

THE EFFECT OF PREFERENTIAL SOLVATION ON RADICAL POLYMERISATION OF METHYL METHACRYLATE

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The effect of acetonitrile–methyl methacrylate mixed solvent viscosity and preferential solvation on both the reaction order with respect to monomer and the determination of transfer constant with acetonitrile is demonstrated on radical polymerisation of methyl methacrylate in acetonitrile at 25°C. The results obtained indicate that due to a preferential solvation of poly(methyl methacrylate) by monomer the polymerisation proceeds at effectively higher monomer concentration than is the analytical one. Methyl methacrylate polymerisation in solvents of different viscosity is of the first order only if monomer concentration is related to viscosity reduced rate of polymerisation, $R_p \cdot \eta^{-0.5}$. Transfer constant of poly(methyl methacrylate) radical with acetonitrile at 25°C after the correction for mixed solvent viscosity and local monomer concentration is $4.4 \cdot 10^{-5}$.

When studying the kinetics of radical polymerisation one observes smaller or larger deviations from the ideal course of reaction. The deviations, such as fractional reaction order with respect to monomer, nonadditivity of transfer constant in a mixed solvent, *etc.* are often quoted.

The effect of polymer solvent viscosity on the termination rate constant of poly(methyl methacrylate) radicals¹ or of polystyrene radicals² has already been described. In many instances by taking corrections for viscosity it is possible to show that the order of viscosity reduced rate of polymerisation with respect to monomer is unity³ or that the transfer constant with solvent can be determined in the usual way⁴. The rate of methyl methacrylate (M) polymerisation which includes mixed solvent viscosity is given by

$$R_p = K[M] \eta^{0.5}, \quad (1)$$

where K is the complex constant which involves the rate constants of initiation, propagation and the rate constant of termination at solvent viscosity being unity, η is the solvent viscosity. The equation (1) indicates, that by neglecting the correction for viscosity the reaction order with respect to monomer becomes inversely proportional to solvent viscosity (Table I). It has also been observed that there are systems which even after the correction for viscosity do not give a reasonable correlation between an experiment and the expected kinetics.

The previous study⁵ of radical polymerisation of methyl methacrylate in cyclohexanone revealed that cyclohexanone prevails over monomer in solvation of poly(methyl methacrylate) chains. In such a system the reaction order with monomer depends, besides viscosity, also on dilution of monomer with respect to cyclohexano-

ne. The present paper quotes the results of methyl methacrylate polymerisation performed in solution when polymer is predominantly solvated by monomer.

EXPERIMENTAL

Methyl methacrylate — a technical product was twice distilled under nitrogen and the purity checked as it is described in our previous communication⁵; the rate of bulk polymerisation was in accord with the values quoted in the literature⁶. Acetonitrile, analytical grade, was dried over CaCl_2 and then distilled under nitrogen, b.p. 80.1°C . 2,2'-Azobis-(isobutyronitrile) was used as a photosensitive initiator; a commercial product (Koch and Light Lab.) was twice recrystallised from ether solution, m.p. $102-104^\circ\text{C}$.

The rate of methyl methacrylate polymerisation was determined by gravimetry. Glass ampoules (transmitting above 330 nm) flushed with nitrogen were filled with monomer, initiator and varied amount of acetonitrile and sealed. Polymerisation was performed in a tempered water bath ($25 \pm 0.05^\circ\text{C}$). Mercury lamp (Tesla, Holešovice RVL-80 without upper cover) was used. The ampoules were rotating at a constant speed around the source of radiation. No polymerisation was observed in the absence of initiator. Polymer was precipitated out by cooled heptane, reprecipitated from chloroform solution and dried to constant weight under vacuum.

Polymer molecular weights were calculated from limiting viscosity numbers $[\eta]$, (an Ubbelohde dilution viscometer was employed) according to the equation valid for benzene and the temperature of 30°C (ref.⁷), $[\eta] = 8.69 \cdot 10^{-5} M^{0.76}$.

Viscosities of methyl methacrylate-acetonitrile mixtures were determined with the use of an Ubbelohde viscometer. Pycnometer holding 10 ml was used for determining their densities. Solvents were degassed prior to measurements under water pump vacuum.

Coefficients of preferential solvation (λ) for individual methyl methacrylate-acetonitrile compositions were determined from the difference of the mixture refraction indexes before and after the swelling of crosslinked PMMA (ref.⁸). Refraction index differences were determined by means of a Brice-Phoenix visual differential refractometer. The λ values served for calculating the methyl methacrylate-acetonitrile mixture composition surrounding the polymer chain⁹

$$\bar{x}'_1 = \frac{Z\bar{x}_1 + \lambda_1 m/V_1}{Z + \lambda_1(m/V_1 - m/V_2)}, \quad (2)$$

TABLE I

Solvent Viscosity and Reaction Order with Monomer (n) at Methyl Methacrylate Polymerisation at 25°C

| Solvent | η , mPa s | n |
|---------------------|----------------|------|
| Acetone | 0.304 | 1.18 |
| Acetonitrile | 0.339 | 1.15 |
| Methyl methacrylate | 0.531 | 1.00 |
| Propyl acetate | 0.551 | 0.99 |
| Cyclohexanone | 2.016 | 0.68 |

where \bar{x}'_1 is the mole fraction of solvent 1 in the vicinity of a polymer chain, \bar{x}_1 is the average molar fraction, m is the molecular weight of a polymer monomer unit, V_1 and V_2 are solvent molar volumes, Z is the parameter representing the number of solvent molecules solvating one monomer unit. Z value is usually evaluated from analogies¹⁰. The authors of ref.⁹ used for calculation $Z = 3$, for the methyl methacrylate-acetonitrile system the best agreement with the experiment was attained with $Z = 2$.

RESULTS AND DISCUSSION

At a solution polymerisation a solvent not only dilutes monomer but also forms with it a binary solvent for a polymer formed. If the components combination is such that the preferential solvation of macromolecules takes place then the change of mixed solvent composition in close vicinity of a polymer chain occurs⁹.

At the polymerisation of methyl methacrylate (M) in cyclohexanone at 25°C the polymer is preferentially solvated by cyclohexanone⁵. The rate of polymerisation (R_p) exhibits lower values than the expected ones calculated according to Eq. (1) with average values of methyl methacrylate concentrations. On the other hand, higher than calculated rates should be observed if a growing macroradical is preferentially solvated by its monomer. It can be expected that this requirement would be met if the monomer is mixed with a poorer solvent for PMMA. Acetonitrile was selected from a number of solvents because in this solvent PMMA has a lower value of the limiting viscosity number at 25°C than in methyl methacrylate.

| Solvent | benzene | methyl methacrylate | acetonitrile |
|-----------------------------------|---------|---------------------|--------------|
| $\eta, \text{cm}^3 \text{g}^{-1}$ | 184 | 130 | 32 |

TABLE II

Polymerisation of Methyl Methacrylate in Acetonitrile at 25°C

Initiator concentration: $1.74 \cdot 10^{-3} \text{ mol dm}^{-3}$, \bar{x}_s acetonitrile mole fraction, R_p rate of polymerisation, \bar{P}_n average degree of polymerisation.

| \bar{x}_s | [M] mol dm^{-3} | $R_p \cdot 10^5$ $\text{mol l}^{-1} \text{s}^{-1}$ | \bar{P}_n |
|-------------|-----------------------------|---|-------------|
| 0 | 9.35 | 21.16 | 1 046 |
| 0.29 | 7.75 | 17.78 | 703 |
| 0.47 | 6.50 | 13.82 | 610 |
| 0.56 | 5.75 | 12.23 | 545 |
| 0.65 | 4.89 | 10.01 | 479 |
| 0.69 | 4.38 | 8.58 | 443 |
| 0.74 | 3.85 | 6.98 | 408 |

Also the fact that acetonitrile is less viscous than methyl methacrylate was taken into account. On addition of acetonitrile to monomer the viscosity of this binary solvent for PMMA decreases and thus the preferential solvation by monomer affects the rate of methyl methacrylate polymerisation more markedly.

The results of methyl methacrylate polymerisation in acetonitrile are summarised in Table II. The monomer conversion *vs* time plots are at the early stages of polymerisation (up to the conversion of about 7%) linear with no sign of acceleration or inhibition. Therefore, we conclude that the polymerisation at certain dilution proceeds under steady state conditions without any change of the initiation rate.

The plot of $\log R_p$ *vs* $\log [M]$ (Fig. 1) gives the straight line 1, which has a lower slope (lower reaction order with monomer) than the curve 2 calculated according to Eq. (1) which includes the methyl methacrylate-acetonitrile viscosity (η). The cause of this difference we attribute to the preferential solvation of poly(methyl methacrylate) growing radical by methyl methacrylate. The following table summarises determined coefficients of preferential solvation (λ_M) for the methyl methacrylate-acetonitrile-PMMA system at 25°C (\bar{x}_s is acetonitrile molar fraction in the mixture)

| | | | |
|---|-------|-------|-------|
| \bar{x}_s , average: | 0.40 | 0.67 | 0.86 |
| \bar{x}_s , in solv. layer: | 0.38 | 0.62 | 0.80 |
| λ_M , $\text{cm}^3 \text{g}^{-1}$: | 0.026 | 0.070 | 0.112 |

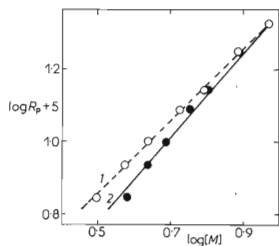


FIG. 1

Rate of Methyl Methacrylate Polymerisation *vs.* Concentration of Monomer in the Mixture with Acetonitrile at 25°C and at Initiator Concentration of $1.74 \cdot 10^{-3} \text{ mol dm}^{-3}$

1 At average monomer concentration (○), 2 calculated according to Eq. (1), ● monomer concentration in the polymer vicinity.

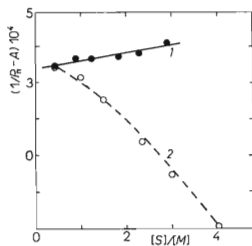


FIG. 2

Transfer Constant Determination at Methyl Methacrylate (M) Polymerisation in Acetonitrile (S) at 25°C (Eq. (3))

$A = (1 + \beta) k_t^0 R_p^0 / 2k_p^2 [M]^2 \eta$. Curves for [M]: 1 in solvating layer, 2 average.

Those measurements indicate that the monomer concentration in the polymer chain vicinity is higher than the average one. If the experimentally determined rate of polymerisation is related to monomer concentration present in the solvated layer, the experimental points shift towards higher monomer concentration and reasonably well agree with the curve 2 in Fig. 1.

The substantiation for using monomer concentration present in the vicinity of the polymer chain can be further documented by determining the transfer constant C_s . The modified equation for calculating C_s , which also includes mixed solvents viscosity⁴ is the following:

$$\frac{1}{\bar{P}_n} = \frac{1}{2} (1 + \beta) \frac{k_t^0 R_p}{k_p^2 [M]^2 \eta} + C_M + C_s \frac{[S]}{[M]} \quad (3)$$

\bar{P}_n is an average degree of polymerisation, β represents participation of disproportionation in the termination reaction, k_t^0 is the rate constant of termination at unit viscosity (1 mPa s), k_p denotes rate constant of propagation, C_M and C_s are transfer constants with monomer and solvent (S), respectively. Graphical solution of the Eq. (3) with the use of average monomer concentrations leads to a nonlinear dependence stretches even to negative values — Fig. 2, curve 2. On the other hand, if the calculation is done with the monomer concentration and the viscosity of the methyl methacrylate–acetonitrile mixture corresponding to the solvated layer then we obtain a straight line with a positive slope. The value of C_s determined by this way is $4.4 \cdot 10^{-5}$.

The kinetics of the preferential solvation equilibrium formation has not so far been quoted in the literature. However, the present views on the diffusion rate of low-

TABLE III

Densities (ρ), Viscosities (η), Excess Viscosity ($\Delta\eta^E$), Excess Molar Volume (ΔV^E), Parameter d from Eq. (4) of Methyl Methacrylate–Acetonitrile Mixture at 25°C

| \bar{x}_s | ρ g cm ⁻³ | η mPa s | $\Delta\eta^E$ mPa s | ΔV^E cm ³ | d |
|-------------|------------------------------|-----------------|-------------------------|---------------------------------|-------|
| 0 | 0.9385 | 0.531 | 0 | 0 | 0 |
| 0.3 | 0.9128 | 0.491 | 0.017 | -0.23 | 0.266 |
| 0.45 | 0.8936 | 0.461 | 0.016 | -0.12 | 0.239 |
| 0.6 | 0.8720 | 0.431 | 0.014 | -0.15 | 0.243 |
| 0.8 | 0.8334 | 0.386 | 0.008 | -0.09 | 0.240 |
| 0.9 | 0.8065 | 0.361 | 0.002 | +0.09 | 0.185 |
| 1.0 | 0.7783 | 0.339 | 0 | 0 | 0 |

molecular components of this system do not exclude the possibility that the preferential solvation equilibrium is established fast enough, *i.e.* during the macromolecule growth. Therefore, the results obtained allow us to assume that the growing radical of methyl methacrylate polymerisation in acetonitrile is surrounded by a mixed solvent whose composition differs from its average composition in the whole system.

The way of quantitative representation of intermolecular interactions in connection with their effect on the course of polymerisation is not at present quite unambiguous. Besides interactions which manifest themselves in the changes of movement rates of macromolecule segments or in preferential solvation of a macromolecule, it is possible to evaluate intermolecular interaction directly from viscometric measurements as it is usual when binary liquid mixtures are studied¹¹. Commonly used characteristics, such as excess viscosity¹², excess molar volume¹¹ and parameter d from the following equation¹¹

$$\ln \eta = \bar{x}_1 \ln \eta_1 + \bar{x}_2 \ln \eta_2 + \bar{x}_1 \bar{x}_2 d, \quad (4)$$

where \bar{x}_1 is component 1 mole fraction, η_1 component 1 viscosity, have for the initial polymerisation mixture the values given in Table III. The positive values of excess viscosity as well as of d parameter and taking into account their magnitudes it is possible to conclude that interactions between unlike molecules prevail in the methyl methacrylate-acetonitrile mixtures and that they are weak¹¹.

Other method for characterising the effect of the mixed solvent on the macromolecule can be seen in determining limiting viscosity number of a PMMA sample in methyl methacrylate-acetonitrile mixture of variable composition. Nevertheless, that acetonitrile is a poorer solvent for PMMA than the monomer, it is interesting that its addition to the monomer causes in the first stage a moderate raise of limiting viscosity number. It means that the polymer coil in this region becomes more bulky than in the neat monomer. This may effect, for example, the rate of termination

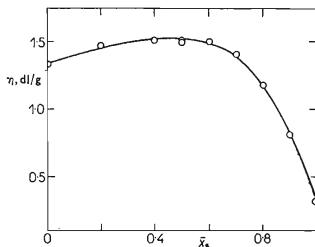


FIG. 3
Limiting Viscosity Number of PMMA vs
Mole Fraction of Acetonitrile (\bar{x}_2) in the
Mixture with Methyl Methacrylate at 25°C

reaction (Fig. 3). However, the characterisation of the mixed solvent which follows from the excess functions (Table III) or from values of limiting viscosity numbers (Fig. 3) does not indicate a correlation with the course of polymerisation. On the other hand, the polymerisation course is in the first place effected by all intermolecular interactions represented by the binary solvent viscosity, and by the coefficient of preferential solvation.

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