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Aqueous Polymerization on Clay Surface. 2. The Polymerization of Methyl Methacrylate on Hydrogen Bentonite: Effect of Monomer Concentration and Temperature

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ABSTRACT

Aqueous free radical polymerizations of methyl methacrylate with the hydrogen bentonite/ethanol system have been accomplished with less transfer to monomer in spite of high monomer concentrations and temperature. The overall initial rate has a first-order dependence on monomer. It is proposed that initiation does not occur in the aqueous phase. The apparent activation energy of 15 kcal/mol corroborates a twofold increase in rate for a 10°C rise in temperature. The frequency of bimolecular termination is quite small as is evident from k_p^2/k_t values at various temperatures.

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INTRODUCTION

Both synthetic and natural aluminosilicates have a wide range of applications in chemical industries. They have been used in polymerizations with free-radical initiators to enhance the reaction. Complexation of aluminosilicates with functional acrylates, e.g., hydroxymethacrylate, followed by initiation and polymerization have been observed [1]. More recent study has revealed the usefulness of clay minerals, particularly bentonite, as free-radical initiator in conjunction with alcohols and thiols in aqueous systems [2]. It has been shown that poly(methyl methacrylate) of $\bar{M}_n \approx 2-4 \times 10^6$ is easily obtainable.

The rate is rather slow and has a half-order dependence on alcohol. A free-radical mechanism has been proposed.

Thermodynamic parameters of polymerization along with other variables, like monomer, initiator concentration, etc., are very important tools in elucidating the reaction mechanism. The present communication deals with the effect of varying monomer concentration and temperature on the aqueous polymerization of methyl methacrylate with the hydrogen bentonite/ethanol initiating system. The polymerizability of acrylonitriles with such an initiating system is also discussed.

EXPERIMENTAL

Methyl methacrylate (MMA) was purified by standard procedures. Preparation of hydrogen bentonite (HB) suspension of average particle size $2 \mu\text{m}$ has been reported in a previous publication [2]. Deionized water was used throughout.

Polymerizations were carried out in well-stoppered dark Pyrex bottles under a nitrogen blanket. HB and MMA were equilibrated at the reaction temperature with intermittent shaking for 4-6 h prior to the addition of ethanol. Poly(methyl methacrylate) (PMMA) isolation and purification methods have been reported [2].

Number-average molecular weights of PMMA samples were determined by viscosity measurements at 30°C in benzene using Ubbelohde viscometers and the following equation given by Fox [3]:

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76}$$

RESULTS AND DISCUSSION

While no polymer was produced either with HB or EtOH alone on prolonged standing at various temperatures and reaction conditions, high molecular weight (10^6) PMMA resulted in the presence of both

the reactants in aqueous medium. It was further observed that the changes in reaction parameters, like temperature, monomer concentration and clay/ethanol concentration, have no effect on the polymerization unless the mixture is shaken intermittently. In fact, only 1-2% PMMA of $\bar{M}_n \approx 10^6$ could be isolated after 12 h at 60°C without shaking. These results lead us to believe that for the polymerization of MMA to initiate with the HB/alcohol system, the monomer molecules have to be near the clay surface. In other words, monomer has to be adsorbed on the clay surface for effective polymerization. Initiation probably does not occur in the aqueous phase (i.e., the initiating species is trapped between the clay layers).

Effect of Monomer Concentration

For a constant ratio of $[\text{HB}]/[\text{EtOH}]$ the conversion increased with increasing concentration of MMA at all temperatures with a parallel increase in \bar{M}_n . Figure 1 illustrates conversion-time plots for aque-

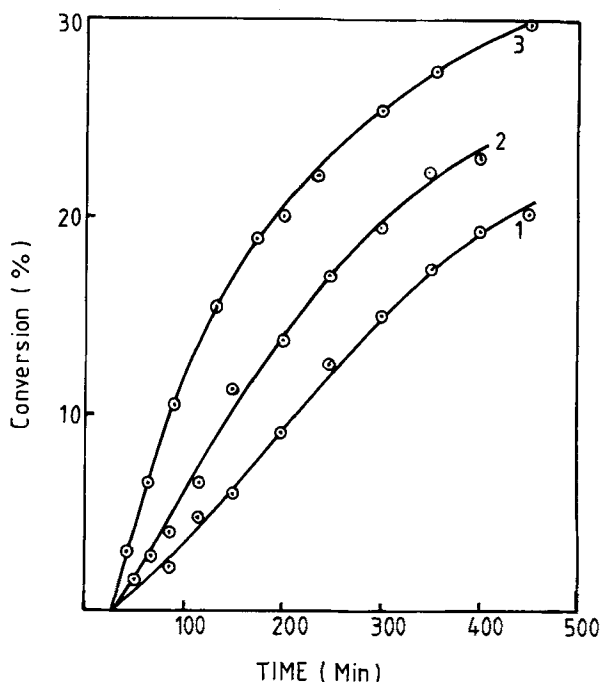


FIG. 1. Time-conversion plots for the aqueous polymerization of MMA at 60°C with HB/EtOH. $[\text{HB}] = 0.887\%$ (w/v); $[\text{EtOH}] = 0.334$ M; and $[\text{MMA}] = 0.749$ M (1), 1.123 M (2), and 1.495 M (3).

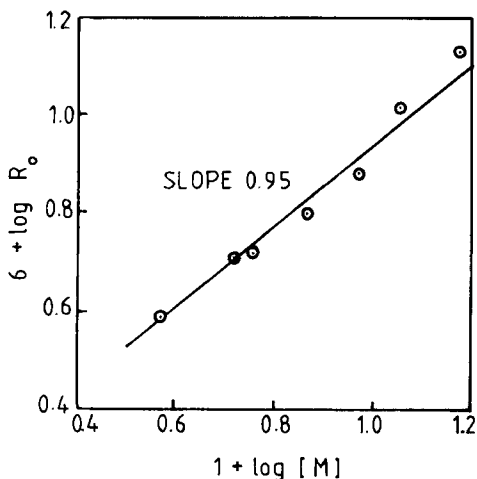


FIG. 2. Plot of $\log R_0$ vs $\log [M]$ for the aqueous polymerization of MMA at 60°C with 0.887% (w/v) HB and 0.334 M EtOH.

ous polymerizations at 60°C . After 5 h of polymerization the conversions were 15, 20, and 25% for 0.749, 1.123, and 1.495 M MMA, respectively. However, longer reaction times resulted in higher conversions. In all polymerizations an induction period was observed and found to be independent of monomer concentration. Separate sets of polymerizations were carried out with varying MMA concentrations to determine the overall initial rates R_0 of the polymerizations from the initial slopes (up to 15% conversions). A nearly first-order dependence of R_0 on monomer concentration (Fig. 2) suggests that strong complexation between HB and MMA is probably negligible. Some R_0 data along with \bar{M}_n values at much higher conversions with different monomer concentrations are shown in Table 1. Although \bar{M}_n values are relatively high the increment in \bar{M}_n is not parallel to the increase in monomer concentration. The number-average moles of PMMA increased with increasing MMA level. This could be due to transfer to monomer because of relatively high monomer concentration and high conversions.

In the previous publication of this series [2], it was pointed out that the initial rate has half-order dependence on ethanol and that transfer to ethanol is absent. Assuming, therefore, that chain transfer to initiator (HB/EtOH) is insignificant, the degree of polymerization is

TABLE 1. Aqueous Polymerization of MMA at 60°C in the Presence of [HB] = 0.887% (w/v) and [EtOH] = 0.343 M

[MMA], M	Conversion, 12 h	$R_0 \times 10^5$, mol/L·s	$\bar{M}_n \times 10^{-6}$	$N_n^a \times 10^6$
0.562	36	0.512	1.38	0.78
0.749	42	0.625	1.50	1.03
0.936	45	0.741	1.58	1.31
1.123	55	1.040	1.71	1.80

^aNumber-average moles of PMMA.

$$\frac{1}{\overline{DP}_n} = \frac{1.85 k_t}{k_p^2} \frac{R_0}{[M]^2} + \frac{k_{tr,M}}{k_p}$$

where k_t , k_p , and $k_{tr,M}$ are rate constants for termination, propagation, and transfer to monomer, respectively. A plot of $1/\overline{DP}_n$ vs $R_0/[M]^2$ would be linear, with $k_{tr,M}/k_p$ as the intercept and $1.85 k_t/k_p^2$ as the slope. Such plots at three different temperatures are shown in Fig. 3. Transfer to monomer is quite small. Values of $k_{tr,M}/k_p$ and k_p^2/k_t are shown in Table 2. The latter are lower than usually encountered in the redox-initiated aqueous polymerizations of MMA [4]. However, they are higher than for homogeneous polymerizations [5]. The increase in k_p^2/k_t with temperature is probably due to the increase in k_p , while k_t is relatively small because of the occlusion of free-radical ends by growing polymer chains inside layers of clay mineral [6, 7]. Generally, an increase in monomer concentration lowers the rate of aqueous polymerization because of the solubility of the polymer in the monomer due to an increase in the frequency of termination [8]. With HB/ethanol, equilibrium exists between the monomer adsorbed on the clay surface and that in the aqueous layer. This equilibrium is shifted when adsorbed monomer is consumed during the polymerization, leading to fresh monomer adsorption. This probably explains the high molecular weights of the polymer obtained with HB/ethanol in spite of the quite high monomer concentration.

TABLE 2. Kinetic and Energy Parameters for the Aqueous Polymerization of MMA with 0.343 M EtOH and 0.887% (w/v) HB at Various Temperatures

Temperature, °C	k_p^2/k_t' L/mol·s	$k_{tr}M/k_p$ $\times 10^5$	E_a' kcal/mol	$2E_p - E_t'$ kcal/mol	E_d' kcal/mol	E_{DP_n} kcal/mol
50	0.84	1.54	15.0	12.2	17.0	-3.2
60	1.67	2.44				
80	4.20	3.36				

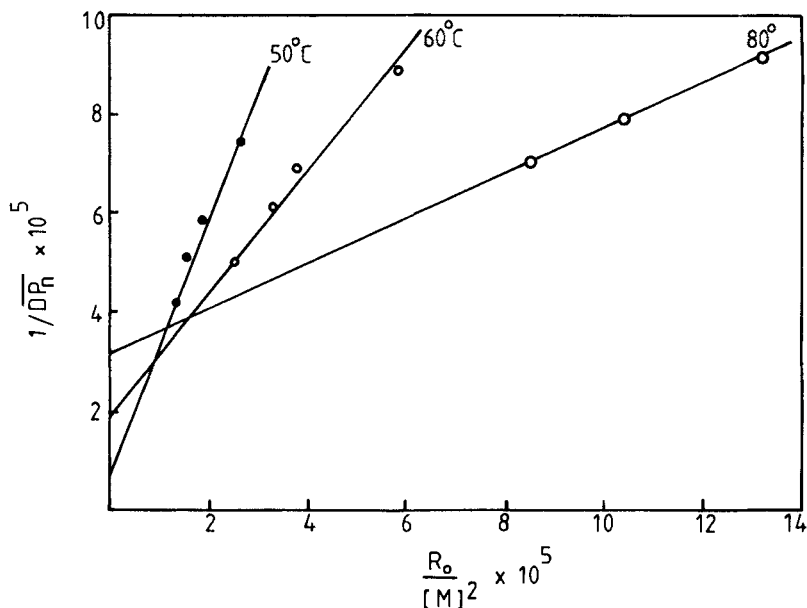


FIG. 3. Plots of $1/\overline{DP}_n$ vs $1/T$ at 50, 60, and 80°C for the aqueous polymerization of MMA with HB/EtOH.

Effect of Temperature and Activation Energy

Both the monomer conversion and R_0 increase with temperature. For the 0.374-M MMA system the rate increased from 5.72×10^{-6} mol/L·s to 1.25×10^{-5} mol/L·s to 3.92×10^{-5} mol/L·s at 50, 60, and 80°C (Fig. 4). An approximately twofold increase in rate for each 10°C rise in temperature resulted. The overall activation energy E_a was determined from the slopes of plots of $\log R_0$ vs $1/T$ for various MMA concentrations (Fig. 5). A value 15.0 kcal/mol is higher than usually obtained for the aqueous polymerization of MMA with redox initiators. This, however, is an apparent activation energy since correction due to the heats of adsorption of MMA on HB has not been made. Other activation parameters, $2E_p - E_t$ and E_d , have been determined from k_p^2/k_t values at 50, 60, and 80°C and calculated by the relation $E_a = E_d/2 + E_p - E_t/2$ (Table 2). E_d is 17.0 kcal/mol

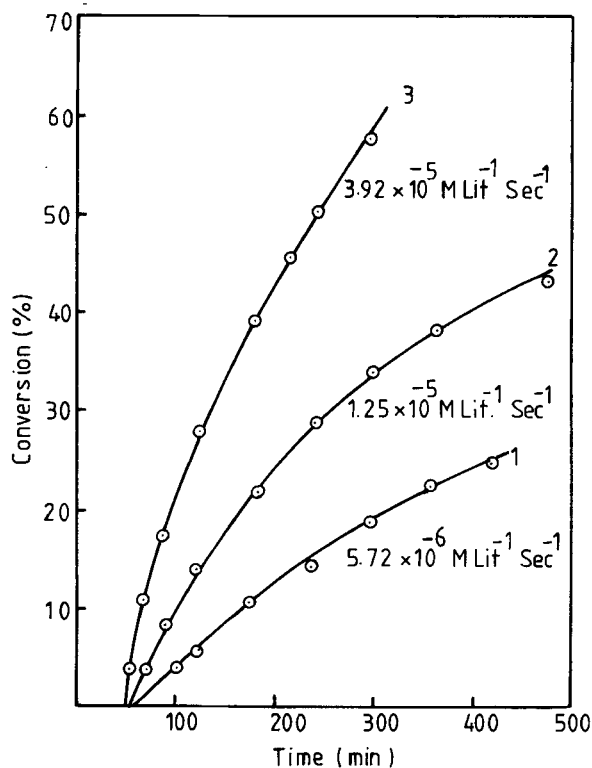


FIG. 4. Time-conversion plots for aqueous polymerization of MMA at 50°C (1), 60°C (2), and 80°C (3); $[MMA] = 0.374 M$; $[HB] = 0.887\%$ (w/v); and $[EtOH] = 0.343 M$.

and is comparable to that obtained by Nayak et al. for the aqueous polymerization of MMA [9]. The activation energy for \overline{DP}_n , calculated from a plot of $\log \overline{M}_n$ vs $1/T$ (Fig. 6), is -3.2 kcal/mol and is suggestive of a system where transfer is not significant. Details of the mechanism of this polymerization system will be communicated later.

Polymerizability of Acrylo- and Methacrylonitriles

An attempt to polymerize acrylonitrile and methacrylonitrile with HB/EtOH in aqueous medium under various experimental con-

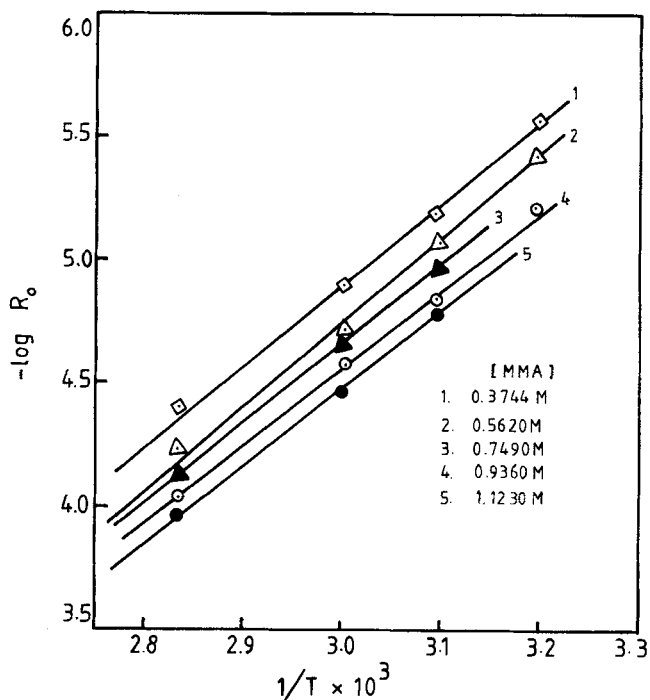


FIG. 5. Arrhenius plots: $\log R_0$ vs $1/T$ with various amounts of MMA with 0.887% (w/v) Hb and 0.343 M EtOH.

ditions failed. The reason for such failure may be the interference of the cations, which exist with the clay mineral, through the $-C\equiv N$ group itself is polarizable and, being attached to the vinyl group, polarization is enhanced. In the process, the vinyl group is deactivated, and attack by free radicals is not favored. The monomers, however, form copolymers with MMA with the same initiating system [10], probably due to their solubility in MMA and initiation through the latter. This observation further supports the free-radical mechanism proposed for the MMA/HB/EtOH (aqueous) system.

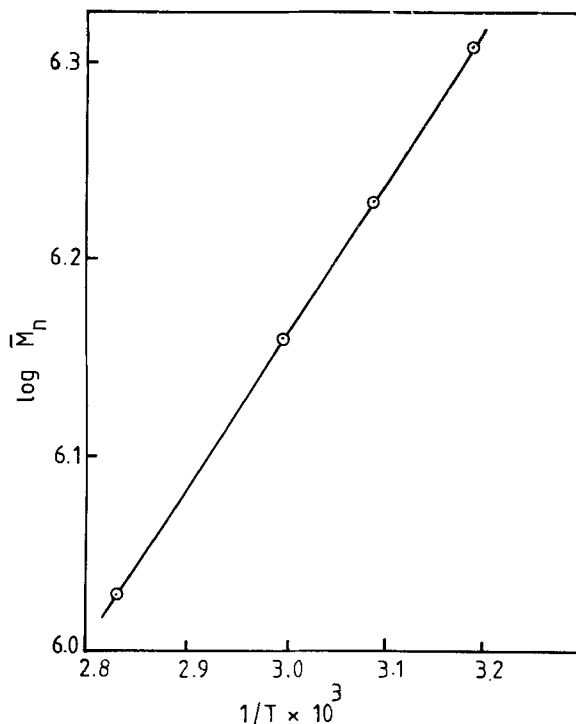


FIG. 6. Arrhenius plots for \bar{M}_n of PMMA: $[MMA] = 0.374 M$, $[HB] = 0.887\%$ (w/v), $[EtOH] = 0.343 M$.

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REFERENCES

- [1] D. H. Solomon and B. C. Loft, *J. Appl. Polym. Sci.*, **12**, 1253 (1968).
- [2] S. Talapatra, S. K. Saha, S. K. Chakravarti, and S. C. Guhaniyogi, *Polym. Bull.*, **10**, 21 (1983).
- [3] T. G. Fox, J. B. Keisinger, and H. F. Mason, *Polymer*, **3**, 71 (1962).

- [4] P. Ghosh and S. Biswas, J. Macromol. Sci.-Chem., **A16**(5), 1033 (1981).
- [5] M. S. Matheson, E. B. Bevilacqua, E. E. Auer, and E. J. Hart, J. Am. Chem. Soc., **71**, 497 (1949); **73**, 1700 (1951).
- [6] C. H. Bamford and A. D. Jenkins, Proc. R. Soc. London, **A228**, 220 (1955); **A216**, 515 (1953).
- [7] C. H. Bamford, A. D. Jenkins, M. C. R. Simons, and M. G. Townsend, J. Polym. Sci., **34**, 181 (1959).
- [8] R. G. W. Norrish and R. R. Smith, Nature, **150**, 336 (1942).
- [9] P. Nayak, B. C. Singh, and T. R. Mohanty, Makromol. Chem., **176**, 873 (1975).
- [10] S. C. Guhaniyogi and S. Talapatra, Unpublished Results.

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