

Aqueous Polymerization of Clay Surface

1. The Polymerization of Methylmethacrylate on Hydrogen Bentonite: Effect of Alcohols

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SUMMARY

Methylmethacrylate has been successfully polymerized to high conversions and high molecular weight polymers with aqueous suspension of hydrogen-bentonite in the presence of aliphatic alcohols. Both extractable and non-extractable polymers were obtained. The overall initial rates of polymerization increased with increasing ethanol concentrations. The constancy in the viscosity average moles of polymer at higher ethanol concentrations indicates that transfer to alcohol was unimportant. E.s.r. and x-ray studies suggest a free radical mechanism for such polymerizations. It has been postulated that interlamellar silicate layers are responsible for generating the free radicals.

INTRODUCTION

Clay minerals, silicates of either aluminium or magnesium, are used in the chemical industry in widely diversified roles like catalysts for cracking (1), alkylation (2), isomerization (3), etc. They have also been used for polymerizing acrylic and vinyl monomers both in the absence and presence of other initiators. Styrene was polymerized by acid clays cationically (4) and by neutral clays via radical-carbonium ion mechanism (5). In the polymerizations of a number of monomers using 2,2'-azobisisobutyramidine hydrochloride in conjunction with kaolin and bentonite, free radicals were generated by decomposing the initiator-clay complex at 60°C (6). Layer aluminosilicate montmorillonite has been reported to form complex with hydroxymethacrylate monomers which spontaneously initiated the polymerization on further monomer addition (7). Most of these systems were aimed to prepare clay-polymer composites for various applications. It is now generally accepted that the catalytic activity of the acid clays is related to the aluminiums in octahedral coordination. These aluminiums at the crystal edges promote carbonium ion reactions (5). They also inhibit the polymerization of methylmethacrylate MMA (8). Some contradictory results on the use of clay minerals as polymerization catalysts have been reported (9,10).

Hydrogen bentonite HB, an aluminosilicate, is a weak Lewis acid. HB preferentially adsorbs initiating or propagating free radicals; or electron transfer from radicals to the Lewis acid

sites occurs. These processes inhibit the polymerization of MMA. The present investigation has been undertaken for several reasons: limited data are available on aqueous polymerizations using clay minerals, HB is known to inhibit non-aqueous polymerization of MMA and lastly, during our scouting experiments with aqueous suspension of HB we observed that only alcohol poisoned HB could polymerize MMA in good yields without using conventional free radical initiators. This paper qualitatively describes the effect of alcohols on the polymerization of MMA in the presence of HB and suggests a probable mechanism.

EXPERIMENTAL

Materials: MMA (BDH) was purified by removing inhibitor and distilling fractionally before use. Rectified spirit (C.P.) was stored over a proportional amount of freshly burnt quicklime, distilled and the middle fraction was collected. n-propanol, isopropanol and n-butanol were dried over anhydrous K_2CO_3 and distilled. Methanol (E. Merck, A.R.), petroleum ether (C.P.), benzene (C.P.), diphenyl picryl hydrazyl DPPH (Sigma) and sodium hexametaphosphate were used as received. Bentonite (Evans Medical Co., England) was processed and an aqueous suspension having particle size $<2\mu$ was obtained by sedimentation (11). Organic matters were removed by gently boiling with H_2O_2 . Excess H_2O_2 was removed by continuous boiling till the test was negative. The bentonite suspension so obtained was then repeatedly and successively passed through columns packed with cation (Amberlite IR 120) and anion (Amberlite IRA 400) exchange resins. The actual HB content in the suspension was determined by evaporating a known volume to complete dryness.

Polymerization: Measured amount of alcohol was added under pure N_2 to known volume of HB suspension in pyrex bottles (outside being painted black), stoppered, shaken vigorously and allowed to equilibrate at the polymerization temperature. The polymerization was started by adding MMA under N_2 and shaking well. Control runs were carried out side-by-side without alcohol. The bottles were withdrawn from time-to-time and the reaction was arrested by adding DPPH solution followed by chilling. The solid mass was separated by centrifugation ($16-17 \times 10^3$ r.p.m.), dried in a vacuum oven at $40^\circ C$ and weighed. Extractable and non-extractable polymethylmethacrylates PMMA's were separated by repeated extraction with benzene and centrifugation. Benzene extracted PMMA was purified by precipitation into a mixture of methanol and petroleum ether followed by drying under vacuum at $40^\circ C$.

Techniques: Except for x-ray diffractions, benzene extracted PMMA's were used for analyses. Intrinsic viscosities were determined in benzene at $30^\circ C$ using Ubellhode Viscometer. \bar{M}_w/\bar{M}_n 's were calculated from GPC counts with a standard PMMA curve, GPC traces were obtained by using a Waters high pressure instrument, RI detector and five μ Styragel columns. E.s.r. spectra were recorded in a Varian E-4X band EPR spectrometer. X-ray diffraction data were obtained with Fe-filtered CoK_α radiation using a camera of 114.83 mm diameter.

RESULTS AND DISCUSSION

The polymerization of MMA at 60°C with aqueous suspension of HB alone yielded ~2% PMMA. Under identical conditions, except in the presence of alcohols, significant amounts of PMMA's were obtained (Table 1). \bar{M}_v 's of PMMA's harvested with alcohols of chain lengths C₁ to C₄ are essentially the same for similar conversions in spite of their different chain transfer constants. Evidently, alcohols do not behave as chain transfer agents in HB/MMA polymerization systems. Not only alcohols but also thiols produced high molecular weight PMMA's in good yield (13). It is noteworthy that a gradual increase in ethanol con-

Table 1

Polymerization of MMA in the presence of different Alcohols: [HB] = 0.8 % (w/v), [MMA] = 0.374 M; [Alcohol] = 0.34 M; total vol. 50 ml, 60°C, 6 hrs.

Alcohol	ϵ^a	$C_A^b \times 10^4$	Conversion (%)	$\bar{M}_v \times 10^{-6}$	$\bar{N}_v^d \times 10^6$
-	-	-	1.5	-	-
Methanol	32.70	0.20	54	1.92	0.52
Ethanol	24.25	0.40	57	1.98	0.54
n-Propanol	20.13	0.69	50	2.00	0.50
Isopropanol	18.41	0.58	49	1.98	0.46
n-Butanol	17.51	0.25 ^c	51	1.80	0.52

^a Dielectric Constant at 25°C

^b Chain transfer constant to alcohol for the free radical polymerization of MMA at 60°C. Data from Ref. 12.

^c Data at 80°C

^d Viscosity average moles of PMMA.

centration resulted in higher yields. A 500 fold increase in ethanol conversion increased from 25% to 68% (Table 2). 100% conversion was not achieved with HB/MMA/ethanol even after a week. \bar{M}_v 's decreased initially but attained a constant value. \bar{N}_v 's increased parallelly and remained constant at $\sim 0.5 \times 10^{-6}$. Evidently, increased amount of ethanol deactivated increased number of octahedral aluminiums and increased the concentration of active sites for the polymerization. The near constancy of \bar{M}_w/\bar{M}_n 's (1.8-1.9) at high ethanol concentrations along with unaltered \bar{N}_v 's strongly rules out transfer to alcohol. The e.s.r. spectra of dry HB soaked with ethanol indicated the presence of odd electron (Fig. 1). Mössbauer spectra of HB failed to identify any transition metal ion. However, we failed to register any odd electron in the aqueous suspension treated with alcohol.

Table 2

Polymerization of MMA in the presence of varying amounts of Ethanol: [HB] = 1.08 % (w/v), [MMA] = 0.374 M, total vol. 50 ml, 60°C, 12 hrs.

Ethanol $M \times 10^3$	Conversion %	$\bar{M}_v \times 10^{-6}$	$\bar{N}_v \times 10^6$	\bar{M}_w/\bar{M}_n
-	2.0	-	-	-
0.86	25.2	4.31	0.11	1.76
3.43	30.7	3.70	0.15	1.88
4.28	35.8	3.12	0.21	1.84
5.13	42.5	2.73	0.29	-
21.40	48.3	2.60	0.35	-
51.30	55.6	2.33	0.45	1.80
102.60	62.9	2.15	0.55	-
307.80	65.4	2.20	0.55	1.95
513.00	68.2	2.40	0.53	1.79

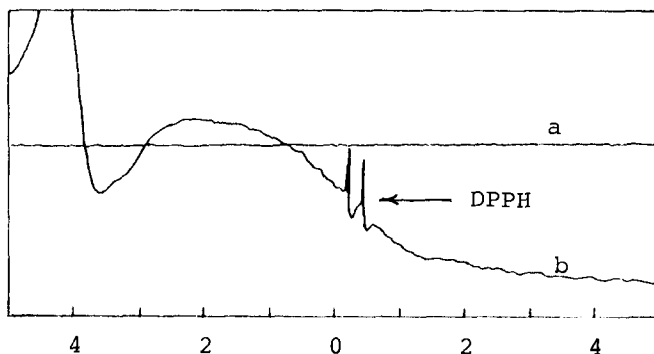
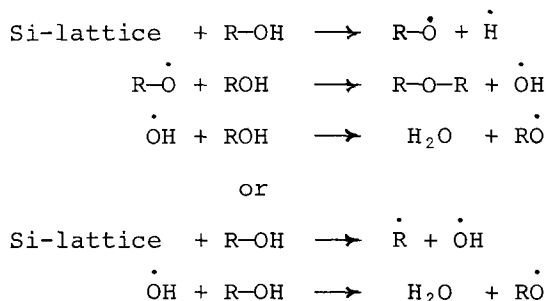


Figure 1: E.s.r. spectra of (a) HB
(b) ethanol treated HB

This is probably due to their extreme low concentration. In the polymerization system the odd electron, therefore, originated from the adsorption of alcohol on HB.

In order to establish the nature of active sites, Al-sites were totally blocked by treating the suspension with sodium hexametaphosphate and the polymerization of MMA was carried out. High yields of PMMA's were obtained only with alcohols.

It was suggested earlier that Al-sites of bentonite cannot promote the polymerization of MMA (8). The availability of H^+ in bentonite is not necessary to induce the polymerization since Na^+ and Cu^{++} forms were as successful only with alcohols (13). These results strongly suggest the free radical generation via the complex formation between alcohols and Si-sites of HB. Dowdy and Mortland also suggested that alcohols can penetrate the near surface of clay crystal lattice (14). This has been further corroborated by polymerizing MMA on quartz surface (200 mesh) in the presence of alcohols. Again, quartz alone failed to do so. With such a knowledge we suggest the following radical forming steps:



It is highly probable that the vacant d-orbital of Si in the lattice stretches the unsymmetrical alcohol molecule to form the radical.

X-ray diffraction data suggest a basal spacing of 14\AA for HB dried at $100\text{--}105^\circ\text{C}$ and, water occupies 4.4\AA . Dekking reported that a 3.3% (w/v) bentonite suspension has a water layer of 35.4\AA (6). Therefore, in aqueous suspension swelling to an extent of 31\AA occurs. On close examination a spacing of 17.9\AA has been found in dry HB-PMMA adduct. This allows two MMA layers (each attached to Si-layer) within the interlamellar space. Thus the frequency of termination between the growing chains would be low since that would involve two interlamellar Si-layers separated by nearly 30\AA . Such an explanation requires free radical initiation to exist on the Si-layer.

In all the polymerizations an induction period of ≈ 90 mins was observed. Higher initial rate of polymerization was associated with higher ethanol concentration (Fig. 2). Though the exact nature of the polymerization with an aqueous HB suspension is still unknown to us at this point, we have found that at conversions below 10% the overall initial rates are 0.89×10^{-5} , 1.28×10^{-5} , 1.66×10^{-5} and 1.81×10^{-5} moles $\text{lit}^{-1} \text{sec}^{-1}$ for 0.39, 0.68, 1.028 and 1.37 M ethanol respectively (Fig. 3). These values are much lower than those for the aqueous polymerizations of MMA using conventional free radical initiators. The overall initial rate in this system is of the order of 0.5 with respect to ethanol.

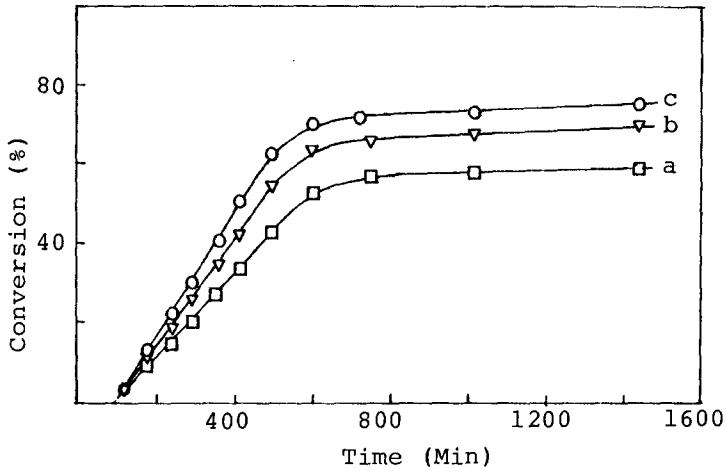


Figure 2: Time conversion plots at (0°C) with [HB]=0.87% (w/v), [MMA]=0.374 M for different ethanol concentration (a) 0.68 M, (b) 1.03 M and (c) 1.37 M

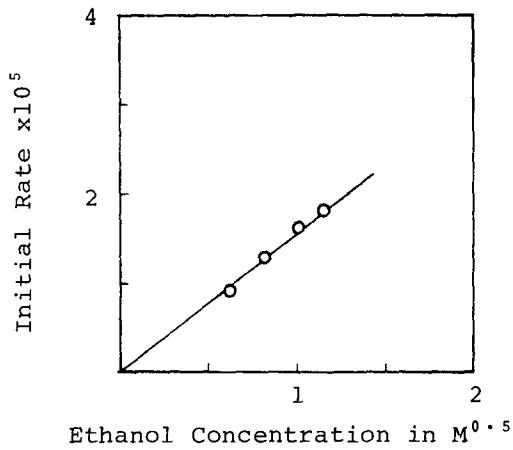


Figure 3: Initial rate of polymerization at (0°C) as a function of $[\text{ethanol}]^{0.5}$
 [HB]=0.87% (w/v)
 [MMA]=0.374 M

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