising for water treatment and selective binding of metals from salt solutions.

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