

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

QUANTITATIVE ANALYSIS OF THE TIME DEPENDENCES OF VISCOSITY

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Conditions of negative thixotropy of poly(methyl methacrylate) solutions were investigated from the quantitative viewpoint, using the rotational viscometer Rheotest with a continuous recording of the dependence of viscosity on time. The analogy between the flow formation of the gel structure bonds and the crosslinking of polymeric chains was used as a basis for deriving the dependence of the effect of negative thixotropy on molecular weight and concentration, or on the limit conditions necessary for the occurrence of the effect (minimum velocity gradient G_{\min}). These relationships are in agreement with the results of measurements of solutions of four fractions and one unfractionated polymer sample.

As we have shown^{1,2}, the effect of negative thixotropy of poly(methyl methacrylate) solutions in low-viscosity solvents manifests itself in a capillary viscometer by an increase in viscosity with the shear stress; in a rotational viscometer, there is a characteristic dependence of the shear stress, τ , or of viscosity on the time of measurement, with a steep rise and a gradual decrease³ after reaching the maximum. To investigate the effect of concentration, molecular weight, temperature, thermodynamic quality of the solvent or the composition of its binary mixture, the results of measurements in a capillary viscometer with a manostat⁴ were mainly used². The flow condition in the capillary are too complex and undefined in these cases and do not allow a quantitative analysis of the results. Therefore, previous measurements made in the Couette rotational viscometer and in capillary viscometers yielded only an approximate information on the character of dependences of negative thixotropy. To obtain a deeper insight into the effect, it appeared necessary that the measurements should be made exclusively in a rotational viscometer, and – if possible – with solutions of several polymer fractions within a wide range of concentrations and molecular weights; this has been the object of the present work.

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EXPERIMENTAL

Material

The polydisperse sample of poly(methyl methacrylate) ($\bar{M}_n = 3.2 \cdot 10^6$) was obtained by block polymerization, initiated with benzoyl peroxide, up to a high conversion. It was divided into four fractions having molecular weights $6.3 \cdot 10^6$, $4.4 \cdot 10^6$, $3.2 \cdot 10^6$ and $1.7 \cdot 10^6$, respectively, by precipitating from benzene solutions with light petroleum and a successive separation into two identical weight parts each time. This procedure⁵ yielded fractions with a narrower distribution of molecular weights than in the case of gradual precipitation. The fractions after isolation were reprecipitated from benzene solutions with gasoline and dried over phosphorus pentoxide at 60°C. One part of the polydisperse sample was reprecipitated in the same way. The molecular weight of both the polydisperse sample and fractions, M , was determined from intrinsic viscosity $[\eta]$ of benzene solutions at $25 \pm 0.05^\circ\text{C}$ according to a relationship suggested by Schulz and Cantow⁶, $[\eta] = 5.7 \cdot 10^{-5} M^{0.76}$. Solvents: Light petroleum (Lachema, Brno) and gasoline (for medical uses, Urx's works, Ostrava) were used for fractionation without further treatment. Benzene, anal. purity grade, for solutions used in the molecular weight determinations, was dried with sodium and redistilled; cyclohexanone, isopropyl alcohol and butyl acetate, all anal. purity grade, were also redistilled.

Viscometry

$[\eta]$ Used in the molecular weight determinations was measured in capillary dilution viscometer of the Ubbelohde type. Correction for the loss of kinetic energy and the end effect was negligible. The method of extrapolation of $[\eta]$ has been described². To measure negative thixotropy, Couette rotational viscometer Rheotest with a S1 rotor was used (Type RV Prüfgeräte-Werk Medingen, Dresden), connected with a registration millivoltmeter (Standard-Kompensationsschreiber GIBI, Zeiss, Jena). The apparatus allowed a continuous registration of the dependence of the shear stress or viscosity on the time of measurement at 24 values of the velocity gradient from 1.5 to 1310 s^{-1} . The volume of solution consumed per one measurement was 25 ml. The measuring cylinders were thermostated to $23 \pm 0.05^\circ\text{C}$ by means of a through-flow thermostat (Ulthathermostat Wobser U-8 Prüfgeräte-Werk Medingen, Dresden). A mixture of cyclohexanone (51.6% by weight) with isopropyl alcohol (about $1-2^\circ\text{C}$ above the θ -temperature) and butyl acetate (about 43°C above the θ -temperature)⁷ were used as solvents. With respect to the polymer degradation by flow³, each experiment required a fresh solution.

RESULTS AND DISCUSSION

Regulation of revolutions of the rotational viscometer used earlier³ was made by means of a servosystem controlled by a feedback according to the revolutions of a tachodynamo; the adjustment of the chosen velocity gradient according to the revolutions of the stroboscope required a certain time after the starting of the motor, during which the gradient sometimes oscillated quite considerably. It was established, with the aid of the above experimental device, that the effect of negative thixotropy took place only if the velocity gradient exceeded a certain minimum value (G_{\min}). The use of the viscometer Rheotest allowed us, at the very beginning of measurements, that is starting from the moment when the driving motor was switched on, to maintain constant revolutions and thus also a constant gradient, given by the

speed gear employed and varying only negligibly with the frequency oscillations of the alternating current used. It appeared at the same time that it is just at the onset of measurements that the velocity gradient has a decisive influence on the initial intensity of the effect of negative thixotropy, and that the increase in the shear stress with time does not occur immediately, but after a certain time (induction period, t_g).

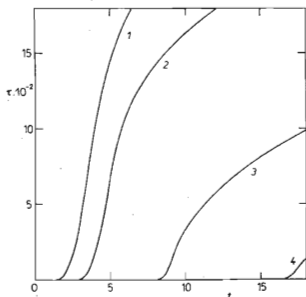


FIG. 1

Dependence of the Shear Stress, τ (dyn cm^{-2}) on Time, t (s), during Measurement of the Polymer Fraction I at a Concentration $c = 0.75 \text{ g dl}^{-1}$

1 $G = 437 \text{ s}^{-1}$, 2 $G = 364 \text{ s}^{-1}$, 3 $G = 243 \text{ s}^{-1}$, 4 $G = 219 \text{ s}^{-1}$.

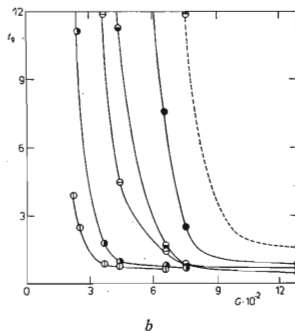
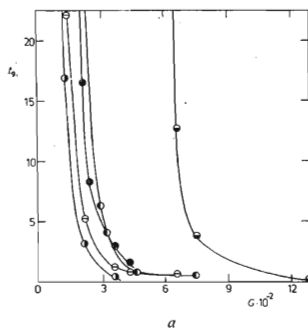


FIG. 2

Dependence of the Period, t_g (s), on the Velocity Gradient G (s^{-1}) for the Polymer Fractions (a) and the Polydisperse Polymer (b) in the Mixture Cyclohexanone-Isopropyl Alcohol

(a) M , c (g dl^{-1}): \bullet $6.3 \cdot 10^6$, $c = 0.75$, \circ $4.4 \cdot 10^6$, $c = 1$, \ominus $1.7 \cdot 10^6$, $c = 1.95$, \oplus $c = 2.1$, \otimes $c = 2.4$; (b) $\overline{M}_\eta = 3.2 \cdot 10^6$; c (g dl^{-1}): \bullet 1, \ominus 1.25, \oplus 1.5 (in butyl acetate: \bullet 1.25, \oplus 1.5, \otimes 1.8). The broken line was calculated according to (12) from two experimental points and the limit value G_{min} .

This period appeared to be — similarly to G_{\min} — a characteristic measure of the effect of negative thixotropy, since it was strongly dependent on the velocity gradient employed, on the concentration of the polymer in the solution and on its molecular weight (Fig. 1). The quantity t_g steeply increases with decreasing velocity gradient, to reach an infinite value at G_{\min} (Figs 2a and 2b). Since these dependences resembled hyperbolas, we made an attempt to linearize them by plotting $t_g G$ vs t_g at a constant molecular weight and concentration of the polymer. It can be seen in Figs 3a and 3b, that the linearization carried out in this way is feasible. Using the slope of the straight lines thus obtained, it was possible to determine G_{\min} with much more accuracy than by direct measurements, as the choice of the velocity gradients with our viscosimeter was too rough.

When investigating the dependence of G_{\min} on concentration and molecular weight (Fig. 4), we can see that at a sufficiently large velocity gradient the effect of negative thixotropy does not occur until a certain minimum concentration has been used; this concentration is lowest at an infinitely large velocity gradient (c_{\min}). The curves also resemble hyperbolas, and we therefore made an attempt to linearize them by plotting cG_{\min} vs G_{\min} . Fig. 5 shows the results of measurements of the polydisperse sample of poly(methyl methacrylate) and its three fractions in the mixture of cyclohexanone and isopropyl alcohol and also of the polydisperse polymer in butyl acetate. The curves are linear to a satisfactory degree; in the case of solutions in the cyclohexanone–isopropyl alcohol mixture they point to an approximately common intercept (~ 40), while in the case of butyl acetate the intercept is considerably larger (~ 200).

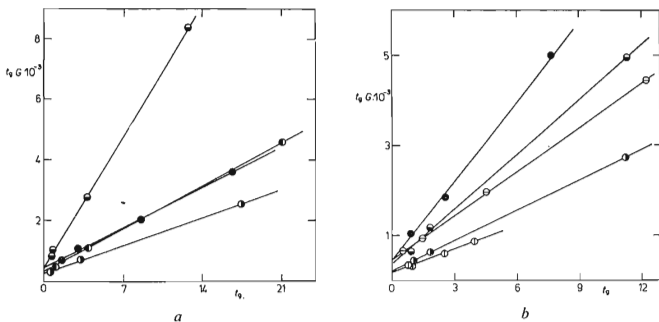


FIG. 3

Dependence of $t_g G$ on t_g (s) for the Polymer Fractions and the Polydisperse Polymer in the Mixture Cyclohexanone Isopropyl Alcohol and in Butyl Acetate

Points designated as in Fig. 2.

The slopes of the straight lines in Fig. 5 represent limit concentration values, c_{\min} . We assumed in the preceding paper² that these values are identical with the concentrations $c_0 = 908M^{-1/2}$ at which all macromolecules in the solution represented by the model of an equivalent sphere just touch each other in cubical packing, that is, need not be entangled. We can see, however, that the minimum concentration c_{\min} which is necessary to obtain the effect of negative thixotropy is 2 to 2.5 times higher than c_0 , and that the ratio c_{\min}/c_0 somewhat increases with increasing c_0 , *i.e.* with decreasing molecular weight (Fig. 6).

The existence of the induction period, t_g , was an incentive for us to compare the effect of negative thixotropy with the process of crosslinking of the polymeric chains⁸. We suppose that each macromolecule of poly(methyl methacrylate) has in its chain a certain number of equivalent groups, capable of linking by a bond of physical type during the flow chain orientation. We describe the rate of formation of these bonds by the differential equation of a bimolecular reaction, where the rate constant is a function of the velocity gradient

$$-(dn/dt) = k(G) n^2 ; \quad (1)$$

here, n is the number of all groups capable of bond formation in 1 ml after a time t , and $k(G)$ is the rate constant. By integrating Eq. (1) we obtain

$$t = (n_0/n - 1)/k(G) n_0 , \quad (2)$$

where n_0 is the initial number of all groups capable of bond formation in 1 ml. If c is the concentration of the polymer in g/dl, \bar{M}_n is the number average molecular weight, \bar{P}_n is the number average degree of polymerization, N is Avogadro's number,

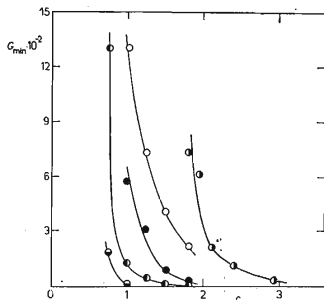


FIG. 4
Dependence of the Values of G_{\min} (s^{-1}) Obtained from the Slopes of the Curves in Fig. 3 or by Direct Measurements on the Concentration of the Polymer, c ($g\ dl^{-1}$)

Molecular weights of the fractions in the cyclohexanone-isopropyl alcohol mixture: ● $6.3 \cdot 10^6$, ● $4.4 \cdot 10^6$, ● $1.7 \cdot 10^6$, unfractionated polymer in the cyclohexanone-isopropyl alcohol mixture ●, in butyl acetate ○.

M_0 is the weight of a monomeric unit, ϱ_0 is the number of the groups capable of bond formation in the monomer, and κ is the fraction of all reacted groups, it holds

$$n_0 = cN\bar{P}_n\varrho_0/100\bar{M}_n, \quad n_0 = cN\varrho_0/100M_0, \quad n = n_0(1 - \kappa). \quad (3), (4), (5)$$

By substituting for n_0 and n from (3) and (5) into (2), we obtain

$$t = (100M_0/k(G) cN\varrho_0) \kappa/(1 - \kappa). \quad (6)$$

The condition for the onset of formation of an infinite network structure is the critical value of the fraction of reacted groups

$$\kappa_g = 1/(\varrho_0\bar{P}_w - 1), \quad (7)$$

where \bar{P}_w is the weight average of the degree of polymerization of the primary chains. By substituting this quantity into (6) we obtain the dependence of the reaction time from the beginning of the experiment to the point of gelation on the initial parameters of the system:

$$t_g = 100M_0/k(G) cN\varrho_0(\varrho_0\bar{P}_w - 2), \quad (8)$$

which, after introducing the weight of a part of the polymeric molecule carrying

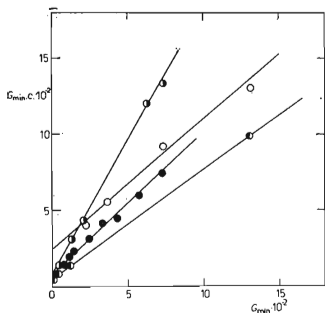


FIG. 5
Dependence of $G_{\min}c$ on G_{\min} (s^{-1})
Points designated as in Fig. 4.

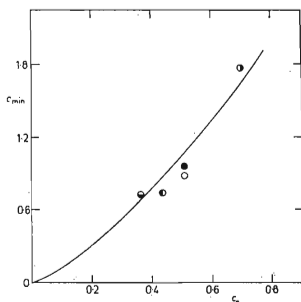


FIG. 6
Dependence of c_{\min} on c_0 ($g\ dl^{-1}$)
Points designated as in Fig. 4.

one group capable of bond formation $a_0 = M_0/\rho_0$ and the weight of the monomeric unit, $M_0 = \bar{M}_w/\bar{P}_w$, becomes

$$t_g = 100a_0^2/k(G) cN(\bar{M}_w - 2a_0). \quad (9)$$

We believe that the quantity thus derived is analogous to the induction period t_g determined experimentally. The change in the viscosity of the solution, caused by a mere formation of major aggregates of macromolecules before the point of gelation, can be neglected in comparison with the impressive change in the viscosity after the formation of the infinite network structure; it could not be observed with the experimental device used in the present work. If we assume that the rate constant $k(G)$ is a linear function of the velocity gradient

$$k(G) = K(G - G_{\min}), \quad (10)$$

where K is the constant of proportionality independent of G , we can see that after substituting this dependence into (9), a relationship is obtained

$$t_g = 100a_0^2/cKN(G - G_{\min})(\bar{M}_w - 2a_0). \quad (11)$$

This relationship can be modified to become

$$t_g G = t_g G_{\min} + 100a_0^2/cKN(\bar{M}_w - 2a_0), \quad (12)$$

representing the linear relationship $t_g G$ vs t_g , as found experimentally in Figs 3a and 3b. According to this plot, the intercept in the y -axis should be inversely proportional to the concentration of the polymer and to its molecular weight. As to the qualitative side, the dependence on the molecular weight is in agreement with the experiments. On the other hand, no quantitative analysis was made, since the distances of the points from the beginning are comparatively large, and no reliable and sufficiently accurate extrapolation was therefore possible. The dependence of the intercept on the concentration of the polymer does not, however, adequately describe the experimentally determined existence of the minimal concentration, c_{\min} . To describe this fact in full, it would be necessary to introduce a kind of "effective concentration", representing the difference between the actual concentration of the polymer and c_{\min} , already into the initial crosslinking conditions.

It seems suitable to point out, in conclusion, that no attempt at suggesting a theory of negative thixotropy has been made in the present work: it should only be regarded as a possible example of the mechanism of flow aggregation of the macromolecular chains, to be used for treatment of the experimental data. Despite the simplifying assumptions, the procedure described above led to a relationship which was in ac-

cordance with the experimental results. An assumption of the existence of a direct proportionality between the rate constant of aggregation, on the one hand, and the velocity gradient at flow, on the other, has already been made by Peterlin⁹, who explained the increase in viscosity in the case of negative thixotropy of the poly(methyl methacrylate) solutions in a high-viscosity chlorinated diphenyl in terms of the mechanism of formation of doublets of macromolecules. We stress once again that in no case there are any reasons for the linear dependence of $k(G)$ on G ; in this work, too, this assumption has been made for its simplicity only.

If reproducible results are to be obtained by the viscometry of solutions exhibiting negative thixotropy, the experimental technique is very exacting. The comparability of the results depends not only on the temperature being exactly maintained throughout the measurements, but also on observing always the same procedure while handling the sample during the process of filling of the viscometer. Moreover, we have also found out, by parallel measurements carried out with some of our poly(methyl methacrylate) solutions on the Weissenberg cone and plate rheogoniometer that the quantitative results greatly depend on the type of the viscometer, or on the width of the slit employed, and do not coincide with the results obtained with Rheotest.

The real mechanism of the effect of negative thixotropy, as well as the character and causes of the forming bonds is not yet known. It can only be assumed that the formation of these bonds requires an orientation of the extended macromolecular coils in the flow, similarly to the flow-produced crystallization of some polymers¹⁰.

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