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INFLUENCE OF THE MOLECULAR PARAMETERS OF POLYACRYLAMIDE ON THE MASS TRANSFER IN TURBULENT WATER FLOWS IN CAPILLARIES

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Polyacrylamide samples of different molecular mass have been obtained under soft conditions by the method of ultrasound destruction. The influence of the concentration and molecular parameters of a polymer additive on the reduced Toms effect in purely aqueous media and in aqueous media containing a surface-active substance and an electrolyte (NaCl) has been analyzed.

A pressing problem of leading industries is increasing the output and decreasing the expenditure of energy of pipelines for forward and backward transportation of organic and inorganic liquids, including emulsions (crude oil first of all) and suspensions [1]. One of the most promising and original methods of solving this problem is decreasing the hydraulic resistance to turbulent liquid flows in a dispersive medium by introduction of comparatively small amounts of natural or synthetic polymers, functioning as additives, into it (Toms effect) [2–5]. Even though the mechanisms of this effect are not clearly understood, it is widely used in various industries and not only for intensification of liquid flows in pipelines. For example, the Toms effect is successfully used for increasing the velocity of travel of above-water and under-water bodies, intensification of drilling processes, and increasing the range of action of fire-hose barrels in the case of suppression of strong fires as well as in medicine and biology [2, 3, 6, 7].

It is difficult to optimize the turbulent liquid flows in actual multicomponent systems by introduction of polymer additives into them because of the peculiar features of the process considered and the vagueness of its mechanism. This is explained, in part, by the fact that the indicated process is characterized by a large number of parameters different in nature that substantially influence the resulting macroscopic Toms effect. The main parameters are the extent, cross-section area, and geometric shape of transient and turbulent flows, the kinetic viscosity of the dispersive medium, the shear stress, the Reynolds number Re, the nature and structure of the defect regions of the surface material of the inner walls of capillaries and tubes, the extent and structural features of a double electric layer (in the case of existence of a charge at the phase boundary) in the near-wall region of a flow, the features of a polymer additive (the nature and composition of alternating links, the value of the molecular mass, the kinetic and thermodynamic flexibility of macromolecules), the nature and quality of the dispersive medium serving as the solvent of the polymer additive, the existence of active ingredients in the system (electrolytes and surface-active substances), the amount of these ingredients, and others [3, 6–12].

Since the Toms effect has a paramount practical importance and the above-described specific features, the systematic study of the influence of the active parameters of a system Z on the resulting macroscopic Toms effect T is of obvious interest. It is very important to correctly select the method of estimating the Toms effect when the dependence $T = f(Z)$ is investigated because, when a concrete parameter Z is varied, all the other active parameters should remain unchanged. The character of the dependence $T = f(Z)$ will change with change in the experimental conditions (e.g., in the case of change from capillaries to pipelines) because of the specific features of the Toms effect, explained by its multifunctionality; therefore, the dependence $T = f(Z)$ obtained under different conditions will be correlational rather than strictly functional. In any case, the empirical dependences $T = f(Z)$ obtained under definite conditions can be used for development of optimum regimes of multicomponent liquid flows in pipelines.

Our main concern in the present work was with the influence of the concentration and molecular parameters of a polymer added to an aqueous dispersive medium on the Toms effect and the behavior of this effect in the case

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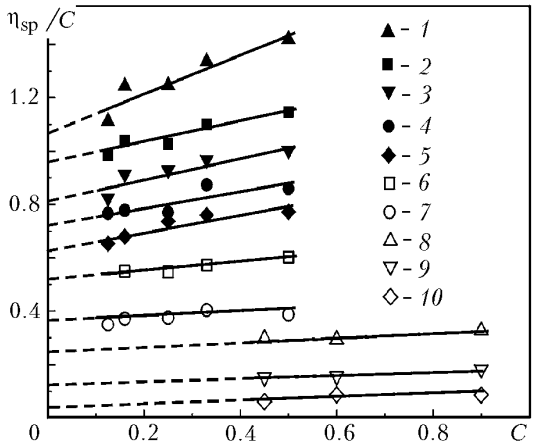


Fig. 1. Concentration dependence of the viscosity numbers of polyacrylamide samples having a different molecular mass $M \cdot 10^3$: 4.54 (1), 3.87 (2), 3.2 (3), 2.77 (4), 2.30 (5), 1.77 (6), 1.08 (7), 0.80 (8), 0.33 (9), and 0.08 kg/mole (10).

of dosed introduction of active elements (a surface-active substance (SAS) or an electrolyte) into it. As in [13, 14], polymers of different molecular mass M were obtained by the method of ultrasound destruction with the use of a UZDN-1 apparatus (operating frequency 22 kHz). As the basic substance, we used a copolymer of acrylamide with sodium acrylate with a low hydrolysis rate $\beta = 1\%$ and a molecular mass $M = 4.54 \cdot 10^3$ kg/mole at a working concentration of solutions of 1 kg/m^3 in the process of ultrasound destruction with an exposure time ranging from 3 to 150 min. The ultrasound destruction was carried out under soft conditions, which made it possible to obtain ten copolymer samples identical in chemical composition and structure of their macromolecules [15]. This was very useful for analysis of the results of subsequent experiments.

To illustrate the efficiency of the ultrasound-destruction method used we present (Fig. 1) the concentration dependences of the viscosity of the ten polymer samples studied, η_{sp}/C. The molecular mass M of the basic polyacrylamide samples was calculated by the Staudinger–Mark–Hauvink formula

$$[\eta] = KM^a , \tag{1}$$

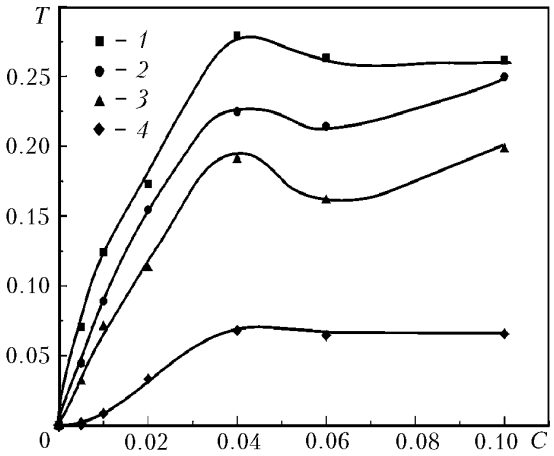
where K and a are constants ($K = 0.69 \cdot 10^{-5}$, $a = 0.78$) [16].

A turbulent liquid flow was controlled by the velocity of the polymer-solution flow v_s in a capillary with a diameter $d = 5 \cdot 10^{-4}$ m and a length $L = 38 \cdot 10^{-3}$ m at a constant pressure produced by an electric pump. To pass from the velocity of a polymer-solution flow v_s to the velocity of a water flow v_w, we measured the masses of the liquids m_s and m_w flowing through the capillary for 30 sec [17]. The values of m_s and m_w were determined with the use of an automatic one-shoulder scale of the A&D Company (Japan). The velocity of the water flow was $v_w \approx 10$ m/sec at $\mathrm{Re} = 5.2 \cdot 10^3$; under these conditions, intensive processes of destruction of macromolecules in the capillary were practically excluded. In the case where short capillaries are used, the value of the Toms effect is conveniently determined with the use of the relative dimensionless parameter T [17, 18]:

$$T = \frac{m_s - m_w}{m_w} = \frac{v_s - v_w}{v_w} . \tag{2}$$

Before conducting a series of experiments on the dependence $T = f(M)$, the basic polymer samples were tested as agents potentially capable of decreasing the hydraulic resistance of turbulent water flows. For all the copolymer samples studied, including the sample having minimum values of M and $[\eta]$, the following criterion inequality was fulfilled [19, 20]:

$$[\eta]\, MQ_{sh} > R\,(t + 273) . \tag{3}$$



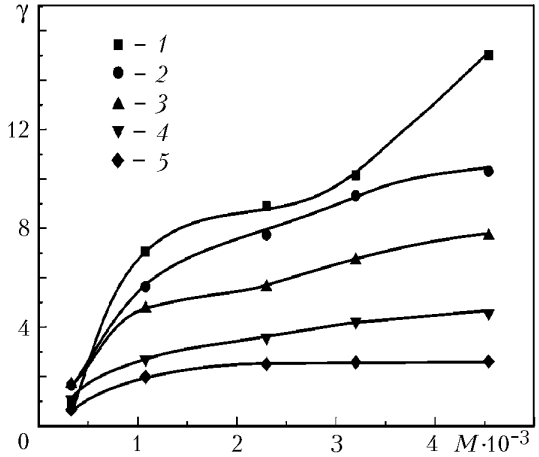


Fig. 2. Concentration dependence of the Toms effect for polyacrylamide samples having a different molecular mass $M \cdot 10^3$: 4.54 (1), 2.30 (2), 1.08 (3), and 0.33 kg/mole (4).

Fig. 3. Dependence of the reduced Toms effect on the molecular mass of polyacrylamide at different concentrations C of it: 0.01 (1), 0.02 (2), 0.04 (3), 0.06 (4), and 0.1 kg/m^3 (5).

Here

$$Q_{sh} = \Delta p \, d/(4L) ; \tag{4}$$

Δp is the differential pressure in the capillary, produced by the electric pump.

If inequality (3) is fulfilled for a concrete polymer additive, this additive can be used as a "quencher" of the turbulence in a liquid flow. The correctness of the testing of polymer additives was supported by subsequent experiments with them: the Toms effect i.e., $T > 0$, was detected for all the basic samples, including the low-molecular polyacrylamide ones.

It is evident from Fig. 2 that the Toms effect depends on the concentration and molecular mass of a polymer additive. The behavior of the empirical dependence $T = f(M)$ at comparatively low Reynolds numbers ($\mathrm{Re} < 1 \cdot 10^4$) is understood: as M increases, the sizes of the macromolecular balls increase and the value of T changes in direct proportion to them [21, 22]. The above-indicated functional relation between M, $[\eta]$, and the root-mean-square radius of a macromolecule $(\overline{h^2})^{0.5}$ follows from the known Flori equation [23]

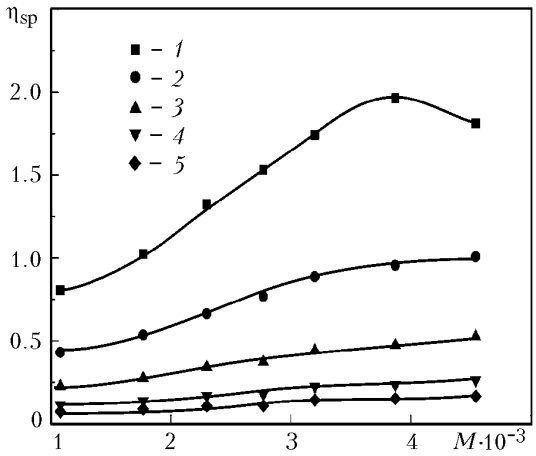
$$(\overline{h^2})^{3/2} \hat{O} = M [\eta] . \tag{5}$$

To obtain more exact and convenient (for comparison) information on the dependence of the Toms effect on M and the polymer-additive concentration C, it is appropriate to pass from the parameter T to the parameter γ [17]:

$$\gamma = T/C . \tag{6}$$

Figure 3 presents the generalized dependences $\gamma = f(M)$, and the dependence of the specific viscosity of aqueous solutions of polyacrylamide η_{sp} on its molecular mass M is illustrated in Fig. 4. According to (5), $(\overline{h^2})^{0.5}$ changes in direct proportion to η_{sp} in the first approximation.

A decrease in the parameter γ with increase in the polymer-additive concentration C points to a decrease in the contribution of the subsequent polymer additives to the resulting macroscopic Toms effect. Comparison of the values of γ and η_{sp}, determined for certain values of M, shows that the dependences $\gamma = f(C)$ and $\eta_{sp} = f(C)$ are antibatic in character.



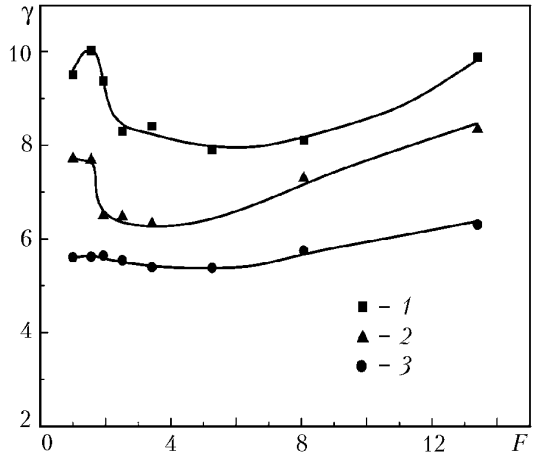


Fig. 4. Dependence of the specific viscosity of aqueous solutions of polyacrylamide on its molecular mass at different concentrations of this polymer C: 0.5 (1), 0.25 (2), 0.12 (3), 0.06 (4), and 0.04 kg/m^3 (5).

Fig. 5. Dependence of the reduced Toms effect on the Shultz parameter for compositions of polyacrylamide with $\overline{M} = 2.3 \cdot 10^3$ kg/mole at different concentrations C of it: 0.01 kg/m^3 (1), 0.02 (2), and 0.04 kg/m^3 (3).

We now consider the influence of the polymer-additive polydispersity with respect to M on the Toms effect. It should be noted that there are only a few publications on this problem [22]. The ten basic samples of acrylamide copolymers obtained by ultrasound destruction were very different in the value of M (by one and a half orders of magnitude) and identical in chemical composition, which allowed us to estimate the influence of their dispersivity with respect to M on the parameters T and γ fairly correctly. As the quantitative criterion of estimation of the polymer-additive polydispersivity with respect to M we used the Shultz parameter F [23]:

$$F = \frac{\overline{M}_{\text{wa}}}{\overline{M}_{\text{na}}} - 1 = \left[\sum_{i=1}^{k} \omega_i M_i \sum_{i=1}^{k} \frac{\omega_i}{M_i} \right] - 1 . \tag{7}$$

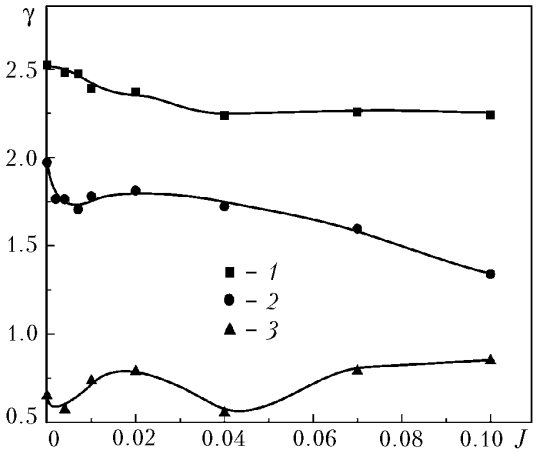
Here, $\overline{M}_{\text{wa}}$ and $\overline{M}_{\text{na}}$ are respectively the weight-average and number-average molecular masses of mixture compositions, ω_i is the weight fraction of the ith mixture component with $M = M_i$, and k is the total number of basic samples in the composition. The normalization condition for all compositions is as follows:

$$\sum_{i=1}^{k} \omega_i = 1 . \tag{8}$$

Polymer compositions with a definite value of $\overline{M} = 2.3 \cdot 10^3$ kg/mole were obtained by mixing the calculated amounts of basic samples having different values of M. For example, for a binary composition of basic samples with $M = M_1$ and $M = M_2$ (it will be assumed for definiteness that $M_1 < \overline{M}$ and $M_2 > \overline{M}$), the weight fraction ω_1 of the sample with $M = M_1$ was calculated by the formula

$$\omega_1 = \frac{M_2 - \overline{M}}{M_2 - M_1} . \tag{9}$$

Figure 5 shows the dependence of the reduced Toms effect on the polymer-additive polydispersity with respect to M. This dependence for the polyacrylamide mixture compositions considered is less pronounced as compared to the analogous dependence for ionogenic acrylamide copolymers with a high content of ionogenic links. This can be explained by the polyelectrolytic properties of the additives [22] and the absence of a polyelectrolytic effect in the co-



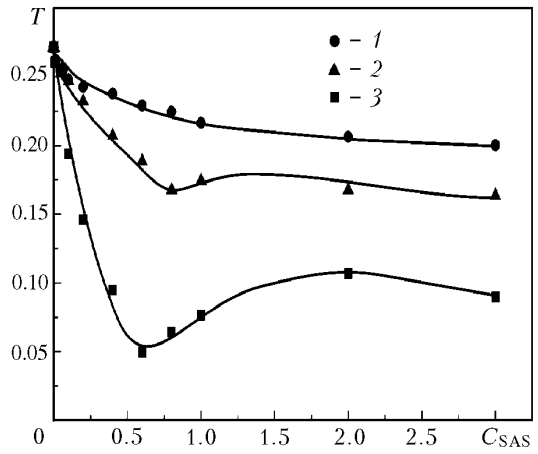


Fig. 6. Dependence of the reduced Toms effect (C = 0.1 kg/m^3) on the ionic strength for samples of polyacrylamide with a different molecular mass $M \cdot 10^{-3}$: 2.3 (1), 1.08 (2), and 0.33 kg/mole (3).

Fig. 7. Dependence of the Toms effect for polyacrylamide with $M = 2.3 \cdot 10^3$ on the concentration of an SAS: 1) ASAS (sulfonol), 2) ASAS (surfagen), 3) CSAS.

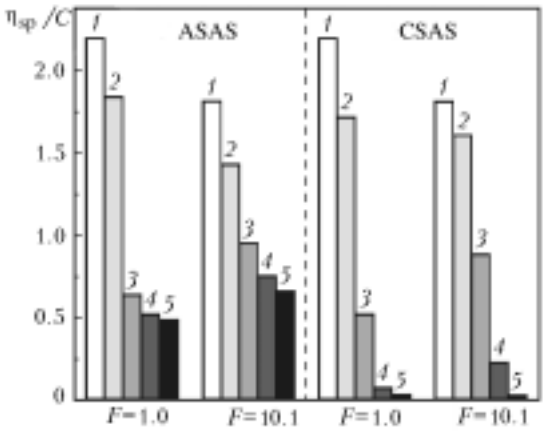
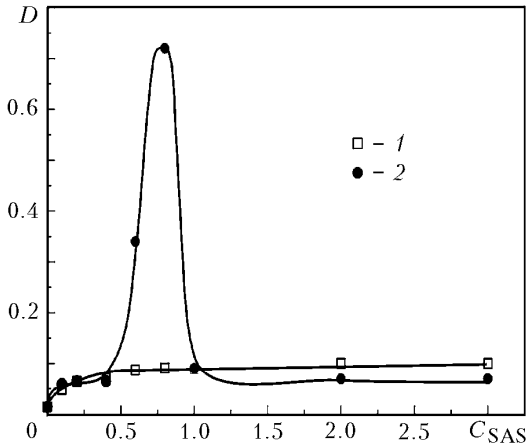


Fig. 8. Dependences of the viscosity numbers of mixtures of polyacrylamide (C = 0.1 kg/m^3; $M = 2.3 \cdot 10^3$ kg/mole) with an ASAS (sulfonol) and a CSAS for polymer systems with a Shultz parameter F = 1 and F = 10.1 for C_{SAS} = 0 (1), 0.1 (2), 0.6 (3), 1 (4), and 2 kg/m^3 (5).

polymers considered that are characterized by a very low degree of hydrolysis. Circumstantial evidence of the truth of this supposition is the weak dependence of the parameter γ of these copolymers on J (J is the ionic force induced by NaCl), presented in Fig. 6; the dependence $\gamma = f(J)$ is very pronounced for acrylamide copolymers with a high content of ionogenic links [24]. For nonionogenic polyacrylamide, the value of η_{sp}/C changes insignificantly with change in the ionic strength of its solutions J in a wide range (the conformational state of the macromolecules changes symbatically with change in this quantity) [3]. When the parameter T of a medium containing an electrolyte or an SAS is calculated by formula (2), m_w should be determined not for water itself but for water with salt (or SAS) additions of the same concentration.

Surface-active substances of different chemical nature can be used as active admixtures for multicomponent dispersive media (oil emulsions first of all). These substances influence the hydrodynamic resistance of turbulent liquid flows and the conformational state of the polymer-additive macromolecules. Therefore, the study of the influence of the nature and concentration of an SAS in polymer additives acting as "quenchers" of turbulent aqueous flows is of



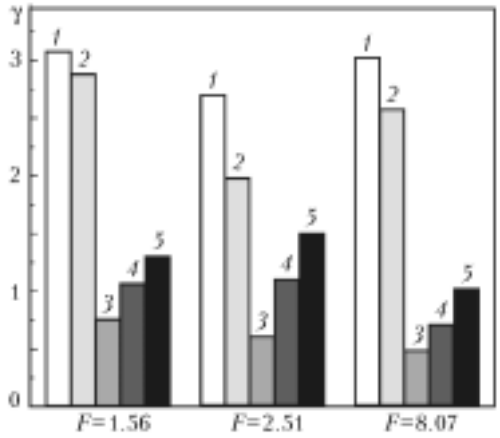


Fig. 9. Dependence of the optical density (λ = 400 nm) of the polyacrylamide ($M = 4.54 \cdot 10^3$ kg, C = 0.1 kg/m^3)–SAS system on the concentration of an SAS: 1) ASAS (sulfonol), 2) CSAS.

Fig. 10. Dependences of the reduced Toms effect for polyacrylamide samples ($\overline{M} = 2.3 \cdot 10^3$ kg/mole, C = 0.1 kg/m^3) with a different polydispersity with respect to M in aqueous solutions containing a CSAS with C_{SAS} = 0 (1), 0.2 (2), 0.6 (3), 1 (4), and 3 kg/m^3 (5).

not only scientific but also practical interest. It is seen from Fig. 7 that the Toms effect depends on the concentration and nature of an SAS, which points to the fact that this admixture substantially influences the macroscopic processes of mass transfer in turbulent flows of polyacrylamide aqueous solutions in capillaries. It should also be noted that the dependences $T = f(C_{SAS})$ are very different for anionic (curves 1 and 2) and cationic (curve 3) SASs, which is, in part, due to the influence of the nature of ionogenic SASs on the conformational state of the additive macromolecules. This supposition is supported by the viscosimetry analysis data (Fig. 8). In the range $C_{SAS} > 1$ kg/m^3, the value of η_{sp}/C and, consequently, the mean-square size of macromolecules $(\overline{h^2})^{0.5}$ decrease with increase in the SAS concentration much more substantially for a cationic SAS (CSAS) than for an anionic SAS (ASAS). The optical densities measured on an FEKM apparatus also point to the significant difference between the effects of ASASs and CSASs on a conformation of polyacrylamide macromolecules. The existence of an extremum (maximum) on curve 2 presented in Fig. 9 and the visually seen cloudiness of solutions point to the tendency for formation of globules in the binary system polyacrylamide–CSAS [25]. This tendency is not characteristic of the polyacrylamide–ASAS system because, for this system, the dependence $D = f(C_{SAS})$ has no extremum and solutions do not cloud at $C_{SAS} \le 3$ kg/m^3.

For the sake of completeness, we investigated the effects of the polymer-additive polydispersity with respect to M on the reduced Toms effect in aqueous media containing an SAS. As is seen from Fig. 10, the reduced Toms effect γ depends not only on the CSAS concentration but also on the parameter F and, consequently on the polymer-additive polydispersity with respect to M.

In conclusion, it may be said that the influence of the molecular parameters of polyacrylamide on the efficiency of its action and the efficiency of action of its binary compositions with SASs serving as agents decreasing the hydraulic resistance to the turbulent liquid flows in pipelines, detected in experiments with short capillaries, can be used for increasing the output of pipelines used for rapid transportation of products in the form of solutions, emulsions, and suspensions.

NOTATION

C, concentration of a polymer in a solution, kg/m^3; C_{SAS}, SAS concentration, kg/m^3; D, optical density; d, diameter of a capillary, m; F, Shultz parameter; $(\overline{h^2})^{0.5}$, mean-square sizes of macromolecules, m; J, ionic strength, H;

L, length of a capillary, m; *M*, molecular mass of a polymer, kg/mole; $\overline{M}$, mean molar mass of a polymer, kg/mole; *m*, mass of the liquid flowing through the capillary, kg; Q_{sh}, shear stress, Pa; R = 8.31, universal gas constant, J/(mole·K); Re, Reynolds number; *T*, parameter characterizing the Toms effect, m^3/kg; γ, reduced parameter characterizing the Toms effect; *t*, temperature of the liquid, ^oC; *Z*, active parameters of the system influencing the Toms effect; *v*, linear velocity of the flow, m/sec; β, weight content of ionogenic groups in the polymer macromolecule, %; η_{sp}, specific viscosity; η_{sp}/C, viscosity number, m^3/kg; $[\eta]$, limiting viscosity number, m^3/kg; λ, wavelength, nm; ω, mass fraction; Φ, Flori constant. Subscripts: w, water; s, solution; sh, shear; sp, specific; na, number-average, wa, weight-average.

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