Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Effect of Some Solvents on the Radical Polymerization of Methyl Methacrylate Studied by Differential Scanning Calorimetry

T. Malavašič[a]; U. Osredkar[a]; I. Anžur[a]; I. Vizovišek[a]
[a] Boris Kidrič Institute of Chemistry, Ljubljana, Yugoslavia

To cite this Article Malavašič, T. , Osredkar, U. , Anžur, I. and Vizovišek, I.(1988) 'Effect of Some Solvents on the Radical Polymerization of Methyl Methacrylate Studied by Differential Scanning Calorimetry', Journal of Macromolecular Science, Part A, 25: 1, 55 — 64

To link to this Article: DOI: 10.1080/00222338808053365

URL: http://dx.doi.org/10.1080/00222338808053365

J. MACROMOL. SCI.–CHEM., A25(1), pp. 55-64 (1988)

EFFECT OF SOME SOLVENTS ON THE RADICAL POLYMERIZATION OF METHYL METHACRYLATE STUDIED BY DIFFERENTIAL SCANNING CALORIMETRY

T. MALAVAŠIČ, U. OSREDKAR, I. ANŽUR, and I. VIZOVIŠEK

Boris Kidrič Institute of Chemistry
61000 Ljubljana, Yugoslavia

ABSTRACT

The course of the isothermal polymerization of methyl methacrylate in different concentrated solutions in toluene, *n*-butyl acetate, cyclohexanone, and dimethylformamide was measured at four temperatures by differential scanning calorimetry. The conversions at the sharp increase of the reaction rate were found to increase with dilution of the reaction mixture. The polymerization enthalpies and the composite rate constants were calculated. The polymerization enthalpies seem to be solvent independent. The composite rate constants for polymerization in butyl acetate are lower and those for polymerization in toluene are equal to the constants for bulk polymerization. They are independent of the concentration of the reaction system. The constants for polymerization in cyclohexanone and dimethylformamide are, however, concentration dependent. An interrelation between the composite rate constants and solubility parameters of the solvents and methyl methacrylate was found. The relative molecular weight averages decrease with decreasing concentration of the reaction mixture. The MW distributions were very broad.

INTRODUCTION

The presence of a solvent in the radical polymerization of vinyl monomers obviously influences the course and mechanism of the reaction, particularly the diffusion-controlled termination [1, 2]. The effect of different solvents, mostly aromatic solvents, on the radical polymerization and on the propagation rate constant has been explained in terms of complex formation of radicals with the solvents [3-7], but the complex formation was not confirmed by NMR [8]. An effect of the solubility parameter was observed for the polymerization of butyl acrylate [9].

In contrast to acrylic acid esters or other vinyl monomers, the course of polymerization of short-chain methacrylic acid esters is specific: the initial stage of the nearly constant reaction rate is prolonged and, therefore, the composite rate constants can be calculated from DSC measurements [10, 11].

The aim of this work was to study the effect of toluene (T), *n*-butyl acetate (BA), cyclohexanone (CON), and dimethylformamide (DMF) (as solvents of very different viscosities and chemical character) on the course of polymerization and the composite rate constants for the polymerization of methyl methacrylate (MMA).

EXPERIMENTAL

Materials

Monomers were freed of inhibitor by washing with 5% NaOH solution and distilled under nitrogen at reduced pressure. The initiator 2,2′-azoisobutyronitrile (AIBN) was recrystallized from absolute ethanol and stored in the dark at -25°C. Solvents were of p.a. grade and distilled before use.

Method

The courses of the isothermal polymerization of 95, 90, 85, 80, and 50 wt% solutions of MMA in T, BA, CON, and DMF were measured at 353, 358, 363, and 368 K with a Perkin-Elmer DSC-2 differential scanning calorimeter. To initiate the polymerization, 50 mmol/L of AIBN was added. Since the reaction rates were proportional to the released enthalpy, relative reaction rates were measured by the ordinate displacement of the DSC curves. The values were comparative ones, given in arbitrary units of millimeter chart displacement. The conversions at the onset of the accelerated reaction were obtained by graphical extrapolation of the initial and the accelerated rate of polymerization [12]. The enthalpies of polymerization and the composite rate constants were calculated from the areas between the DSC curves and the baseline, which were obtained by back-extrapolation of the straight line after the polymerization was terminated. The calorimeter was calibrated with the melting enthalpy of indium. The DSC curves were digitized on-line and processed by computer.

The molecular weight averages of the poly(methyl methacrylates) (PMMA) obtained were measured by gel permeation chromatography (GPC) relative to polystyrene standards. A Waters pump Model 510, μ-Styragel columns with pore sizes of 10^{-5}, 10^{-6}, 10^{-7}, and 5×10^{-8} m, and a differential refractometer were used as a detector. The measurements were performed in tetrahydrofuran with a flow rate of 60 mL/h.

RESULTS AND DISCUSSION

The polymerizations of MMA at different concentrations in toluene at 363 K are shown in Fig. 1. Similar curves were obtained with the other three solvents. It can be seen that the time of the nearly constant reaction rate increases and that the relative initial and maximal rates in the accelerated reaction rate region decrease with dilution. The values for all the systems are given in Table 1.

On comparing the relative initial rates, it can be seen that the differences between solvents are in the range of the experimental error, with a tendency to be lower in BA and higher in DMF. The values increase in the measured temperature range from 353 to 368 K by a factor of ~3.

The influence of the type of solvent and, even more, of the solution concentration is much more noticeable for the relative maximal rates in the region of the gel effect. The decrease of the maximal rates with dilution is lowest for CON. The maximal rates in 80% solutions were lower than the initial rates for T and DMF at 363 and 368 K. The same phenomenon was observed for BA at 368 K. Accelerated reaction was not observed for any 50% solutions.

The conversions at the onset of the accelerated reaction in the measured temperature interval were found to be independent of temperature for any concentration (Table 2). The conversions at the onset of the sharp increase of reaction rate are highest in T solutions.

The polymerization enthalpies, extrapolated to 100% MMA, are in the range 59 ± 3 kJ/mol for all measured systems.

The conversion is proportional to the released enthalpy of polymerization.

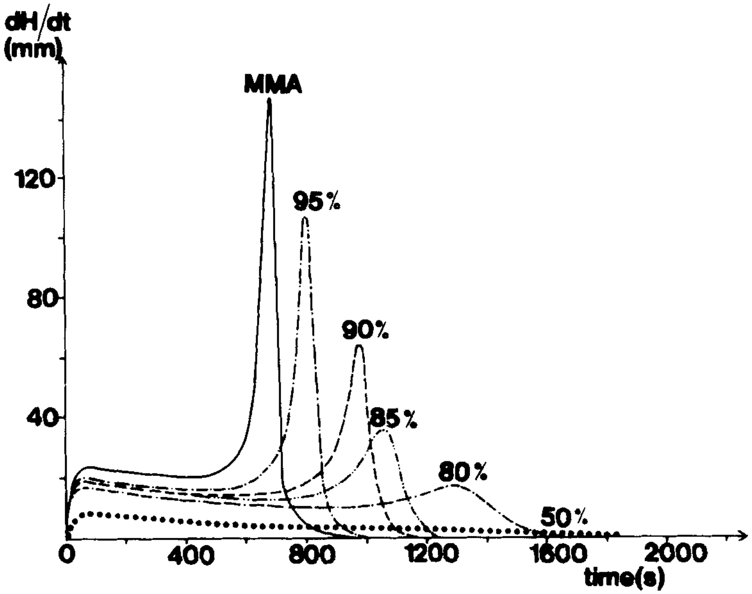

FIG. 1. Courses of isothermal polymerization of MMA in 95, 90, 85, 80, and 50 wt% solutions in toluene at 363 K, [AIBN] = 50 mmol/L.

From plots of ln $(A/A - a)$ vs time [10] (where A is the total area and a is the partial area to time t between the DSC curves and the baseline), the composite first-order polymerization rate constants k' were calculated (Table 3). Since k' is equal to the polymerization rate R_p divided by the concentration of the monomer [M], they should be equal for all concentrations if the solvent does not influence the reaction mechanism:

$$k' = k_p(fk_d[I_0]/k_t)^{1/2} = R_p/[M], \qquad (1)$$

where k_p, k_d, and k_t are the rate constants for polymerization, initiator dissociation, and termination; and $[I_0]$ is the initial initiator concentration.

It can be seen that k' for polymerization in T does not differ from that for bulk polymerization, while k' in BA is lower and independent of concentration. In CON, and even more in DMF, k' increases with dilution of the reaction mixture.

No relation between the rate constants and the viscosity of the solvents

TABLE 1. Relative Initial Rates and Maximal Rates in the Gel Effect Region for Solution Polymerization of MMA in Toluene (T), *n*-Butyl Acetate (BA), Cyclohexanone (CON), and Dimethylformamide (DMF) at Different Concentrations of the Reaction Mixtures[a]

Temperature, K	95%				90%				85%				80%			
	T	BA	CON	DMF	T	BA	CON	DMF	T	BA	CON	DMF	T	BA	CON	DMF
	Relative initial rates[b]															
353	9.7	8.1	10.1	11.3	9.8	8.3	9.8	12.1	9.2	8.0	9.5	10.3	7.3	7.2	6.8	10.7
358	13.8	11.8	14.4	15.0	13.6	12.1	14.4	15.8	13.6	9.8	13.8	14.3	11.6	10.4	12.6	15.7
363	20.4	16.8	21.4	21.2	20.2	17.2	20.8	22.4	19.1	14.6	19.4	20.9	16.9	14.9	18.8	21.9
368	29.8	23.8	29.8	30.2	27.8	23.9	29.2	30.0	27.0	20.7	27.1	28.5	24.5	21.0	25.6	29.5
	Relative maximal rates[b] at the gel effect															
353	69.9	65.4	70.6	73.1	47.9	45.9	55.6	54.2	30.1	32.1	36.4	33.0	14.7	16.3	22.3	18.9
358	85.8	80.6	87.4	91.8	56.0	54.3	65.6	63.8	33.8	35.3	42.9	35.5	15.8	17.7	25.2	19.9
363	106.6	95.4	108.2	104.6	64.6	62.0	77.6	72.2	35.6	29.7	47.6	38.7	16.3	18.1	27.1	19.7
368	117.8	110.2	120.6	122.2	68.0	64.9	86.4	76.2	36.8	29.7	49.6	39.7	16.5	18.9	26.9	20.2

[a] In wt%; [AIBN] = 50 mmol/L.

[b] In arbitrary units of millimeter chart displacement per 10 mg of reaction mixture.

TABLE 2. Conversions[a] at the Onset of the Accelerated Reaction Rate in the Solution Polymerization of MMA in Toluene (T), *n*-Butyl Acetate (BA), Cyclohexanone (CON), and Dimethylformamide (DMF) at Different Concentrations

	Concentration, wt%			
Solvent	95	90	85	80
T	47.1	56.9	60.7	69.0
BA	47.0	51.7	54.9	63.9
CON	45.1	50.0	57.6	62.9
DMF	47.7	54.4	57.9	63.5

[a] In %; [AIBN] = 50 mmol/L.

could be found. However, the difference between solubility parameters of the solvents and MMA was found to be related to k' as follows: The solubility parameter of BA is smaller than that of MMA, and k' for polymerization in BA is smaller than k' for bulk polymerization and independent of concentration. The solubility parameters of T and MMA are very near, and k' for the polymerization in T and in bulk are equal. The solubility parameters of CON and DMF are higher than the solubility parameter of MMA, and k' for the polymerization of MMA in CON and DMF is higher than for bulk polymerization and dependent on concentration (Table 4).

The observed differences in overall rate constants and rate of polymerization as a function of solubility parameter can be explained by changes in the monomer concentration in the neighborhood of the growing radical due 1) to differences in the miscibility of monomer and solvent and 2) to differing expansion of polymer molecules.

The relative molecular weight averages are given in Table 5. The MW distributions for polymers synthesized in 95% solutions were very broad but became narrower with dilution of the reaction mixture. The measurements for the same sample varied when repeated, especially for the 95% solutions, which could be ascribed to the increased pressure in the GPC columns due to the accumulation of microgel often present in methacrylic acid esters polymers.

TABLE 3. Composite Rate Constants, k', for the Polymerization of MMA in Toluene (T), *n*-Butyl Acetate (BA), Cyclohexanone (CON), and Dimethylformamide (DMF)[a]

Temperature, K	$k' \times 10^3$, s^{-1}																				
		95%				90%				85%				80%				50%			
	100%	T	BA	CON	DMF	T	BA	CON	DMF	T	BA	CON	DMF	T	BA	CON	DMF	T	BA	CON	DMF
353	0.46	0.46	0.39	0.47	0.50	0.46	0.39	0.50	0.53	0.46	0.40	0.48	0.50	0.43	0.39	0.50	0.57	0.48	0.38	0.63	0.85
358	0.67	0.67	0.57	0.67	0.68	0.66	0.59	0.74	0.75	0.68	0.56	0.71	0.72	0.64	0.57	0.71	0.82	0.67	0.53	0.82	1.13
363	0.95	0.98	0.80	0.98	0.99	0.97	0.84	1.05	1.07	0.98	0.82	1.01	1.04	0.94	0.81	1.01	1.16	0.94	0.85	0.98	1.29
368	1.34	1.45	1.18	1.41	1.40	1.38	1.21	1.52	1.47	1.38	1.21	1.44	1.48	1.31	1.13	1.42	1.61	1.47	1.12	1.45	1.63

[a] [AIBN] = 50 mmol/L.

TABLE 4. Viscosities, Solubility Parameters, and Composite Rate Constants (k') for the Polymerization of MMA in Bulk and in Solutions in Toluene (T), *n*-Butyl Acetate (BA), Cyclohexanone (CON), and Dimethylformamide (DMF)[a]

Solvent	Viscosity, mPa·s at 25°C	Solubility parameter × 10^{-3} [13], $(J/m^3)^{1/2}$	$k' \times 10^3, s^{-1}$			
			100%	95%	80%	50%
BA	0.688	17.31		0.39	0.39	0.38
T	0.552	18.23		0.46	0.43	0.48
CON	2.20	20.21		0.47	0.50	0.63
DMF	0.802	24.84		0.50	0.57	0.85
MMA	0.565	18.0	0.46			

[a] At 353 K; [AIBN] = 50 mmol/L.

TABLE 5. Relative Molecular Weight of Poly(Methyl Methacrylates), Synthesized at Different Concentrations[a] in Toluene (T), *n*-Butyl Acetate (BA), Cyclohexanone (CON), and Dimethylformamide (DMF)[b]

Solvent	$\overline{M}_w \times 10^{-4}$				
	95%	90%	85%	80%	50%
T	14.4	9.2	8.7	8.0	2.5
BA	14.9	10.0	9.2	8.1	2.5
CON	15.3	9.5	9.0	7.4	2.7
DMF	16.2	9.1	8.7	5.5	2.4

[a] In wt%.

[b] At 358 K.

CONCLUSIONS

The initial rates and maximal rates of polymerization in the gel effect region decrease and the conversions at the sharp increase of reaction rate increase with dilution of the reaction system. The values are also dependent on the solvent. In 50% solutions the strongly accelerated reaction was not observed any more.

The composite rate constants vary with the solvent. For polymerization in BA they are lower and for polymerization in T they are equal to the constants for bulk polymerization, and for both solvents they are independent of concentration from 95 to 50 wt%. The constants for polymerization in CON and DMF are higher than for bulk polymerization, and they increase with dilution. The rate constants were found to be independent of solvent viscosity but dependent on their solubility parameters.

The relative molecular weight averages of PMMA and the breadth of the distributions decrease with dilution. Due to microgel present in the samples, the values were not reliable enough to make firm conclusions from these measurements.

REFERENCES

[1] A. M. North and G. A. Reed, *Trans. Faraday Soc.*, *85*, 859 (1961).

[2] A. M. North and G. A. Reed, *J. Polym. Sci., Part A*, *1*, 1311 (1963).

[3] D. B. Anderson, G. M. Burnett, and A. C. Govan, *Ibid.*, 1465 (1963).

[4] G. Henrici-Olivé and S. Olivé, *Z. Phys. Chem.*, *48*, 35 (1966).

[5] C. H. Bamford and S. Brumby, *Makromol. Chem.*, *105*, 122 (1967).

[6] Gy. Fenyvesi, A. Fehervari, T. Földes-Berezsnich, and T. Tudös, *J. Macromol. Sci.-Chem.*, *A22*, 203 (1985).

[7] M. Kamachi, D. J. Liaw, and S. Nozakura, *Polym. J.*, *13*, 41 (1981).

[8] P. E. M. Allen and B. O. Bateup, *Eur. Polym. J.*, *9*, 1283 (1973).

[9] M. Kamachi, M. Fujii, S. Ninomiya, S. Katsuki, and S. Nozakura, *J. Polym. Sci., Polym. Chem. Ed.*, *20*, 1489 (1982).

[10] T. Malavašić, I. Vizovišek, S. Lapanje, and A. Može, *Makromol. Chem.*, *175*, 837 (1974).

[11] T. Malavašić, U. Osredkar, I. Anžur, and I. Vizovišek, *J. Macromol. Sci.-Chem.*, *A19*, 987 (1983).

[12] T. Malavašić, U. Osredkar, I. Anžur, and I. Vizovišek, *J. Therm. Anal.*, *29*, 697 (1984).

[13] H. Burell in *Polymer Handbook,* 2nd ed. (J. Brandrup and E. H. Immergut, eds.), Wiley-Interscience, New York, 1975, IV 337-359.

Received March 3, 1987
Revision received June 11, 1987