Influence of Poor Solvents in Radical Polymerizations of Methyl Methacrylate

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ABSTRACT: Radical polymerizations of methyl methacrylate (MMA) were carried out in the presence of poor solvents for poly(methyl methacrylate) (PMMA) at 60°C. At 40 vol% or above of n-hexane and at 50 vol% of cyclohexane, the solutions became turbid during polymerization and the polymers precipitated. But the precipitates were not observed in methanol (≤ 50 vol%). The kinetic order of the initiator was 0.5 when no precipitate was observed, but it became less than 0.5 when the precipitate was present. Under homogeneous conditions, the values of $(1+x)k_t/k_p^2$ were determined from the relations between $1/P_n$ and R_p, and varied with the viscosity of the system. When a precipitate was observed, k_t/k_p^2 could not be determined. It is concluded that when a precipitate is observed, the propagating radical grows large enough to precipitate by itself and the termination rate decreases.
KEY WORDS Radical Polymerization / Methyl Methacrylate / Poor
Solvent / Inhomogeneous System / Kinetic /

Radical polymerizations of vinyl monomers in good solvents have been well studied.[1] However, radical polymerizations in poor solvents for polymer have not been established well. For example, in the radical polymerization of styrene in poor solvents Barton et al.[2] reported that k_t (termination rate constnat) was proportional to the reciprocal viscosity of the system, but Cameron et al.[3] reported that k_t was smaller than that in a good solvent.

Since the above results on styrene polymerization are in disagreement, we investigated radical polymerizations of styrene in poor solvents and got different results[4] from those as follows: (1) in both methanol (30, 40, and 50 vol%) and isopropanol (40 and 50 vol%), turbidity and precipitation were observed, but in cyclohexane and n-hexane no turbidity or precipitation was observed; (2) when turbidity and precipitation were observed, the termination rate was markedly enhanced, but when

not observed, this rate constant varied with the reverse viscosity of the medium as in good solvents.[5]

In this study, we carried out radical polymerizations of methyl methacrylate (MMA) in methanol, cyclohexane, and n-hexane, and found phenomenon contrary to that in styrene polymerization.

EXPERIMENTAL

MMA was washed with 5% NaOH aq solution and water, dried over anhydrous Na_2SO_4 and distilled under reduced nitrogen pressure three times. AIBN (α,α'-azobisisobutyronitrile) was recrystallized from methanol. Methanol, cyclohexane and n-hexane were purified by the methods described in "Organic Solvents."[6]

MMA, AIBN and poor-solvent (≥ 50 vol%) were placed in a Pyrex glass tube and the

mixture was degassed by the freezing–pumping–thawing method. Then the tube was sealed off and placed in a thermostat water bath at 60°C. Poly(methyl methacrylate) (PMMA) was precipitated with cool methanol, filtered and dried under vacuum. The rate of polymerization (R_p) was determined from the weight of polymer. The average degree of polymerization (P_n) was determined from the intrinsic viscosity ([η]) of benzene solution at 30°C according to eq 1. The values of $(1+x)k_t/k_p^2$ were determined from the slopes of the relations between $1/P_n$ and R_p according to eq 2.

$$\log P_n = 3.420 + 1.13 \log[\eta] \qquad (1)$$

$$1/P_n = (1+x)(k_t/k_p^2)(R_p/[\text{MMA}]^2) + C_m$$
$$+ C_s[\text{S}]/[\text{MMA}] + C_i[\text{AIBN}]/[\text{MMA}] \quad (2)$$

RESULTS AND DISCUSSION

In the radical polymerization of styrene, turbidity and precipitate were observed in methanol ($\geqq 30$ vol%),[4] while not even turbidity was observed in the polymerization of MMA in methanol. On the other hand, turbidity and precipitation were observed in the polymerizations of MMA in cyclohexane (50 vol%) and n-hexane ($\geqq 40$ vol%), but in the polymerizations of styrene in the above poor solvents, turbidity and precipitation were not observed.

R_p determined gravimetrically are listed in Table I and R_p dependences on initiator concentration are shown in Fig. 1 (a)—(c). The values of R_p for a [methanol] = 10—50 vol%, [cyclohexane] = 10—40 vol% and [n-hexane] = 10—40 vol% in which no turbidity was observed were proportional to the square root

Table I. Results of radical polymerizations of MMA in poor-solvents at 60°C

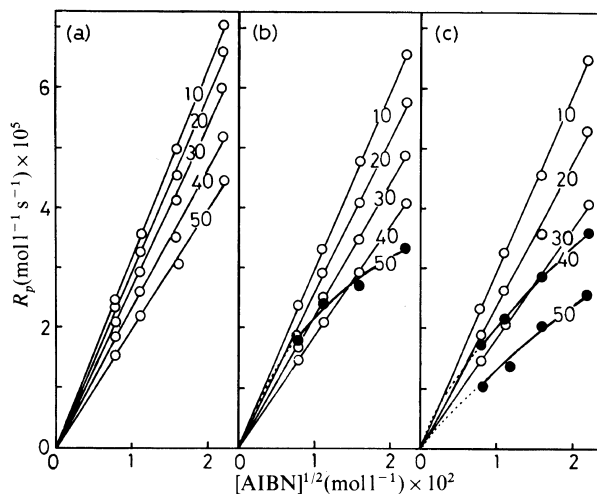| [MMA]	[AIBN] $\times 10^4$	Methanol		Cyclohexane		n-Hexane	
		$R_p \times 10^5$	$(1+x)k_t$	$R_p \times 10^5$	$(1+x)k_t$	$R_p \times 10^5$	$(1+x)k_t$
vol%	mol l^{-1}	mol l^{-1} s^{-1}	k_p^2	mol l^{-1} s^{-1}	k_p^2	mol l^{-1} s^{-1}	k_p^2
90	4.92	7.07		6.56		6.46	
	2.46	4.95	53	4.78	64	4.54	61
	1.22	3.58		3.30		3.25	
	0.61	2.44		2.36		2.32	
80	4.92	6.60		5.75		5.31	
	2.46	4.54	54	4.08	63	3.58	70
	1.22	3.26		2.88		2.64	
	0.61	2.31		2.01		1.86	
70	4.92	6.00		4.91		4.10	
	2.46	4.13	55	3.46	68	2.83	87
	1.22	2.91		2.50		2.02	
	0.61	2.07		1.69		1.45	
60	4.92	5.14		4.08		3.62	
	2.46	3.51	57	2.90		2.82	
	1.22	2.59		2.09		2.14	
	0.61	1.81		1.40		1.73	
50	4.92	4.42		3.33		2.56	
	2.46	3.03	54	2.72		2.03	
	1.22	2.18		2.14		1.33	
	0.61	1.51		1.56		1.04	

Figure 1. Dependence of R_p on AIBN concentration in methanol: (a), cyclohexane; (b), n-hexane, (c), at 60°C. Numbers and black circles in the figures indicate vol% of poor-solvent and precipitation, respectively.
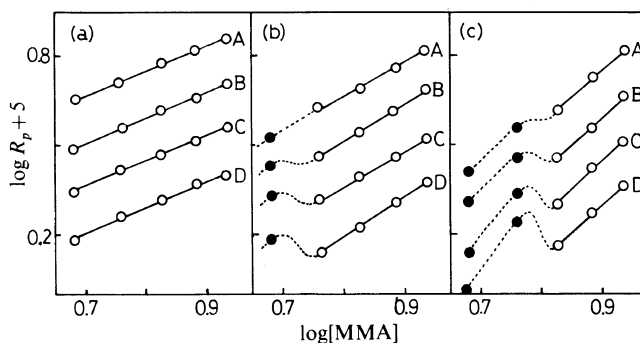

Figure 2. Dependence of R_p on MMA concentration in methanol; (a), cyclohexane; (b), n-hexane; (c), at 60°C. Black circles indicate precipitation. [AIBN](mol l^{-1}) × 10^4: A, 4.92; B, 2.46; C, 1.22; D, 0.61.

of [AIBN] as shown in Figure 1. However, the plots of R_p in the cases of [cyclohexane] = 50 vol% and [n-hexane] = 40 and 50 vol% against the square root of [AIBN] deviated from the proportional relation, especially at low [AIBN]. Although the deviation is similar to that caused by the primary radical termination, it is not caused by primary radical termination.[7] Because in these cases, R_p increased at low [AIBN] as shown in Figure 1, while R_p should decrease at high [AIBN] in the case of primary termination.

The dependence of R_p in methanol, cyclo-hexane and n-hexane on [MMA] is shown in Figure 2(a)—(c). The plots of log R_p against log[MMA] in methanol showed linear relationships as in Figure 2(a), but the plots in cyclohexane and n-hexane deviated markedly with MMA concentration of precipitate observed as shown in Figure 2(b), (c). The deviation was remarkable at low [AIBN].

From these results, we consider the following: As a propagating radical becomes large enough to coil and poor solvent can separate the polymer radical and solution, the end radical should be occluded in the coil. So the
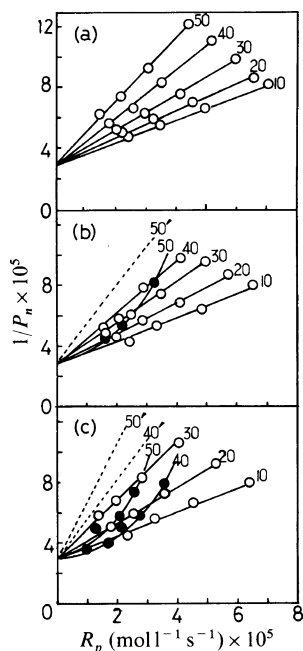
Figure 3. Relations between $1/P_n$ and R_p in methanol; (a), cyclohexane; (b), n-hexane; (c), at 60°C. Numbers and black circles in the figures indicate vol% of poor-solvent and precipitation, respectively. The broken lines indicate the relations supposed if the system was homogeneous. The same intercept as solid line was taken because of small chain transfer constant to cyclohexane or n-hexane and the slope was derived on the basis of $(1+x)k_t/k_p^2$ determined from the relation in Figure 4.

Figure 4. Plots of $(1+x)k_t/k_p^2$ against $1/\eta$. ⊕, methanol; ⊕, cyclohexane; ⊖, n-hexane.

termination reaction is suppressed, but the propagation reaction should not be affected. As a result, R_p is enhanced when a precipitate is observed.

In order to examine the influence of poor solvents on the termination step, $1/P_n$ was plotted against R_p in Figure 3(a)—(c). As shown in Figure 3, linear relationships were obtained in methanol (10—50 vol%), cyclohexane (10—40 vol%), and n-hexane (10—30 vol%). It suggests that under homogeneous conditions, polymerization proceeds by the ordinal mechanism of radical polymerization. The values of $(1+x)k_t/k_p^2$ were determined from the slopes and are listed in Table I. The plots of the values against the reciprocal of the viscosity of the system were almost on the line
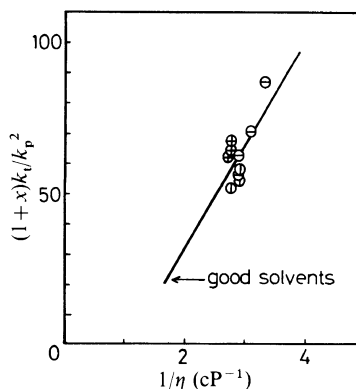
obtained for the polymerizations in good solvents (Figure 4). This also indicates that polymerizations in these systems proceed by the same manner as in good solvents and poor solvents do not affect the termination process unless polymer precipitates.

On the other hand, when a precipitate was observed ([cyclohexane] = 50 vol% and [n-hexane] = 40 and 50 vol%), the plots deviated far below the relations (broken lines in Figure 3) supposed if the systems were homogeneous, and showed curves. Therefore the values of $(1+x)k_t/k_p^2$ in these cases could not be determined, but the values estimated from the tangent of the curves were smaller than those from the broken lines.

We consider from the smaller $(1+x)k_t/k_p^2$ and larger R_p at lower AIBN concentration that the propagating PMMA radical becomes large enough to precipitate by itself, the radical is occluded in the coil and termination reaction is prevented.

Contrary to the poly MMA radical, the propagating polystyryl radicals were not large enough to precipitate by themselves, radicals clustered in poor solvent and termination reaction was enhanced. After termination, the polymers gathered and precipitated.

The main issue is precipitation. Cameron et al.[3] also studied the radical polymerizations of MMA in poor solvents but did not mentioned

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the importance of precipitation. It is concluded that poor solvents are not different from good solvents until polymer precipitates.

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