Reactions Catalyzed by Minerals.   Part III.
The Mechanism of Spontaneous Interlamellar Polymerizations in Aluminosilicates

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Synopsis

The spontaneous polymerization of hydroxymethacrylate monomers by the layer aluminosilicate montmorillonite is reported.   Saturation of montmorillonite by acrylic monomers gives interlayer complexes of three types, only one of which is susceptible to spontaneous polymerization.   Electron-donating sites situated within the silicate lamellae initiate the spontaneous polymerization which it is suggested proceeds by a mechanism involving radical-anions.   The results of this study together with those reported previously are used to explain the variety of effects noted when aluminosilicates are added to or heated with vinyl or acrylic monomers.

INTRODUCTION

The polymerization of vinyl or acrylic monomers which are held in specific orientations has received increasing attention from polymer chemists in recent years, partly because of the possibility that polymers produced in this manner could have unique properties.   Of the various substrates that have been used to orient the monomer prior to polymerization, the lamellar aluminosilicate montmorillonite is particularly attractive, since the nature of the silicate surface is well established and the monomer or polymer complexes with this mineral can be examined readily by x-ray diffraction.   Additional interest in montmorillonite as the substrate has come from the studies of Blumstein[1] who has demonstrated that polymers formed between the silicate layers possess unusual resistance to thermal degradation.   Blumstein used conventional free-radical initiators and γ-radiation to polymerize the monomer/montmorillonite complexes.   Furthermore, Glavati et al.[2] have found that polymerization of acrylonitrile/-montmorillonite complexes by γ-radiation gives stereospecific polymers.

In this paper we report the spontaneous polymerization of hydroxymethacrylate monomers in a montmorillonite/monomer complex and suggest a mechanism for this polymerization.   Previous reports of other polymerization reactions in the presence of montmorillonite are discussed in relation to the proposed mechanism.

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EXPERIMENTAL

Methyl methacrylate and all solvents used were purified as described in Part I.[3] N-Methylol acrylamide (60% aqueous solution) (Cyanamid) was used without further purification. Hydroxyethyl methacrylate and hydroxypropyl methacrylate (Rohm and Haas) were passed through columns of alumina to remove peroxides.

The benzidine blue test was carried out by adding the mineral to a saturated solution of benzidine hydrochloride in water. This reagent gives a blue radical-cation with oxidants. It is used to indicate the oxidation state of transition metals in the silicate lattice.

Minerals

The two Wyoming bentonites commonly used as reference sources of montmorillonite (Volclay ex. American Colloid Company, and Aquagel ex. Baroid Division of National Lead Corp.), were used in all experiments unless otherwise indicated. The bentonites were purified by first removing the heavy mineral impurities by sedimentation in water, then dialyzing against distilled water (1 week) to remove soluble salts. The purified montmorillonites were dried in the air at 20°C. They contained 9–10% water. They gave no color reaction with benzidine reagent.

The montmorillonites obtained in the above manner contained a mixture (60% Na^+, 30% Ca^{++}, 10% Mg^{++}) of cations in the exchange sites. Homoionic montmorillonites (Na^+, Ca^{++}, Co^{++}) were prepared by treating the purified natural clay with $1N$ solutions of the appropriate chloride until saturation was achieved, and washing with distilled water until chloride free. The clay gels were freeze dried. The homoionic montmorillonites did not give a color with benzidine. The oxidized montmorillonites were obtained by heating the clays, purified as above, in air at 110°C. They gave strong blue colors with benzidine.

Chemically reduced clays were prepared by treating the oxidized clays with dilute aqueous hydrazine or by the electrochemical method of Leach et al.[4] They gave no color with benzidine.

Polyphosphate-treated montmorillonites were prepared by adding 0.5% (by wt. of clay) of a polyphosphate (Calgon marketed by ICIANZ Ltd.) in water to a 5% suspension of the required montmorillonite. The viscosity of the slurry dropped rapidly on adding the polyphosphate. The treated clay was washed twice with water and then freeze dried.

Preparation of Monomer/Montmorillonite Complexes

The monomer was added to the montmorillonite and the formation of the interlamellar complex was followed by x-ray diffraction. The interlamellar spacings obtained are shown in Table I. Similar results were obtained when the clay used was dried under reduced pressure, or when the excess monomer was removed by washing with petroleum ether, b.p. 40–60°C., which because of its relatively nonpolar character does not displace mono-

TABLE I

Interlamellar Spacings of Monomer Complexes in Montmorillonite

Monomer	C-axis repeat distance of complex, (A.)	Inter-lamellar spacing, A.[a]	Complex type (see Fig. 1)
Ethyl acrylate	16.1	6.8	1
Glycidyl acrylate	17.0	7.7	1
Methyl methacrylate	17.0	7.7	1
Hydroxyethyl methacrylate	17.3	8.0	3
Hydroxypropyl methacrylate	17.3	8.0	3
Glycidyl methacrylate	17.0	7.7	1
Butyl methacrylate	12.8	3.5	2
Lauryl methacrylate	12.7	3.4	2
Dimethylaminoethyl methacrylate	12.9	3.6	2
tert-Butylaminoethyl methacrylate	15.4	6.1	2

[a] Thickness of silicate lamella taken as 9.3 A. This value is calculated from the results of Radoslovich,[5] and differs from those used by Blumstein[6] or Friedlander and Fink[7] who have confused the basal spacing given by x-ray diffraction (9.6 A.) with the thickness of the silicate layer. The basal spacing is the thickness of the silicate layer plus the space taken up by the dehydrated exchangeable cations.

mer adsorbed between the silicate layers. The oxidized and polyphosphated reduced forms of the clay all gave similar complexes.

Polymerization of Monomer/Montmorillonite Complexes

Complexes of each of the monomers listed in Table I with the montmorillonite described above were prepared, washed with petrol, and allowed to stand (48 hr.) at room temperature. Each complex was then washed with alcohol and then water; in all cases x-ray diffraction at 100°C. gave the 9.6 A. spacing typical of montmorillonite. Examination of the alcohol/water liquors showed that an oil had been extracted from the HEMA and HPMA complexes with the reduced montmorillonites; no reaction products were found from the other monomer complexes. The oil from the HEMA/reduced montmorillonite complex had infrared absorption bands corresponding to hydroxyl and ester–carbonyl. The band due to carbon–carbon unsaturation was absent. The montmorillonites recovered by washing out the low molecular weight oil gave a dark blue color with benzidine.

The monomer complexes were also stood (48 hr.) in contact with excess monomer. The HEMA, HPMA, and N-methylol acrylamide complexes with reduced montmorillonites became rubbery or hard. The other monomers could be removed unchanged by washing as described above. N-Methylol acrylamide was polymerized by montmorillonite but x-ray data could not be obtained because the monomer lost formaldehyde during the drying of the specimen prior to x-ray diffraction.

A range of commercially available bentonites was examined for catalytic activity in the polymerization of HEMA, and the results are in Table II.

TABLE II

The Relation Between Activity in Polymerizing Hydroxyethyl Methacrylate and the Benzidine Blue Test for a Range of Bentonites

Parent bentonite[a]	Activity with HEMA	Color with benzidine	Color with benzidine after oxidation[b]
Volclay[c]	+	Pale blue	Very dark blue
Aquagel[d]	+	Pale blue	Very dark blue
Otay, California	+	None	Dark blue
Upton, Wyoming	+	None	Dark blue
Little Rock, Arkansas	−	Pale mid-blue	Dark mid-blue
Clay Spur, Wyoming	−	Mid-blue	Dark mid-blue
Hi Jel[e]	−	Mid-blue	Mid-blue
Aberdeen, Mississippi	−	Dark blue	Dark blue
Sin Procedencia, Argentina	−	Mid-blue	Very dark blue
Red Hill, U.K.	−	Very dark blue	Very dark blue
Newcastle, N.S.W., Aust.	−	Dark blue	Very dark blue
Gellibrand, Vic., Aust.	−	Dark blue	Very dark blue
Marburg, Q'ld., Aust.	−	Mid-blue	Dark blue
Andamooka, S.A., Aust.	−	Pale mid-blue	Mid-blue
Cardabia, W.A., Aust.	−	Dark blue	Dark blue

[a] All these montmorillonites give the interlamellar spacings shown in Table I with the appropriate monomers.

[b] Clays oxidized by heating at 100°C. in air (1 hr.).

[c] Registered trademark of American Colloid Co.

[d] Registered trademark of National Lead Corp.

[e] Registered trademark of Georgia Kaolin Co.

The polymerization of HEMA/reduced montmorillonite complexes in contact with excess monomer proceeds more readily at elevated temperatures; for example, a tough rubbery block forms in 5 hr. at 50°C. or 24 hr. at 20°C.

The influence of water content of the clay on the polymerization is shown in Table III. No significant differences in the interlamellar monomer spacing was noted with variation in the water content of the clay.

The mineral/poly(HEMA) reaction mass, after washing with alcohol to remove monomer, gave an x-ray diffraction spacing of 13.6–14.0 A. This indicates the presence of poly(HEMA) between the silicate lamellae. The rate of polymerization of the HEMA complex in excess HEMA was

TABLE III

The Effect of Water on the Polymerization of HEMA on Montmorillonite

Water content (w/w) of clay	Time to form rubbery block at 50°C. (hr.)
9% (air dry)	5
20%	1.5
27%	>1
38%	1.0
70%	7

TABLE IV
Rate of Polymerization of HEMA by Montmorillonite at Room Temperature

Contact time, hr.	Proportion of polymer complex[a]	Appearance of mixture
1	0	Mobile clay/monomer slurry
2	0	Mobile slurry
3	0	Mobile slurry
4	0[b]	Mobile slurry
5	0.02	Clay mass beginning to be rubbery Clay settles quickly
6	0.04	Clay slightly rubbery, settles rapidly
7	0.05	Rubbery coherent mass of clay
500	1.00	Tough rubbery block of clay-filled polymer in excess monomer

[a] Measured by the ratio of the intensity of the (001) x-ray reflection of the polymer complex to the total intensity of the (001) reflections of the reaction mixture.

[b] This clay contained 1% by weight of external polymer as determined by the weight loss at 600°C. minus that of the original montmorillonite.

followed by x-ray diffraction. Samples were washed to remove monomer before examination. The results are in Table IV.

Attempted Separation of Poly(HEMA)/Montmorillonite Complex

A poly(HEMA)/montmorillonite reaction mass, prepared as above, was extracted with acetone (95 hr.) to remove unchanged monomer, and then 2-ethoxy ethanol, a good solvent for poly(HEMA) (72 hr.). No polymer was extracted from the polymerized mass.

The reaction mass was treated with 40% HF at 0°C. (24 hr.) and the reaction mixture treated as described for montmorillonite/poly(methyl methacrylate) complexes.[6] The product isolated had absorption bands at 1190 and 2290 cm.$^{-1}$; these bands were not present in poly(HEMA) but are present in some fluorine-containing compounds. A similar product was obtained by the action of HF on poly(HEMA), prepared by the benzoyl peroxide initiated polymerization of HEMA.

Adsorption of Poly(HEMA) by Montmorillonite

Oxidized montmorillonite was added to a 4% solution of poly(HEMA) in HEMA. After 5 hr. at room temperature, the mineral phase was separated and washed thoroughly with alcohol. X-ray diffraction at 100°C. showed a 14.0 A. basal spacing, characteristic of a poly(HEMA)/montmorillonite complex.

Electron Spin Resonance Studies

The ESR studies were performed at room temperature on a Varian model V4501 spectrometer using 100 Kc./sec. field modulation and a
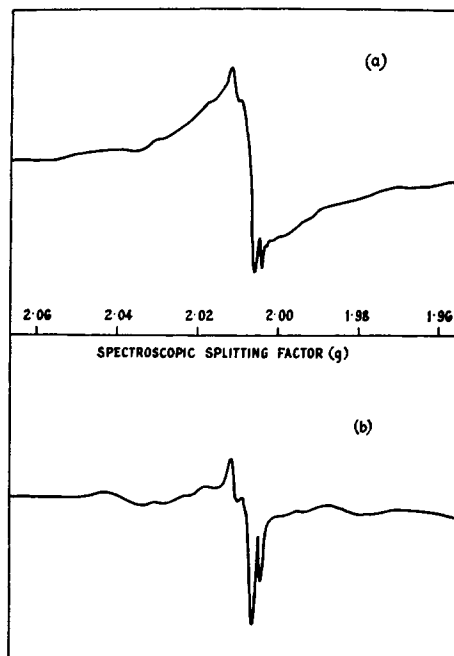
Fig. 1. ESR spectra of TCNE–clay complexes: (a) the region around $g = 2$ in the ESR spectrum of tetracyanoethylene on reduced Volclay; (b) the ESR spectrum of reduced Volclay in the same region. The g values were determined by comparison with the Mn^{++} peaks in Keramot whose peak positions had previously been established with a proton probe.

microwave frequency of 9.1 Gc./sec. The only changes in the spectra were in the region with a spectroscopic splitting factor (g) about 2. The ESR spectrum of tetracyanoethylene/reduced Na^+ Volclay [Fig. 1(a)], was run on a complex obtained by first drying the clay at 70°C. and 10^{-3} mm. Hg and then adding a degassed solution of tetracyanoethylene in benzene. The spectrum of dry reduced Na^+ Volclay in benzene is given in Figure 1(b). When tetracyanoethylene solution was added to oxidized Na^+ Volclay the ESR signal did not change. Degassed tetracyanoethylene solution had no detectable ESR signal.

DISCUSSION

The x-ray diffraction data (Table I) can be interpreted in terms of the formation of three types of monomer/montmorillonite complexes. Type I (Fig. 2), consists of two monomer layers lying flat between each pair of silicate lamellae; Blumstein[6] has suggested that the methyl methacrylate/-montmorillonite complex is of this type. The aminomethacrylates form complexes which contain only one monomer layer lying flat (Type 2, Fig. 2). The third type of complex (Type 3, Fig. 2), is formed by the hydroxy
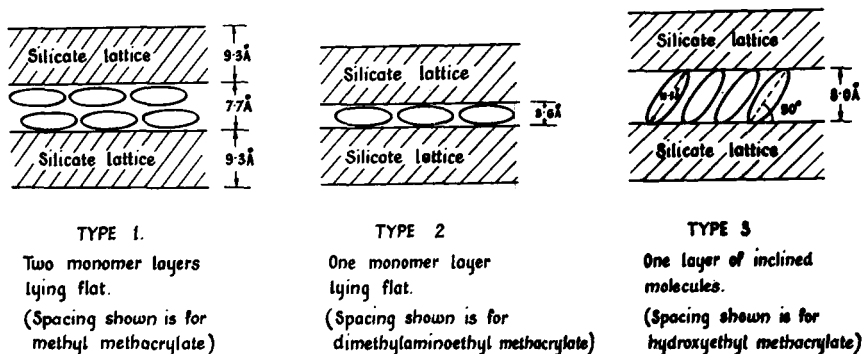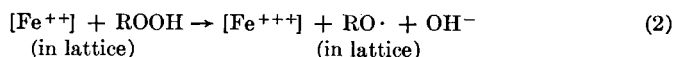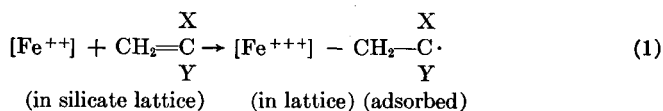
TYPE 1.

Two monomer layers
lying flat.

(Spacing shown is for
methyl methacrylate)

TYPE 2

One monomer layer
lying flat.

(Spacing shown is for
dimethylaminoethyl methacrylate)

TYPE 3

One layer of inclined
molecules.

(Spacing shown is for
hydroxyethyl methacrylate)

Fig. 2. Schematic representation of monomer–montmorillonite complexes.

methacrylates and consists of a layer of monomer molecules standing at an angle to the silicate lamellae. The suggestion of inclined orientation is not novel and is well established for montmorillonite complexes with alcohols,[8] fatty acids,[9] and amines.[10]

Of the monomer complexes listed in Table I, only those with type 3 orientation (HEMA, HPMA) polymerize. This suggests that in this type of compound, the hydroxyl group gives an inclined orientation favorable for initiation and propagation of the polymerization.

A number of observations suggest that the mineral initiates the polymerization of HEMA by acting as a reducing agent. Thus it has been shown that the mineral is oxidized in the process of initiating the polymerization, that oxidation of the mineral prior to adding the monomer destroys the catalytic activity, and that reduction of the mineral inactivated by oxidation regenerates the activity. Examination of a range of bentonites has confirmed that the mineral acts as a reducing agent in this polymerization; bentonites which were inactive in the polymerization of HEMA were in the oxidized form and could be activated by reduction. Treatment of the mineral with sodium polyphosphate, which coats the crystal edges,[11] does not inhibit the polymerization in excess monomer. Therefore, the polymerization is not initiated at the lamellar edges and the reducing sites are located along the silicate lamellae.

Two mechanisms consistent with the above observations are shown in eqs. (1) and (2). (Iron is shown as the oxidizable atom in the silicate lattice although other transition metals can be present.)

$$[Fe^{++}] + CH_2{=}\overset{X}{\underset{Y}{C}} \rightarrow [Fe^{+++}] - CH_2{-}\overset{X}{\underset{Y}{C}}\cdot \qquad (1)$$

(in silicate lattice)   (in lattice) (adsorbed)

$$[Fe^{++}] + ROOH \rightarrow [Fe^{+++}] + RO\cdot + OH^- \qquad (2)$$
(in lattice)   (in lattice)

In mechanism 1 electron transfer from the mineral to the double bond gives the radical-anion; this mechanism is similar to that proposed for the

polymerization of olefins by transition metal catalysts.[12] It is most likely that the anion would be destroyed rapidly by reaction with proton donors associated with the mineral surface (—OH of monomer, water molecules). The free radical formed from the radical-anion could then propagate between the mineral sheets: termination by transfer to the mineral surface or crystal edge[13] would give rise to the low molecular weight polymer that was found in the absence of excess monomer. Where monomer is present outside the clay complex, some chains propagate from between the clay layers. The conditions under which the external polymer grows (room temperature, high monomer concentration, low radical concentration) would lead to a high molecular weight poly(HEMA) which because of its highly polar nature would be absorbed strongly onto and between the clay surfaces. The possibility of poly(HEMA) migrating into the interlamellar region has been confirmed by adsorption studies; Greenland's[14] work on poly(vinyl alcohol)/montmorillonite systems also shows that interlayer complexes can form by polymer adsorption. X-ray diffraction results (Table IV) are consistent with the montmorillonite polymer complex forming by adsorption.

The feasibility of radical-anion formation on montmorillonites is supported by the reaction of tetracyanoethylene (TCNE) with montmorillonite (Volclay). ESR spectra (Fig. 1) show that the reduced form of the clay is oxidized by TCNE which in the process is converted to the radical-anion.[15] Oxidized Volclay did not react with TCNE.

The accelerating effect of water on the reaction (Table III) is also in accord with an electron transfer mechanism since it has been noted previously that water increases the rate of oxidation of benzidine where the clay acts as an electron acceptor.[16] The precise mechanism by which water aids electron transfer reactions has yet to be defined.

Mechanism (2) involves the well-known hydroperoxide/transition metal system. Evidence not in support of Mechanism (2) is that oxygenation of the monomer prior to complex formation does not accelerate the rate of polymerization. However, the possibility that traces of oxygen adsorbed on the mineral surface cause rapid hydroperoxidation, or that the hydroperoxide content is not rate determining cannot be discounted.

Irrespective of the initiating reaction the suggested propagation stage involves free radicals—the most likely intermediates for the chain growth of a methacrylate under the conditions used.

The mechanisms proposed in this and previous papers[3,13] contribute to a rational explanation of the apparently contradictory influences shown by clay minerals on polymer-forming reactions. Thus, one of the apparent anomalies of montmorillonite was its ability to promote the polymerization of monomers where propagation presumably involved only cations (butene-2)[17] or only radical or anionic intermediates (acrylamide, 4-vinyl pyridine)[7] and to inhibit other polymer-forming reactions.[13] To explain these effects it is essential to consider the heterogeneous nature of the layer silicate structure which enables the mineral to be either an electron acceptor

or an electron donor. Thus, montmorillonite has strong electron accepting sites at the crystal edge where monomers such as styrene are converted to radical-cations. Within the silicate lamellae transition metals can act as electron donor or acceptor sites depending on their oxidation state. The electron donor sites within the silicate lamella can reduce monomers to radical-anions; a prerequisite for this reaction is that the monomer forms a suitable interlamellar complex.

The influence of the mineral on polymer forming reactions which are initiated by conventional free radical initiators is distinct from the spontaneous polymerizations. The influence of the mineral on these reactions is the result of the mineral reacting with the active intermediates.[13] The spontaneous polymerizations involve mineral–monomer interaction.

These reaction possibilities are illustrated in Scheme 1. It should be noted that reports that "dispersed" sodium montmorillonite is an active catalyst for the spontaneous polymerization of methyl methacrylate[18] are not at variance with the above suggestions; the "dispersion" process consisted of vibration milling of the montmorillonite monomer mixture; bond fission of the silicate to give free radicals is more than likely under these conditions.
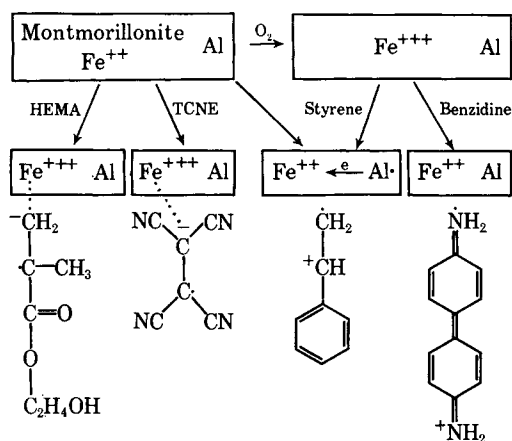
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