

INVESTIGATION OF THE CONDITIONS OF NEGATIVE THIXOTROPY OF POLY(METHYL METHACRYLATE) SOLUTIONS IN LOW-VISCOSITY SOLVENTS. I.

INFLUENCE OF POLYMER CONCENTRATION, TEMPERATURE AND THERMODYNAMIC QUALITY OF SOLVENT

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Negative thixotropy has already been described for a series of polymer solutions. A comprehensive survey can be found in a paper by Savins¹. The investigations made to date are dealing only with a qualitative description of the effect, and the change of the solution structure to a gel-like substance caused by flow is explained by the authors of these investigations only in terms of the formation of aggregates of oriented particles due to the velocity gradient without finding out the actual cause of these changes. So far, bonds forming the gel structure have not been identified in any system.

In our earlier papers²⁻⁵ we have investigated the negative thixotropy effect in solutions of poly(methyl methacrylate) and the copolymers of the ester with the mother acid in low-viscosity solvents (1–2 cP). In contrast with the results obtained by Peterlin and coworkers⁶⁻¹⁴ in their measurements carried out with poly(methyl methacrylate) solutions in a high-viscosity solvent (chlorinated diphenyl, $\eta_s \sim 10$ P), we have demonstrated that this effect is not necessarily due to an extraordinarily high viscosity of the solvent, but in the first place to its poor thermodynamic quality. Its intensity strongly depends on the concentration of the polymer in the solution, on the temperature and molecular weight. With solutions having negative thixotropy, an increased value of the Huggins constant¹⁵ has also been established, which indicates an increased degree of aggregation of macromolecules even in considerably diluted solutions.

In the present work, an attempt has been made to express quantitatively some relationships between the conditions producing the above effects. We believe that this might be a route leading to an elucidation of the changes in the molecular structure of the solution, which take place during the change of the macrostructure.

EXPERIMENTAL

Poly(methyl methacrylate) was obtained by radical polymerization initiated with benzoyl peroxide. The polymer was reprecipitated from a benzene solution with gasoline for medical uses (Urx's Works, Ostrava) and dried over phosphorus pentoxide at 60°C. The fractions were obtained by gradual precipitation of the polymer from the benzene solution with pure petroleum ether (Lachema, Brno), and also reprecipitated.

Viscometry

The mixture containing a weighed amount of the polymer and solvent was shaken in a sealed flask at 50–60°C until it was dissolved. The solution was filtered through an S 1 glass filter without applying an additional pressure, in order to prevent the possible degradation of the polymer by flow in the capillaries of the filter.

Viscometric measurements of benzene solutions at five concentrations were performed in a diluting capillary viscometer of the Ubbelohde type. After determination of intrinsic viscosities by extrapolation according to Heller¹⁶, the results were employed in the estimation of the Θ -temperature by a procedure described earlier²; the molecular weights were calculated by means of the relationship $[\eta] = 5.7 \cdot 10^{-5} M^{0.76}$ (ref.¹⁷).

The dependence of the viscosity on the shear stress in solutions of the polymer in the mixture of cyclohexanone (51.6% by weight) and isopropyl alcohol (both solvents were analytical purity grade, distilled) was measured in viscometers of two types. The rotational viscometer was of the Couette type with an external rotor and was made at the Institute of the Scientific Instruments, Brno. The apparatus allowed a continuous recording of the shear or viscosity in dependence on time within the range of velocity gradients from 4.025 to 3.420 s⁻¹. The Ostwald capillary viscometer for the investigation of the dependence of viscosity on the shear stress with a manostat added¹⁸, which allowed a variation of overpressure within 18 degrees (within the range from 5 to 1000 mm Hg), was employed as a "single pass" viscometer: after the side arm was filled with solution by means of a pipette, the flow time was measured of the solution which was squeezed in the capillary from the lower to the upper mark of the bulb. Each measurement was carried out only once, always using a fresh solution.

RESULTS AND DISCUSSION

We have shown in a preceding paper⁴ that during the measurements carried out with poly(methyl methacrylate) solutions in a rotational viscometer the phenomenon of negative thixotropy can be observed, if the velocity gradient overpasses a certain minimum value G_{\min} . This quantity, which is an important criterion of the phenomenon, was measured by the author in solutions in the mixture of cyclohexanone (51.6% by weight) and 2-propanol at 23°C (about 1–2°C above Θ) in dependence on the concentration of the solution, and also in dependence on temperature at a concentration of 1.2 g/dl. In the case of an unfractionated polymer having molecular weight $3.4 \cdot 10^6$ the effect of negative thixotropy rapidly decreases with decreasing concentration below 1 g/dl (Fig. 1), and a higher velocity gradient G_{\min} must be used to produce this effect. It follows from the comparison of the volume occupied by one molecule in the solution with its dimensions that the concentration 0.4 to 0.5 g/dl, at which the curve tends to an infinite value of G_{\min} (the so-called critical concentration c_0), corresponds to a state in which the macromolecules just yet need not overlap and form entanglements. For an unfractionated polymer having the molecular weight $3.4 \cdot 10^6$, intrinsic viscosity at the Θ -temperature $[\eta]_{\Theta} = 0.968$ dl/g and the Flory parameter $\Phi = 2.87 \cdot 10^{21}$, we obtain from the relationship

$$\overline{(r_0^2)}^{1/2} = ([\eta]_{\Theta} M / \Phi)^{1/3} \quad (1)$$

the root mean square end-to-end distance of the macromolecule in an infinitely dilute solution $\overline{(r_0^2)}^{1/2} = 1.05 \cdot 10^{-5}$ cm. The volume occupied by one macromolecule in the solution is given by the expression

$$V = 10^2 M / Nc, \quad (2)$$

where N is the Avogadro number and c is the concentration of the polymer in g/dl. For the concentration from 0.4 to 0.5 g/dl, this volume lies within $1.41 \cdot 10^{-15}$ to $1.13 \cdot 10^{-15}$ cm³, and the diameter of a sphere inscribed in this space is $1.12 \cdot 10^{-5}$ to $1.04 \cdot 10^{-5}$ cm.

If we substitute $[\eta]_{\Theta} = K_{\Theta} M^{1/2}$ into relationship (1), it is possible to derive a general dependence of the critical concentration of the polymer on the molecular weight. From the conditions of

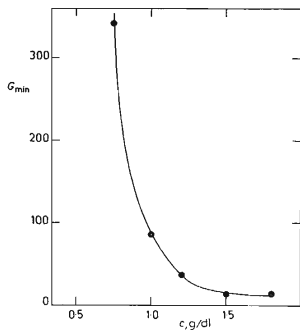


FIG. 1

Dependence of G_{min} (s^{-1}) on the Polymer Concentration, Measured on a Rotational Viscometer at 23°C

Solutions of unfractionated polymer ($\bar{M}\eta = 3.4 \cdot 10^6$) in the mixture of cyclohexanone (51.6% by weight) with 2-propanol. For the solution $c = 0.5$ g/dl, G_{min} is > 3420 s^{-1} .

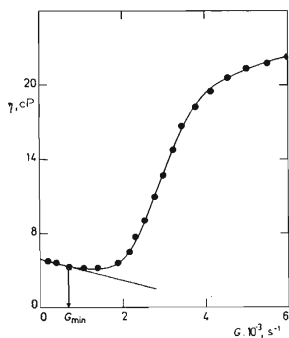


FIG. 2

Dependence of the Viscosity (η) in cP on the Velocity Gradient (G), Measured on a Capillary Viscometer at 23°C

Values taken from an earlier work² for a solution of the polymer fraction ($M = 6.3 \cdot 10^6$) in the mixture of cyclohexanone (51.6% by weight) and 2-propanol ($c = 0.497$ g/dl).

overlapping of the spheres of macromolecules in the solution it follows that

$$K_{\Theta} M^{3/2} / \Phi = M / 10^{-2} N c_0, \quad (3)$$

whence

$$c_0 = 10^2 \Phi / N K_{\Theta} M^{1/2}. \quad (4)$$

On calculating the expression for the poly(methyl methacrylate) solution ($K_{\Theta} = 0.526 \cdot 10^{-3}$), a conclusion can be drawn that the critical concentration depends indirectly on the square root of the molecular weight

$$c_0 = 908 M^{-1/2}. \quad (5)$$

A disadvantage of the rotational viscometer consisted in a large amount of the solution needed (c. 40 ml for one experiment). Therefore, in the case of solutions of those polymer fractions which were at disposal in a limited quantity only, a more economical procedure for investigation of the effect of negative thixotropy had to be used, *viz.* measurements of the dependence of viscosity η on the shear stress τ in a capillary "single pass" viscometer with a manostat (5 to 15 ml for one experiment). Besides, the highest attainable velocity gradient in the rotational viscometer was not sufficient to produce the effect at lower concentrations and molecular weights. As has been shown in an earlier work², the negative thixotropy also affects the η vs τ dependence: it exhibits a minimum instead of a monotonous decrease, which is usual in the systems without negative thixotropy.

To determine the critical value of the velocity gradient G_{\min} from measurements carried out

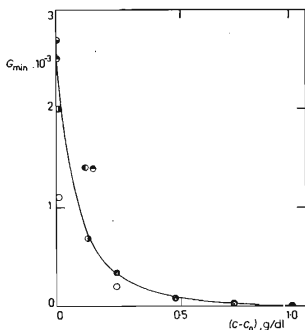


FIG. 3

Dependence of G_{\min} (s^{-1}) on $(c - c_0)$ for Polymer Solutions in the Mixture of Cyclohexanone (51.4% by Weight) and 2-Propanol at 23°C

Rotational viscometer, unfractionated polymer ($M\eta = 3.4 \cdot 10^6$) ●; capillary viscometer, molecular weights of fractions: ○ $6.3 \cdot 10^6$, ● $5.76 \cdot 10^6$, ● $3.7 \cdot 10^6$, ● $2.94 \cdot 10^6$, ○ $\bar{M}\eta = 3.4 \cdot 10^6$ (unfractionated polymer).

on the capillary viscometer, the dependence of viscosity ($\eta = \eta_s \eta_{rel}$) on the velocity gradient ($G = \tau/\eta$) was used; the viscosity was calculated from the dependence η_{rel} vs. τ (η_s being the viscosity of the solvent). The η - G curves had a typical course, given by the superposition of the normal non-Newtonian decrease in viscosity due to the deformation and orientation of the macromolecules and the effect of negative thixotropy at $G > G_{min}$. To determine G_{min} with more exactitude, the knowledge of the η - G dependence, undeformed by negative thixotropy, would be necessary. Since this dependence is not known, we drew a straight line through the initial points, and assumed the velocity gradient at which this line deviates from the experimental curve to be G_{min} (Fig. 2). The assemblies of the results obtained (Table I) are also reasonably satisfied by values obtained for two fractions having molecular weights $3.7 \cdot 10^6$ and $6.3 \cdot 10^6$, although the necessary data were not obtained by measurements on the "single pass" viscometer (cf. ref.²). The dependence of G_{min} on $(c - c_0)$, common for polymers of different molecular weights (Fig. 3), corroborates the view that the entanglements of intertwined polymeric coils play an important role in the effect of negative thixotropy.

The formation of the gel structure by flow was strongly temperature-dependent (Fig. 4): by increasing the temperature by several degrees above Θ , it was possible to suppress the effect completely. The most appropriate criterion of the magnitude of the effect would consist in the ratio of viscosity measured at a certain shear stress to the viscosity which the solution would have at a given shear stress, if there were no effect of negative thixotropy, and if there existed only the non-Newtonian decrease of viscosity with the shear stress. Owing to the fact that this value cannot be determined reliably, we accepted as a criterion the ratio of viscosity measured on a capillary viscometer at the highest attainable shear stress ($\tau = 1050 \text{ dyn cm}^{-2}$) to the viscosity η_0 , measured without an overpressure ($\tau \approx 8 \text{ dyn cm}^{-2}$). At the same time, the intrinsic viscosi-

TABLE I

G_{min} Values of the Solutions of Poly(Methyl Methacrylate) Fractions in the Mixture of Cyclohexanone (51.6% by Weight) and 2-Propanol at 23°C

$M \cdot 10^{-6}$	c_0 , g/dl	c , g/dl	G_{min} , s ⁻¹
3.4 ^a	0.493	0.750	342 ^b
		1.000	86 ^b
		1.250	36 ^b
		1.500	14 ^b
		1.750	14 ^b
		0.500	1 100 ^c
		0.750	200 ^c
6.3 ^c	0.362	0.373	2 000 ^c
		0.497	700 ^c
5.76	0.378	0.500	1 400 ^c
3.7 ^c	0.472	0.470	2 500 ^c
		0.627	1 400 ^c
2.94	0.530	0.500	2 700 ^c

^a Unfractionated polymer. ^b Determined on a rotational viscometer. ^c Determined on a capillary viscometer. ^d Ref.².

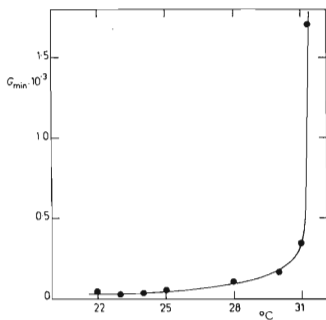


FIG. 4

Dependence of G_{\min} (s^{-1}) on Temperature ($^{\circ}C$) on a Rotational Viscometer
Polymer solution (cf. Fig. 1), concentration 1.2 g/dl.

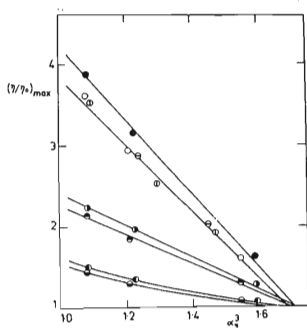


FIG. 5

Dependence of $(\eta/\eta_0)_{\max}$ on the Expansion Factor (α_n^3)

Solutions in the mixture of cyclohexanone (51.6% by weight) and 2-propanol; $c = 0.5$ g/dl, unfractionated polymer, $M = 3.4 \cdot 10^6$ (\odot at $23^{\circ}C$, $26^{\circ}C$, and $28.2^{\circ}C$); polymer fractions, $M = 6.3 \cdot 10^6$ (\bullet $c = 0.497$, \circ $c = 0.373$, \ominus $c = 0.248$), $M = 3.7 \cdot 10^6$ (\circ $c = 0.627$, \ominus $c = 0.470$, $\omin�$ $c = 0.313$) at 23° , 25° , and $30^{\circ}C$.

Solutions in the mixtures of cyclohexanone (54 and 57% by weight) and 2-propanol: $\omin�$ unfractionated polymer, $M = 3.4 \cdot 10^6$, $23^{\circ}C$, $c = 0.5$ g/dl.

ties of the above solutions were determined on a Ubbelohde capillary viscometer without overpressure, and the expansion coefficients $\alpha_n^3 = [\eta]/[\eta]_0$ were calculated as a measure of the thermodynamic quality of the solution. The dependence $(\eta/\eta_0)_{\max}$ vs. α_n^3 (Fig. 5) is slightly curved and tends to $\alpha_n^3 = 1.7$ at $\eta/\eta_0 = 1$, regardless of molecular weight of the fractions and concentration of the solutions. It can be concluded, therefore, that the suppression of the effect of negative thixotropy by improving the thermodynamic quality of the solvent is the same, be it due to an increase in temperature or to an increase in the cyclohexanone fraction in its mixture with 2-propanol, and it can be expressed for both cases only by a change of the expansion of the macromolecular coil.

While measuring the intrinsic viscosity of solutions in thermodynamic poor solvents, *i.e.* under conditions when the effect of negative thixotropy is observed, Bohdanecký¹⁵ established that the values of the Huggins constant k_H were extremely high. This finding confirms the strong tendency toward aggregation of macromolecules even in highly dilute solutions. According to the plot k_H vs. α_n^3 (*cf.* ref.¹⁵), we can see the connection between the effect of negative thixotropy in more concentrated solutions and their aggregation in more dilute ones: the increase in the Huggins constant disappears roughly at an expansion coefficient which corresponds to the suppression of the effect of negative thixotropy (*cf.* Fig. 5).

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