

High conversion polymerization of methyl methacrylate in the presence of poly(methyl methacrylate) of different relative molecular mass

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Received 12 August 1982

Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

The initial rate of heat evolution for methyl methacrylate polymerization (v_0) is decreased by adding poly(methyl methacrylate) into the polymerization system. The effect of poly(methyl methacrylate) on the value of v_0 is a function of concentration and relative molecular mass of poly(methyl methacrylate). The addition of polymer does not significantly influence the maximum rate of polymerization, but shortens the time needed to reach it as well as the overall time period of polymerization. In the presence of solvent cyclohexanone the value of v_0 is not affected by poly(methyl methacrylate) addition.

Начальная скорость тепловыделения (v_0) при полимеризации метил-метакрилата понижается при добавлении полиметилметакрилата в полимеризационную систему. Влияние полиметилметакрилата на скорость v_0 является функцией концентрации и относительного молекулярного веса полиметилметакрилата. Добавление полимера не изменяет существенно максимальную скорость полимеризации, но сокращает время необходимое для ее достижения и также общий полупериод полимеризации. В присутствии циклогексанона как растворителя значение v_0 не зависит от добавки полиметилметакрилата.

The decrease in initial rate of polymerization due to a polymer added into the system, the so-called negative template effect [1] is documented by many examples in the literature [2—5]. In spite of this fact, the nature of this effect is not, however, reliably explained [4—7]. In the papers dealing with the effect of added polymer on polymerization kinetics hitherto published the attention is mainly given to initial

stage of polymerization. The effect of added polymer on the course of polymerization in the whole region of monomer conversion has not been studied adequately by now. This is quite surprising because of a great practical importance of such studies, e. g. for preparation of high impact polystyrene. It was therefore the aim of this work to appreciate the influence of the added polymer of different relative molecular mass on the course of polymerization up to high monomer conversions in the presence and/or absence of solvent. As a model system methyl methacrylate—poly(methyl methacrylate) was selected.

Experimental

Methyl methacrylate was purified by repeated distillation under reduced pressure of nitrogen (100 Pa). Cyclohexanone was purified by thermostating at 90 °C, stirring and bubbling with nitrogen for 2 h in the presence of 1 mass % of iron(II) sulfate. Afterwards, it was filtered, dried with anhydrous calcium chloride and distilled under reduced pressure of nitrogen at 110–120 °C. 2,2'-Azobisisobutyronitrile was purified by twofold crystallization from ethanol and its melting point was 103.5 °C. Poly(methyl methacrylate) of different relative molecular mass was prepared by polymerization of methyl methacrylate using various concentrations of 2,2'-azobisisobutyronitrile as initiator [8].

For the measurement of the heat evolved during polymerization a differential scanning calorimeter DSM-2M (USSR) was used. The polymerization mixtures were prepared by mixing a solution of poly(methyl methacrylate) in methyl methacrylate with a solution of 2,2'-azobisisobutyronitrile in methyl methacrylate or in the mixture of methyl methacrylate with cyclohexanone. The calorimetric measurements were performed according to the procedure described in paper [9]. The presented results of experimental measurements are arithmetic means of two measurements at least.

Results and discussion

A typical calorimetric record of methyl methacrylate bulk polymerization is represented in Fig. 1. After a relatively short induction period (*ca.* 300 s) the rate of polymerization heat evolution reaches in the course of 20–50 s the initial value v_0 . The section of practically constant rate of polymerization v_0 is subsequently succeeded by a rapid increase in the rate of polymerization heat evolution which reaches the maximum value v_{\max} and afterwards gradually decreases to attain the zero value. The zero rate of polymerization heat evolution indicates that the polymerization is practically finished (limiting monomer conversion > 90 %).

It results from Fig. 1 as well as from the values in Table 1 that an addition of poly(methyl methacrylate) influences the value of v_0 while the value of v_{\max} remains without any significant change. In general, the functional dependence of

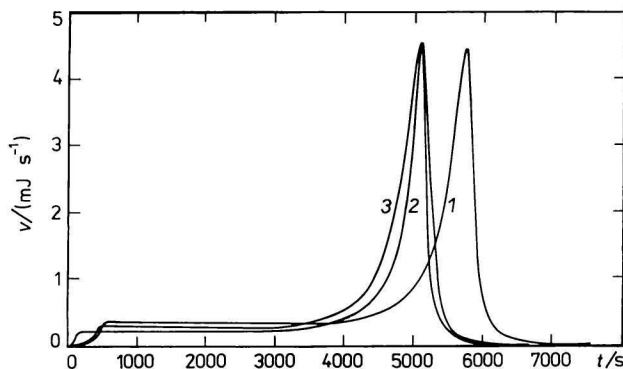


Fig. 1. Variation of the rate of heat evolution (mJ s^{-1}) with time (s) for methyl methacrylate bulk polymerization in the presence and/or absence of the added poly(methyl methacrylate) of viscometric relative molecular mass of 160 000. Concentration of 2,2'-azoisobutyronitrile $5 \times 10^{-2} \text{ mol dm}^{-3}$, temperature 60°C .

1. Without any addition of poly(methyl methacrylate), mass of polymerization mixture 8.42 mg; 2. 1 mass % of poly(methyl methacrylate) referred to methyl methacrylate, mass of polymerization mixture 7.45 mg; 3. 5 mass % of poly(methyl methacrylate) referred to methyl methacrylate, mass of polymerization mixture 8.14 mg.

the ratio of the initial polymerization rate in the presence of a polymer and of the initial polymerization rate in the absence of a polymer is described by a plot [4] with minimum and the position of this minimum is determined not only by concentration but also by relative molecular mass of the added polymer. This seems to be valid also for the case of methyl methacrylate polymerization in the presence of poly(methyl methacrylate) (Table 1).

The overall period of exothermic peak (of polymerization) varies in the range 5900—7000 s. The time of polymerization gets shorter by the effect of poly(methyl methacrylate) addition and this reduction is more conspicuous at higher concentration and especially if poly(methyl methacrylate) of higher relative molecular mass is used. The reaction time necessary to reach the maximum rate of polymerization heat evolution also decreases in the presence of added poly(methyl methacrylate) (Fig. 1), which means that the gel effect takes place at lower conversions when compared with the conversions necessary for inception of the gel effect in the absence of added poly(methyl methacrylate).

The retarding effect of the added poly(methyl methacrylate) on the initial rate of polymerization [1] is eliminated by the effect of solvent. The ratio $v_{0, \text{PMMA}}/v_0$ in the presence of solvent approximates the value of 1 (Table 2). Possible causes of elimination of the effect of the added polymer on the initial rate of polymerization

Table 1

Variation of the initial v_0 and maximum v_{\max} rate of heat evolution for methyl methacrylate bulk polymerization and polymerization heat ΔH with concentration and relative molecular mass of the added poly(methyl methacrylate)
Concentration of 2,2'-azoisobutyronitrile $5 \times 10^{-2} \text{ mol dm}^{-3}$, temperature 60°C

PMMA ^a	w/mass % of PMMA referred to monomer	$\frac{v_0}{\text{J mol}^{-1} \text{ s}^{-1}}$	$\frac{v_{0, \text{PMMA}}^b}{v_0}$	$\frac{v_{\max}}{\text{J mol}^{-1} \text{ s}^{-1}}$	$\frac{\Delta H^c}{\text{kJ mol}^{-1}}$	$\frac{\Delta H^d}{\Delta H'}$
—	—	4.7	1.00	66.3	−56.6	1.00
19 400	1	4.6	0.99	66.6	−53.5	0.95
	3	4.1	0.87	64.0	−51.5	0.91
	5	3.9	0.85	60.3	−50.5	0.89
	1	4.7	0.99	64.4	−54.2	0.96
61 000	3	4.3	0.93	63.8	−53.3	0.94
	5	3.9	0.84	60.4	−49.7	0.88
	1	3.0	0.65	66.7	−47.8	0.85
160 000	3	3.7	0.80	63.2	−49.6	0.88
	5	4.2	0.89	61.6	−50.2	0.89

a) Poly(methyl methacrylate) of a given viscometric relative molecular mass.

b) The ratio $v_{0, \text{PMMA}}/v_0$ is referred to initial rates of polymerization heat evolution in the reaction mixture containing the added poly(methyl methacrylate) and in the reaction mixture without any addition of poly(methyl methacrylate).

c) For methyl methacrylate bulk polymerization the values of $-55.7 \text{ kJ mol}^{-1}$ and $-58.2 \text{ kJ mol}^{-1}$ were reported [12, 13] for 74.5 and 76.8°C , respectively.

d) $\Delta H' = -56.6 \text{ kJ mol}^{-1}$.

Table 2

Variation of the ratios of initial rates of heat evolution, reaction heats and maximum rates of heat evolution for methyl methacrylate polymerization in the presence and/or absence of poly(methyl methacrylate) with cyclohexanone (CHx) concentration in the reaction mixture
Concentration of 2,2'-azoisobutyronitrile $5 \times 10^{-2} \text{ mol dm}^{-3}$, temperature 60°C

$\frac{[\text{CHx}]}{\text{mol dm}^{-3}}$	$\frac{v_{0, \text{PMMA}}^a}{v_0}$	$\frac{\Delta H_{\text{PMMA}}^a}{\Delta H'}$	$\frac{v_{\text{max}}}{\text{J mol}^{-1} \text{ s}^{-1}}$	$\frac{v_{\text{max, PMMA}}^a}{\text{J mol}^{-1} \text{ s}^{-1}}$
—	0.93	0.94	66.3	63.8
0.48	0.95	0.99	55.3	57.6
0.96	1.02	0.98	45.2	41.7
1.35	0.99	0.99	36.3	39.8
1.93	0.97	1.03	26.5	27.7

a) Index PMMA in $v_{0, \text{PMMA}}$, $v_{\text{max, PMMA}}$, and ΔH_{PMMA} denotes the values obtained for these quantities in the system containing 3 mass % of poly(methyl methacrylate) of viscometric relative molecular mass of 61 000. Mass fraction is referred to monomer and solvent or only to monomer; $\Delta H' = -56.6 \text{ kJ mol}^{-1}$.

have been discussed in previous paper [1]. With respect to eventual influence of solvent on polymerization kinetics [10], it is necessary to make some pertinent corrections for the determined value of the rate of polymerization. This circumstance was taken into consideration in summarization of the data given in Table 2. The added solvent significantly reduces the value of v_{max} , i.e. suppresses the gel effect [11] of methyl methacrylate polymerization. If the concentration of solvent is high enough (for the case discussed this concentration is 4.8 mol dm^{-3}), the gel effect is not to be observed. From these experimental results one could therefore conclude that in the presence of solvent the kinetic differences between polymerization system with added polymer and polymerization system without added polymer are practically eliminated.

The decrease in the values of reaction heats of polymerization accompanied by a decrease in the values of initial polymerization heat evolution rates (Table 1) is evidently due to difficulties in preserving the calibration of the DSC instrument for the whole period of experiments. The calibration was accomplished by melting a standard substance with known latent heat of fusion. Such melting process proceeds rapidly and a calibration based on this process would not allow for the heat losses during lengthy polymerization [14]. However, it has recently been shown [15] that the heat of methyl methacrylate polymerization does not depend on reaction rate, i.e. time of polymerization, if this time is relatively short (less than 30 min). In such instance the reasonable value of the polymerization heat is obtained.

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Translated by R. Domanský