Rheological Properties of an Interpolymer Complex Formed Between Poly(acrylic acid) and Methyl Cellulose

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ABSTRACT: Some rheological properties of an interpolymer complex formed in the mixtures of aqueous solutions of poly(acrylic acid) and methyl cellulose are investigated. In a diluted state, the complex exhibits polyelectrolyte properties, and in the shear field, it flows like a pure poly(acrylic acid) solution. From the experimental data obtained from the mixture flow in a longitudinal field, an effective relaxation time was calculated. It turned out to be higher than that for the initial components. The deviation of the experimental values of the viscosity from the calculated additive ones allowed us to determine the critical molecular weight of the poly(acrylic acid) below which the complex is not formed: $M_{cr} \approx 6 \times 10^4$, which is one order of magnitude higher than for the mixtures of spatially complementary macromolecules. The increase of the total polymer concentration in the mixture first leads to an increase of the complex size. Further increase of the polymer concentration and transition to the semidiluted state decreases the complex size and also decreases its solubility in water. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1523–1528, 1999

Key words: interpolymer complex; polyelectrolyte; elongational and shear flow fields

INTRODUCTION

An interpolymer complex (IPC) is a compound formed in mixed solutions as a result of the interaction of two or more compatible polymers. For example, an IPC can be formed between two oppositely charged polyelectrolytes due to covalent bonding [solutions of poly(acrylic acid) (PAAc) + polyethyleneimine[1]] and also through hydrogen bonding between nondissociated groups of a polyacid and proton-acceptor groups of a noncharged polymer [PAAc acid + polyoxyethylene[2,3] or PAAc + poly(vinyl alcohol)[4]]. Studies of the mechanisms of the interaction between synthetic polymers help in the understanding and prediction of some properties of proteins and biological cells. From a practical point of view, similar investigations of polymer–micelle complexes[5] lead to the development of new effective methods of wastewater treatment.

The formation, structure, and properties of complexes based on two interacting chemically and spatially complementary flexible-chain polymers were described in detail in many articles.[1–7] However, there are but few works that studied the interaction between two spatially noncomplementary macromolecules, such as a flexible polyelectrolyte and a rigid-chain polymer (e.g., PAAc + hydroxyethylcellulose[8,9]). How this influences the complex formation and its properties is an open question.

In our work, an IPC formed between PAAc and methyl cellulose (MC) was investigated. The complex formation in the mixture of aqueous solu-

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tions of these polymers was proved by different methods (see ref. 10). The goals of the work were to study some rheological properties of the IPC formed in a mixture of aqueous solutions of PAAc and MC and to remind the reader that rheology is a powerful tool for the investigation of IPCs.

EXPERIMENTAL

Materials

In our work, we used four samples of PAAc: three of them, of molecular weights 3.7×10^4, 1.2×10^5, and 2.5×10^6, determined in a $2N$ NaOH aqueous solution at 25°C using the Mark–Kuhn–Hauwink equation $[\eta] = 1.5 \times 10^{-3}M^{0.54}$ (ref. 11), were synthesized at the Institute of Macromolecular Compounds, and the fourth one of $M = 4.5 \times 10^5$ was produced by Aldrich (Milwaukee, WI).

The MC used of $M = 2.3 \times 10^5$, with a degree of substitution of 1.6, was produced by NPO Polymersyntez (Vladimir, Russia). The sample was purified from impurities and lyophilized, and the molecular weight was determined in an aqueous solution at 20°C using the Mark–Kuhn–Hauwink equation $[\eta] = 2.8 \times 10^{-3}M^{0.63}$ (ref. 12), with $[\eta] = 6.8$ g/dL.

The mixtures of PAAc and MC were prepared by direct mixing of the initial aqueous polymer solutions of the same concentrations in different proportions; thus, the total polymer concentration in the mixture was kept constant during each experiment. The concentrations were varied from 0.1 to 2.0 g/dL. The experiments were performed at 25°C.

Methods

The rheological tools used are as follows:

- A capillary Ubbelohde viscometer having a solvent (water) flow time of 125 s;
- Two concentric rotational cylinder rheometers, "Rheotest-4" (Germany), and a viscometer for low viscosities (manufactured at the Institute of Petrochemical Synthesis, Moscow) with the gaps between cylinders of 0.78 and 0.47 mm, respectively; and
- An experimental setup for generating a longitudinal hydrodynamic field between two opposite coaxial capillaries. The capillaries were placed into a vessel with looking win-

dows. The solution was sucked into capillaries and a critical flow gradient, g_{cr}, at which the solution stretched between two capillaries becomes birefringent was measured. The scheme and detailed description of the setup were given in ref. 13.

RESULTS

A straightforward method for testing a mixture's compatibility is to measure the dependence of the mixture specific viscosity on its composition in a capillary viscometer. The procedure is well known and described in the literature.[2,4,14–16] For the mixture of MC with PAAc of four molecular weights, the result is presented in Figure 1. The concentration of the initial polymer solutions here was 0.1 g/dL for all the mixtures. The dashed lines show the additive dependence of the viscosity of each mixture, η_{add}, on its composition, which corresponds to the absence of the interaction between the components. In the first approximation, it can be calculated from the following expression:

$$\eta_{add} = \eta_{sp\,1}(C_1) + \eta_{sp\,2}(C_2) \tag{1}$$

Figure 1 Dependence of the mixture's specific viscosity on its composition: PAAc of (1) $M = 3.7 \times 10^4$, (2) 1.2×10^5, (3) 4.5×10^5, and (4) 2.5×10^6. The dashed lines are for the corresponding additive dependencies.

Figure 2 Determination of the critical molecular weight of PAAc.

$\eta_{sp\ 1}(C_1)$ and $\eta_{sp\ 2}(C_2)$ being the specific viscosities of each polymer measured in water, and C_1 and C_2, the polymer concentrations in the mixture, $C_1 + C_2 = $ const.

From Figure 1, it is clear that for the mixtures of MC with PAAc in the range of molecular weights from 10^5 to 2.5×10^6 there is a positive deviation of experimental data from the calculated additive viscosity. Keeping in mind the results of velocity sedimentation and potentiometric titration experiments (a detailed study was presented in ref. 10), one can conclude that an IPC is formed in these mixtures.

One of the criteria of IPC formation is the magnitude of the deviation of the experimental values of viscosity from the calculated additive ones. The maximal difference between the experimental values of η_{sp} and the corresponding η_{add} were calculated as follows:

$$\Delta\eta = (\eta_{sp} - \eta_{add})_{max}/\eta_{add} \qquad (2)$$

The dependence of $\Delta\eta$ on the molecular weight of the PAAc is shown in Figure 2. For the mixtures of MC with PAAc of molecular weights lower than 6×10^4 $\Delta\eta = 0$, there is no difference between the experimental and calculated additive viscosities. A complex is not formed in these mixtures (or, at

least, the increase of its size compared with the initial macromolecules is negligibly small). Thus, all further rheological studies will be performed on the mixture of MC with PAAc of $MM = 4.5 \times 10^5$.

When investigating the physicochemical properties of IPCs, one of the main questions is to what extent the complex is retaining the properties of the initial components. The capillary viscometry was again used to check if the complex is keeping polyelectrolyte properties from the PAAc. The dilution of the mixture MC : PAAc = 1 : 1 with water was performed and compared with the analogous dependence for the PAAc.

The result of the dependence of η_{sp}/C on the polymer concentration (for the mixture, on the total polymer concentration in the mixture) is given in Figure 3. The mixture shows a behavior typical for polyelectrolyte solutions. This is a predictable result because in this mixture the IPC is formed due to the hydrogen bonding between non-dissociated groups of PAAc and proton-acceptor groups of MC.[10] The charged groups of the PAAc are not involved in the complex formation, and as a consequence, the complex is a polyelectrolyte.

Another important characteristic of a polymer solution is its flow in hydrodynamic fields of different geometries. An example of the interpoly-

Figure 3 Demonstration of polyelectrolyte properties of the IPC based on PAAc ($M = 4.5 \times 10^5$) : MC = 1 : 1. The open circle corresponds to the aqueous PAAc solution of the same molecular weight.

log η (Pa s)

Figure 4 Shear-rate dependence of the viscosity of (1) MC, (2) PAAc, and their mixtures (3) PAAc : MC = 3 : 1 and (4) PAAc : MC = 1 : 3. Total polymer concentration in the mixture is 0.1 g/dL.

mer complex behavior in shear and longitudinal fields is given in Figures 4 and 5, correspondingly. The total polymer concentration is 0.1 g/dL.

In a diluted state, the initial components show a different behavior in the shear field (Fig. 4). MC is a Newtonian liquid below the critical overlap concentration (which is ≈0.15 g/dL for this molecular weight). PAAc has a Newtonian plateau at low shear rates and the beginning of a non-linear regime at high shear rates. PAAc shows a shear thinning phenomenon because of the polyelectrolyte effect which is present at low PAAc concentration. The interpolymer complex, being also a polyelectrolyte (as shown in the previous paragraph), has a similar dependence of the viscosity on the shear rate to that of the PAAc.

For the solutions flowing in the longitudinal field, the threshold rate gradient g_{cr} leading to considerable uncoiling of a polymeric chain is dependent on the time of the deformation relaxation τ of the macromolecule as a whole. According to the dumbbell model,[17] $\tau = 0.5/g_{cr}$. It was not possible to measure g_{cr} for the PAAc solution because the segments of the PAAc macromolecule are not optically anisotropic. In our case, this method is sensitive only to the effects connected with MC, which has an intrinsic optical anisotropy. Thus, the obtained value of τ is, in fact, the effective

relaxation time. Both types of the MC macromolecules, those "reacted" with the PAAc and the ones which are free in the mixture, contribute to the effective relaxation time.

The dependence of τ on the mixture composition is presented in Figure 5. It shows a maximum at the same mixture composition as for the dependence of η_{sp} (see Fig. 1, curve 3). If there should not be any interaction between the polymers, the effective relaxation time should decrease monotonically with the decrease of the MC concentration in the mixture. The obtained result shows that this method is sensitive to a complex formation in a mixture even if one of the components is not optically anisotropic. The increase of the effective relaxation time in the mixture as compared with the relaxation time of MC indicates that the size of the complex is larger than that of the initial components.

The rheological behavior in the shear field of the mixture PAAc + MC in a semidiluted regime (1.0 and 2.0 g/dL) is presented in Figure 6(a,b), correspondingly. Here, MC and its mixtures with PAAc show a nonlinear dependence of the viscosity on the shear rate. It should be noted that mixtures containing more than 50% of PAAc are turbid, this effect being more pronounced for mixtures prepared from the initial 2.0 g/dL polymer solutions. In this case, some mixtures have the same viscosity as that of the initial PAAc solution [see Fig. 6(b)].

Figure 5 Effective relaxation time versus mixture composition (IPC in the elongational flow field).

(a)

(b)

Figure 6 Shear-field behavior of mixtures in a semidiluted state. (a) Total polymer concentration in the mixture of 1.0 g/dL: (1) MC; (2) PAAc; (3) PAAc : MC = 7 : 93; (4) PAAc : MC = 1 : 1; (5) PAAc : MC = 73 : 27; (6) PAAc : MC = 93 : 7. (b) Total polymer concentration of 2.0 g/dL: (1) MC; (2) PAAc; (3) PAAc : MC = 7 : 93; (4) PAAc : MC = 2 : 3. The dependencies of viscosity on the shear rate for IPC of compositions PAAc : MC = 92 : 8, 4 : 1, and 7 : 3 coincides with the data for the PAAc solution.

In a few days, a separation into two phases for the mixtures prepared from 2.0 g/dL solutions and containing more than 70% of the PAAc solu-

tion in the mixture was observed. The mixture of PAAc : MC = 73 : 27 was centrifuged for 10 h at 5×10^4 s^{-1}. The sediment and the solution were separated, lyophilized, and analyzed by IR spectroscopy. The spectra showed that the sediment consists of both MC and PAAc in the proportion 70 : 30 and the solution was mainly of PAAc, meaning that the complex was precipitated and the excess of the PAAc remains in the solution.

DISCUSSION

As was shown in Figure 2, the size of the IPC is larger than the size of the initial components when the molecular weight of PAAc is higher than $\approx 6 \times 10^4$. This result is similar to the one obtained by different authors studying IPC formation between two flexible polymers (see, e.g., refs. 3, 7, and 18–20). The existence of a minimum chain length is a consequence of the cooperative character of such interpolymer interactions. The difference is in the values of the critical molecular weights M_{cr}. In a mixture of two interacting flexible polymers, complexes are not formed when one of the components is almost an oligomer: $M_{cr} = 4 \times 10^3$ (ref. 3) or 1.5×10^3 (ref. 18). In our case, the critical molecular weight of PAAc is one order of magnitude higher because PAAc and MC are not spatially complementary and also because of the presence of hydrophobic groups in MC.

An analysis of the influence of the polymer concentration (in the region from 0.1 to 2 g/dL) on the complex formation was performed using the parameter $\Delta\eta$ (see exp. 1). The experimental dependencies of the specific viscosity on the mixture composition were obtained on the capillary Ubbelohde viscometer for different polymer concentrations and compared with the calculated additive viscosities using the procedure described in the previous section. For the semidiluted region, the values of the viscosities at $\gamma = 10^2$ s^{-1} obtained on rotational viscometers were used (we chose the shear rate of 10^2 s^{-1} because the same shear rates are realized in the capillary viscometer).

The result is presented in Figure 7. For the concentrations lower than 1 g/dL, the increase of the total polymer concentration in the mixture leads to an increase of the values of $\Delta\eta$, which means increase of the size of the complex. This result coincides with the one obtained for a pair of

Figure 7 $\Delta\eta$ dependence on the total polymer concentration in the mixture.

flexible-chain polymers [PAAc + poly(vinyl alcohol)] forming an interpolymer complex.[19] The reason is that with increase of the polymer concentration PAAc and MC form associates in the initial aqueous solutions and thus the complex consists of several macromolecules of both types.

The difference with the complexes formed by other macromolecules, for example, in the mixtures of PAAc + PEO[18] or PAAc + PVA,[19] is that a further increase of the total polymer concentration in the mixture PAAc + MC leads to decrease of the size of the complex (see Fig. 7) and its solubility in water. This result is mainly the consequence of the hydrophobicity of MC. The complex here consists of MC and PAAc; thus, its solubility in water is lower than that of a pure PAAc. The increase of the total polymer concentration in the mixture decreases the number of water molecules per each macromolecule, which is why the complex containing the MC macromolecules precipitates in the mixture complex + PAAc. The concentration region when the complex solubility starts to decrease is the transition to the semidiluted state.

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