

Effect of Pressure on the Precipitation and Sol-Phase Aqueous Polymerization of Methyl Methacrylate

BAIJAYANTIMALA MOHANTY, SUNANDA K. PALIT, and MUKUL BISWAS,* *Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India*

Synopsis

Effect of pressure (atmospheric to 120 kg/cm²) on the K₂S₂O₈-Na₂S₂O₄-initiated aqueous polymerization of methyl methacrylate has been studied at 25°C. When the concentrations of the redox initiator are so adjusted as to obtain the separating polymer phase as a coarse coagulum, the conversion, rate, and molecular weight of polymerization tend to rise initially with increase of pressure up to a certain value and fall subsequently to a limiting value. However, these parameters fall monotonously with an increase in pressure when the polymer phase separates out as a fine colloid at a lower concentration of the initiator. The initial rise in rate is consistent with an increase in k_p and or a decrease in k_t under high pressure; the ultimate fall in rate may be due to a decrease in the diffusion of monomer from the aqueous phase to the growing polymer radical site. The fall in the molecular weight with pressure is explained on the basis of enhanced monomer transfer. In the colloidal range the pressure dependence trend is related to the stability of the colloidal phase. The rate is proportional to the square root of the product of K₂S₂O₈-Na₂S₂O₄ and varies linearly as the first power of the monomer concentration as also observed under normal pressure conditions. The MWD values of the polymers are ca. 2.5 and do not change with applied pressure.

INTRODUCTION

A fairly recent review by Ogo¹ highlighting the effect of high pressure on vinyl polymerization reveals that there is no useful information on the effect of pressure on aqueous polymerization systems. Preliminary experiments studying the effect of pressure on the aqueous polymerization of methyl methacrylate and acrylonitrile² initiated by K₂S₂O₈-Na₂S₂O₄ redox system revealed that up to a certain extent even a modest pressure accelerates the rate and enhances the molecular weight in relation to the atmospheric pressure polymerization. It is indeed unusual that such liquid phase reactions should be so sensitive to the prevailing pressure particularly when the latter is in the modest range from atmospheric to ca. 120 kg/cm². In order to endorse these observations and explain the conspicuous pressure effect, the detailed kinetics of the aqueous polymerization of MMA-K₂S₂O₈-Na₂S₂O₄ system have been studied in the pressure range, atmospheric to 120 kg/cm².² The

*To whom all correspondence should be addressed.

choice of the system is particularly significant because this happens to be a much investigated and apparently well-understood process.³ At low concentrations of the redox initiators, the polymerization under atmospheric pressure occurs in a fine colloidal phase with rate and molecular weight depending on the stability³ of the separating colloidal phase of the polymer in the aqueous medium. With increase in the concentrations of $K_2S_2O_8$ and $Na_2S_2O_4$, the fine sol changes to a milky phase and ultimately to a coarse coagulum. The rate and molecular weights are decreased under these conditions.³

This article will focus the salient kinetic aspects of the system under the pressure range mentioned and the distinctive influence of pressure on the precipitation and the sol-phase polymerization, respectively. These results are significant in that they reveal a conspicuous pressure dependence of the kinetic parameters under rather a modest pressure range as compared with the 1000–3000 kg/cm² range reportedly used for the solution polymerization of methyl methacrylate initiated by benzoyl peroxide,⁴ 2,2'-axobisisobutyronitrile,⁵ and 1,1'-azobiscyclohexane-1-carbonitrile.⁶

EXPERIMENTAL

Methyl methacrylate, Merck-Schuchardt (99%), stabilized with 100 ppm hydroquinone was washed with a small amount of sodium hydroxide solution (10%). The monomer was dried over anhydrous sodium sulfate, and finally fractionated. Potassium persulfate ($K_2S_2O_8$) and sodium dithionite ($Na_2S_2O_4$), both E. Merck, were used without further purification. Double distilled water was prepared by distilling ordinary water with alkaline permanganate in an all-glass setup.

POLYMERIZATION

The polymerizations were carried out by transferring calculated aliquots of deaerated water, monomer, initiator ($K_2S_2O_8$), and activator ($Na_2S_2O_4$) under nitrogen in a dry-cleaned glass liner. The glass liner containing the reaction mixture was placed inside the autoclave, which was sealed and flushed adequately with nitrogen. The pressure inside the reactor was raised to the desired level by introducing purified and dried nitrogen gas under pressure. After a specified residence period, e.g., 2 h, the glass liner containing the reaction mixture was taken out and the entire liquid mixture was poured in methanol quantitatively. The precipitated polymer was isolated by filtration, dried at 60°C, and subsequently characterized.

CHARACTERIZATION

Intrinsic viscosities of the polymers were determined in THF at $35 \pm 0.1^\circ\text{C}$ with an Ubbelohde viscometer. The \bar{M}_v values were calculated by using the relation⁷

$$[\eta] = KM^\alpha, \quad \text{where } K = 5.05 \times 10^{-4} \quad \text{and} \quad \alpha = 0.50 \text{ (THF)}$$

Molecular weight distributions (MWD) were determined by GPC using a Waters Associates Model 244 unit with the following accessories:

Injector:	Waters 46 K
Columns:	Dupont Zorbox Trimodel set
RI detector:	Waters R 401
UV detector:	Waters 440
Solvent:	THF (20 μ L, 0.5% w/v)
Standard:	Polystyrene (MWD 1.06)

The IR spectra of the polymers were recorded on a Perkin-Elmer 237B spectrophotometer in KBr pellet.

^{13}C -NMR spectra were obtained on a JEOL GX 400 FT NMR spectrometer (100 MHz ^{13}C -NMR) in CDCl_3 and benzene- d_6 at 70°C.

The polymerizations are accompanied by phase separation owing to the insolubility of PMMA in water. At the concentration range of $\text{K}_2\text{S}_2\text{O}_8$ ($1.84 \times 10^{-3}\text{M}$) and $\text{Na}_2\text{S}_2\text{O}_4$ ($6.7 \times 10^{-4}\text{M}$) used in these experiments, a coarse coagulum is obtained. The polymer is white in color and is recovered as a powdery mass after usual processing.

IR spectra of PMMA obtained at atmospheric pressure and at higher pressures are virtually similar to one another.

^{13}C -NMR spectra analyses of PMMA obtained at three different pressures (1, 20, and 126 kg/cm^2) do not reveal any difference between isotactic, heterotactic, and syndiotactic configurations.⁸

KINETIC CHARACTERISTICS

Figure 1 shows two typical conversion time isobars and $[\eta]$ -time isobars obtained with a particular polymerization recipe at pressure 20 and 11 kg/cm^2 , respectively. The conversion-time and the molecular weight-time plots are linear up to 2 h, indicating steady behavior over this time. In view of this, all rate calculations were made from conversions realised over 2 h.

Effect of Pressure on Polymerization

This was studied by carrying out the polymerization at different pressures with a fixed concentration of MMA, $\text{K}_2\text{S}_2\text{O}_8$, and $\text{Na}_2\text{S}_2\text{O}_4$, respectively. Figure 2 represents the variation of percent conversion and rate with applied pressure. Figure 3 represents the variation of \bar{M}_v with applied pressure. It is observed that initially, as the pressure is raised from atmospheric to 20 kg/cm^2 , conversion as well as rate increases consistently. With further increase of pressure these parameters start falling to a limiting value.

The initial increase in conversion and rate with pressure has also been reported in several instances.⁹ This behavior may be explained conventionally in terms of an increase in chain propagation rate¹⁰ and/or a decrease in the rate of termination of chain ends.¹⁰

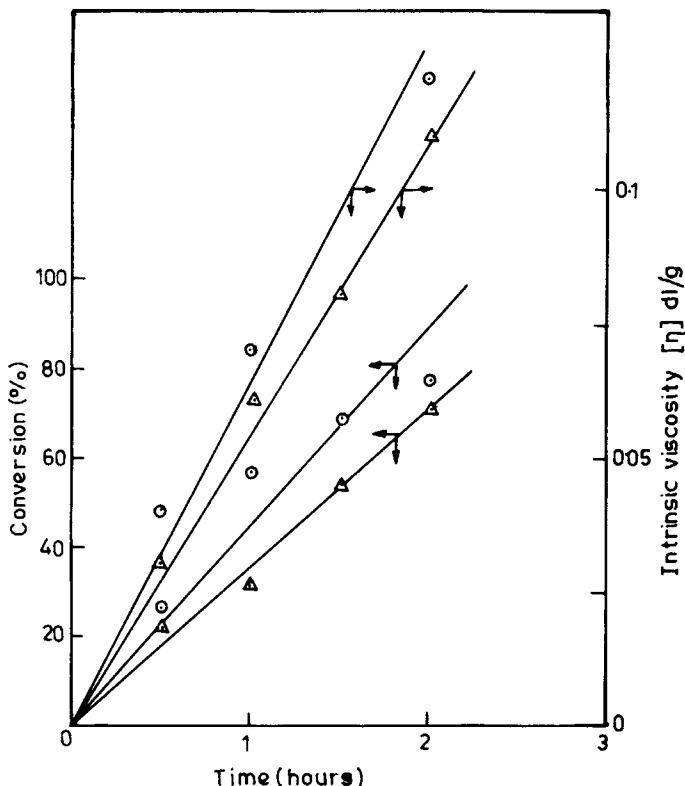


Fig. 1. Variation of percentage conversion and viscosity average molecular weight with time. Polymerization conditions: $[MMA] = 0.48M$; $[K_2S_2O_8] = 2.58 \times 10^{-3}M$; $[Na_2S_2O_4] = 6.7 \times 10^{-4}M$; temp $25^\circ C$; pressure = 20 kg/cm^2 and 11 kg/cm^2 .

However, it is likely that, as the pressure is raised, some of the primary radicals generated from the redox system are also lost by increased collision. This would imply a decrease in conversion and rate.¹⁰

Beyond the optimum pressure limit, the conversion, as well as the rate, fall with pressure. It is possible that under these conditions diffusion of monomer from the aqueous medium to the growing polymer radical site is gradually impaired¹⁰ as the system tends to become more dense on exposure to higher pressures. Relevantly, Sasuga and Takehisa¹¹ have confirmed from pressure-volume relation studies with methacrylic, acrylic esters, and acrylonitrile that monomer molecules indeed undergo short-range alignment under pressure even in the liquid state. The pressure range used by Sasuga is higher than the same in this study. Nevertheless, chances of some alignment cannot be overruled completely in this case.

Such alignments will evidently create a situation, which will disfavor diffusion of monomer molecules, thus aligned, to the propagation site to a larger extent than when they are randomly distributed in the solution normally in the absence of any pressure. Accordingly, a fall in conversion or rate would be expected.

However, the actual situation is more complex because of the possibility that chain termination may be reduced too in this denser matrix. The fact

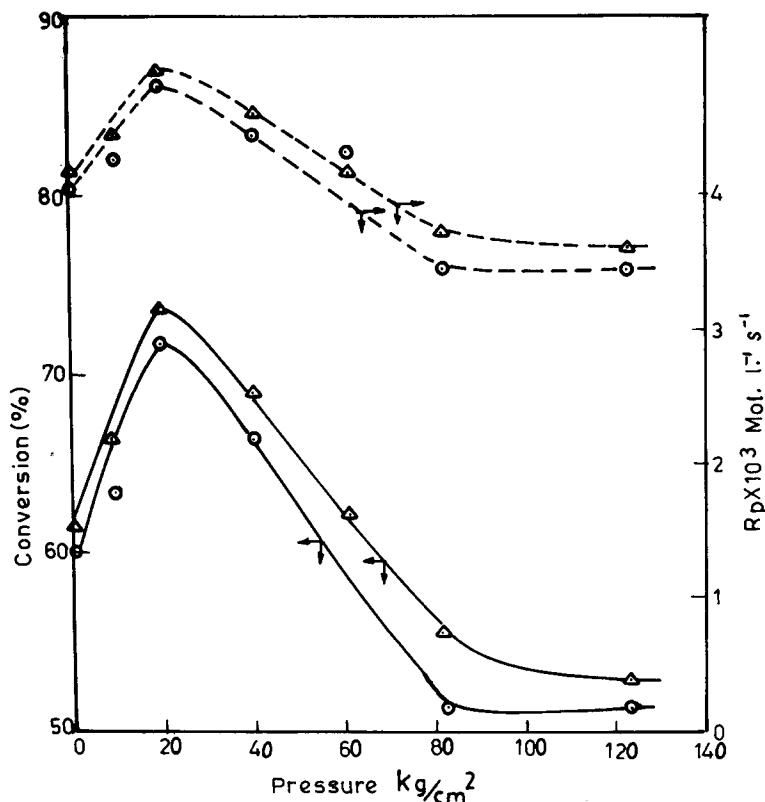


Fig. 2. Dependence of percentage conversion (—) and rate (---) of polymerization on pressure: $[MMA] = 0.48M$; $[Na_2S_2O_4] = 6.7 \times 10^{-4}M$; temp $25^\circ C$; $[K_2S_2O_8] = 1.84 \times 10^{-3}M$ (○) and $2.58 \times 10^{-3}M$ (Δ).

that the overall rate falls is suggestive of the possibility that decrease in the propagation rate due to decreased diffusion will kinetically outweigh the chance of an increase in rate due to decrease in termination. Indeed instances are known¹⁰ where rates of solution polymerization have been observed to fall with increase in the pressure.

The molecular weights of the polymers tend to rise initially with increasing pressure and fall thereafter (Fig. 3). This may imply that bimolecular transfer reaction between polymer radicals and monomer molecules becomes important in the increasing pressure range. However, the possibility of an exclusive chain transfer in this system is overruled since the conversions are also affected considerably which endorse that termination is important as well in the system.

The propagation step of many radical polymerizations has been shown to be favored by pressure in the liquid phase as would be expected for reactions accompanied by a reduction in molar volume.⁹ The overall activation volume ΔV_{pol}^\ddagger of the polymerization has been calculated as -32.3 and -28.5 cm³/mol for two different concentrations of $K_2S_2O_8$, respectively, from the usual $\log[-dM/dt]$ vs. pressure plots over the initial pressure range (atmospheric -120 kg/cm²), where the conversions rise linearly with pressure.

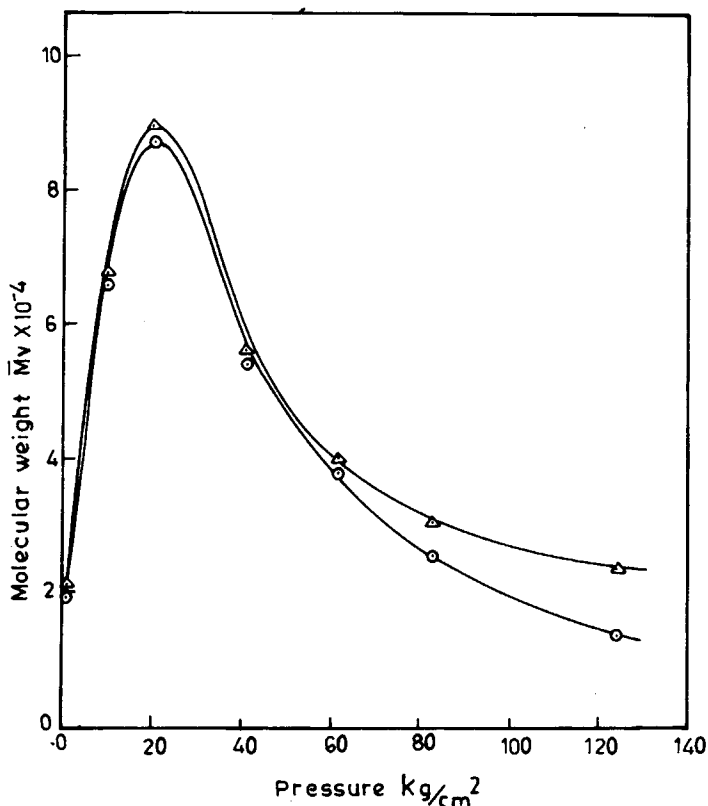


Fig. 3. Variation of molecular weight with pressure. Polymerization conditions for (O) and (Δ) are same as in Figure 2.

Pressure Effect vs. the Nature of the Physical State of the Polymerization System

Data so far presented correspond to polymerization conducted under the condition that the separating polymer phase appears as a coarse coagulum. When the initiator concentration is so adjusted that the separating phase appears as a fine colloidal sol, the system exhibits a pressure effect distinct from the same with a coarse coagulated polymer phase. Figure 4 represents the variation of conversion and molecular weight with pressure and clearly demonstrates a consistent fall in the conversion, rate, and molecular weight with pressure. Evidently, the trend is typically different from that revealed in Figure 3 for a coagulated polymer system. In the light of the results of Palit et al.,^{2,3,12,13} such a fall in rate and molecular weight may be associated with a decrease in the stability of the separating phase. The validity of the contention in the present system is amply demonstrated by the results of Figure 5, which indicate that the overall stability of the colloidal phase as measured in terms of the coagulation value of NaCl^{2,3,12} as the coagulating electrolyte falls almost parallel with the rate and the molecular weight.

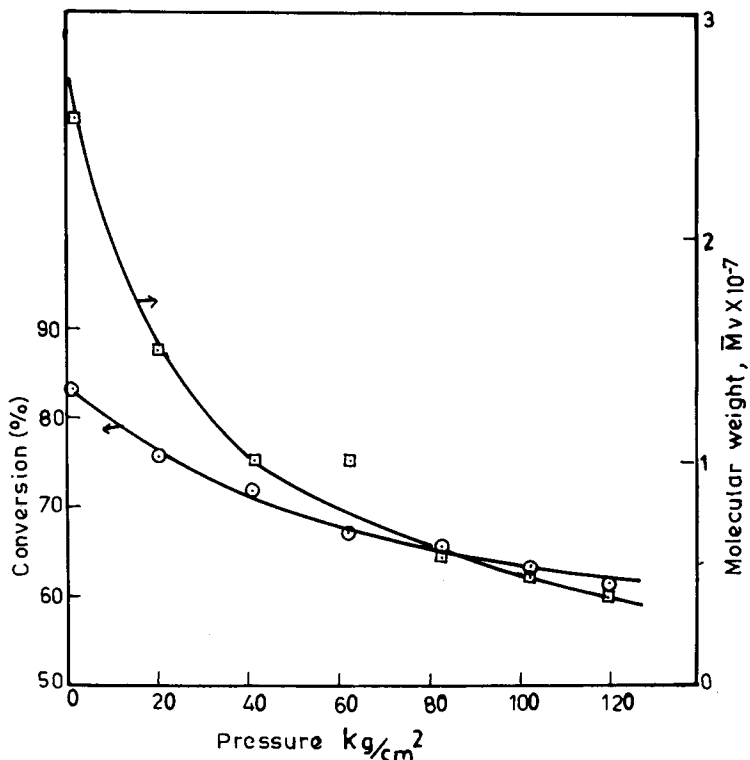


Fig. 4. Variation of percent conversion and molecular weight with separating polymer phase as a fine colloid with pressure: $[MMA] = 0.096M$; $[K_2S_2O_8] = 1.84 \times 10^{-4}M$; $[Na_2S_2O_4] = 6.7 \times 10^{-5}M$; time 2 h; temp 25°C.

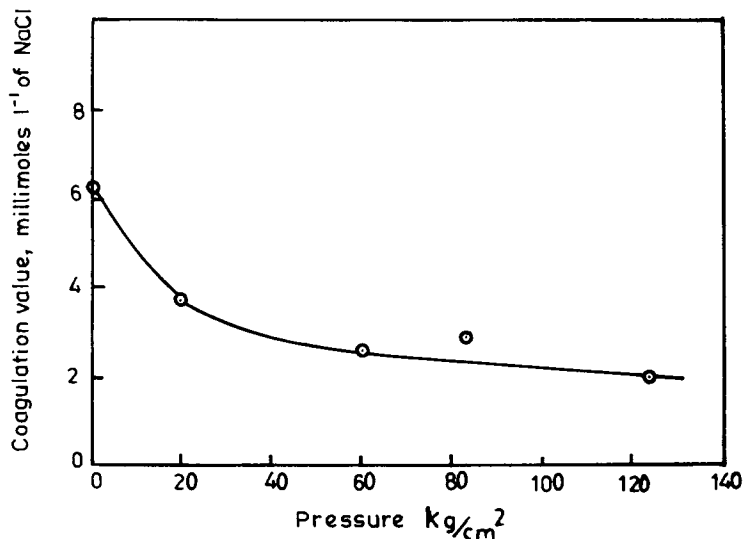


Fig. 5. Variation of coagulation value of the separating polymer (colloid) phase with pressure. The polymerization condition of Figure 5 is same as in Figure 4.

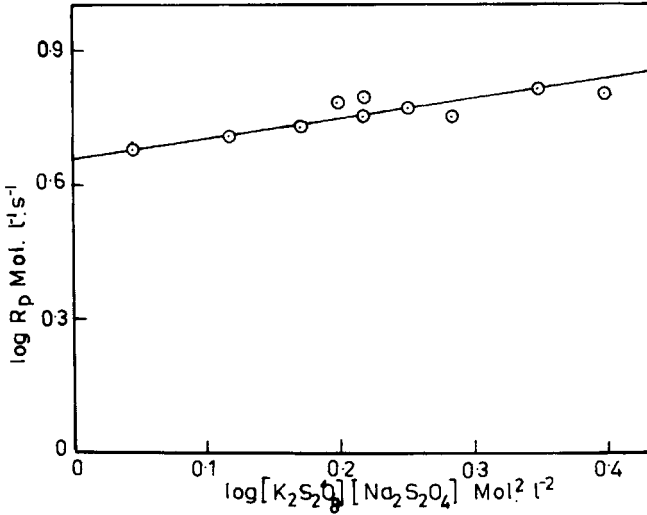


Fig. 6. Dependence of the logarithm plot of rate vs. product of the $[K_2S_2O_8]$ and $[Na_2S_2O_4]$: $[MMA] = 0.48M$; time 2 h; temp $25^\circ C$; pressure 20 kg/cm^2 .

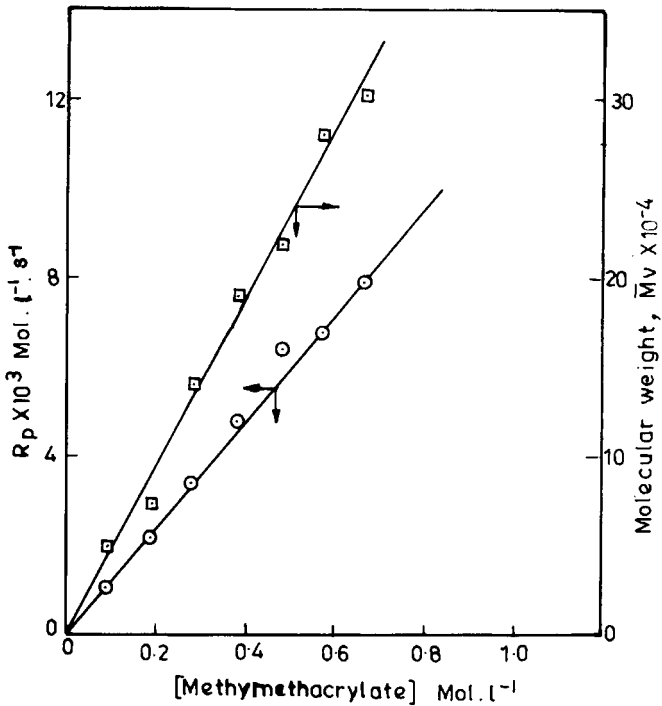


Fig. 7. Dependence of rate and molecular weight on monomer concentration: $[K_2S_2O_8] = 4.8 \times 10^{-3}M$; $[Na_2S_2O_4] = 27.1 \times 10^{-4}M$; time 2 h; temp $25^\circ C$; pressure 20 kg/cm^2 .

TABLE I
Rate and DP of Aqueous Polymerization of Methyl Methacrylate at 25°C at Atmospheric and High Pressure (20 kg/cm²)

	$[K_2S_2O_8][Na_2S_2O_4]$ $\times 10^6$ (mol ² /L ⁻²)	$R_p \times 10^3$ (mol L ⁻¹ s ⁻¹)	$[C]/R_p \times 10^3$ (s)	$10^3/DP$	k_m/k_p
1a ^a	1.72	4.21	0.408	0.237	
	2.22	4.47	0.496	0.400	
	1.07	4.14	0.257	0.256	0.75×10^{-4} ^b
	3.74	4.40	0.848	0.552	
	4.98	4.28	1.160	0.771	
1b ^a	2.46	6.09	0.407	0.71	
	3.74	6.30	0.592	1.02	2.5×10^{-4}
	6.24	6.34	0.983	1.42	
	1.73	5.09	0.339	0.68	

^a Polymerization at 25°C [MMA] = 0.48M. (1a) runs conducted at atmospheric pressure, (1b) at high pressure (25 kg/cm²).

^b Other reported k_m/k_p values are 0.27×10^{-4} ¹⁵ and 0.12×10^{-4} ¹⁶.

Dependence of Rate on the Concentrations of the Redox Initiator and MMA

Figures 6 and 7 show that, at 20 kg/cm², rate varies as the square root of $[K_2S_2O_8][Na_2S_2O_4]$ and the first power of $[MMA]$, which is similar to the behavior reported under normal pressure.¹⁴

Evaluation of k_m/k_p

Earlier in the text the suggestion has been made that the fall in the molecular weight beyond the maximum (Fig. 3) beginning at a particular pressure of 20 kg/cm² is partly due to enhanced transfer to growing chains with monomer. To lend credence to this contention, k_m/k_p has been calculated in the present polymerization conducted at 2×10^6 Pa and at atmospheric pressure following the procedure due to Onyon et al.¹⁴ The usual relationship¹⁴

$$\frac{1}{\overline{DP}} = \frac{d[P]/dt}{-d[M]/dt} = \frac{k_m[M][X] + 2k_{td}[X]^2 + k_{tc}[X]^2}{k_p[M][X]}$$

has been used where $[M]$ and $[X]$ are the concentrations of methyl methacrylate and radicals and k_m , k_p , k_{td} , and k_{tc} are the usual rate constants. It has been tacitly assumed that transfer to solvent (H₂O) and to the redox catalyst moiety is absent. Denoting $[C]$ as the product $[K_2S_2O_8][Na_2S_2O_4]$, the steady state condition gives

$$2fk_d[C] = 2(k_{td} + k_{tc})[X]^2$$

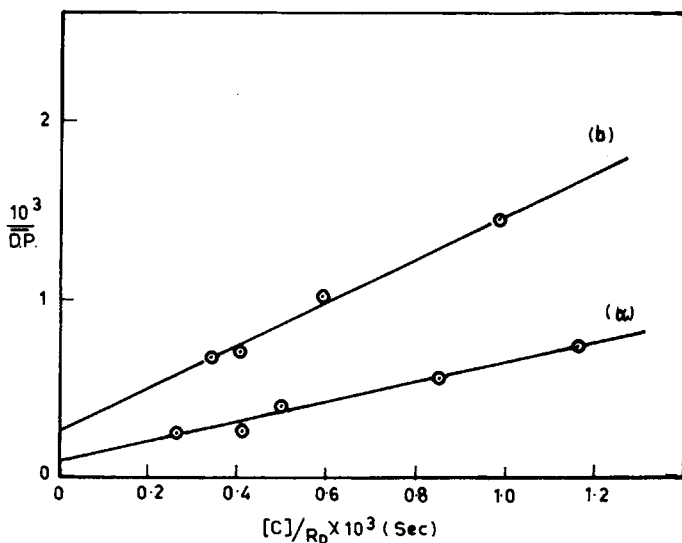


Fig. 8. Evaluation of k_m/k_p under normal (a) and high pressure 20 kg/cm² (b).

TABLE II
Effect of Pressure on Molecular Weight Distribution

Polymer ^a	\bar{M}_w	\bar{M}_n	MWD ^b
a	392,450	159,750	2.46
b	375,970	146,670	2.56
c	275,550	110,500	2.49

^aPMMA: a = atmospheric pressure, b = 20 kg/cm², and c = 120 kg/cm². All polymerizations conducted at 25°C with [MMA] = 0.48M, [K₂S₂O₈] = 1.84 × 10⁻³M, and [Na₂S₂O₄] = 6.7 × 10⁻⁴M.

^bStandard: polystyrene, \bar{M}_n = 100,530, \bar{M}_w = 108,340, MWD = 1.08.

and putting¹⁴

$$x = k_{td}/k_{tc} + k_{td}$$

$$\frac{1}{\overline{DP}} = \frac{fk_d[C](1+x)}{k_p} + \frac{k_m}{k_p}$$

Results of k_m/k_p determination are summarized in Table I and the Mayo plot is shown in Figure 8. Evidently k_m/k_p is higher under high pressure (20 kg/cm²) than under atmospheric pressure conditions which endorse the suggestion.

Molecular Weight Distribution

Molecular weight distributions were studied for three PMMA samples in the present system prepared (a) under atmospheric condition, (b) at a pressure 20 kg/cm² (maximum rate and molecular weight, Figs. 2 and 3), and (c) at the highest pressure zone [(C) 120 kg/cm², Figs. 2 and 3]. Relevant results summarized in Table II indicate that the distributions are usually broad (2.5) and that they are not affected by the superincumbent pressure at least in the range studied in the system. The broad distributions are consistent with a transfer/termination controlled polymerization.

Thanks are due to the authorities of I. I. T., Kharagpur, India for facilities.

References

1. Y. Ogo, *Macromol. Chem. Phys. Rev.*, **C-24**, 1 (1984).
2. B. Mohanty, S. K. Palit, and M. Biswas, *J. Appl. Polym. Sci.*, **32**, 2969 (1986).
3. S. R. Palit and T. Guha, *Polym. Sci.*, **34**, 243 (1959); T. Guha, M. Biswas, S. R. Konar, and S. R. Palit, *J. Polym. Sci., Part A*, **2**, 1471 (1964).
4. J. A. Lamb and K. E. Weale, *Symposium on the Physical Chemistry of High Pressure*, Soc. Chem. Ind., London, 1963, p. 229.
5. T. Imoto and H. Asai, *Nippon Kagaku Zasshi*, **85**, 149 (1964).
6. M. Yokawa, Y. Ogo, and T. Imoto, *Makromol Chem.*, **163**, 135 (1973).
7. H. Inagaki and S. Kawai, *Makromol Chem.*, **79**, 42 (1964); see also G. V. Schulz and Z. Kirste, *Phys. Chem. (N.F.)*, **30**, 171 (1961).
8. B. Mohanty, S. K. Palit, and M. Biswas, *Polym. J.*, **19**, 931 (1987).
9. K. E. Weale, *Chemical Reactions at High Pressure*, Spon, London, 1967, pp. 206-238.
10. F. M. Merrett and R. G. W. Norrish, *Proc. Roy. Soc.*, **A206**, 309 (1951).

11. T. Sasuga and M. Takehisa, *Macromol. Sci. Chem.*, **A12**(9), 1343 (1978).
12. M. Biswas and S. R. Palit, *J. Sci. Ind. Res.*, **20B**, 160 (1961).
13. M. Biswas, T. Guha, and S. R. Palit, *J. Ind. Chem. Soc.*, **42**, 509 (1965).
14. P. F. Onyon, *J. Polym. Sci.*, **22**, 19 (1956).
15. G. Henrice Olive, S. Olive, and G. V. Schulz, *Makromol. Chem.*, **23**, 207 (1957).
16. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949).

Received September 3, 1987

Accepted September 14, 1987