STUDY OF RHEOLOGICAL PROPERTIES OF AQUEOUS PECTIN SOLUTIONS

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The study is devoted to the rheological behavior of aqueous solutions of pectin, a natural polysaccharide, which is a polyelectrolyte and has a spectrum of physiological activity. It is shown that the polyelectrolyte nature of the polymer introduces significant features into its rheological behavior. These features are manifested in the form of low values of the activation energy of viscous flow, in the absence of an anomaly in the viscous flow of solutions above the crossover point, as well as in the existence of a concentration region in which macromolecules are in contact with each other, but do not form a fluctuation network of meshes.

Keywords: polymer, polyelectrolyte, viscosity, rheological properties, fluctuation network, concentration of crossover.

Introduction

The research of rheological characteristics of polymer solutions is of great theoretical and practical interest. The theoretical interest is due to the fact that the dependence on viscosity on shear rates, strain, and the concentration of polymers in solutions, the temperature of the process can result in the conclusion about its structural and physical conditions [1–2]. The practical interest is conditioned by the fact that polymer's viscosity and its anomalies define the conditions of polymer processing [3–4].

The rheology of nonionic polymer solutions has a long history and is well studied [5–9]. For these solutions the boundary of concentration regimes of polymer solutions is clearly defined. The role of this boundary plays the crossover point that is defined as the concentration of solutions at which the overlapping of macromolecular coils and the formation of a network of meshes begins [1]. The crossover point characterizes the transition of the regime from the diluted to semi-diluted solutions and change in the mechanism of mass transfer of macromolecules. In the diluted area the translational mechanism of mass transfer is realized, in the semi-diluted area the reptational mechanism is realized [6].

The rheological behavior of polyelectrolytes is less studied. The presence of electrostatic repulsion between polymer ions can affect both the value of the crossover point and the formation of the mesh of entanglements [10–15]. Unfortunately, the experimental data on the study of the rheological properties of polyelectrolyte solutions are currently insufficient to draw unambiguous conclusions about the mechanism of the change in concentration regimes. In this regard, the aim of this work was to study the rheological behavior of aqueous solutions of pectin, a natural polysaccharide, which is a polyelectrolyte and has a spectrum of physiological activity [16–17].

Experimental

The object of the research is pectin (PC) of citrus origin produced by SIGMA-ALDRICH. The character-

istic viscosity was defined using Ubelode viscometer and calculated using the Baranov's method [18], which makes it possible to exclude the influence of the polyelectrolyte swelling effect on the intrinsic viscosity. According to this method, the value of $\frac{\partial \ln(\eta_{relative})}{\partial C}$ at each point of the dependence of $\ln \eta_{relative}$ on the polymer concentration in solution C can be considered as the current value of the intrinsic viscosity:

$$[\eta]^* = \frac{\partial \ln(\eta_{relative})}{\partial C}, \quad (1)$$

where $\eta_{relative}$ is the value of relative viscosity of polymer solutions. It is obvious that with $C \rightarrow 0$ the value of $[\eta]^*$ corresponds to the initial slope of the dependence of $\ln \eta_{relative}$ on C and coincides with the value of the intrinsic viscosity $[\eta]$ which describes the behavior of an isolated macromolecule.

Rheological measurements of aqueous solutions of PS were carried out on a Haake Mars III modular dynamic rheometer at 25 ± 1 °C in an oscillatory mode. Since tests in the oscillatory mode must be performed in the area of linear viscoelasticity, initially, based on the dependences of the storage modules and losses on the stress amplitude obtained at a constant oscillation frequency, the optimal amplitude values corresponding to constant values of the modules (linear viscoelastic region) were determined. For PC solutions in the interval from 0.05 to 20% in the range of amplitudes from 0.1 to 10 Pa and oscillation frequencies from 0.1 to 10 Hz, the solution corresponded to the region of linear viscoelasticity, since the values of the modules did not depend on the voltage amplitude. The activation energy of viscous flow of the studied systems E_a in the temperature range from 15 to 80 °C was estimated using the Arrhenius–Frenkel–Eyring equation (2) and calculated by the least squares method:

$$\eta = A e^{\frac{\Delta E_a}{RT}}, \quad (2)$$

where R is the universal gas constant, A is the pre-exponential factor.

Results and discussion

It is known that polymers in solutions can exist in different concentrate modes [1–2; 5]. In the regime of

diluted solutions with the concentration of C less than the concentration of crossover $C^*=1/[\eta]$, where $[\eta]$ is the intrinsic viscosity, macromolecules of nonionic polymers are isolated from each other. They do not interact with each other, and the viscosity of the solution increases with an increasing concentration according to the linear law $\eta \sim C^\delta$, where $\delta = 1.00$.

In this area of concentration in the rheological point polymer solution behaves like newton liquid the viscosity of which doesn't depend on shear rate or oscillation frequency.

At the concentration of C greater than C^* macromolecules interact with each other and the viscosity depends on the concentration according to the power law $\eta \sim C^\delta$, where $\delta > 1.00$. At the same time, upon going to the region of semi-diluted solutions, the nature of the dependence of viscosity on the shear rate changes, namely, the viscosity of polymers decreases with an increase in the shear rate (or oscillation frequency), i.e. solutions of nonionic polymers behave in the overwhelming majority of cases as a pseudoplastic liquid.

The increase in the concentration is accompanied by formation of the network of meshes with the concentration of C_e that can be easily defined at the beginning of a sharp increase in viscosity. A sharp increase in the intensity of viscosity growth is due to the fact that, upon going from a diluted solution to a semi-dilute solution, the mass transfer mechanism changes (from translational to reptational), which is associated precisely with the formation of a fluctuation mesh of entanglements [6].

However, the rheological behavior of polyelectrolytes has its own features. For example, in nonionic solutions the fluctuation network of meshes is formed almost immediately after reaching the crossover point. Respectively, the value of C^* coincides with the value

of C_e . However, in the nonionic solutions there is electrostatic repulsion of like-charged chains, which can prevent the coils from penetrating into each other and the formation of a network of meshes. Therefore, in the solutions of polyelectrolytes there can be the area of semi-diluted solutions in which coils touch each other, but do not form the network of meshes. The presence of such an area is discussed, for example, in [19–23].

Indeed, a sharp increase in the dynamic viscosity of PC solutions and the transition from one concentration regime (diluted solution) to another (semi-diluted) occurs not at a crossover concentration with $C^*=1/[\eta]$, but somewhat later (fig. 1).

As it is seen from the data in fig. 1, in the temperature range 15–80 °C, the concentration of the formation of the network of meshes C_e , determined by the onset of a sharp increase in viscosity, corresponds to a solution with a concentration of 2.5–3.0 g/dl. Considering that the values of intrinsic viscosity that were determined using Baranov's method are $[\eta] = 5.0$ dl/g at 20 °C and $[\eta] = 4.8$ dl/g at 80 °C, the crossover point with $C^*=1/[\eta]$ for these polymers corresponds to concentrations of 0.2 and 0.21 g/dl, respectively. As it is seen from the data in fig. 1, reaching the crossover point does not affect the polymer flow mechanism. In this regard, we can speak about the presence of a transition region from a diluted region to a semi-diluted region, in which the macromolecules contact with each other, but do not form the network of meshes. It is obvious that in transition area with an increase in concentration there is a gradual compression of macromolecular coils due to their contact and overcoming the forces of electrostatic repulsion. Only after this the network of meshes forms in the system.

Fig. 1. Concentration dependence of complex viscosity at a temperature of 15 (1), 20 (2), 30 (3) 40 (4), 60 (5) and 80 (6) °C for pectin solutions.

The difference in the rheological behavior of the polyelectrolyte solution is also evidenced by the shape of the viscosity curves (*fig. 2*). As it is known, when testing polymer solutions in the oscillation mode the dependence of the viscosity on angular velocity (oscillation frequency) is studied. As we can see from the data in *fig. 2*, the pectin solutions with the concentration 2 g/dl in the temperature range from 15 to 80 °C behave like newton liquids, i.e. their viscosity range does not depend on the oscillation frequency (*fig. 2*, *curves 1–5*). The pectin solution with the concentration of 5 g/dl in the temperature range from 40 to 80 °C behaves like newton liquids (*curves 6–7*), but the decrease in temperature below 30 (*curves 8–10*) results in a typical (for pseudoplastic fluids) change in viscosity with the oscillation frequency, namely, the viscosity decreases with the oscillation frequency.

Thus, all curves shown in *fig. 2* characterize the solutions with the concentration greater than the cross-over point. But only when the concentration of the polymer in the solution exceeds the value of C_e , the viscosity curves take the form that pseudoplastic liquids should have.

The formation of fluctuation network of meshes is also reflected in the concentration dependence of the activation energy of viscous flow. In *fig. 3* we can see that a kink in the concentration dependence of the activation energy of a viscous flow, indicating a change in the mechanism of mass transfer in a solution, occurs at the values corresponding to the concentration at which the mesh of entanglements is formed. The activating energy values of viscous flow PC are low and in the case of diluted solutions coincide in order of magnitude with the activation energy of the viscous flow of the solvent, which agrees with the experimental data for other polyelectrolytes [19; 23–25].

Fig. 2. Dependence of the complex viscosity on the oscillation frequency for pectin solutions of concentration 2 (1–5), 3 (6, 7) and 5 g/dl (8–10) at a temperature of 80 (1, 6), 60 (2), 40 (3), 30 (6, 8), 20 (4, 7, 9), 15 °C (5, 10).

Fig. 3. Dependence of the activation of the viscous flow of pectin solutions on its content in the solution.

Fig. 4. Dependence of the accumulation modulus (1) and losses (2) for pectin solutions at temperatures of 20 (a) and 80 °C (b) on its content in the solution.

An examination of the dependences of the accumulation and loss modulus on the concentration of PA in solution also showed that a sharp increase in the values of the accumulation and loss moduli begins in the concentration range of the order of C_e (fig. 4).

It can be noted that at temperatures of 15–30 °C, a concentration equal to 10 g/dl is determined, at which the storage modulus becomes greater than the loss modulus, i.e. the viscoelastic fluid becomes an elastic-viscous body (fig. 4a). In this case, the polymer liquid loses its fluidity. At temperatures of 40–80 °C in the entire investigated concentration range, the accumulation modulus has lower values than the loss modulus, i.e. PC solution behaves like a viscoelastic fluid (fig. 4b). The difference in the behavior of PS solutions at different temperatures is obviously due to the fact that the number of nodes of the fluctuation network at elevated temperatures is significantly less than at low temperatures.

All in all, our study of PS solutions showed that the polyelectrolyte nature of the polymer introduces significant features into its rheological behavior. These features are manifested in the form of low values of the activation energy of viscous flow, in the absence of an anomaly in the viscous flow of solutions above the crossover point, as well as in the existence of a concentration region in which macromolecules are in contact with each other, but do not form a fluctuation network of meshes.

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