

CYCLOHEXANONE AS TRANSFER AGENT FOR POLY(METHYL METHACRYLATE) RADICAL

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Radical polymerisation of methyl methacrylate in cyclohexanone was studied at 60°C. In this system, the intensity of substitution reactions (transfer constant) of poly(methyl methacrylate) radical with cyclohexanone varies with the composition of the initial polymerisation mixture. The minimum value of the transfer constant C_s , being approximately $6 \cdot 10^{-5}$ at the molar ratio of the solvent in the polymerisation mixture 0.6, is observed when absolute values of the excess viscosity $\Delta\eta^E$ as well as the excess free energy of activation of the flow Δ^*G^E are the highest. The decrease of the transfer constant with dilution is explained in terms of the intensity variation of intermolecular interactions of the like and unlike molecules. Other factors, such as the variation of the rate of termination, were found to be less important.

We have observed that the polymerisation of methyl methacrylate in cyclohexanone yields polymer which has higher molecular weight than it should have with respect to the monomer dilution. When calculating C_s according to Mayo's relation generalised for system with any type of initiation and termination of radicals^{1,2}, the phenomenon described above manifest itself in the decrease of C_s with decreasing monomer concentration. The graphical solution does not give a straight line with the slope equal to the value of C_s , but a concave curve. In one of the earlier studies³ the authors determined C_s for polystyrene radical with cyclohexanone from an analogous dependence and plotted a straight line, but in fact a concave curve would fit the points more precisely. It may well be that this is the reason why in the comprehensive list of published transfer constants of poly(methyl methacrylate) radical this characteristics of substitution reactions with cyclohexanone is not listed.

Further work was directed to polymerisations of methyl methacrylate in cyclohexanone which should show to what extent this anomalous behaviour of transfer constant is connected with the intensity of substitution reactions. The molecular weights observed were not considered only from the point of view of the chain transfer with cyclohexanone but also the variation of the viscosity of the medium and its effects on other elementary reactions of the polymerisation were taken into account.

EXPERIMENTAL

Methyl methacrylate was purified in the usual way. Just before the use the last traces of polymerisation impurities were removed by prepolymerization, the conversion of which was about

2–3% (in the presence of 0.01% of benzoyl peroxide) and distillation of the residual monomer in nitrogen atmosphere under reduced pressure⁴. The polymerisation of the monomer purified in this way initiated with 2,2'-azobis(isobutyronitrile) ($5 \cdot 10^{-3}$ mol/l) at $60 \pm 0.05^\circ\text{C}$ exhibited the rate $(1.931 \pm 0.035) \cdot 10^{-4}$ mol l⁻¹ s⁻¹, which is in good agreement with the data published by others^{1,5}. Cyclohexanone, anal. grade, was freed from hydroperoxides by heating with anhydrous ferro sulphate and distilled under nitrogen; b.p. $155.6^\circ\text{C}/760$ Torr.

Polymerization of methyl methacrylate, initiated by 2,2'-azobis(isobutyronitrile) ($5 \cdot 10^{-3}$ mol/l) was performed in sealed glass ampoules in nitrogen atmosphere at $60 \pm 0.05^\circ\text{C}$. Solvent molar ratio varied from 0 to 0.74. Conversion of monomer to polymer was determined gravimetrically; 5 to 7 samples was measured for each dilution. Polymer was isolated by precipitating the ampoule contents with heptane. The maximum conversions were about 10%. The rates of polymerisation were calculated by the least square method.

The degree of polymerisation was determined by measuring the viscosity of benzene solutions of poly(methyl methacrylate) in a Ubbelohde dilution viscometer at 30°C ; the measurement was done with the samples obtained from the polymerisations which were stopped at 4–6% conversion of monomer to polymer. The calculation of \bar{P}_n from $[\eta]$ was done according to the relation⁶ $[\eta] = 8.69 \cdot 10^{-5} M^{0.76}$. The viscosities of cyclohexanone-methyl methacrylate solutions were determined with the use of an Ubbelohde viscometer fitted with a capillary having 0.534 mm in diameter. The densities of the cyclohexanone-methyl methacrylate solutions were determined pycnometrically.

RESULTS

For the determination of the transfer constant, C_s , of poly (methyl methacrylate) radical with cyclohexanone we have used the following data. The rate of polymerisation, R_p , and the degree of polymerisation, \bar{P}_n , were determined at different solvent (S) to monomer (M) ratios (Table I). The transfer constants were calculated for each monomer concentration according to the following equation:

$$1/\bar{P}_n - A = C_s \cdot [S]/[M], \quad (1)$$

where

$$A = C_m + \frac{1}{2}(1 + \lambda) \delta^2 \cdot R_p/[M]^2. \quad (2)$$

The equation does not include the transfer with initiator, which is admissible for the initiator we used— 2,2'-azobis (isobutyronitrile)¹. The values of other parameters needed for the calculation were taken from the literature data. The reported ratio of the rate constant of termination k_t to the square of the rate constant of propagation k_p^2 denoted as δ^2 is, for methyl methacrylate at 60°C in the range^{5,7-8} of 70–75; we have used the value 72 given by Houwink and Staverman⁵. The ratio of disproportionation and recombination is in Eq. (1) given by the symbol λ whose value under our experimental conditions⁹ is 0.75. The value of the rate constant of monomer transfer (C_m) at 60°C is $1 \cdot 10^{-5}$ (ref.¹⁰). The calculated transfer constants C_s in dependence on the molar ratio of cyclohexanone in the polymerisation system are given in Fig. 1. Nevertheless that there was no reason to assume any variation of the rate of initiation¹¹ R_i , we have determined this value both in bulk and cyclohexanone solution. The induction period was determined with the use of 1,1-diphenyl-2-picrylhydrazyl. The value of R_i at 60°C and initiator concentration of $5 \cdot 10^{-3}$ mol/l was in bulk polymerisation $8.8 \cdot 10^{-8}$ mol/l s and in solution polymerisation ($\bar{x}_s = 0.59$) $9 \cdot 10^{-8}$ mol/l s. The efficiency of initiation, referring to the rate constant of spontaneous decomposition of the initiator at the same temperature, was about 0.85. This value is in good agreement with the data published by other authors who quote the initiation efficiency of 2,2'-azobis(isobutyronitrile)¹² 0.6–0.8.

TABLE I

Polymerization of Methyl Methacrylate (M) in Cyclohexanone (S) at 60°C Initiated with 2,2'-Azobis(isobutyronitrile) ($5 \cdot 10^{-3} \text{ mol l}^{-1}$)

\bar{x}_s Molar ratio of the solvent, R_p rate of polymerization ($\text{mol l}^{-1} \text{ s}^{-1}$), \bar{P}_n average degree of polymerisation, k_t^* termination constant ($\text{l mol}^{-1} \text{ s}^{-1}$), C_s and C_s^* transfer constants.

\bar{x}_s	S M	$R_p \cdot 10^4$		$1/\bar{P}_n \cdot 10^4$	$k_t^* \cdot 10^{-7}$	$C_s \cdot 10^4$	$C_s^* \cdot 10^4$
		exp.	ref. ³				
0	0	1.93	2.08	2.192	2.70	—	—
0.17	0.20	1.79	1.75	2.432	2.56	3.52	3.95
0.26	0.35	1.70	1.53	2.876	2.21	2.24	2.64
0.34	0.51	1.51	1.40	2.983	2.28	1.42	1.59
0.59	1.42	1.01	0.88	4.713	2.02	0.69	0.62
0.70	2.29	0.84	0.70	5.356	1.88	0.44	0.85
0.74	2.85	0.58 ^a	0.39	5.357	1.24	0.02	1.05

^a Initiator concentration $2.5 \cdot 10^{-3} \text{ mol/l}$.

TABLE II

Viscosities of Methyl Methacrylate-Cyclohexanone Mixtures (η), Values of Excess Molar Free Energy of Activation of the Flow (Δ^*G^E) and of Excess Molar Volume (ΔV^E)

Parameter d was calculated from Eq. (4).

\bar{x}_s	η , cP	Δ^*G^E , cal mol ⁻¹	ΔV^E , cm ³	d
25°C				
0	0.531	0	0	0
0.2	0.638	-49.3	0.071	-0.522
0.4	0.769	-96.4	0.130	-0.682
0.5	0.847	-118.3	0.126	-0.802
0.6	0.946	-131.1	0.156	-0.927
0.7	1.110	-116.1	0.142	-0.939
0.8	1.308	-97.5	0.117	-1.899
1.0	2.016	0	0	0
60°C				
0	0.359	0	0	0
0.2	0.421	-43.6	0.028	-0.413
0.5	0.552	-87.6	0.111	-0.534
0.8	0.797	-68.4	0.087	-0.650
1.0	1.109	0	0	—

The decreasing values of C_s with dilution of the monomer indicate an anomalous behaviour of this system in comparison with usual solution polymerisations. As k_t is usually effected by the viscosity in the first place^{13,14} the variation of the rate constant of termination k_t with increasing viscosity of the mixture could be expected. Moreover from the deviations from the rectilinear dependence of the viscosity or of the logarithm of viscosity vs mixture composition, it is possible to obtain information regarding the type and the degree of interactions of components of binary liquid mixtures¹⁵⁻¹⁷. Therefore, we have measured the viscosities of starting polymerisation mixtures of methyl methacrylate with cyclohexanone (Table II). In Fig. 2, there are given excess viscosities $\Delta\eta^E$ calculated according to the equation $\Delta\eta^E = \eta - (\bar{x}_1\eta_1 + \bar{x}_2\eta_2)$; where η is the viscosity of the mixture and the subscripts (1) and (2) refer to the components. Similarly the excess molar free energy of activation of the flow Δ^*G^E exhibits negative deviations (Table II). The values of Δ^*G^E were calculated from the equation $\Delta^*G^E = RT[\ln \eta V - (\bar{x}_1 \ln \eta_1 V_1 + \bar{x}_2 \ln \eta_2 V_2)]$, where V is the molar volume of the mixture calculated according to the relation $V = (M_1\bar{x}_1 + M_2\bar{x}_2)/\rho$; values of the mixtures density ρ were determined experimentally; V is the molar volume of the mixture, the subscripts (1) and (2) refer to the components; R is the gas constant and T is the temperature in K. In contrast to the

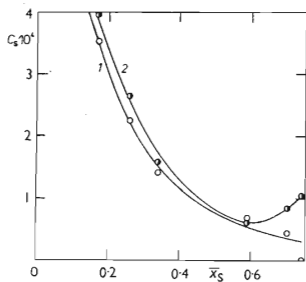


FIG. 1

Variations of Transfer Constant of Poly(Methyl Methacrylate) Growing Radical with Cyclohexanone in Dependence on Molar Ratio of Cyclohexanone (\bar{x}_s) in Polymerising Mixture at 60°

1 C_s , calculated with constant value of k_t ;
2 C_s^* , k_t^* as a function of \bar{x}_s was used in calculation.

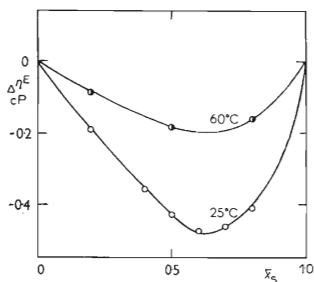


FIG. 2

Excess Viscosity $\Delta\eta^E$ in Dependence on Composition of Methyl Methacrylate-Cyclohexanone Mixture

functions mentioned above, the excess molar volumes $\Delta V^E = V - (\bar{x}_1 V_1 + \bar{x}_2 V_2)$ have the positive deviation from the rectilinear course (Table II).

DISCUSSION

Cyclohexanone as a Solvent for Methyl Methacrylate Polymerisation

As the linearity of the dependence $1/\bar{P}_n - A$ vs $[S]/[M]$ given by Eq. (1) is impaired, it is necessary to check the polymerisation system from the viewpoint of keeping constant condition at dilution. From the measurements of viscosities of the mixtures with different $[S]/[M]$ ratios it follows, that right from the beginning of the polymerisation at 60°C the viscosity increases from 0.35 cP in monomer to 1.11 cP in cyclohexanone. According to North and coworkers^{13,14} at such an increase of viscosity, the rate constant of termination falls down approximately four-times. The variations of k_t , assumed in the quoted papers, are so extensive that they should manifest themselves not only in the decrease of δ^2 but also in marked increase of the rate of polymerisation. This is substantiated by the fact that, besides added cyclohexanone a manifold increase in viscosity is caused by the polymer formed during polymerisation^{11,15}. But the experimentally determined conversions exhibit rectilinear dependence on time of polymerisation without showing any acceleration. The rates of bulk polymerisations determined from the polymerisations which were stopped at maximum con-

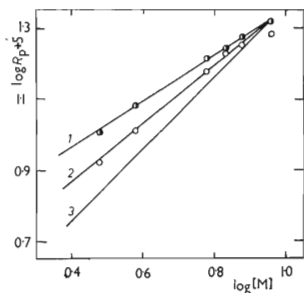


FIG. 3

Dependence of Rate of Solution Polymerisation of Methyl Methacrylate (R_p) on Monomer Concentration at 60°C

R_p : 1 calculated on the assumption that k_t varies according to (ref.¹³) and that the variation corresponds to the viscosity of initial polymerisation mixtures, 2 experimentally determined value, 3 theoretical value calculated from Eq. (3).

versions up to 8% are in good agreement with the rates determined from the following relation:

$$R_p = K_M \cdot [M] \cdot [I]^{0.5} \text{ (mol l}^{-1} \text{ s}^{-1}\text{)}, \quad (3)$$

the value of $K_M = 3.28 \cdot 10^{-4}$ at 60°C was taken from ref.¹.

The rates R_p determined for diluted monomer are higher than the calculated rates. The reaction order with respect to monomer is 0.8, which is quite close to unity, as it is assumed in the previously quoted equation (Fig. 3). The lower value than one indicates that the value of k_t falls with increasing cyclohexanone concentration. Therefore, assuming that other rate constants remain unchanged, we have calculated from Eq. (3) the values of k_t^* and δ^{*2} , respectively, which correspond to the experimentally determined value of R_p (Table I). The values calculated in this way indicate the variations of k_t caused by the presence of cyclohexanone and not by an increasing viscosity during the polymerisation system.

The rate constant of propagation k_p was several times reported^{13,16} to be unaffected at such a low viscosity of the medium. Also the rate of initiation can be considered to be independent of the composition and the viscosity of the mixture¹¹. On the basis of the literature data and own experimental results we think that it is justifiable to consider only the changes of k_t , and take other elementary rate constants of polymerisation unchanged. C_s^* values, calculated from corrected values of δ^{*2} , vary with dilution of the system similarly as C_s values (Table I, Fig. 1), with the exclusion of \bar{x}_s higher than 0.6. The facts so far quoted give us the reason to believe that the observed decrease of C_s and C_s^* , respectively, with dilution is due to an altered rate of the substitution reaction.

Transfer Constant and Intermolecular Interactions in the System Monomer-Solvent

From the study of the substitution reactions of radicals follows, that the intensity of the reaction is influenced also by intermolecular interactions of the components. It is assumed that the reactivity of a medium, or of a radical, depends on the concentration of the components which form molecular complexes, e.g. electron donor-acceptor complexes^{17,18}. Transfer reactions of radicals are probably effected also by intermolecular forces of some other character^{19,20}. The curves representing the dependence of C_s on the composition of the transfer agent may exhibit either positive and negative deviation from the additivity rule or to proceed through an inflexion.

In the polymerising system methyl methacrylate-cyclohexanone, the C_s values decrease considerably with increasing cyclohexanone concentration. A very similar phenomenon was observed by Olaj¹⁷ when diluting styrene with tetrachloromethane. The fall of the intensity of the substitution reactions is ascribed to the electron donor-acceptor complex which has lower reactivity than the individual free components. However, the presence of such a complex could not be proved with certainty by spectroscopic measurements.

The transfer constants C_s^* , which can be taken as more precise data than C_s , do not fall monotonously in the studied range of \bar{x}_s , but exhibit a curve with the minimum at $\bar{x}_s \sim 0.6$ (Fig. 1). The minimum value of C_s^* was found at the same composition of the mixture monomer-solvent at which also the functions $\Delta\eta^E$ and Δ^*G^E exhibit minimum values. Hence, it is possible to seek a direct connection between the force of interactions of molecules in the system and the intensity of substitution reactions.

Negative deviations of the viscosity or of $\Delta\eta^E$ in the dependence on the composition of binary liquid mixtures, which were also observed with methyl methacrylate-cyclohexanone mixtures, become more apparent the disperse forces are responsible for the components interactions²¹⁻²³; as a more objective measure for the interaction forces is considered the parameter d from the following equation

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

The calculated values of d for methyl methacrylate and cyclohexanone are quoted in Table II. Relatively high negative values of $\Delta\eta^E$ and of the parameter d should indicate the absence of specific interactions between unlike molecules²³. The large changes of d observed also indicate the variation of the intensity of interactions of like molecules with dilution of the monomer with cyclohexanone²¹. Therefore, it is possible to judge that in the system studied the interactions among cyclohexanone molecules take place at increasing dilution of methyl methacrylate with cyclohexanone. Decreasing values of \bar{C}_s with increasing \bar{x}_s could be explained by the formation of a ternary system which includes cyclohexanone associates of lower reactivity at substitution reactions than free cyclohexanone.

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