# Rheokinetics of free-radical polymerization

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The authors elaborate theoretical concepts and obtain mathematical relations describing the increase in viscosity of reactive masses during bulk free-radical polymerization. The results obtained are confirmed experimentally for free-radical polymerization of alkyl methacrylates and styrene.

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## INTRODUCTION

Quantitative analysis of the processes of polymer synthesis is usually based on the elucidation of the mechanism of a reaction and on the determination of its kinetic regularities. However, when going over from an experimental set-up to an industrial reactor it is important to take into account also the transfer regularities for the reactive media, namely their rheological and thermal properties. The most sensitive parameter that changes sharply during polymerization is the viscosity of the reactive medium, since in the process of polymer formation a transition from a low-viscosity liquid to a high-viscosity polymer melt is accomplished, i.e. the viscosity may change by 7–8 and even more decimal orders. This explains the importance of the problem concerning regularities of the increase in viscosity during polymerization (and polycondensation). The results of some viscometric measurements are presented in the literature. These results, however, are random and give no indication of the general regularities of this phenomenon, which are associated with fundamental properties of the polymerizing systems. On the other hand, the nature of the change in viscosity of reactive media during the formation of polymers is determined by the mechanism and kinetic regularities of a specific reaction, as well as by the properties of the reactive medium, which is a dispersion (or a solution) of the polymer being formed. The 'rheokinetic' approach based on these considerations has been developed for some cases[1–4]. The present work is devoted to such a rheokinetic treatment of free-radical polymerization reactions, taking the formation of polystyrene and various polymethacrylates as an example. In all cases under consideration we shall be dealing with homogeneous polymerization, i.e. processes in which the polymer being formed is soluble in its own monomer or in the solvent used. We shall also consider some specific cases of the formation of heterogeneous systems and associated changes in viscometric transitions.

## THEORY

The increase in the viscosity of a reactive medium during polymerization is determined both by an increase in the molecular mass of the polymer formed and by an increase in its content in the system. These changes in molecular mass and polymer content depend on the kinetics and the mechanism of polymerization. In the general case, the reactive mass can be considered as a solution of the polymer formed in the initial monomer. The viscosity of such a solution is a function of the average chain length $\bar{N}$ of the polymer being formed and of its concentration $\phi$:

$$\eta = f(\bar{N}, \phi)$$

The viscosity of a homogeneous reactive mass, which is a single-phase polymer solution, may be expressed by the following formula:

$$\eta = K\phi^b \bar{N}^a \tag{1}$$

where $K$, $a$ and $b$ are constants. The choice of the formula for specifying the dependence $\eta = f(\bar{N}, \phi)$ is not critical. The power law in equation (1) has been used by us for convenience of analysis. The applicability of this formula to describing viscous properties of reactive systems was demonstrated in a number of our works as well as in independent studies by other authors[5].

In the case of block polymerization, the mass fraction of the polymer formed in a reactive system is equal to the degree of conversion of monomer, i.e.

$$\phi = \beta = ([M]_0 - [M])/[M]_0$$

where $[M]_0$ and $[M]$ are the initial and the current concentrations of the monomer. For thermal initiation of polymerization, the current concentration of the initiator is expressed as follows[6]:

$$[I] = [I]_0 \exp(-k_i t) \tag{2}$$

where $[I]$ is the current concentration, $[I]_0$ is the initial concentration of the initiator, $k_i$ is the rate constant of initiation, and $t$ is time.

In the simplest case of free-radical processes (without taking into account the chain transfer reaction and for chain termination by joining the radicals) the changes in the number-average degree of polymerization $\bar{N}$ and the degree of conversion $\beta$ are described by the following relations[6]:

$$\bar{N} = \frac{[M]_0\beta}{[I]_0(1 - e^{-k_i t})} \qquad (3)$$

$$\ln(1 - \beta) = \frac{2\sqrt{f}\,k_g}{k_0^{1/2}k_i^{1/2}}[I]_0^{1/2}(1 - e^{-k_i t}) \qquad (4)$$

where $k_g$ and $k_0$ are the rate constants for the growth and termination of the chain, respectively, and $f$ is the initiator efficiency.

If we take the degree of conversion $\beta$ or time $t$ as an independent variable, we can then write the expressions describing the change in the viscosity of a reactive system:

$$\eta = K\beta^b \left(\frac{[M]_0\beta}{[I]_0(1 - e^{-k_i t})}\right)^a \qquad (5)$$

or

$$\eta = K_1[I]_0^{-a}\left[1 - \exp\left(-\frac{2\sqrt{f}\,k_g}{k_0^{1/2}k_i^{1/2}}[I]_0^{1/2}(1 - e^{-(1/2)k_i t})\right)\right]$$
$$\times [1 - \exp(-k_i t)] \qquad (6)$$

where $K_1 = K[M]_0$.

Thus, if we know the rate constants of the elementary reactions and the rheological properties of the solution of a polymer in its own monomer or in the solvent used, we can, using equations (5) and (6), give a complete rheological description of the change in the viscosity of reactive media during free-radical polymerization. In this case, the kinetic constants are assumed to be invariable, i.e. we remain in the range of moderate degrees of conversion at least until an increase in the viscosity affects $k_0$ (ref. 6). Incidentally, the boundaries of this range are not defined beforehand; they can be established only by comparing the obtained theoretical dependences with the experimental results.

The above complete expressions can be considerably simplified. By expanding the functions in these expressions into power series and confining ourselves to linear terms (for $\beta \ll 1$ and $k_i t \ll 1$), under the condition that the molecular mass of the polymer formed remains unchanged and the yield at the initial stages of the reaction increases linearly, we obtain the following simple formula describing the change in the viscosity of the reactive mass with the degree of conversion:

$$\eta = \theta\beta^b \qquad (7)$$

where

$$\theta = K_1\left(\frac{k_g}{k_0^{1/2}}\sqrt{2f}\,k_i^{-1/2}[I]_0^{-1/2}\right)^a$$

is a constant.

If we consider the change in viscosity with time, we can write

$$\eta = \theta_1 t^b$$

where

$$\theta_1 = K_1\left(\frac{k_g}{k_0^{1/2}}\sqrt{2f}\right)^{a+b}(k_i[I]_0)^{(1/2)(b-a)} \qquad (8)$$

The above formulae describe in a sufficiently simple form the increase in viscosity during the initial stages of free-radical polymerization and make it possible to reveal quantitatively the role of the principal determining factors: the values of the kinetic constants and the initiator concentration.

It is interesting to consider the corollaries following from the formulae obtained, which concern the role of the initiator concentration $[I]_0$ and temperature $T$ in the isothermal case. The quantity $[I]_0$ enters in the constants $\theta$ and $\theta_1$ in formulae (7) and (8). If we express its effect explicitly, these formulae can be written in the form:

$$\eta = \theta'[I]_0^{-(1/2)a}\beta^b \qquad (9)$$

and

$$\eta = \theta_1'[I]_0^{(1/2)(b-a)}t^b \qquad (10)$$

where $\theta'$ and $\theta_1'$ are constants whose physical meaning can be easily established from the above formulae.

Hence, for $\beta = $ constant, the viscosity is proportional to $[I]_0^{-a/2}$ and for $t = $ constant it is proportional to $[I]_0^{(b-a)/2}$, where the exponents $a$ and $b$ characterize the viscous properties of solutions. In other words, the role of $[I]_0$ can be judged by the results of independent measurements of the rheological properties of polymer solutions.

The reaction temperature affects the yield and the molecular mass of the polymer formed in different ways. We can compare the values of the viscosity of a reactive medium at various temperatures corresponding to a constant degree of conversion. If we take into account that the quantities $k_i$, $k_g$, $k_0$ and $K_1$ in equation (7) can be represented as exponential functions of temperature, each with its own value of the activation energy, it turns out that:

$$\eta = A \exp\left[E + a(U_g - \tfrac{1}{2}U_0 - \tfrac{1}{2}U_i)/RT\right] \qquad (11)$$

where $A$ is the pre-exponential factor, $E$ is the activation energy of the viscous flow, and $U_i$, $U_g$ and $U_0$ are the activation energies of initiation, growth and termination of the chain, respectively.

We can then find a certain 'apparent' value of the activation energy of the process of increase in viscosity at an arbitrarily chosen value of $\beta = $ constant. When plotting the dependence of $\eta(\beta)$ on $T$ in $\ln \eta$ versus $T^{-1}$ coordinates for $\beta = $ constant, the activation energy is given by the following relation:

$$E_\beta = E + a(U_g - \tfrac{1}{2}U_0 - \tfrac{1}{2}U_i) \qquad (12)$$

If we compare the temperature dependences of $\beta$ corresponding to isoviscous states of reactive masses while plotting this dependence in $\ln \beta$ versus $T^{-1}$ coordinates (for $\eta = $ constant),we shall obtain the following expression for the apparent 'activation energy':

$$E_\eta = -\frac{E + a(U_g - \tfrac{1}{2}U_0 - \tfrac{1}{2}U_i)}{b} \qquad (13)$$

When considering the temperature dependence of

viscosity of a reactive mass at a fixed value of the polymerization time $t$ = constant (i.e. when plotting the ln $\eta$ versus $T^{-1}$ dependence for $t$ = constant), the activation energy will be determined as

$$E_t = E + (a+b)(U_g - \tfrac{1}{2}U_0) + \tfrac{1}{2}(b-a)U_i \qquad (14)$$

For the most important case from a practical point of view, the temperature dependence of the time for the attainment of a certain viscosity level $\eta^*$ = constant is determined by the 'activation energy' expressed in the following form:

$$E_\eta = -\frac{E + (a+b)(U_g - \tfrac{1}{2}U_0) + \tfrac{1}{2}(b-a)U_i}{b} \qquad (15)$$

Thus, the concept of activation energy becomes ambiguous and depends on the conditions under which a comparison is made and on the nature of the quantities whose temperature dependence is considered. Naturally, in all these cases the concept of 'activation energy' has equivalent meaning and reflects the sum of different elementary processes. This concept simply characterizes the temperature dependence of the parameter under consideration.

The formulae and relations obtained above allow experimental verification. This question will be considered in the following section.

## EXPERIMENTAL RESULTS AND DISCUSSION

It was interesting to verify the relations above for a wide range of materials. For this purpose, we studied a homologous series of alkyl methacrylates: methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), octyl methacrylate (OMA), as well as styrene. The characteristics of the initial monomers are given in *Table 1*.

Before polymerization, the monomers were purified by fractional distillation under vacuum. Benzoyl peroxide was used as an initiator. The monomer was purified of atmospheric oxygen prior to polymerization. The

viscosity of the polymerizing system and the degree of conversion were determined simultaneously by the dilatometric method[7]. Besides, the viscous properties of model systems—solutions of polymers in their monomers—were determined. Poly(alkyl methacrylate)s used for this purpose were obtained by the method of block polymerization under the same conditions as were used for studying the rheokinetics of polymerization. The values for the molecular masses of the polymers were determined with the help of the viscometric method (*Table 2*).

Besides the original experimental results, we also analysed the experimental results on the free-radical polymerization of styrene[8]. In all these cases, we speak of bulk polymerization, i.e. in the medium of its own monomer.

When conducting polymerization in a solvent, we should consider the polymer solution in a mixture of solvents, consisting of a low-molecular-weight liquid and the initial monomer. In this case we must take into account the fact that the composition of such a mixture changes continuously as the monomer is consumed.

First of all, let us consider the influence of initial concentration of initiator, $[I]_0$, and of temperature on the nature of the increase in viscosity. This makes it possible to determine independently the numerical values of the exponents $a$ and $b$ in formulae (7)–(10) and (12)–(15), and to compare them with the values obtained in the model analysis of the viscous properties of polymers in their own monomers. Independent measurements of these quantities in different experiments and comparison of the results is a criterion for the correctness of the theoretical results. The corresponding dependences are represented by the formulae.

The values of the exponents $a$ and $b$ are determined from the rheokinetic data by plotting the dependences $\eta([I]_0)$ for $\beta$ = constant and $\eta(\beta)$ for $[I]_0$ = constant in log–log co-ordinates. *Figures 1* and *2* show the $\eta(\beta)$ dependence for free-radical polymerization of MMA, BMA and styrene. It is seen that the $\eta(\beta)$ dependence is represented by two segments of straight lines, which clearly resemble the similar concentration dependence $\eta(\phi)$ of the viscosity of the polymer solution. The slopes of the straight lines obtained correspond to the values of the exponent $b$ presented in *Table 3*.

The value of the exponent $a$ is determined by plotting the dependence $\eta([I]_0)$ for $\beta$ = constant, which is based on formula (9), or the dependence $\eta([I]_0)$ for $t$ = constant, which allows us to determine the value of $a$ for a known value of $b$, by equation (10). The corresponding dependences for MMA and BMA are shown in *Figure 3*. The dependences for $\beta$ = constant obey a power law. The exponent $-a/2$ is calculated from the slope. A comparison of the values of the exponents $a$ and $b$ obtained from various experiments is made in *Table 3*.

**Table 1** Characteristics of the monomers employed

| Monomer | Symbol | $d$ (gcm$^{-3}$) | $n_D^{20}$ | B.p. (°C) |
|---|---|---|---|---|
| Methyl methacrylate | MMA | 0.936 | 1.4130 | 100 |
| Ethyl methacrylate | EMA | 0.907 | 1.4140 | 117 |
| Butyl methacrylate | BMA | 0.895 | 1.4215 | 163 |
| Octyl methacrylate | OMA | 0.864 | 1.4373 | 105 (5 mmHg) |
| Styrene | St | 0.906 | 1.5468 | 145 |

**Table 2** Molecular masses of the investigated polymers

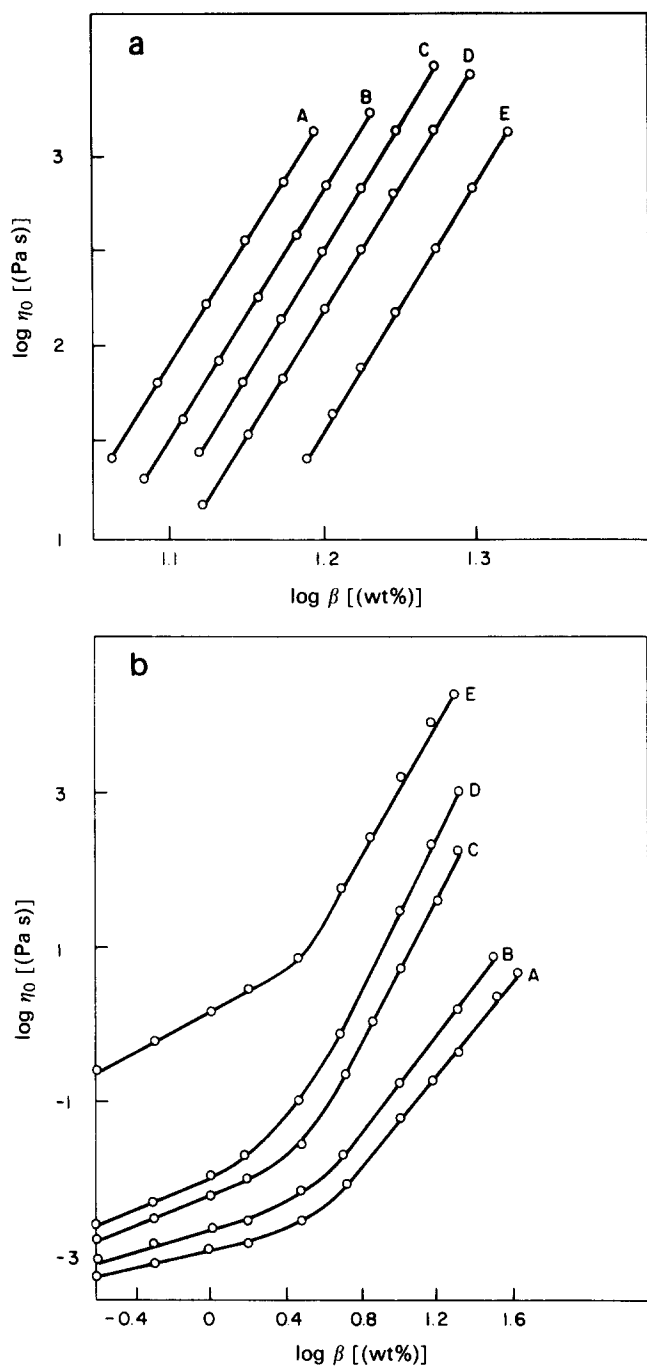| Polymer | Symbol | Solvent | $T$ (°C) | $K \times 10^5$ (ref. 16) | $\alpha$ (ref. 16) | Interval of molecular mass, $M \times 10^{-5}$ |
|---|---|---|---|---|---|---|
| Poly(methyl methacrylate) | PMMA | Acetone | 25 | 7.5 | 0.7 | 1–30 |
| Poly(ethyl methacrylate) | PEMA | Methyl ethyl ketone | 23 | 2.83 | 0.79 | 3.4–20 |
| Poly(butyl methacrylate) | PBMA | Benzene | 30 | 4.0 | 0.77 | 2.6–66 |
| Poly(octyl methacrylate) | POMA | Methyl ethyl ketone | 23 | 4.47 | 0.69 | 2.0–7.4 |
| Polystyrene | PS | Benzene | 30 | 10.6 | 0.74 | 0.4–1.0 |

Figure 1 Dependence of the initial Newtonian viscosity $\eta_0$ on the degree of conversion $\beta$ of (a) polymerizing MMA and (b) polymerizing BMA. (a) $T=70°C$; $[I]_0$ (wt%): curve A, 0.02; B, 0.05; C, 0.075; D, 0.1; E, 0.15. (b) $T=60°C$, $[I]_0$ (wt%): curve A, 1.0; B, 0.8; C, 0.2; D, 0.1; E, 0.05



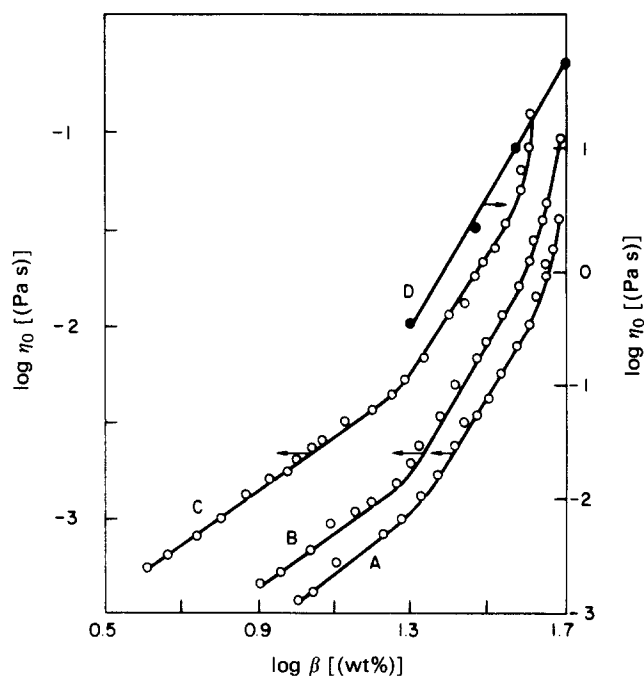Figure 2 Dependence of the initial Newtonian viscosity $\eta_0$ on the degree of conversion $\beta$ of polymerizing styrene. $T=80°C$ (curves A–C), 100°C (curve D); $[I]_0$ (wt%): curve A, 1.5; B, 1.3; C, 1.0; D, 0

It can be seen from this table that the numerical values of $a$ and $b$ determined from kinetic data and from the analysis of rheological properties of polymer solutions in their respective monomers practically coincide.

Apparently, the most general conclusion that can be drawn from the experimental data above and from their processing consists of the proof that the reactive mass can be treated as an analogue of a solution of stable macromolecules in their monomer. On the other hand, the possibility of applying the theoretical relations above indicates that up to rather high degrees of conversion, at which the rheokinetic measurements were made, the kinetic constants may be assumed to be invariable. Otherwise, it should be expected that the experimental results would not obey the simple regularities following from the assumption about the constancy of kinetic constants.

Let us now consider the temperature dependence of the viscosity of a reactive system during free-radical polymerization and find the values of the apparent 'activation energy' by formulae (12)–(15). As we have mentioned above, the temperature dependence of the growth in viscosity is affected by the conditions under whidh the

Table 3 Comparison of the exponents $a$ and $b$ obtained from the rheokinetic measurements and viscometry of solutions

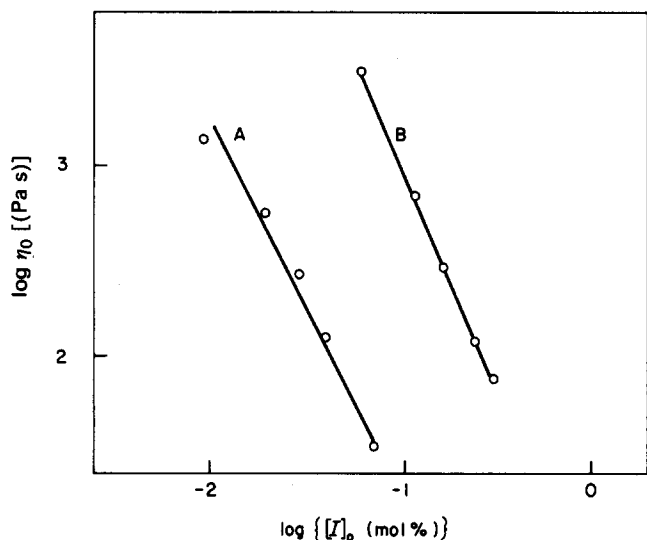| | a | | | | b | | | |
|---|---|---|---|---|---|---|---|---|
| | From rheokinetic measurements | | From viscometry of solutions | | From rheokinetic measurements | | From viscometry of solutions | |
| | 1* | 2** | 1 | 2 | 1 | 2 | 1 | 2 |
| PMMA | 1.0 | 3.4 | 1.0 | 3.4 | 1.0 | 12.8 | 1.0 | 13.0 |
| PEMA | 1.0 | 3.4 | — | 3.4 | 0.8 | 4.2 | — | — |
| PBMA | 1.0 | 3.4 | 1.0 | 3.4 | 0.9 | 4.0 | 0.85 | 3.9 |
| POMA | 1.0 | 3.4 | — | — | 0.8 | 4.5 | 0.8 | 4.4 |
| PS | 1.0 | 3.4 | 1.0 | — | 0.8 | 5.5 | 0.9 | 5.5[11] |

\* *Figure 1*
\*\* *Figure 2*

**Figure 3** Dependence of the initial Newtonian viscosity $\eta_0$ on the initial concentration $[I]_0$ of the initiator for polymerizing MMA (curve A; $T=70°C$, $\beta=16$ wt%) and BMA (curve B; $T=60°C$, $\beta=26$ wt%)
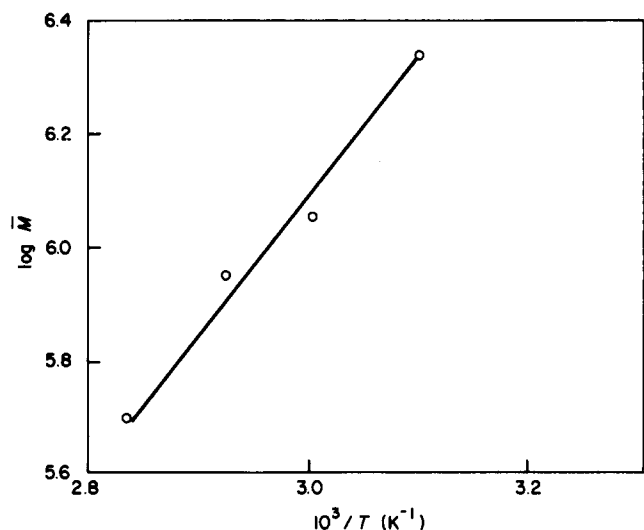


**Figure 4** Dependence of the molecular mass $\bar{M}$ o PMMA on the polymerization temperature $T$: $[I]_0=0.2$ wt%

comparison was made. In other words, this dependence is determined by the values of the activation energy of the viscous flow, and that of the chain initiation, growth and termination reactions. In the general case, the change with temperature in the degree of polymerization of the polymer formed during free-radical polymerization is determined by the sum of the temperature dependences of the rate constants of chain initiation, growth and termination reactions. The activation energy of this process can be written as follows:

$$U_{\bar{N}} = U_g - \tfrac{1}{2}U_0 - \tfrac{1}{2}U_i$$

The value of $U_{\bar{N}}$ required to calculate the apparent 'activation energies' was estimated from the dependence of the polymer molecular mass on polymerization temperature (*Figure 4*). For PMMA, this value was found to be equal to about $4.8 \times 10^4$ J mol$^{-1}$, which is in a good agreement with the literature data[6]: $U_i = 1.3 \times 10^5$ J mol$^{-1}$, $U_g - \tfrac{1}{2}U_0 = 1.9 \times 10^4$ to $2.1 \times 10^4$ J mol$^{-1}$.

The value of $E_\beta$ obtained by plotting $\ln \eta$ versus $T^{-1}$ (*Figure 5*, curve A) was found to be $1.4 \times 10^5$ J mol$^{-1}$. This value satisfies formula (12) for $a=3.4$ and the activation energy of the viscous flow $E=2.1 \times 10^4$ to $2.5 \times 10^4$ J mol$^{-1}$. The latter value corresponds to the experimental results obtained in the medium range of compositions of PMMA solutions in its monomer. On considering the change in the value of $E$ required to attain a constant viscosity level irrespective of the temperature variation (*Figure 5*, curve B), we obtained $E_\eta = 1.1 \times 10^4$ to $1.3 \times 10^4$ J mol$^{-1}$, which corresponds to formula (13) for $a=3.4$ and $b=13$.

The determination of the constants $a$ and $b$ in the formula for the concentration dependence of viscosity is only one particular application of the relations obtained. Apart from this, by using formulae (7) and (8), it is possible to calculate directly the change in viscosity with time or the dependence on the degree of conversion under different conditions. Such a calculation was performed for the series of alkyl methacrylates under study. The kinetic constants for the monomers under investigation, required for calculations, are given elsewhere[6,9-12]. The value of the initiator efficiency $f$ in formula (4) was taken to be 0.8. Naturally, this introduces a certain, though not very significant, amount of arbitrariness.

The results of calculations and their comparison with the experimental dependence are shown in *Figures 6* and *7*. The results obtained show good agreement between the experimental and theoretical dependences for $\eta(\beta)$ and $\eta(t)$. A certain discrepancy at high $[I]_0$ for PMMA can be attributed to the recombination of radicals and to a
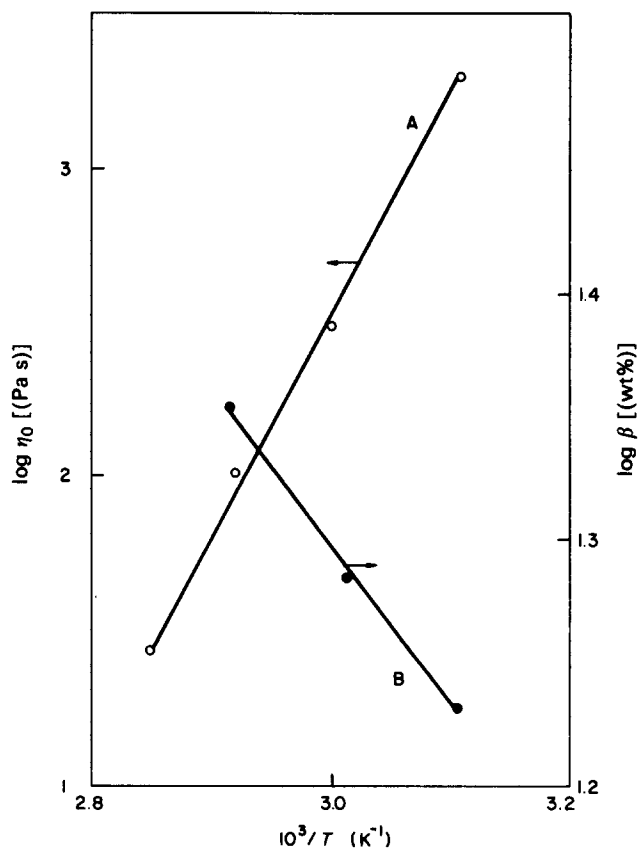


**Figure 5** Dependence of the initial Newtonian viscosity $\eta_0$ of the reactive mass for $\beta=18$ wt% (curve A) and the degree of conversion $\beta$ for $\eta^*=500$ Pa s (curve B) on the polymerization temperature of MMA; $[I]_0=0.2$ wt%
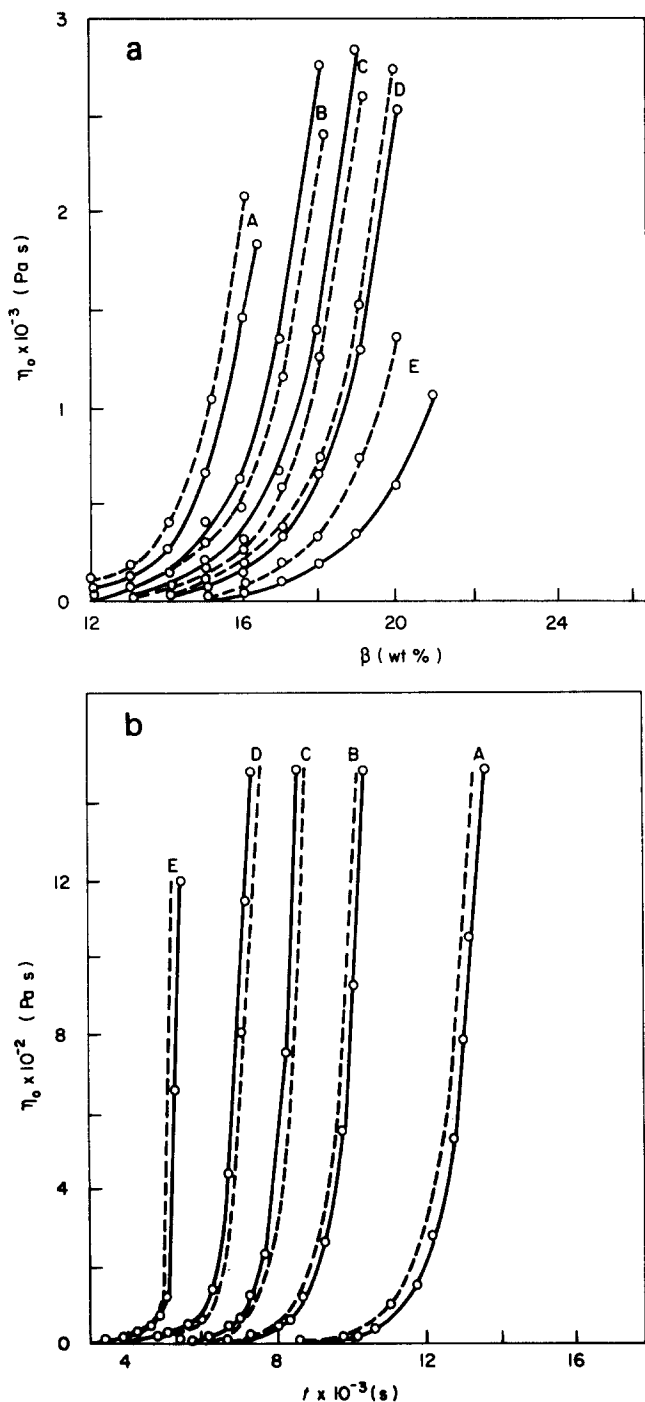
Figure 6 Dependence of the initial Newtonian viscosity $\eta_0$ on (a) the degree of conversion $\beta$ of MMA and (b) the polymerization time $t$. [I]$_0$ (wt%): curves A, 0.02; B, 0.05; C, 0.075; D, 0.1; E, 0.15. Broken curves have been calculated theoretically.

decrease in initiator efficiency $f$ that was not taken into account.

Thus, the coincidence of a large body of the experimental data with the proposed theoretical relations indicates that our rheokinetic approach to the analysis of the change in viscosity during radical polymerization correctly explains the basic regularities of the process. Besides, on the basis of the general behaviour of viscous properties of polymer solutions, this fact enables us to predict quantitatively the nature of the increase in viscosity in reactive media during homogeneous polymerization as a function of basic factors: initiator con-

centration, temperature and time. The relations above were obtained on the assumption that the kinetic constants are invariable, which is apparently true in the cases under consideration up to high degrees of conversion. In particular, this means that the change in viscosity in the conversion intervals under consideration is not affected at all by the attainment of the gel point, irrespective of whether this point exists for the systems studied.

The results indicate, particularly, that the deviation of the experimental dependence from the theoretical functions obtained for the simplest kinetic scheme may serve, on increasing degree of conversion, as a quantitative criterion for the variation of the kinetic constants during polymerization.

The nature of the increase in viscosity may also change during phase transition: in the course of the reaction[13,14]. We observed this in experiments on the polymerization of MMA in a solvent–precipitant mixture (*Figure 8*). The mixture consisted of cyclohexane as precipitant and toluene as solvent. The MMA monomer also served as a solvent for the polymer formed. During polymerization the dissolving power of the medium decreased as MMA was consumed, and at a definite degree of conversion the conditions of phase separation were attaihed, and the homogeneous system transformed into a heterogeneous one. In this case we observe an extreme change in the viscosity during polymerization, as was reported for the first time elsewhere[15]. At the beginning of polymerization, the viscosity increased with increasing degree of conversion (in the homogeneous system). However, on attainment of a definite degree of conversion, the dissolving power of the medium reduced to such an extent that the polymer precipitated as a dispersion, thereby causing pronounced turbidity of the system. Naturally, the viscosity of the mass also decreased, since the polymer concentrated in the precipitated phase. With increasing degree of conversion the viscosity of the heterogeneous
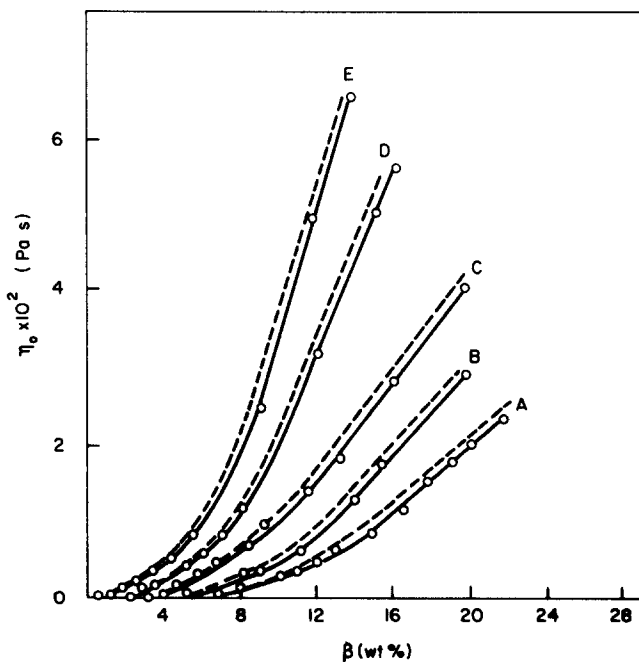


Figure 7 Dependence of the initial Newtonian viscosity $\eta_0$ on the degree of conversion $\beta$ of polymerizing EMA. $T=70°C$, $\bar{M} \times 10^{-5}$ of PEMA: curves A, 3.4; B, 4.5; C, 8.0; D, 10; E, 20. Broken curves have been calculated theoretically
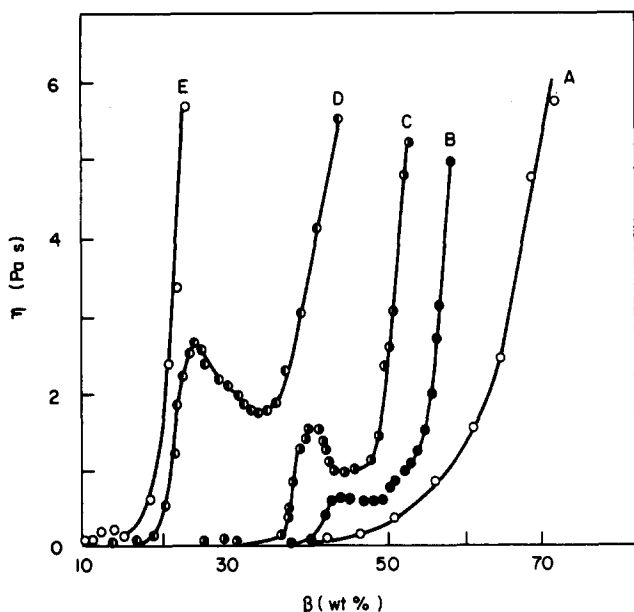
**Figure 8** Dependence of viscosity $\eta$ for $\gamma=0.32$ s$^{-1}$ on the degree of conversion $\beta$ of polymerizing MMA in a precipitant–solvent medium. Mixture composition, MMA: cyclohexane:toluene (wt%) respectively: curve A, 50:15:35; B, 50:30:20; C, D, 50:32.5:17.5; E, 50:37.5:12.5; $\bar{M} \times 10^{-4}$ of PMMA: curve A, 19; B, 0.11; C, 0.26; D, 25; E, 31

medium once again increased. Upon increasing the concentration of the precipitant in the system, the polymer phase was precipitated at lower degrees of conversion, as expected.

## CONCLUSIONS

Comparison of the predictable regularities of the viscosity variation in a reactive medium upon homogeneous free-radical polymerization with the experimental data shows that, on the whole, the reactive medium may be treated as a solution of the polymer formed in its own monomer, and that the presence of a free radical does not affect the

viscous properties of the polymerizing system. For this reason the constants $a$ and $b$ that characterize the rheological behaviour of the solutions in the formula $\eta = K\phi^b \bar{N}^a$ determine the regularities of the effect of initial concentration of initiator and of temperature on the rate of increase in viscosity. Moreover, such an approach can be used to predict the variation of viscosity and also to solve, in principle, the inverse problem—to evaluate the kinetic constants from measurements of the change in viscosity of the reactive mass. The rheokinetic analysis permits us to determine the constancy or the variation of the elementary kinetic constants in the course of polymerization.

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