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RHEOLOGY OF HYDROPHOBICALLY MODIFIED POLYMERS

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A study has been made of the rheological characteristics of the aqueous and water-salt solutions and gels of one class of hydrophobically modified polymers: acrylamide copolymers with a hydrophobic monomer which can be either acrylamide with a hydrophobic "tail" consisting of 9 or 12 carbon atoms or methacrylate with the same "tail." It has been shown that a sharp growth in the viscosity of the solutions and in the limiting stress, the highest Newtonian viscosity, and the elastic modulus of the gels is the greater, the larger the length and the number of hydrophobic groups in the copolymer and the smaller the amount of a surfactant in the process of its synthesis, which leads to a hydrophobicity growth of the copolymer. Consideration has been given to the role of the number of charges introduced into the copolymer apart from the hydrophobic groups and to other factors determining the rheological properties of the gels and their resistance to temperature.

Introduction. Water-soluble polymers and copolymers whose main chain is hydrophobic but a small number of the side or end nonpolar groups has been introduced into the macromolecules are called hydrophobically modified (HM) polymers. Hydrophobic interactions occur between these groups in water, i.e., such polymers are capable of self-associating. This process can be both intramolecular (when the concentration of the polymer in the solution is lower than the concentration of overlapping of the coils $C^{'}$), and then the solution viscosity sharply drops, and intermolecular (when $C > C^{'}$), and then the solution viscosity sharply increases.

Hydrophobic interactions that cause the aggregation of small nonpolar groups contained in the macromolecules of water-soluble polymers in a polar medium were first discovered in studying protein conformations [1]. The essence of these interactions is that the molecules of water, due to the hydrogen bonds between them, gather around nonpolar groups, forming icebergs of a sort. This changes the water structure completely and leads to an entropy change unfavorable in energy terms. In recent years, another explanation for hydrophobic interactions has been proposed; such interactions have been explained by the association of nonpolar groups that is not related to the entropy decrease, i.e., by the phenomenon well known in the physics and chemistry of polymer solutions when the polymer–polymer interaction is larger than the polymer–solvent interaction. Since hydrophobic interactions of cooperative character in proteins are one of the strongest types of nonchemical interactions, scientific effort since the end of the 1960s has gone into the creation of HM self-associating synthetic polymers [1]. The widest acceptance has been gained by three types of such polymers: 1) cellulose derivatives, mainly ethyl cellulose with end epoxy groups [3]; 2) polyethylene glycols with end urethane groups [4]; 3) copolymers of the acrylamide proper with acrylate (methacrylate) or with acrylamide into which one has introduced side nonpolar groups [5, 6].

In this work, we have investigated the aqueous and water-salt solutions and gels of the latter of the above classes. We studied both binary copolymers (consisting of two components: a) acrylamide (AAm) and HM acrylamide, i.e., "*amide*" copolymers, and b) acrylamide and HM methacrylate, i.e., "ether" copolymers) and ternary copolymers (consisting of three components: AAm, the mentioned HM monomer, and a monomer containing charged groups). Taking into account the mutual influence of hydrophobic and charged groups [7], one can purposefully control the properties of the solutions and gels of these copolymers. The chemical formulas of the copolymers are given below:

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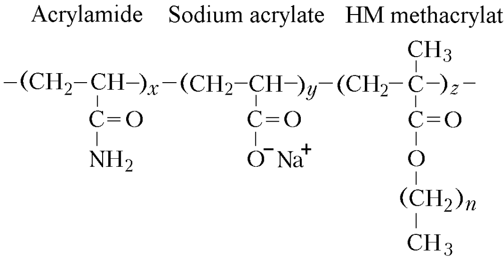
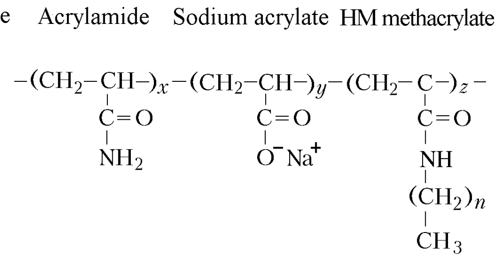


$$-(CH_2-CH(CONH_2)-)_x-(CH_2-CH(COO^-Na^+)-)_y-(CH_2-C(CH_3)(CO-O-(CH_2)_n-CH_3)-)_z-$$



$$-(CH_2-CH(CONH_2)-)_x-(CH_2-CH(COO^-Na^+)-)_y-(CH_2-C(CO-NH-(CH_2)_n-CH_3)-)_z-$$

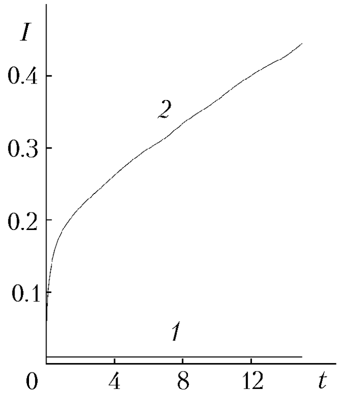


Fig. 1. Reversible creep of a 2% gel of a ternary ester copolymer of composition 1-C12/3.5SA below $\tau_{\lim}$ [1) G = 130 Pa] and the irreversible creep of a 2% gel of a copolymer of composition 0.5–C12/3.5SA above $\tau_{\lim}$ [2) G = 9 Pa]. I, Pa^{-1}; t, min.

This work was aimed at mastering synthetic techniques of production of copolymers and at varying the level of their hydrophobicity and charge for creation of physical gels possessing a wide range of rheological properties (elastic modulus, yield stress, viscosity above the yield stress) and resistance to higher-than-average temperatures.

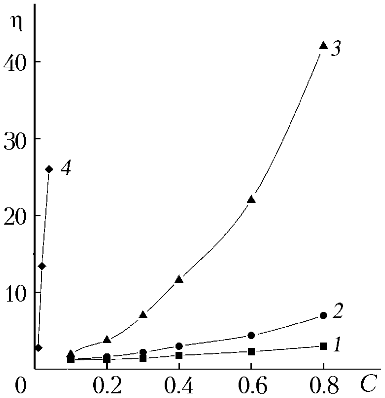
Since the presence of nonpolar groups even of a very small size and in very small quantities leads to the insolubility of the initial monomers in water, one produces HM copolymers by a specific method of micellar copolymerization [8, 9].

Experimental. The method of micellar copolymerization is as follows. One adds to water a surfactant, most frequently the anionic surfactant sodium dodecyl sulfate in whose micelles nonpolar groups are solubilized, and then carries out radical copolymerization of the above monomers. We used ammonium persulfate as the initiator of copolymerization. The reaction was carried out at $50^{o}C$ for 5 h at a pH of 3.5–9. On completion of the copolymerization, the residual surfactant was removed by precipitating the solution into methanol.

We thoroughly dried the polymer and preparated its solutions of different concentration in water or in a 2 wt.% solution of salt (NaCl).

The viscosity of low-concentrated solutions (to 0.6 wt.%) was measured in an Ubbelohde capillary viscosimeter; as the concentration of the solutions increased, we measured their viscosity on VPN-1 rotational viscosimeters of constant stresses [10] or Haake viscosimeters. We employed the static and dynamic methods to characterize the gels.

We measured the temporal progress of the deformation of a specimen (creep ε) in the regime of a constant static shear stress (τ = const). From the data obtained we determined the compliance ($I = \varepsilon/\tau$), the static shear modulus (G, the inverse of the compliance), the limiting shear stress or the yield stress ($\tau_{\lim}$), whose presence is the main rheological characteristic of a physical gel, which enables one to differentiate it from a solution, and the viscosity $\eta = \tau/(d\varepsilon/dt)$. For stresses below $\tau_{\lim}$ progressing is only the reversible creep, whose value is time-independent, and the flow of the system is absent (i.e., it is a gel); for stresses above the yield stress there occurs irreversible creep, determining the viscosity of the system in its flow. In physical gels, we can have flow with an undestroyed structure in the regime of creep where the grid nodes destroyed by stress have time to recover over the period of application of the stress. Such systems are characterized by flow with the highest Newtonian viscosity [11]. An example of different rheological behavior of HM-copolymer gels below and above $\tau_{\lim}$ is given in Fig. 1. One can determine, in the same



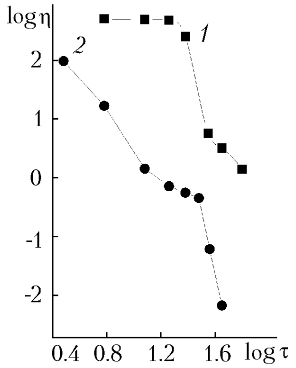


Fig. 2. Influence of the number and length of hydrophobic groups in HM binary copolymers on the concentration of the beginning of an increase in the viscosity and the rate of its growth: 1) 3-C9; 2) 5-C9; 3) 1-C12; 4) 1-C18; η, mPa·sec; *C*, wt.%.

Fig. 3. Flow curves of 2% gels of binary uncharged ester copolymer of compositions: 0.2-C12 (1) and 0.5-C9 (2). log η, Pa·sec; log τ, Pa.

regime, the stress at which the gel structure is destroyed in an avalanche-type manner. Therefore, the regime τ = const is frequently more informative for characteristics of physical gels than the most frequently used dynamic method of measurement of G' and G'', employing which we also characterized the gels produced.

Results of the Experiments and Their Discussion. In synthesizing HM polymers, one can vary the following parameters. In the binary copolymers, we changed the hydrophobic-group length that was 9 and 12 carbon atoms (C9 and C12) in this work, the number of hydrophobic groups (within 0.5–3 mole % C9 and 0.2–1.5 mole % C12)*, and synthesis conditions. The latter include: the content of a surfactant in synthesis (2–4 wt.%), the concentration of monomers in the initial solution, the pH of a medium (3.5–9), and the temperature and duration of the reaction. In ternary copolymers, these parameters additionally include the number (mole %) of charged groups in the copolymer. We added sodium acrylate (SA) (charged group COO^-); the content of these groups in a copolymer amounted to 2–20 mole %.

Let us consider the influence of all the mentioned factors on the rheological properties of solutions and gels of HM polymers.

Hydrophobicity (Length, Number, and Character of Distribution of Hydrophobic Groups in a Copolymer Chain). The main result of the addition of hydrophobic groups to a macromolecule is a sharp growth in the viscosity of diluted solutions. It begins with a concentration of the copolymer of about 0.2 wt.%; then the viscosity begins to intensely rise with increase in the concentration, and when the concentration is 2 wt.%, the system is a physical gel in which the aggregates of the hydrophobic groups represent nodes of a physical grid relating macromolecules. The longer the hydrophobic groups, the smaller the number of them that can be added to a copolymer without the loss of its solubility in water. Thus, according to [12], the maximum number of C12 groups in a binary amide copolymer amounts to 0.25 mole %. The longer the hydrophobic groups and the larger their number, the lower the concentration of the copolymer in the solution for which we have a viscosity jump and the more intense the rise in the viscosity (Fig. 2).

The hydrophobicity level of the copolymer increases with the length and number of hydrophobic groups, and the nodes of the gel grid which determine the gel's elastic modulus and viscosity above the yield stress accordingly become stronger. This is quite obvious from Fig. 2, which gives the flow curves of 2% systems copolymer–solvent for C12 and C9 binary ester copolymers with a small number of hydrophobic groups. In the case of this concentration the copolymer with a longer hydrophobic group forms a gel, and one observes flow of this gel with the highest Newtonian viscosity above τ_{lim}, while for a smaller length of the hydrophobic group we have flow with non-Newtonian viscosity, i.e., the system represents a solution.

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[*] In what follows we place mole % of a hydrophobic group before the number of carbon atoms in it, for example, 05–C12; mole % of the charged sodium-acrylate groups is given after the dash.

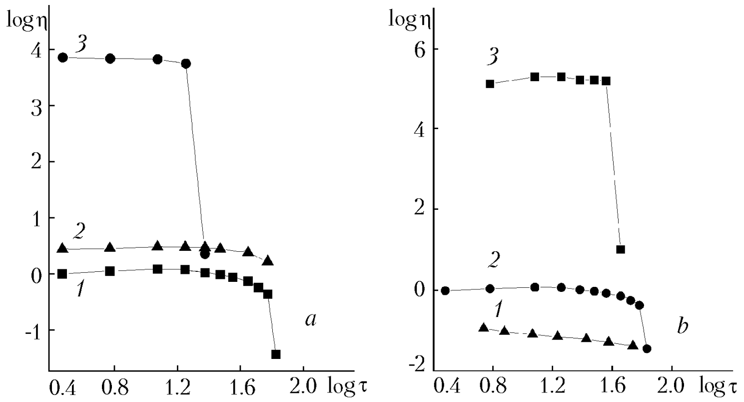
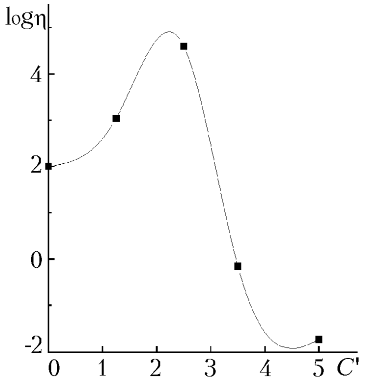


Fig. 4. Dependences of the flow curves of the ternary copolymer 1-C9/5SA on the content of a surfactant in synthesis (a): 1) 3, 2) 2.5, and 3) 2 wt.% and of the same copolymer on the number of hydrophobic groups for a content of the surfactant of 2.5 wt.% (b): 1) 0.5, 2) 1, and 3) 2 mole % of C9. log η, Pa·sec; log τ, Pa.



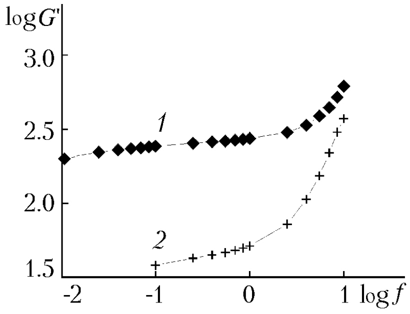
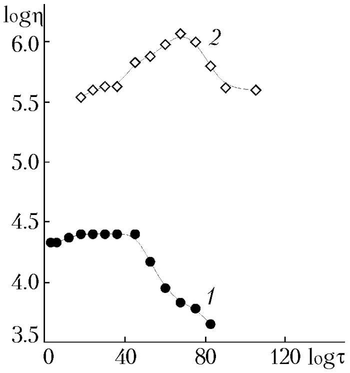


Fig. 5. Dependence of the viscosity above $\tau_{\lim}$ of 2% gels of ester ternary copolymers on the content of the charged groups of SA in the chain. log η, Pa·sec; C', mole % of SA.

Fig. 6. Comparison of the dynamic modulus of ester (1) and amide (2) ternary copolymers of composition 0.5-C9/10SA. log G', Pa; log f, Hz.

However, the hydrophobicity level depends not to a lesser (and sometimes to a greater) extent on the distribution of hydrophobic groups in the copolymer chain, which is determined by the amount of the surfactant in the system in synthesis. In the presence of the surfactant molecules, there form mixed micelles of the surfactant with nonpolar copolymer groups that are stronger than the domains formed by the hydrophobic groups in the absence of a surfactant. Therefore, the rigidity of the gel, i.e., the elastic modulus, is substantially influenced by the relation of the number of hydrophobic groups in the copolymer and of surfactant molecules. The smaller the amount of surfactant in synthesizing a copolymer, the more nonpolar tails (hydrophobic groups) gather in each surfactant micelle, which contributes to the occurrence of a block structure of the copolymer instead of the static distribution of hydrophobic groups in the chain. Such a structure determines the high strength of the domains which make up the nodes of a physical grid combining hydrophilic chains. The block character of the structure (presence of blocks in it) is a dominant factor of association and it largely determines the hydrophobicity level of the system [13]. Figure 4a gives as an example the dependence of the flow curves of gels on the amount of surfactant in synthesis on one ternary copolymer of composition 1-C9/5SA. It is obvious that, as the amount of the surfactant decreases from 2.5 to 2 wt.%, the viscosity of the gel increases by more than three orders of magnitude. A comparison of these data to the data of Fig. 4b on the viscosity growth with increase in the number of hydrophobic groups in the same polymer (from 0.5 to 2 mole %) for the same amount of surfactant shows that, by changing the number of hydrophobic groups for the same content of the



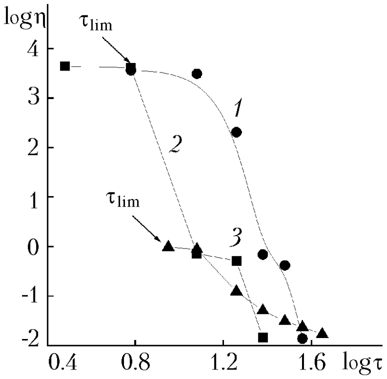


Fig. 7. Curves of flow of 2% gels of the polymers: 1) 1.5-C9/10SA and 2) 3-C9/20SA. log η, Pa·sec; log τ, Pa.

Fig. 8. Influence of the number of C12 groups in ester copolymers on the viscosity of 2% gels above their yield stress: 1) 0.5-C12, 2) 0.7-C12, and 3) 1-C12. log η, Pa·sec; log τ, Pa.

surfactant and by changing the content of the surfactant for a constant number of hydrophobic groups, one can attain the same quite significant result.

Role of the Charged Groups in the Chain of a Ternary Copolymer. Introduction of charges into the macromolecule of an HM copolymer produces two different effects. The first of them is that, when the number of hydrophobic groups is constant, a small number of charges leads, due to the electrostatic interaction between them (repulsion of like charges), to an increase in the size of surfactant micelles and accordingly a larger number of hydrophobic groups in them, i.e., again to an increase in the hydrophobicity level. This in turn leads to an increase in the yield stress, the elastic modulus, and the viscosity of the gels.

As the number of charged groups increases further, the electrostatic interaction becomes so strong that it destroys hydrophobic domains. Therefore, the dependence of the viscosity on the content of SA in the ester copolymer is extremum in character, as is obvious from Fig. 5. It is important that the maximum of this dependence hold the same value for different lengths of hydrophobic groups in the copolymer (C9 or C12).

It is of interest to note that this maximum corresponds to different contents of SA in the case of amide and ester copolymers: in amide copolymers, it is attained for a higher content of SA (10 mole %) whereas in ester copolymers it is attained for 2.5 mole % of SA. For the same contents of SA there are maxima of the limiting shear stress and the stress corresponding to the avalanche-like destruction of the gel structure.

The difference in the content of charges corresponding to the maximum of the rheological parameters is one manifestation of the difference in the character of these two types of HM copolymers for ester and amide gels. As is obvious from Fig. 6, the addition of acrylamide to a ternary copolymer (amide copolymer) leads, all other things being equal, to a *lower* dynamic elastic modulus of the gels than the addition of HM methacrylate (ester copolymer). This can be a result of the higher hydrophobicity of the amide chain than that of the ester chain and of the presence of one additional group CH_3 in the ester chain of methacrylate as compared to acrylamide. However, it is precisely due to the higher-than-average hydrophilicity of the amide chain that one can introduce more hydrophobic groups into ternary amide copolymers (with preservation of the solubility of HM copolymers in water and water-salt solutions). Thus, one can add only 0.7 mole % of C12 groups to an ester copolymer and 1 mole % of C12 groups to an amide copolymer for the same content of charges. This, naturally, increases the level of hydrophobicity of the copolymers and enables one to produce solutions and gels of amide copolymers with "*higher*" rheological characteristics.

The analogous effect manifests itself with increase in the content of the charges themselves in the chain of a ternary copolymer (the second effect of increase in the number of charges). Whereas the Newtonian viscosity of the gel significantly drops with increase in the number of charges, with the number of hydrophobic groups being constant, the same increase in the content of charges enables one to add more hydrophobic groups to the copolymer and thus to increase the viscosity and other rheological properties of the gel. This is quite obvious from the example given in Fig. 7. In the case of short hydrophobic groups (C9) one is able to add only 3 mole % of C9 groups to the amide

TABLE 1. Dependence of the Rheological Characteristics of Ternary Copolymers on Their Composition

Composition of the ternary copolymer	Amount of the surfactant in synthesis, wt.%	Elastic modulus G, kPa	Newtonian viscosity, Pa·sec
Ester 0.5-C9/2.5SA	4	40	$3 \cdot 10^4$
Ester 0.5-C9/5SA	3	–	0.90
Amide 0.5-C9/5SA	3	–	0.11
Ester 0.5-C9/5SA	2	40	$4 \cdot 10^5$
Ester 0.5-C12/5SA	3	6.7	$3.5 \cdot 10^3$
Amide 1-C9/10SA	2	33	$7.8 \cdot 10^3$
Amide 1-C12/10SA	3	110	$3 \cdot 10^5$
Amide 15-C9/5SA	2	50	$2 \cdot 10^5$

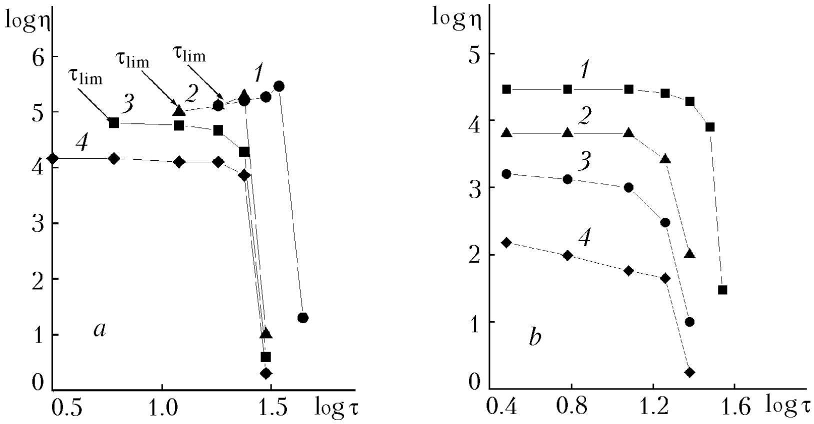


Fig. 9. Curves of flow of 2% gels of 0.8-C12/5SA copolymers synthesized with 2.5 (a) and 4 wt.% of the surfactant (b) at different temperatures: 1) 20, 2) 40, 3) 60, and 4) 80°C. log η, Pa·sec; log τ, Pa.

copolymer to which, when the number of charges is the most favorable (10 mole %), one can add only 1.5 mole % of C9 groups; this leads to a sharp increase in the gel viscosity. It is of interest that, apart from the high viscosity and elastic modulus of the gels, this ternary copolymer shows the so-called "shear-thickening" behavior, i.e., its viscosity increases with increase in the shear stress in a certain interval of stresses rather than decreases.

Table 1 gives the rheological characteristics for some of the investigated HM copolymers, which enables one to evaluate the influence of the copolymer structure on the properties of the gels. It is obvious that the amide copolymers of compositions 1-C12/10SA and 1.5–C9/10SA possess the highest elastic moduli and Newtonian viscosity.

Further increase in the number of C12 hydrophobic groups for the same content of charges does not lead to an improvement of the rheological properties; conversely, it is accompanied by a sharp drop in the viscosity as a result of the too high hydrophobicity of such copolymers, which causes phase stratification of the HM copolymer–water system. As is obvious from Fig. 8, upon the attainment of the limiting shear stress, stratification is so rapid and deep that the Newtonian flow does not manifest itself at all and one is able to measure only very low values of the viscosity, which correspond mainly to the viscosity of the solvent.

The above results yield that there exists the optimum hydrophobicity level of copolymers for attaining the required rheological properties of the gels; this level is determined by a combination of the number and length of hydrophobic groups and the content of charges and a surfactant. Depending on a fine balance of the enumerated factors, one can change the rheological properties of the gels of HM copolymers within a wide range, which allows purposeful control of them. In particular, these copolymers can show all the rheological types of behavior in solutions and gels: decrease and increase in the viscosity with growth in the stress or the rate of shear and constancy of the viscosity with change in the indicated parameters.

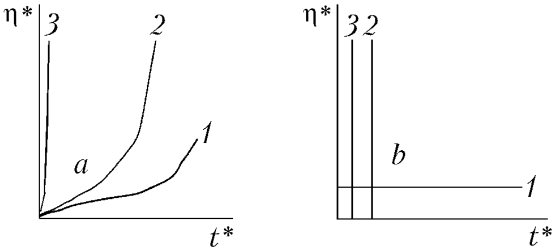


Fig. 10. Diagram of the specific formation of HM-copolymer gels: a) rise in the solution viscosity with time in formation of physical gels (with concentrations of: 1) 1, 2) 2, and 3) 3 wt.%); b) absence of gelation of the 1% solution of an HM copolymer (1) and instantaneous viscosity growth of its solutions in gelation (with concentrations of: 2) 2 and 3) 3%).

Resistance of HM Copolymers to Higher-Than-Average Temperatures. Figure 9 gives the temperature dependence of the curves of flow of 2% copolymer gels of composition 0.8–C12/5SA which have been produced for different amounts of a surfactant in synthesis. It is obvious that for a small amount of the surfactant, which increases the hydrophobicity level of the system, it is characterized by the presence of the shear stress up to 60^oC and preserves a very high Newtonian viscosity up to 80^oC. With increase in the amount of the surfactant in synthesis, which leads to a decrease in the hydrophobicity of the copolymer, the limiting shear stress disappears and the viscosity significantly drops with increase in the temperature. The analogous regularity is observed with decrease in the copolymer hydrophobicity due to the decrease in the number or length of hydrophobic groups. It is significant that one can select the conditions of production of HM copolymers which allow attainment of their fairly high thermal resistance.

Specific Properties of the Gels of HM Polymers. The gels of HM copolymers are totally thixotropic. From all the given flow curves it is obvious that the viscosity drops in an avalanche-type manner at a certain critical stress in the gels. In all the gels, the viscosity is recovered to the initial level during one hour.

The gels of HM ternary copolymers possess one more interesting specific property shown in Fig. 10. In ordinary physical gels, for example, gelatin gels, we have a monotonic growth in the viscosity with time to the attainment of the gel point and the same growth in the elastic modulus after the gel point. Unlike these systems, the gel of an HM copolymer is formed instantaneously, without the preliminary viscosity growth: as is obvious from Fig. 10b, a 1% solution does not form a gel at all, while 1 and 3% gels are formed instantaneously. We may assume that such behavior is associated with the preliminary formation of hydrophobic aggregates in the solution, which are combined into a grid network instantaneously in practice.

Summing up, we may say that HM self-associating copolymers are a new polymer type enabling us to substantially increase the viscosity of highly diluted solutions and to produce strong physical gels with low concentrations, which is of great interest for many application fields of practical importance.

CONCLUSIONS

Hydrophobically modified copolymers are one type of polymers with side groups capable of a strong specific interaction (they are frequently called stickers). The presence of such groups leads to the self-association of the polymers. The main characteristic property of HM polymers is a sharp growth (of orders of magnitude) in the viscosity of their diluted solutions, beginning with a nearly C' concentration; this process usually ends with the formation of a physical gel with a concentration 1–2 wt.% of the HM polymer in the solution. The viscosity of the gels above their yield stress and the elastic modulus of the gels depend on the number and length of hydrophobic groups, the type of HM copolymer and its microstructure (presence of blocks), the content of a surfactant in synthesis, and the number and type of charged groups in the ternary copolymer. In most cases, the viscosity decreases with increase in the temperature and the rate of shear (or the shear stress), but when the hydrophobic groups are numerous we can have a viscosity growth with increase in the rate of shear (shear stress). Control of the synthesis parameters enables us to purposefully change the rheological properties of the systems, which is of great practical importance.

NOTATION

τ, shear stress, Pa; $\tau_{\lim}$, limiting shear stress, Pa; G, shear modulus, Pa; G', accumulation modulus, Pa; G'', loss modulus, Pa; I, compliance, Pa^{-1}; η, viscosity, mPa·sec; t, time, min; C, concentration of the copolymer, wt.%; C', concentration of SA, mole %; f, frequency, Hz. Superscripts and subscripts: *, dimensionless quantities; lim, limiting.

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