RHEOLOGICAL PROPERTIES OF HIGH MOLECULAR WEIGHT POLYMER SOLUTIONS

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The possibility of using known techniques of study of the physicochemical characteristics of high weight polymers to obtain information on the structure of solutions of high polymers in which reduction in turbulent resistance occurs is shown.

Many experiments have established the fact that turbulent resistance is decreased by addition to a low molecular weight solvent of high polymers with a linear long chain structure. Depending on the type of polymer, optimum mass concentration varies from 0.005 to 0.75% (see, for example, [1-3]). The varying effectiveness of high polymer additives, which usually can be compensated to some degree by varying concentration [1], manifests itself in peculiarities of the solution structure [2, 4]. Methods of qualitative analysis of polymer solution structure based on accurate experimental techniques have led to the compilation of hydrodynamic characteristics of various flows [2, 5, 6]. In addition, by using known methods for the study of physicochemical characteristics of high polymers [7, 8], information can be obtained on the structure of high polymer solutions by viscosimetric measurements.

Studies were performed with a capillary constant pressure viscosimeter with liquid thermostabilized to ±0.05°C (Fig. 1). Constant drop with discharge in the capillaries, measured by a set of manometers and piezometric tubes, was maintained by throttling nitrogen into the manostat of the viscosimetric vessel. Liquid flow rate was determined by weighing on an ADB-300m analytical balance a glass container which intercepts the liquid stream with simultaneous switchon of the SK-1N timer. A set of glass capillaries of diameter $(0.2\text{-}4.2)10^{-3}$ m and length 0.09-1.425 m ensured that measurements were performed in the shear stream rate range $\gamma = 25\text{-}8 \cdot 10^5$ sec^{-1}. In accordance with Boussinesq's recommendation [9], the capillaries had a smooth entrance configuration.

Calibration experiments with transformer oil of known viscosity and distillate at t = 5-25°C determined the Hagenbach correction m to the Poiseuille equation.

$$\eta = \frac{\pi r^4 \Delta P}{8LQ} - m\frac{\rho Q}{\pi 8L}, \tag{1}$$

on the basis of which the tension at the capillary wall during polymer solution flow was calculated:

$$\tau = \frac{r}{2L}\left(\Delta P - m\frac{\rho Q^2}{\pi^2 r^4}\right). \tag{2}$$

Using Eq. (1), the correction m was written as the difference of two dimensionless ratios:

$$m = \mathrm{Eu} - \frac{L}{d}\,\frac{32}{\mathrm{Re}}. \tag{3}$$

The experimental data (~150 points) in the range Re = 500-2000, Eu = 5-35, and L/d = 200-450 were approximated with a mean square error of ~6% by the following functions:

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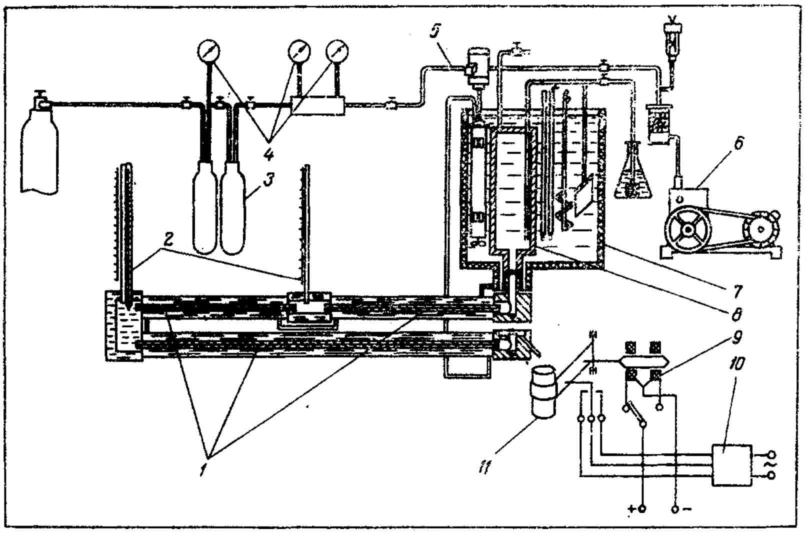

Fig. 1. Schematic diagram of viscosimetric apparatus. 1) capillaries; 2) piezometric tubes; 3) manostat; 4) manometer; 5) pneumosystem; 6) VN-461 vacuum pump; 7) TS-24 thermostat; 8) viscosimetric vessel; 9) electromagnet; 10) SK-1N timer-calibrator; 11) receiving vessel.

$$m = 1.5\mathrm{Eu}^{-0.08}, \tag{4}$$

$$m = 1.13\left(\frac{d}{L}\,\mathrm{Re}\right)^{0.072}. \tag{5}$$

In [10], for glass capillaries with smooth entrance and exit, correction m as a function of Reynolds number was obtained experimentally in the form

$$m = 0.037\,\mathrm{Re}^{0.5}. \tag{6}$$

Equation (6) disagrees with the data obtained significantly, which is evidently connected with the fact that the effect of the relative length L/d is absorbed into Eq. (6).

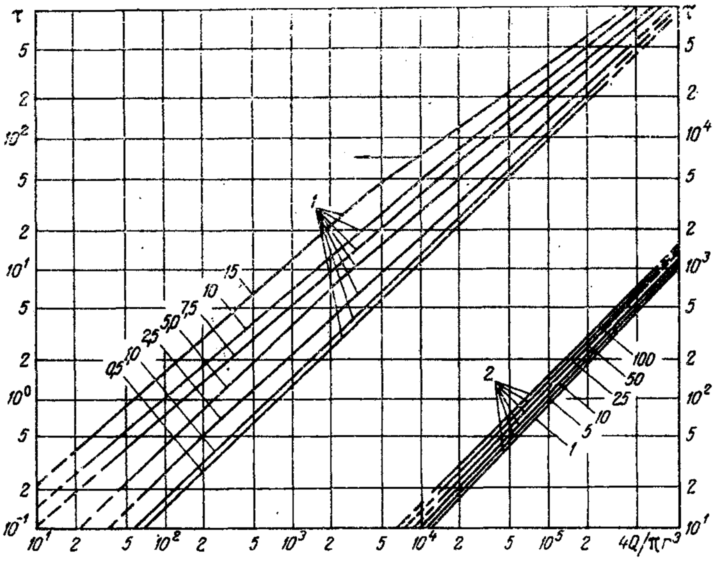

Fig. 2. Polymer solution flow curves in logarithmic anamorphosis: 1) CMC, 2) PAA. Numbers on curves indicate 1) $C \cdot 10^3$, 2) $C \cdot 10^5$. τ, N/m²; $4Q/\pi r^3$, sec⁻¹.

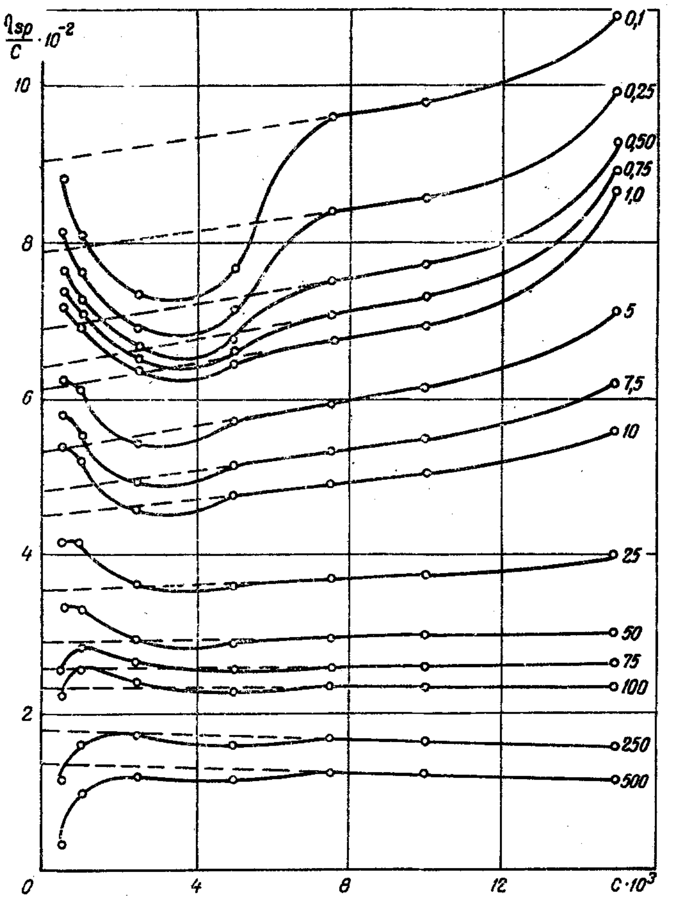

Fig. 3. Reduced viscosity of CMC solutions versus concentration. Numbers on curves are values of $\dot{\gamma}\cdot 10^{-3}$, sec^{-1}.

Using power approximations of consistency flow curves $\tau = f(4Q/\pi r^3)$ of water solutions of polyacrylamide (PAA) and the sodium salt of carboxymethylcellulose (CMC), it was established that use of Eq. (4) or Eq. (5) with Eq. (2) instead of the generally employed m = 1.12 permits a significant improvement in the accuracy of the values of the consistency index K' and the non-Newtonian behavior index n'.

Continuous transformation of the high polymer solution structure with change in concentration and shear strain rate, which is reflected in the flow curves (Fig. 2), may be revealed by using known concepts of the concentration dependence of the reduced viscosity [7, 8]:

$$\frac{K\dot{\gamma}^{n-1} - 1}{\eta C} = [\eta] + K_1[\eta]^2 C. \qquad (7)$$

The parameter K_1 for a concrete solution characterizes both direct interaction of the molecules with each other, reflecting the kinetics of fluctuating multiplet contacts, and that transmitted through the solvent (hydrodynamic interference in dilute solutions). In shear flow the equilibrium interaction of the macromolecules is disrupted, and with increase in shear rate the hydrodynamic orientation, decreasing the extinction angle, leads to reduction in the mutual contact time of molecular associations, which finally is reflected in both decrease in characteristic viscosity and in decrease in the Haggins parameter [7, 8].

The curves obtained for reduced viscosity of CMC solutions as functions of concentration and shear rate (Fig. 3), while reflecting the structural changes which occur, indicate one more peculiarity. This is that at C < 0.75% a viscosity anomaly is observed, connected with passing the "critical concentration." Developing the concepts of Staudinger, the viscosity anomaly in weakly concentrated polymer solutions is presently related to "uncoiling" of macromolecular associations and adsorption processes on the solid walls. The "critical concentration" C_* decreases significantly with increase in molecular weight and depends on interaction between macromolecules and solvent. Numerous investigations have shown that the concentration dependence of η_{sp}/C for $C < C_*$ is determined by the ionogenic properties of the

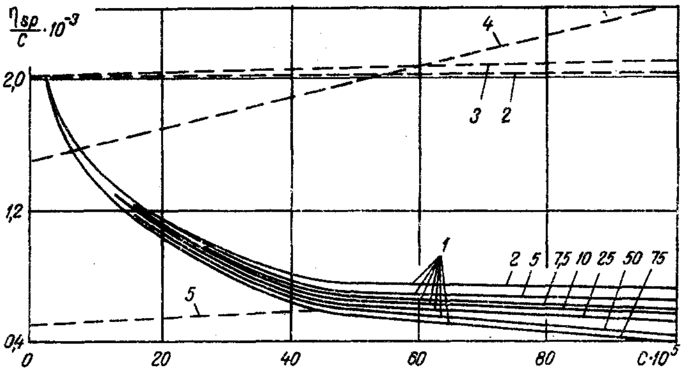

Fig. 4. Concentration dependence of reduced viscosity of water solutions of PAA (1), PEO (2, 3, 4) and guar gum (5). 1) Authors' experiments; 2, 3) data of [11]; 4, 5) data of [1]. Numbers on curves, 1) $\dot{\gamma} \cdot 10^{-4}$, sec^{-1}; 2) $\dot{\gamma}$ = 160-350 sec^{-1}; 3) 25; 4) 0.1-10; 5) (0.3-300)$\cdot 10^3$.

macromolecules. In solutions of polyelectrolytes at high dilutions a continuous increase in η_{sp}/C is observed, produced by polyelectrolytic swelling of polymer associations, while for nonionogenic macromolecules a decrease in η_{sp}/C as a function of shear rate or indifference of η_{sp}/C to solute concentration is more characteristic [7, 8].

The experimentally obtained curve of reduced viscosity of PAA versus concentration and shear rate clearly illustrates polyelectrolytic swelling in the concentration range $C < C_*$, while the calculated curves of $\eta_{sp}/C = f(C)$ using the data of [1, 11] indicate the nonionogenic properties of the solutes polyethylene oxide (PEO) Polyox WSR-301 and guar gum (Fig. 4). The differing character of the curves $\eta_{sp}/C = f(C, \dot{\gamma})$ for PAA, PEO, and guar gum also indicates such structural peculiarities as the internal rigidity of the PAA macromolecule in comparison to the more flexible PEO and guar gum macromolecules. According to the data of [11], in the range $\dot{\gamma}$ = 160-350 sec^{-1} hydrodynamic orientation is compensated by the corresponding effect of PEO macromolecule elongation. With decrease in shear rate contact interactions between the macromolecules become more and more significant, and as $\dot{\gamma} \to 0$, the molecules evidently form a continuous three dimensional lattice structure (Fig. 4). The varying $[\eta]$ values obtained for PEO are probably the consequence of unequal molecular weights of the Polyox WSR-301 samples used in [1] and [11].

A continuous viscoelasticity in the high polymer solutions, which is a consequence of macromolecule interaction, appears at low values of shear rate, differing for each polymer. Thus, in CMC solutions the viscoelastic properties are preserved to higher shear rates ($K_t \to 0$ at $\dot{\gamma} \geq 5 \cdot 10^4$ sec^{-1}) than in PEO solutions, in which hydrodynamic forces disrupt macromolecular bonds even at $\dot{\gamma} > 160$ sec^{-1}. The polymer solutions studied here have a common characteristic peculiarity, in that the limiting values of the Toms effect are observed at $C < C_*$ (Figs. 3, 4). In this connection the results of [12] are of great interest, where on the basis of an experimentally observed adsorption of Polyox WSR-301 molecules, which is characteristic of $C < C_*$, the effect of reduced resistance is explained. Some differences in the rheodynamics of PEO and PAA solutions characterized by macromolecular rigidity from PEO and CMC solutions where, as mentioned above, viscoelasticity is characteristic at low shear rates and orientation effects are characteristic at high shear rates were noted in [13, 14].

Thus, the physicomechanical structural characteristics of polymer-solvent systems complement the traditional rheological parameters of non-Newtonian behavior and must be considred in compiling results of various rheodynamic experiments.

NOTATION

τ	is the stress at capillary wall, N/m^2;
r	is the capillary radius, m;
L	is the capillary length, m;
ΔP	is the measured pressure drop along capillary with liquid flow, N/m^2;
Q	is the liquid flow rate in capillary, m^3/sec;
ρ	is the density, kg/m^3;
η	is the viscosity, $N \cdot sec/m^2$;

m	is the Hagenbach correction;
d	is the capillary diameter, m;
w_m	is the mean liquid velocity across capillary, m/sec;
$Eu = \Delta P/\rho w_m^2$	is the Euler number;
$Re = \rho d w_m/\eta$	is the Reynolds number;
$\dot{\gamma}$	is the shear strain rate, sec^{-1};
n, n', K, K'	are the rheological parameters determined for sections of flow curves rectilinear in logarithmic anamorphosis;
C	is the mass concentration;
C_*	is the "critical "concentration";
K_1	is the Haggins parameter;
$\eta_{sp} = (K\dot{\gamma}^{n-1} - 1)\eta^{-1}$	is the reduced viscosity;
$[\eta] = \lim\limits_{C\to 0} (K\dot{\gamma}^{n-1} - 1)/(\eta C)$	is the characteristic viscosity.

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