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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Effect of Synthesis Conditions on Molecular Characteristics of Acrylamide Copolymers with Acrylic Acid, Carriers of Cationic Biologically Active Substances

E. B. Tarabukina, A. I. Amirova, E. L. Shul'tseva, and M. V. Solovskii

Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

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Abstract—Methods of molecular hydrodynamics and optics were used to study properties of aqueous solutions of acrylamide copolymers with acrylic acid. Dependences of the molecular characteristics of the copolymers on their synthesis conditions were determined and conditions were found in which the process of radical copolymerization of acrylamide with acrylic acid yields water-soluble carboxyl-containing acrylamide copolymers with molecular masses not exceeding 4×10^4 Da.

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Water-soluble macromolecular (with molecular masses of 5×10^5–5×10^6 Da) acrylamide (AA) copolymers with salts of unsaturated carboxylic and sulfonic acids are widely used as flocculants and soil structuring agents [1–4]. At the same time, low-molecular-weight anionic copolymers of acrylamide may also be of considerable interest, because there is a published evidence that polyacrylamide (PAA) is nontoxic for warm-blooded animals [1]. The low toxicity of PAA opens prospects for the use of reactive low-molecular-weight AA copolymers, including copolymers with carboxy groups, as highly hydrophilic polymers, carriers of biologically active substances (BASs). AA copolymers remain poorly studied in this regard. Linear AA copolymers are mostly used to modify BASs of protein nature [5, 6], and cross-linked polymers serve to incorporate various BASs and cells into a polyacrylamide gel and to obtain biogels suitable for gel chromatography of natural and synthetic polymers [7].

The aim of our study was to synthesize low-molecular-weight [with molecular masses of (2–3.5) $\times10^4$ Da] AA copolymers with acrylic acid (AAc), suitable for use as carriers of cationic BASs, and to examine the dependence of the molecular characteristics of the copolymers obtained on their synthesis conditions. The above limitation on the molecular masses (*MM*) of synthetic bionondegradable copolymers, BAS carriers, is due to the necessity for their complete removal from the organism after the biological effect of an attached BAS is executed. This removal is only possible for polymers with certain size of macromolecules, which can be filtered off by kidneys. The molecular mass of linear polymers of this kind should not exceed (3.5–4)$\times10^4$ Da [8]. Therefore, another goal of the study was to examine the molecular and hydrodynamic characteristics of the resulting AA–AAc and to determine synthesis conditions of the copolymers in which their characteristics can be controlled.

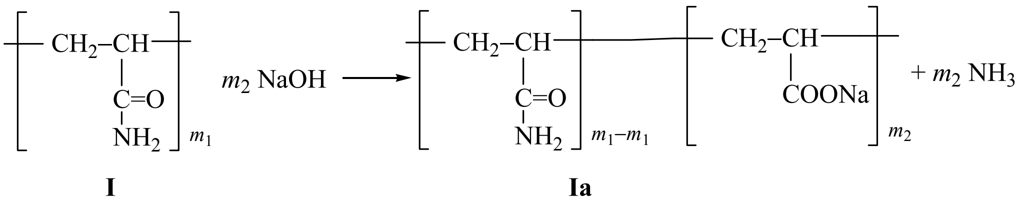
It should be noted that, despite the prolonged and sufficiently detailed analysis of PAAc and PAA properties, results of different studies are not always consistent and, occasionally, are even contradictory, i.e., there is no common opinion about the hydrodynamic and conformational behavior of these homopolymers. Consequently, prediction or calculation of molecular characteristics of the copolymers on the basis of published data poses certain difficulties, the more so as mainly macromolecular polymers have been studied. Experimental determination of these characteristics is more reliable.

The target AA–AAc copolymers were obtained both by alkaline hydrolysis of a low-molecular-weight PAA and by joint polymerization of AA and AAc.

Homopolymerization of AA. To obtain a low-molecular-weight PAA, we performed homopolymerization of AA in isopropanol, which is an effective carrier of a growing polymer chain (PAA *MM* controlling agent) and, for comparison, in ethanol. In doing so, we varied both the content of the initiating agent, azobis(isobutyronitrile) (AIBN) (Table 1, run nos. 1–3) and the AA concentration (run nos. 4–8) in the starting solution. To preclude imidization in the course of the reaction, the polymerization was carried out at a comparatively low temperature (50°C). It can be seen from the data in Table 1 that, even in the case of polymerization in dilute solutions ($[M^0] = 5$ wt %, run nos. 1–4), we obtained AA polymers in high (94–98%) yield. This confirms the high polymerization activity of acrylamide. It is important that low-molecular-weight AA polymers [$M = (0.35–3.6) \times 10^4$ Da] were obtained in all cases. It should, however, be noted that polymerization in ethanol yields AA homopolymers (I-1)–(I-3) with a higher polydispersity in *MM* [$(M_\eta)_w/(M_\eta)_n = 2.9–4.4$] than that of the polymers (I-4)–)I-8) obtained in isopropanol [$(M_\eta)_w/(M_\eta)_n = 1.7–2.2$]. Therefore, we chose the polymerization in isopropanol as the main method for synthesis of low-molecular-weight polymers. Values of *MM* decrease as the initiator concentration increases (Table 1, run nos. 1–3), which is characteristic of radical polymerization processes. The results of run nos. 4–8 (Table 1) of AA polymerization demonstrate that, as the AA concentration $[M_0]$ in the starting solution increases, values of *MM* of the PAA being formed become larger. This dependence is linear (Fig. 1), which also agrees with the fundamental aspects of the radical polymerization. The PAA obtained in run no. 8 was used in experiments on hydrolysis.

AA–AAc copolymers synthesized by alkaline hydrolysis. According to published data [9], a specific feature of the acid hydrolysis of PAA is that insoluble reaction products are formed as a result of imidization. Because of the complicating influence of the imidization, the acid hydrolysis method has not been used to obtain hydrolyzed PAA derivatives. It seems to be more appropriate to synthesize these compounds by hydrolysis in alkaline media, and just this technique was used to obtain PAA (I-8).

Alkaline hydrolysis of PAA (**I**) yields AA copolymers with AAc salts (**Ia**) by the scheme



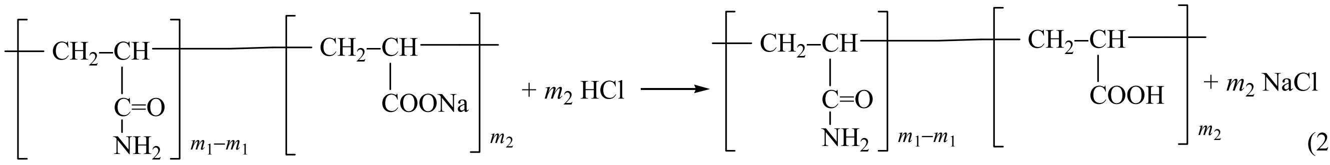
$$\left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{|}}{CH}-\right]_{m_1} \; m_2\,NaOH \longrightarrow \left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{|}}{CH}-\right]_{m_1-m_1}\left[-CH_2-\underset{COONa}{\underset{|}{CH}}-\right]_{m_2} + m_2\,NH_3 \qquad (1)$$

I **Ia**

Table 1. Heterophase polymerization of AA in alcohols at 50°C

Run. no.	Polymerization conditions			Polyacrylamide						
	$[M_1^0]$	[AIBN]	solvent	designation	yield in 24 h, %			$(M_\eta)_w \times 10^{-3}$	$(M_\eta)_n \times 10^{-3}$	$(M_\eta)_w/(M_\eta)_n$
	wt %					1 N $NaNO_3$	H_2O			
1	5	1.0	Ethanol	I-1	98.0	0.29	0.20	24.5	5.5	4.4
2	5	3.0	″	I-2	99.5	0.25	0.18	19.0	4.7	4.0
3	5	4.5	″	I-3	94.0	0.17	0.16	10.7	3.6	2.9
4	5	4.5	Isopropanol	I-4	98.3	0.08	0.11	3.5	2.1	1.7
5	10	4.5		I-5	99.2	0.09	0.12	4.3	2.5	1.7
6	20	4.5		I-6	98.1	0.23	0.26	17.0	8.0	2.1
7	30	4.5		I-7	91.5	0.32	0.35	28.0	12.5	2.2
8	40	4.5		I-8	94.7	0.39	0.41	36.0	16.0	2.2

To obtain AA–AAc copolymers (**II**), we acidified the solution produced by an alkaline hydrolysis of PAA with an HCl solution to pH 2.0 [scheme (2)]. Sodium chloride formed in reaction (2) was removed by dialysis:



$$\left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{\underset{|}{CH}}}-\right]_{m_1-m_1}-\left[-CH_2-\underset{COONa}{\underset{|}{CH}}-\right]_{m_2} + m_2\,HCl \longrightarrow \left[-CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{\underset{|}{CH}}}-\right]_{m_1-m_1}-\left[-CH_2-\underset{COOH}{\underset{|}{CH}}-\right]_{m_2} + m_2\,NaCl \quad (2)$$

II

We carried out the hydrolysis of PAA (I-8) in a 0.6 M NaOH solution at the initial polymer concentration of 0.3 M. In doing so, we varied the temperature and duration of the hydrolysis process. Table 2 lists the results of experiments on alkaline hydrolysis of PAA (I-8). It follows from the data in Table 2 that the hydrolysis occurs at a high rate at a temperature of 100°C and low alkali concentration (Table 2, run nos. 9–11). The degree of PAA hydrolysis, q, is 50.7% already in 15 min and increases to 60.5% in 1 h. Lowering the reaction temperature at the same process conditions makes q smaller. The yield of hydrolysis products upon dialysis is 58–76%.

Noteworthy is that the characteristic viscosity (from 0.37×10^{-2} to 0.16×10^{-2} cm^3 g^{-1}) of the hydrolysis products decreases as q increases (from 13.1 to 60.5%). This indicates that the effective hydrodynamic radius of molecules of hydrolyzed PAA decreases, because the characteristic viscosity is sensitive to the size of macromolecules. In particular, the decrease in the hydrodynamic size of the macromolecule of AA–AAc copolymer may be caused by intrachain hydrogen bonds formed via intramolecular contacts between hydroxy OH groups of AAc units and C=O groups of AAc or AA units of a coiled polymer chain. At the same time, the decrease in [η] may be due to a decrease in *MM* as a result of polymer destruction. Therefore, the question why [η] decreases is of fundamental importance.

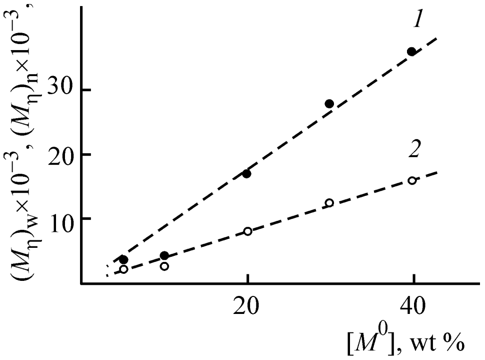


Fig. 1. (*1*) $(M_\eta)_w$ and (*2*) $(M_\eta)_n$ of PAA vs. the initial concentration of the AA monomer, $[M^0]$ in AA polymerization in isopropanol at 50°C. [AIBN] = 4.5 wt %.

To solve this problem, we used sedimentation-diffusion and light-scattering methods, which are absolute techniques for determining MM, because they require no preliminary calibration or any assumptions about the internal structure of a macromolecule. The values of *MM* and hydrodynamic characteristics [η], S_0, D_0, R_h^D of AA–AAc copolymers (II-3) and (II-7) were compared with the respective values for the starting PAA (I-8) (Table 3).

As [η] decreases at an increasing degree of hydrolysis, the translational diffusion coefficient increases and, accordingly, the hydrodynamic radii R_h^D calculated from these values become smaller. It should be noted that that the value of R_h^{DLS}, extrapolated to zero concentration, and R_h^D found at low concentrations almost coincide for sample (II-7) (Table 3). It can also be seen that, as the content of AAc units increases, *MM* decreases from $M_{SD} = 5.7\times10^4$ Da for the starting PAA to $M_{SD} = 2.3\times10^4$ Da for a copolymer with 50.7% carboxy units, i.e., the *MM* of the low-molecular-weight polymers is more than two times smaller. These data indicate that, under the chosen conditions, the alkaline hydrolysis of PA is accompanied by destruction of the main molecular chains and the smaller size of macromolecules is mostly due to the decrease in the *MM* of hydrolyzed PAA (AA–AAc copolymer), compared with the starting PAA.

This result seems to be unexpected, because the hydrolysis was performed under rather mild conditions: at comparatively low temperatures and not too high content of the alkali. However, effects of this kind have been observed previously in thermal destruction of macromolecular ($M = 2.4\times10^6$ Da) PAA in aqueous solutions of Na_2SO_4 at 75°C [10]. In [11],

Table 2. Alkaline hydrolysis of low-molecular-weight PAA (I-8); [NaOH] = 0.6 M, [PAA] = 0.3 M

Exp. no.	Starting PAA, $[\eta]\times10^2$, cm^3 g^{-1}	Hydrolysis conditions		Hydrolysis product (AA–AAc copolymer)			
		T, °C	τ, min	designation	yield, %	m_2, %[a]	$[\eta]\times10^2$, cm^3 g^{-1}
9	0.40	100	60	II-1	64.0	60.5	0.16
10	0.40	100	30	II-2	59.2	52.0	0.17
11	0.40	100	15	II-3	58.0	50.7	0.19
12	0.40	60	60	II-4	76.3	44.6	0.24
13	0.40	37	60	II-5	70.6	17.0	0.27
14	0.40	30	60	II-6	68.3	13.1	0.37
15[b]	0.40	60	60	II-7	71.7	32.3	0.21

[a] $m_2 = q$ (degree of hydrolysis, %). [b] [NaOH] = 0.3 M.

Table 3. Molecular parameters of polyacrylamide and AA copolymers with AAc, produced by alkaline hydrolysis and radical copolymerization

Polymer	m_2, %	$[\eta]\times10^2$, cm^3 g^{-1}	ν, cm^3 g^{-1}	S_0, Sv	$D_0\times10^7$, cm^2 s^{-1}	$M_{SD}\times10^{-3}$	$M_w\times10^{-3}$	R_h^D, nm	R_h^{DLS}, nm	$A_0\times10^{-10}$, erg deg^{-1} mol$^{-1/3}$
I-8[a]	0.00	0.33	0.73	1.7	3.30	57	–	6.3	–	3.2
II-7[b]	32.3	0.21	0.69	1.8	4.50	36	30	4.6	4.6	3.1
II-3[b]	50.7	0.19	0.66	1.6	5.60	23	–	3.7	–	3.1
II-13[c]	31.1	0.20	0.69	2.0	4.30	41	–	4.8	–	3.3
II-14[c]	34.7	0.32	0.69	2.1	3.47	50	–	5.5	–	3.1

[a] PAA. [b] AA–AAc copolymers produced by alkaline hydrolysis of sample (I-8). [c] AA–AAc copolymers produced by radical copolymerization.

the kinetics of thermal decomposition of commercial macromolecular AA copolymers with Na acrylate was studied in relation to the temperature and ionic strength of the solutions used. In this case, destruction occurred at temperatures of 26 to 40°C. At higher temperatures, Kurenkov et al. [11] observed an increase in the *MM*, caused by imidization of amide groups and by intermolecular cross-linking; a decrease in the ionic strength decelerated the decomposition slower.

In the case under study, the *MM* steadily decreases both on making the hydrolysis longer and on raising the temperature of the medium up to 100°C. On the one hand, this indicates that AIBN, which might lead to imidization and cross-linking of polymers, is fully expended. On the other hand, the mechanism of decomposition of AA–AAc copolymer chains is not quite clear. Probably, the rupture of C–C bonds at elevated temperatures occurs at "weak" links of the copolymer, e.g., at places of "head-to-head" linking of AA units [12].

It should be noted that the hydrolysis of PAA under the chosen conditions and the accompanying thermal degradation of the low-molecular-weight AA–AAc copolymer result in that the *MM* and m_2 change simultaneously. In the process, the *MM* of hydrolyzed PAA is the smaller, the deeper the hydrolysis. The relationship between the *MM* of the AA–AAc copolymer and the degree of hydrolysis in the composition range under study can be described by the equation $M/M_1 = 1–1.17\times10^{-2}m_2$, where M_1 and M are the molecular masses (M_{SD}) of the starting and hydrolyzed PAA, respectively, and the amount of AAc units is expressed in molar percent. This relation can be used to prognosticate the corresponding characteristics in synthesis of low-molecular-weight AA–AAc copolymers by alkaline hydrolysis.

AA–AAc copolymers synthesized by radical copolymerization. The heterophase copolymerization was performed in isopropanol, ethanol, and 1 : 1 (v : v) mixture of these alcohols in the presence of AIBN

Table 4. Heterophase copolymerization of AA (M_1) with AAc (M_2) at 50°C

Run. no.	Starting monomer mixture					AA–AAc copolymer				
	$[M_1^0]$	$[M_2^0]$	$[M_1^0] + [M_2^0]$	[AIBN]	solvent	designation	yield in 24 h, %	m_2, mol %	$[\eta]\times 10^2$, $cm^3 g^{-1}$	$(M_\eta)_w \times 10^{-3}$ $(M_{SD} \times 10^{-3})$
	mol %		wt %							
16	80	20	20	4.5	Isopropanol	II-8	99.5	20.1	0.16	10
17	80	20	20	3.0	″	II-9	99.5	18.8	0.23	19
18	80	20	30	3.0	″	II-10	99.8	20.0	0.32	27
19	80	20	40	3.0	″	II-11	99.5	19.6	0.36	33
20	80	20	30	3.0	Isopropanol + ethanol, 1:1	II-12	99.8	20.0	0.40	39
21	68	32	30	4.5	The same	II-13	99.7	31.1	0.20	(41)
22	65	35	30	3.0	Ethanol	II-14	96.9	34.7	0.32	(50)

(Table 4). The molecular mass of the copolymers obtained in quantitative yield increased with the concentration of monomers in the starting mixture (Table 4, run nos. 17–19) and also upon replacement of isopropanol with the mixture of alcohols (run nos. 18 and 20). In this case, raising the AIBN concentration made it possible to diminish the *MM* (Table 4, run nos. 16 and 17). As already noted, the *MM* of copolymers with high content of AAc units was determined by sedimentation-diffusion analysis.

Copolymers (II-3), (II-7), and (II-9)–(II-13), synthesized in the study, are well soluble in water, contain a sufficient number of reactive carboxy groups, and have molecular masses not exceeding 4×10^4 Da, the value admissible for linear bionondegradable polymers. Therefore, they can be used to modify properties of basic BASs, such as, e.g., antibiotics: aminoglycosides and biogenic amines.

AA–AAc copolymers suitable for use as BAS carriers were synthesized by both radical polymerization and alkaline hydrolysis. However, preference should be presumably given to the alkaline hydrolysis of PAA. The synthesis of PAA is simpler than the copolymerization of AA and AAc both in technological regard (only a single monomer is to be prepared) and in choosing conditions for obtaining a product with prescribed properties. In this case, thermal degradation of PAA units, which accompanies the hydrolysis, can be employed to control the *MM* of a copolymer being formed.

EXPERIMENTAL

Acrylamide (Germany) was twice recrystallized from benzene. Found, %: C 50.34, H 7.08. Calculated, %: C 50.65, H 7.03. mp = 84.5°C. Acrylic acid (Sigma) was twice distilled over molecular sieves in the presence of a polymerization inhibitor, Methylene Blue. The fraction with bp = 48°C was collected (22.6 gPa). Found: d_4^{20} 1.0511, n_D^{20} 1.4200, MR 17.35 $cm^3 g^{-1} mol^{-1}$. Calculated: MR 17.12 $cm^3 g^{-1} mol^{-1}$.

Azobis(isobutyrodinitrile) was recrystallized from a 1 : 5 chloroform : ethanol mixture. The yield of purified AIBN was 76.2%. Found, %: C 57.91, H 7.27. Calculated, %: C 58.53, H 7.31. mp = 103°C.

Anhydrous isopropanol and distilled ethanol (Vekton, Russia) were used without additional purification.

Polyacrylamide and acrylamide copolymers with acrylic acid were obtained by heterophase polymerization of AA or copolymerization of AA with AAc in isopropanol, ethanol, or mixtures of these alcohols at 50°C in ampules in an atmosphere of argon in the presence of AIBN. After the (co)polymerization was complete, the ampule was opened and the precipitated polymer was many times treated with acetone (analytically pure), collected on the filter, and dried in a vacuum.

Polyacryloamide was hydrolyzed in a 0.6 N NaOH solution in a flask equipped with a stirrer and a reflux condencer at varied process temperature and duration. After the reaction was complete, the pH of the target solution was brought to 2.0 by addition of a 1 N HCl solution and the mixture was dialyzed against water in the course of 3 days. The hydrolysis product was isolated by liophilic drying.

The composition of the AA–AAc copolymers synthesized by both methods was determined by potentiometric titration of carboxy groups with a 0.1 N NaOH solution in a pH-673 titrator. The structure of the AA–AAc copolymers synthesized by both methods was confirmed by IR spectroscopy. IR spectra were measured on a Bruker IFS spectrometer in pellets with potassium bromide. The IR spectra of AA–AAc copolymers contain, in contrast to the IR spectrum of PAA, a new absorption band at 2580 cm^{-1}, associated with stretching vibrations of –OH of the carboxy group.

The characteristic viscosity [η] was measured with an Ubbelohde viscometer: in a 1 N $NaNO_3$ solution at 30°C and in water at 25°C for polyacrylamide. The characteristic viscosity of AA–AAc copolymers was measured under the conditions of a suppressed polyelectrolyte effect in 1 N $NaNO_3$ solutions.

The molecular mass of PAA and AA–AAc copolymers containing ≤20 mol % AA units was calculated by the formula

$$[\eta] = 3.73\times10^{-4}M_w^{0.66}, \qquad (1)$$

known for PAA in 1 N $NaNO_3$ [12]. This formula was found using weight-average values of *MM* (M_w). The relation

$$[\eta] = 6.8\times10^{-4}M_n^{0.66}, \qquad (2)$$

reported for PAA in water, was found from the number-average *MM* (M_n). With the viscosities of the synthesized PAA measured in these solvents and the *MM* found using formulas (1) and (2) designated as $(M_\eta)_w$ and $(M_\eta)_n$, respectively, we calculated their ratio, $(M_\eta)_w/(M_\eta)_n$. Strictly speaking, determination of the *MM* from the experimentally measured characteristic viscosity yields the so-called hydrodynamic viscosity-average molecular mass M_η, which differs from both M_n and M_w [13] and the ratio $(M_\eta)_w/(M_\eta)_n$ is not a true polydispersity parameter. Therefore, we used this ratio only for a comparative qualitative estimate of the MMD width.

The molecular mass M_{SD} of copolymers with a high content of AAc units (>20 mol %) and the *MM* of a PA sample used to obtain AA–AAc copolymers by hydrolysis were determined from results of a sedimentation-diffusion analysis of solutions of these polymers by the Svedberg formula

$$M_{SD} = \frac{S_0}{D_0}\,\frac{RT}{1-\bar{v}\rho_0},$$

where S_0 and D_0 are the sedimentation and diffusion constants; *T*, absolute temperature; *R*, universal gas constant; $\bar{v}$, specific partial volume; and ρ_0, solvent density.

The translational friction of macromolecules both in the free state (translational diffusion) and in a centrifugal field in an analytical ultracentrifuge (fast sedimentation) was studied in a 1 N $NaNO_3$ solution in water. In doing so, we used in both cases the method of artificial formation of a solution–solvent interface. The position (in sedimentation analysis) or shape (in diffusion analysis) of the interface was recorded as a function of the process duration. The diffusion and sedimentation diagrams were processed using the standard procedures [14].

The diffusion experiments were performed at 25°C in a Tsvetkov diffusion-meter [14, 15] equipped with a polarization interferometer, in dilute solutions with concentrations $c < 0.1\times10^{-2}$ g cm^{-3}. We assumed that the diffusion coefficient *D* is independent of c at these concentrations, as is commonly the case for polymers [14], and D_0 was taken to be equal to the *D* obtained. The dependences of the dispersion of the diffusion boundary, 1/k, on time τ, from whose slope rates D was found, were linear. Figure 2 shows a $1/k$–τ plot for a solution of a PAA sample further subjected to alkaline hydrolysis [Tables 1 and 2, sample (I-8)].

An analytical ultracentrifugation was performed on an MOM 3180 ultracentrifuge (Hungary) at a rotor rotation speed of 45 000 rpm and temperature of 21°C. The range of polymer concentrations was (0.06–0.6)× 10^{-2} g cm^{-3}. The semilog dependences of the coordinate of the sedimentation boundary on time were linear, which made it possible to determine the sedimentation coefficients S corresponding to the final concentration from the slope of the straight lines. The sedimentation constants S_0 were found by extrapolation of S to an infinite dilution, which is illustrated in Fig. 3 for a copolymer sample (II-3) (Table 3). The values of S_0, as also those of D_0, were reduced to a temperature of 20°C, with the solvent viscosity and density taken into account.

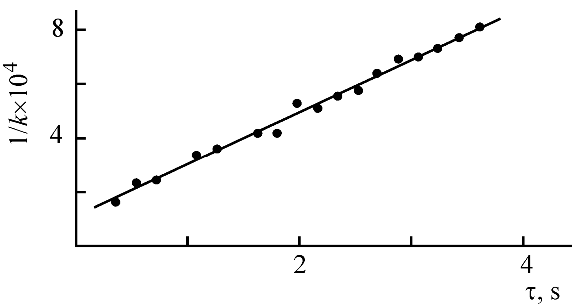


Fig. 2. Dispersion $1/k$ of the diffusion boundary of a solution of PAA sample (I-8) vs. the time τ. Solution concentration 0.053×10–2 g cm^{-3}.

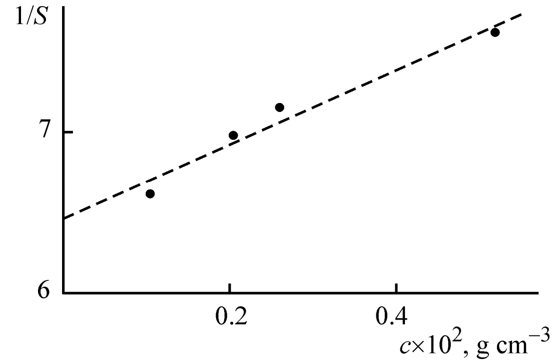


Fig. 3. Inverse sedimentation coefficient $1/S$ [S, Sv^{-1}] vs. the concentration c for a solution of the AA–AAc copolymer [sample (II-3)].

The specific partial volume $\bar{v}$ was found from the buoyancy factor, which was, in turn, determined from the slope rate of the dependence of the density of the polymer solution on its concentration. The density was measured using a pycnometer with a volume of 1.84 cm^3. Values of $\bar{v}$ were measured for PAA and AA–AAc copolymers produced from PAA by alkaline hydrolysis. The values of $\bar{v}$ decrease as the content of AAc units in the copolymer increases [Table 2; samples (I-8), (II=3), and (II-7)]. For samples (II-13) and (II-14), values of $\bar{v}$ were calculated from the content of AAc units, close to that of copolymer (II-7).

It should be noted that the values of the hydrodynamic invariant A_0, determined for the polymers and AA–AAc copolymers under study by the formula [16, 17]

$$A_0 = \eta_0\left(\frac{D_0}{T}\right)^{2/3}\left\{\frac{[\eta]S_0R}{100(1-\bar{v}\rho_0)}\right\}^{1/3},$$

where η_0 is the solvent viscosity, are close to the average experimental value $A_0 = 3.2\times10^{-10}$ erg deg^{-1} mol$^{-1/3}$ for flexible-chain polymers in good solvents [16, 17]. This fact points to the mutual correspondence of the hydrodynamic quantities S_0, D_0, and $[\eta]$, obtained using methods of molecular hydrodynamics, and to the reliability of the *MM* calculated from these parameters.

The molecular mass M_w of one of the copolymers [Table 2, sample (II-3)] was also measured by the static light-scattering method. The intensity of light scattered by a solution in the concentration range $c = (0.4–1.0)\times10^{-2}$ g cm^{-3} was measured on a Photocor installation (Russia). A Spectra-Physics He–Ne laser with an emission wavelength $\lambda_0 = 632.8$ nm served as a source of light. The solutions and solvent were purified using Millex (PVDF) filters with a pore size of 0.45 μm. M_w was calculated the Debye method [18, 19] because no angular dependence of the scattering was observed. The absence of the angular dependence of scattering, which points to a small size of scattering particles, gave no possibility to estimating their inertia radius.

The increment in the refractive index, *dn/dc* (*n* is the refractive index of the solvent) was measured with an IRF-23 refractometer. It was found to be, within the experimental error, 0.18±0.02 cm^3 g^{-1} for both the AA homopolymer [Table 1 and 3, sample (I-8)] and the AA–AAc copolymer [Table 2 and 3, sample (II-7)]. Therefore, it can be assumed that the compositional inhomogeneity of the AA–AAc copolymer and, accordingly, the different polarizabilities of dissimilar units of the copolymer do not exert any strong influence on its optical properties and, consequently, on the value of M_w, found by the light-scattering method. The optical constant

$$H = \frac{4\pi^2 n_0^2 (dn/dc)^2}{N_A\lambda_0^4},$$

used to calculate M_w from light-scattering data, was 2.35×10^{-7} mol g^{-2} cm^{-2} (n_0 is the refractive index of the solvent, and N_A Avogadro number).

The hydrodynamic radius R_h^{DLS} of sample (II-7) was measured by the method of correlation laser spectroscopy (dynamic light scattering) on the light-scattering installation used to determine M_w. The correlation function of the scattered-light intensity was determined using a Photocor-FC correlator with 288 channels; data were processed by the method of cumulants. The value of R_h^{DLS}, found at finite concentrations, was extrapolated to $c = 0$. The strong

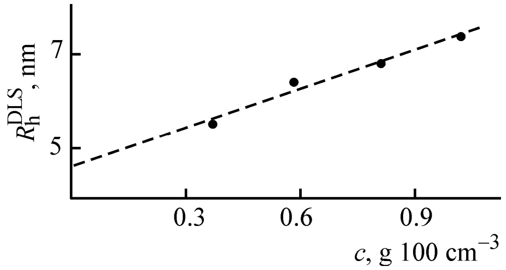


Fig. 4. Hydrodynamic radius R_h^{DLS} of macromolecules of the AA–AAc copolymer (II-7) vs. the concentration c.

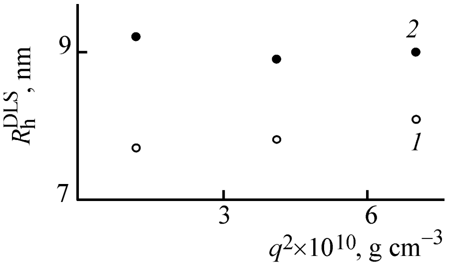


Fig. 5. Hydrodynamic radius R_h^{DLS} of macromolecules of sample (II-7) vs. the squared wave vector, q_2, for copolymer concentrations of (*1*) 0.4×10^{-2} and (*2*) 0.8×10^{-2} g cm^{-3}.

concentration dependences of the hydrodynamic radius (Fig. 4) indicates that there are intermolecular interactions in solutions of the copolymers under study, which may have both hydrodynamic and thermodynamic nature. In this case, we observed a nearly complete absence of an angular dependence of the hydrodynamic sizes, which is illustrated by the plot of R_h^{DLS} against squared wave vector

$$q = \frac{4\pi n_0}{\lambda_0} \sin \frac{\theta}{2},$$

shown in Fig. 5 for two concentrations.

The independence of R_h^{DLS} from the scattering angle is characteristic of small particles. The data furnished by the method of dynamic light scattering are in agreement with the result obtained using the static light-scattering technique and presumably indicate that there is no molecular aggregation (no coarse particles) in the region of dilute solutions of the copolymer under study.

The effective hydrodynamic radius R_h^D of macromolecules were also found from the diffusion constant in terms of the impermeable-sphere model. The equation for calculation of R_h^D

$$R_h^D = k_B T(6\pi\eta_0 D_0),$$

where k_B is the Boltzmann constant was derived using the Stokes formula $f = 6\pi\eta_0 R_h^D$ for the translational friction coefficient f of a hydrodynamically equivalent spherical particle.

CONCLUSIONS

(1) A low-molecular-weight polyacrylamide (3500–36 000 Da) was synthesized in quantitative yield by radical polymerization of acrylamide.

(2) It was shown that alkaline hydrolysis of low-molecular-weight polyacrylamide is accompanied by thermal degradation of the polymer backbone and the degree of hydrolysis increases with the process temperature and duration.

(3) It was demonstrated that, in heterophase acrylamide copolymerization with acrylic acid in alcohols, the molecular mass of the copolymers being formed increases in the order isopropanol > isopropanol + ethanol (1 : 1) > ethanol and the content of carboxy groups in the copolymers grows with the amount of AAc in the starting monomer mixture.

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