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Hydrophobically Associating Water-Soluble Polymers: A Dramatic Growth of Solution Viscosity and the Specificity of Physical Gel Formation

Lidiya Z. Rogovina,* Victor G. Vasil'ev, Nataliya A Churochkina, Tatiyana I. Pryakhina

Institute of Organoelement Compounds of Russian Academy of Sciences, 28 Vavilov Str, 117813 Moscow, Russia

SUMMARY: The rheological properties of dilute and semidilute solutions (viscosity) and physical gels (elasticity modulus) of hydrophobically modified self-associated binary polymers (formed by micellar polymerization of acrylamide and methyl methacrylate with side hydrophobic groups (HG) containing 9, 12 and 18 C-atoms), and terpolymers (the same monomers and a charged component – sodium acrylate) are studied. The dependences of properties on the length, form (linear or branched) and the number of HG and charges is established. It is shown that a very small number of linear HG leads to a considerably higher solution viscosity, starting at a smaller concentration compared with the effects of a larger number of branched HG. Solutions of terpolymers of concentration 2-3 wt. % form physical gels that are thixotropic. After dilution, the polymers suddenly form gels at certain concentrations without the preliminary stage of viscosity growth.

Introduction

Hydrophobic interactions were first discovered in proteins.[1)] Since they are strong interactions, it was of interest to realize similar interactions in water-soluble hydrophilic synthetic polymers by the introduction of hydrophobic side groups. In the last 15-20 years, self-associating polymers were studied by large groups of scientists, with hydrophobic modifications being performed on different classes of polymers: cellulose derivatives, fluorine derivatives, and acrylic and methacrylic polymers obtained by radical polymerizations.[2-5)] In the last case, the hydrophobic groups (HG) were side groups attached to N or O atoms of one of the monomers. The copolymers were obtained by means of water micellar polymerization, i.e., in the presence of a surfactant that helped to dissolve a part of HG in water. In spite of this fact, only small amounts of HG were introduced into the macromolecules; enough, however, to increase substantially the solution viscosity, resulting from strong aggregation of the HG. In some cases these aggregates formed such strong junctions that physical networks (physical gels) were formed.[6-8)] Their properties has been found most interesting and they have many practical applications.

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The Binary Copolymers and the Measurement of Solution Viscosity

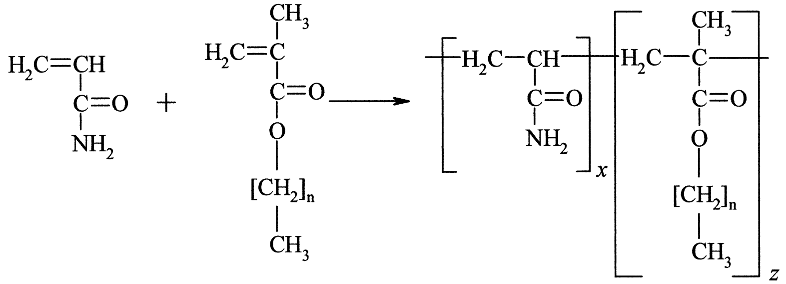
We have compared copolymers with linear and branched HG. The later were synthesized at the University of Leeds and provided for us by Dr. Schlumberger.

Branched HG, containing 9 carbon atoms; can be introduced in a macromolecule in comparatively large amounts of 3 and 5 mol %; HG containing 12 carbon atoms – up to 1.5 mol %, only; and the content of those containing 18 carbon atoms cannot exceed 1 mol %. At the same time, polymers containing linear HG are much more difficult to dissolve; it is possible to introduce not more than 0.5 mol % of HG containing 9 carbon atoms, and only 0.2 mol % of HG containing 12 carbon atoms. The reaction proceeds with 2-4 wt % of surfactant (SDS) and 10^{-3} mol·l^{-1} of sodium persulfate as initiator.

The molecular weights of the copolymers were measured by size exclusion chromatography and light scattering to be equal to $0.5\text{-}1 \cdot 10^6$.

The viscosity of dilute solutions was measured using a Scott viscometer; that of more concentrated solutions, using a viscometer providing constant shear rate; and the viscosity of the most concentrated or more hydrophobic solutions and the properties of the physical gels, on a home-made viscometer at constant shear stress.

The monomers, acrylamide and methacrylates modified with a hydrophobic side group containing *n* CH_2 groups, and the copolymer from these monomers were as follows:



As can be seen in Fig. 1 and 2, in spite of much smaller amount of linear HG in the binary copolymers, starting from 0.5-0.6 wt % of the polymer, the solution viscosities of both polymers with linear HG rise dramatically and reach 100 Pa s at the concentration of 2 wt %, whereas the viscosity of the polymer with 5 mol % of branched C9 groups is only 0.5 Pa s at the same concentration.

The viscosity of the 0.2 mol % C12 polymer is close to that of the polymer containing 1 mol % of very long, but branched C18 groups. Therefore one can see that the form and length of the HG change the solution viscosity by 5-6 orders of magnitude.

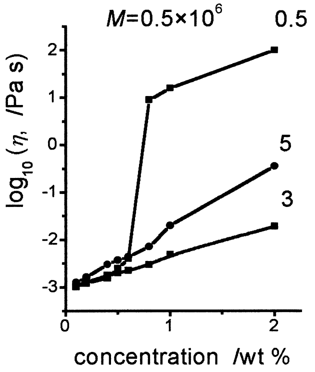


Fig. 1: Comparison of concentration dependences of aqueous solution viscosities of C9 polymers, prepared by Schlumberger (3 and 5 mol %) and in Moscow (0.5 mol %).

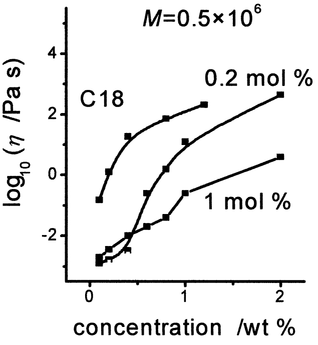


Fig. 2: Comparison of concentration dependences of aqueous solution viscosities of C12 polymers, prepared by Schlumberger (1 mol %) in Moscow (0.2 mol %) and of Schlumberger's C18 polymer (1 mol %).

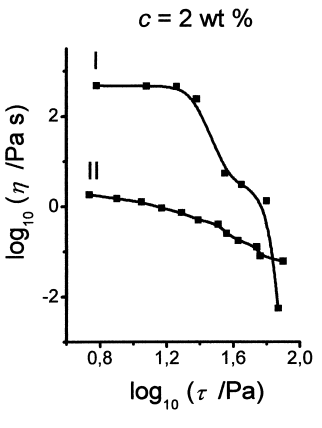


Fig. 3: Comparison of flow curves of 2 % solutions of Moscow and Schlumberger C12 polymers: I: 0.2 mol % of linear HG, II: 1 mol % of branched HG.

The same behavior can be observed in the Fig. 3 for the flow curves of 2 wt % solutions of polymers with linear and branched groups.

It is important that in all the polymers, the viscosity drops not only with the shear rate, but also with temperature increase, although the hydrophobic interactions strengthen as temperature increases. Supposedly, this behaviour is the result of the very small amount of HG in the macromolecules. The amount is just enough to increase viscosity, but not sufficient to modify its temperature coefficient which is determined by the structure of the whole macromolecule.

Charged Terpolymers

The charged terpolymers were obtained in the same manner as the binary ones, but a third, charged monomer was added, in our case, sodium acrylate (SA). The effect of SA concentration on the viscosity of a 0.5 mol % C9 terpolymer with linear HG is shown in Fig. 4. As one can see, a relatively small amount of SA leads to very high solution viscosity. This is the result of the swelling of the charged coils leading to the stronger aggregation of HG. However, further increase in SA concentration results in such a large chain extension that aggregates decompose. Consequently, the dependence of terpolymer viscosity on the charge concentration is expressed by a curve with very sharp maximum, as shown in Fig. 5. It is important that the large number of charged groups in the macromolecule tolerates a large number of HG.

As shown in Fig. 6, using the example of flow curves, the introduction of salt reduces solution viscosity. This behaviour is in contrast to uncharged hydrophobically modified polymers, where an addition of salt strengthens hydrophobic interactions and results in a viscosity increase.

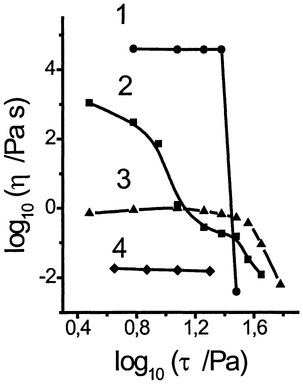


Fig. 4: Dependence of flow curves of 2 wt. % solutions of the 0.5 mol % C9 terpolymer on the amount of ionic groups in the macromolecule: 1-2.5 mol % SA; 2-1 mol %SA; 3-3.5 mol % SA; 4-5 mol % SA.

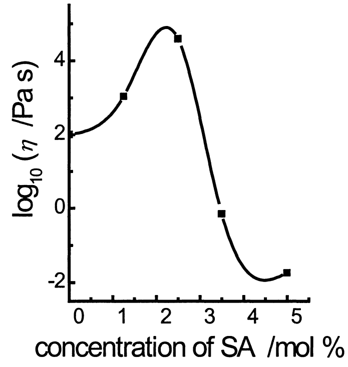


Fig. 5: Dependence of viscosity of 0.5 mol % C9 terpolymer solution on the amount of sodium acrylate.

The temperature dependence of the viscosity of salt-containing, charged terpolymer solutions shown in Fig. 7 in Arrhenius coordinates, gives a very small value of viscous-flow activation energy (8-10 kJ·mol^{-1}). Since the activation energy characterizes the strength of the structural elements that prevent flow, its small value points at the weakness of aggregates of the charged terpolymers in salt solution. At the same time, the activation energies of aqueous solutions of the charged polymers with small amount of charges, as shown in Fig. 8, are large: 105 kJ·mol^{-1} for 0.4 mol % C12, 2.5 mol % SA, and 54 kJ·mol^{-1} for 0.5 mol % C9, 2.5 mol % SA polymers. This behaviour shows that the aggregates formed by C12 are much stronger than the aggregates formed by C9 containing polymers.

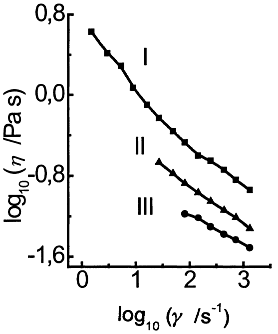


Fig. 6: Influence of salt on the flow curves of a 2 wt % solution of 1.5 mol % C12, 18 mol % SA terpolymer at 25^{0}C: I-water, II-0.2 wt % CaCl$_2$, III- 2 wt % NaCl. γ is the shear rate.

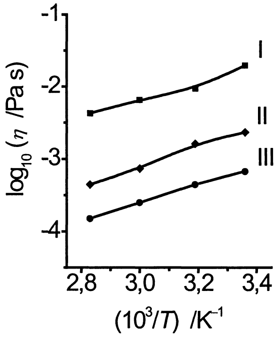


Fig. 7: Temperature dependence of viscosity in Arrhenious coordinates of 2 % solutions of 1.5 mol % C12, 18.5 mol % SA terpolymer: I-water, II-0.2 wt % CaCl$_2$, III-2 wt % NaCl.

Some terpolymers, in contrast to binary polymers, show a shear thickening behaviour that is not very sharply pronounced. An example is shown in Fig. 9. This behaviour can be the result of a transition from intramolecular to intermolecular linkages between hydrophobic groups.

Physical Gel Formation

Charged polymers with small amount of charges that develop very strong aggregates, can form physical gels. Fig. 10 shows the creep curves of 3 wt % physical gel of terpolymer 1 mol % C9, 2.5 mol % SA. This gel has the limiting stress $\tau = 6$ Pa, below which the system does not flow. The deformation is reversible; after removing the stress it goes to zero. At higher stresses (for example $\tau = 45$ Pa – curve 2), irreversible deformations develop and the system can flow. The elasticity modulus of the gel is 67 Pa.

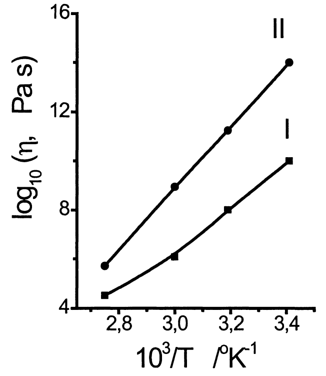


Fig. 8: Temperature dependence of viscosity in Arrhenious coordinates of 0,5 mol % C9, 2.5 mol % SA (I) and 0.4 mol % C12, 2.5 mol % SA (II) terpolymers.

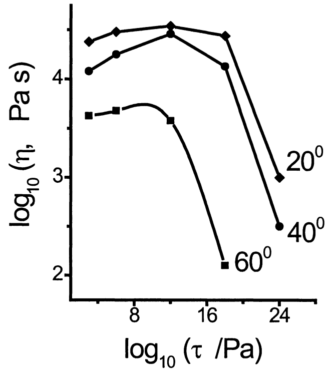


Fig. 9: Flow curves of 2% wt % of terpolymer 1 mol % C9, 10 mol % SA in 2 wt % NaCl solution at different temperatures.

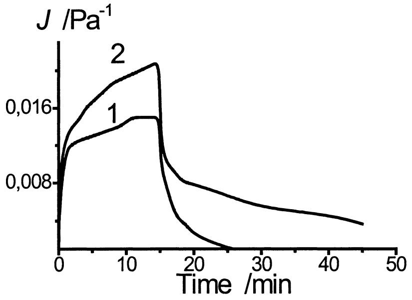


Fig. 10: Creep curves for 3 wt % physical gel of 0.4 mol % C12, 2.5 mol % SA ($M = 10^6$) polymer at $\tau = 6$ Pa (1) and $\tau = 45$ Pa (2).

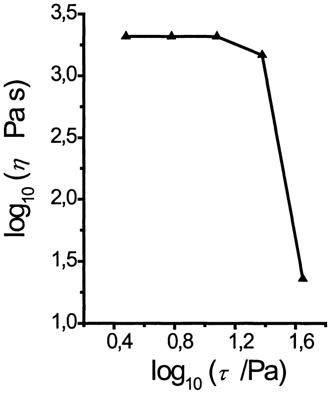


Fig. 11: The dependence of viscosity on the shear stress for 2 wt % gel of 0.4 mol % C12, 2.5 mol % SA ($M = 10^6$) polymer demonstrating the thixotropy of the physical gel: the gel decomposes at high stress and fully restores its properties within one hour after removal of the stress.

The physical gel is a thixotropic system. As shown in the Fig. 11, its viscosity is very high and constant over a wide stress interval. At higher shear stress the gel is destroyed completely.

However, 1 hour after removal of the stress, the viscosity is restored and has the same value at all stresses as before destruction.

A physical gel from a hydrophobically modified polymer has a special feature. As shown in Fig. 12, gelatine gels of different concentration, as well as other physical gels, are characterized by an increase of viscosity before an elasticity modulus appears. The increase is the faster the higher is the concentration of the initial solution. In contrast to this behaviour, the terpolymer solutions of different concentrations do not change in viscosity with time. Instead, they suddenly form gels at 2 or 3 wt %, without a preliminary stage of viscosity increase, as shown in Fig. 13. The change can be a result of the very fast integration of large aggregates, previously formed from HG.

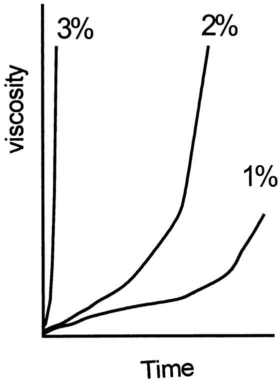


Fig. 12: Schematic rise of viscosity during gelatine gelation in 1, 2, and 3 wt % aqueous solutions.

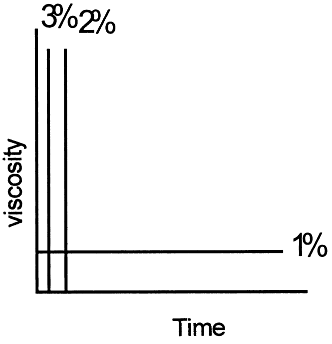


Fig. 13: Illustrating spontaneous gelation of 2 and 3 wt % solutions of polymer of 0.4 mol % C12, 2.5 mol % SA

Conclusions

The rheological properties of hydrophobically modified, charged binary and ternary copolymers (having linear and branched side groups C9, C12 and C18) that have been obtained by micellar polymerization are irregular in certain respects.

The more CH_2 groups in the monomer, the smaller the amount of HG that can be introduced into the copolymer. The solution viscosity rises much more dramatically in the presence of linear HG than in the case of HG that are branched. The difference reaches 5-6 orders of magnitudes. The dependence of solution viscosity of terpolymers on the concentration of charges is characterized by a curve with a marked maximum corresponding to a relatively small number of charges; the strongest hydrophobic aggregates are formed at this composition. The more charges, the larger the amount of HG that can be introduced into the macromolecule. The addition of salt leads to a significant drop in viscosity. A physical gel is formed from 3 wt. % terpolymer solution. It is thixotropic; it does not exhibit a preliminary stage of viscosity rise prior to gelation. The gel is formed suddenly at a concenration of 2-3 wt %. The phenomenon is the result of a very quick integration of previously formed large hydrophobic aggregates.

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