

Reactions Catalyzed by Minerals. Part II. Chain Termination in Free-Radical Polymerizations

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Synopsis

The influence of aluminosilicates and magnesium silicates on the free-radical polymerization of methyl methacrylate is discussed. The relationship between the structure of the mineral and its ability to inhibit radical reactions is considered, and it is concluded that aluminum in octahedral coordination is mainly responsible for the inhibition. Mechanisms which account for the termination reaction are proposed and supported by studies of the reaction of stable free radicals with the minerals.

INTRODUCTION

The modification of an organic polymer system by the addition of pigments and/or fillers is practiced widely in the formulation of plastics, rubbers, and surface coatings for industrial use. The pigment or filler may be added to reduce damage to the organic polymer by irradiation, to provide filling properties in a coating composition used for surface preparation, to perform a decorative function, or to influence and modify the mechanical properties of the system. Many common pigments (TiO_2 , ZnO , carbon black) are now known to be active chemically when used with thermosetting organic polymers, but, in general, the fillers (with the exception of carbon black in rubber compositions) have been regarded as being chemically inert.

Many of the common fillers (china clay, talc) belong to the class of aluminum and magnesium silicates known as the clay minerals. Recently it has been shown that these minerals catalyze a number of polymerization reactions if adsorbed water is removed by drying under mild conditions.¹ Other reports also suggest that the clay minerals are not chemically inert. In some polymer compositions they are claimed to adversely affect cross-linking reactions, for example, in the curing of an unsaturated polyester with styrene^{2,3} which involves free-radical intermediates. Therefore we have examined the influence of clay minerals on the free-radical polymerization of methyl methacrylate and on a number of model reactions, with particular emphasis on the mechanism by which the mineral influences the reactions, and the significance of these effects to the formulation of polymer-filler compositions.

EXPERIMENTAL AND RESULTS

The methyl methacrylate and the solvents used were purified as described in Part I.¹

The minerals used were micronized to give a particle size of approximately 2 μ . Polyphosphate-modified minerals were prepared as follows. The mineral (100 g.) was added with stirring to water (200 ml.) in which was dissolved a sodium polyphosphate (4.0 g., Calgon marketed by ICIANZ Ltd.). The treated mineral was separated by centrifuging the solution. The process was repeated and the polyphosphate modified mineral washed with water (5 times 100 ml.) and freeze-dried.

Benzoyl peroxide assay was 98%. Triphenylmethyl radical solution was prepared as follows. Triphenylchloromethane (2.0 g.) was dissolved in anhydrous benzene (20.0 ml.) and the solution purged with nitrogen. The nitrogen atmosphere was maintained while zinc dust (5.0 g., large excess) was added and the mixture shaken (30 min.). The yellow solution containing the triphenylmethyl radical was filtered and diluted with anhydrous benzene as required.

Visible spectra were recorded on a Beckmann ratio recording spectrophotometer (Model DK2).

ESR spectra were recorded on a Varian X-band spectrophotometer at 100 KHz. Modulation.

NMR spectra were recorded on a Varian A-60 spectrometer.

Thermal Polymerization of Methyl Methacrylate in the Presence of Minerals

The mineral (2.0 g. dried at 110°C./2 mm.) or polyphosphate-treated mineral, methyl methacrylate (28.0 g.), and benzene (28.0 g.) were heated under reflux (2 hr.) in a 100-ml. round-bottomed flask fitted with a stirrer, the speed of which was controlled at 300 rpm. An atmosphere of nitrogen was maintained throughout the experiment.

The reaction mixture was cooled rapidly, filtered through a sintered glass funnel (porosity 3) and the residue washed with benzene (10 \times , 5 ml.) and then acetone (10 \times , 5 ml.).

Poly(methyl methacrylate) was precipitated by slowly adding the filtrate to a large excess of methanol which was being stirred. The precipitated polymer was filtered off, dried at 35–40°C./10 mm., and weighed.

The polymers were redissolved in benzene and reprecipitated for molecular weight measurements. The relative viscosity was measured in an Ostwald viscometer tube at 25°C. with ethylene dichloride as the solvent. Molecular weights were calculated from eq. (1):

$$M = 1.47 \times 10^6 (N_r - 1 - \ln N_r)^{0.65} \quad (1)$$

where N_r = efflux time of polymer solution/efflux time of solvent. The results are reported in Table I.

The efficiency of the procedure was checked by subjecting the mineral, after washing as above, to continuous extraction with benzene (48 hr.) and

TABLE I
Thermal Polymerization of Methyl Methacrylate in the
Presence of Minerals

Mineral present	Yield of polymer, %	Molecular weight of polymer $\times 10^{-4}$
None	3.68	1.364
Attapulгите	Nil	—
Kaolin	0.51	2.882
Montmorillonite	0.680	3.051
Talc	2.20	2.543
Polyphosphated attapulгите	1.115	2.840
Polyphosphated kaolin	0.71	2.220
Polyphosphated talc	2.29	2.761

then acetone (48 hr.). The combined solvent extracts yielded only trace quantities of polymer. The mineral was then dissolved in HF (40%). No significant amounts of polymer residues remained after this treatment.

The possibility that the reduced yield of polymer was the result of the clay catalyzing the depolymerization of polymer, rather than inhibiting its formation was discounted by the following experiment. Poly(methyl methacrylate)(0.23 g.) in benzene (50 g.) was heated with kaolin (4.0 g.) as described above for 2 hr., then the polymer recovered by solvent extraction with benzene followed by acetone. The viscosity-average molecular weight of the poly(methyl methacrylate) recovered (0.21 g., 91.5%) was the same as the starting material.

An attempt was made to detect low molecular weight compounds which could possibly arise from the termination reaction. Methyl methacrylate was heated with attapulгите as described above for 48 hr., analysis by gas-liquid chromatography with a 6-ft. column packed with 15% squalene on Chromosorb P, a temperature of 100°C., a flow rate of 75 ml./min. of carrier gas (40/60 = hydrogen/nitrogen), and a flame ionization detector, did not reveal any impurities in the recovered monomer.

Benzoyl Peroxide-Initiated Polymerization of Methyl Methacrylate in the Presence of Minerals

The mineral (4.0 g. dried at 110°C./2 mm.), methyl methacrylate (56.0 g.), benzene (56.0 g.), and benzoyl peroxide (0.0998 g.) were heated in a 250-ml. round-bottomed flask as described above. Samples were taken during the reaction and the yield and molecular weight of the polymer determined. The results obtained are shown in Table II. The benzoyl peroxide content was measured on the samples by titration using the KI/thiosulfate method. In the absence of a mineral the following results were obtained (the peroxide content of the solution has been expressed as a percentage of the original figure); after 15 min., 91% peroxide; 30 min., 83% peroxide; 45 min., 75% peroxide; 60 min., 68% peroxide. In the presence of the minerals the peroxide decomposition was similar to that recorded above.

TABLE II
Benzoyl Peroxide-Initiated Polymerization of Methyl Methacrylate
in the Presence of Minerals

Time, min.	Yield of polymer, with various minerals present, %				
	None	Attapulgite	Poly- phosphated attapulgite	Kaolin	Poly- phosphated kaolin
15	15.0	8.2	10.3	10.0	12.2
30	28.0	16.0	19.7	19.9	23.1
45	32.0	22.4	26.2	26.5	29.7
60	35.0 ^a	26.0 ^b	28.7 ^c	29.0 ^d	32.5

^a M.W. = 8.87×10^5 .

^b M.W. = 9.44×10^5 .

^c The polyphosphated minerals formed extremely fine suspensions in the polymer solutions and separation was difficult. Molecular weights were therefore not measured.

^d M.W. = 9.12×10^5 .

Reaction of Triphenylmethyl Radicals with Clay Minerals

All experiments were carried out in a dry box under an atmosphere of nitrogen. The clay (dried 4 hr. at 110°C./2 mm.), was added to a benzene solution of triphenylmethyl radicals. After standing, the ESR and visible spectra of the solution and of the clay were run. The experiments were repeated with the use of polyphosphate-treated clays. The visible spectra of the mineral-triphenylmethyl radical suspensions were obtained by shaking the mixture thoroughly and running the spectra of the suspension.

Attapulgite, kaolin, and montmorillonite and triphenylmethyl gave an absorption at 24,000 and 22,700 cm.^{-1} : these bands are displaced by 300–400 cm.^{-1} from the spectrum of triphenylmethyl carbonium ion recorded by Anderson.⁴ Such a shift is not unreasonable because of the known influence of solvents on the position of the absorption bands: the reference spectrum of the carbonium ion was run in sulfuric acid solution and that of the clay samples in benzene. No absorption corresponding to the triphenyl carbanion was observed.

The ESR spectra of the mineral-triphenylmethyl radical suspensions showed that the radical was still present when the mineral used was talc, and only a small reduction in radical signal occurred with polyphosphated montmorillonite, polyphosphated kaolin, or polyphosphated attapulgite, (decreasing order of radical signal). No radical signal was found with kaolin or montmorillonite.

In a similar experiment attapulgite was added to a benzene solution of triphenylmethyl radicals (approximately 0.4 g.). After standing (10 min.) the mixture was filtered and the clay residue washed with benzene (5 \times , 10 ml.) and then acetone (5 \times , 10 ml.). The solvent was removed from the combined filtrates by evaporation under reduced pressure and the residue crystallized from ethanol. Crystals of triphenylcarbinol (0.25 g.) formed, and these after recrystallization from ethanol have a melting point of 163–

165°C. The melting point was not depressed by admixture with an authentic specimen of triphenylcarbinol.

The infrared and NMR spectra of the product were identical to those of an authentic sample of triphenylcarbinol.

The possibility of the triphenylmethyl carbonium ion being formed by an alternative route involving triphenylmethane was investigated because it has been reported that some aluminosilicates activated under more drastic conditions than used here, are capable of promoting such a reaction. Using similar conditions to those described above for triphenylmethyl radicals, triphenylmethane was recovered unchanged, in 95% yield, from attapulgite after standing for 24 hr. The recovered product has a melting point and mixed melting point of 93–94°C.

ANAL. Calcd. for $C_{19}H_{16}$: C, 93.4%; H, 6.55%. Found: C, 93.3%; H, 6.66%.

Reaction of Benzidine with Clay Minerals

The clay minerals were dried under the conditions used in the polyphosphate treatment. Benzidine hydrochloride solution was then added to the mineral and the intensity of the color that developed was noted. Kaolin gave a very pale blue color, whereas polyphosphated kaolin did not produce any detectable blue; attapulgite gave a medium blue color, whereas the polyphosphated attapulgite gave only a pale blue; talc gave no color development when treated with benzidine.

Polyphosphate treatment of the montmorillonite (Volclay) used in the polymerization experiments did not significantly reduce the intensity of the color when treated with benzidine; both minerals gave a deep blue color. The difficulty in distinguishing between the treated and untreated mineral is due to the relatively small number of electron accepting sites at the edge compared to the number of transition metal sites along the silicate layer in Volclay. It was, however, found possible to show that edge effects were significant in a montmorillonite (Otay) having a low transition metal content. This material gave a medium blue color with benzidine, and the polyphosphated mineral gave a pale blue.

TABLE III
Properties of Vulcanized Rubbers

Filler present	Cure	Ultimate	Elonga-	Modulus,		Split tear, lb./in. thickness	Hardness
		tensile strength, psi	tion at break, %	psi	psi		
Kaolin	10 min. at 160°C.	1640	810	200	350	200–190	53
	20 min. at 160°C.	2600	590	600	1310		62
	30 min. at 160°C.	2560	570	600	1300		64
Polyphosphate	10 min. at 160°C.	2640	700	380	930		61
Modified kaolin	20 min. at 160°C.	2880	590	550	1250	190–170	65
	30 min. at 160°C.	2800	580	560	1400		66

Evaluation of Polyphosphate-Treated Kaolin in Rubber

Kaolin and polyphosphate treated kaolin were processed into a rubber mix using the following formula: SBR 1502, 500 parts (by weight); sulfur, 15 parts; cyclohexyl benzothionyl sulfide, 10 parts; zinc oxide, 25 parts; coumarone resin, 37.5 parts; clay, 260 parts. The rubber mixes when cured gave the results shown in Tables III and IV.

TABLE IV
Results of du Pont Abrasion Tests of Vulcanized Rubbers^a

Stock	Weight before testing, g.	Weight after testing, g.	Loss in weight, g.	Specific gravity	Avg. vol. loss, cm. ³
Kaolin stock	5.070	4.280	0.790	1.24	0.643
	5.070	4.265	0.805		
Polyphosphate-modified kaolin stock	4.498	3.646	0.852	1.25	0.670
	4.455	3.632	0.823		

^a These evaluations were carried out by The Olympic Tyre and Rubber Company. We gratefully acknowledge their assistance.

Evaluation of Polyphosphate-Treated Kaolin in an Unsaturated Polyester

Treated and untreated kaolin was processed into the following formula: clay (15 parts by weight), Crystic 196 (unsaturated polyester marketed by Monsanto Chemical Company) (15 parts), and butyl acetate (15 parts) were dispersed in a ball mill to a Hegman gage reading of 1.0. To this were added 30 parts Crystic 196 and 5 parts styrene and ground for 1 hr. Then 38 parts Crystic 196, 12 parts styrene, and 0.31 part cobalt naphthenate solution (6% cobalt) were added with stirring; 2.0 parts methyl ethyl ketone peroxide was added immediately prior to use.

Gel points of each formulation were measured on a Cambridge Techne automatic gel timer. The polyester containing kaolin gelled in 85 min., and that containing the polyphosphate-modified kaolin in 61 min.

DISCUSSION

The free-radical polymerization of methyl methacrylate initiated thermally or by the decomposition of benzoyl peroxide was inhibited by all the clay minerals examined (Tables I and II). The presence of the mineral results in an increase in the molecular weight of the polymer formed and in a reduction of the yield of polymer. These observations (lower yield, higher molecular weight) suggest that the mineral reduces the number of free radicals available for chain initiation or propagation.

Control experiments have shown that the low yield of polymer formed when a mineral is present is not the result of enhanced rates of depolymerization of poly(methyl methacrylate) and that in the case of the benzoyl

peroxide-initiated reaction enhanced or inhibited decomposition of the initiator does not occur. The last observation is supported by other findings on the decomposition of free radical initiators in the presence of inorganic compounds with electron-accepting properties; for example, Imoto et al.⁵ have shown that the rate of decomposition of azoisobutyronitrile is not affected by zinc chloride.

It is not unexpected that the introduction of a substance with a high surface area into a polymerization system would reduce the radical concentration by surface collisions. However, this explanation alone does not account for the observed results, since the minerals vary in their effectiveness as polymerization inhibitors but have comparable surface areas under the experimental conditions used.

Furthermore, selective coating of the crystal edge (a small percentage of the total surface area) by a polyphosphate treatment⁶ reduces significantly the ability of the mineral to inhibit the polymerization of methyl methacrylate. These results demonstrate that the crystal edge is of prime importance in assigning a mechanism for the inhibition. This is substantiated by the greater inhibition shown by attapulgite compared with kaolin; both are aluminosilicates, but differ in that attapulgite has a greater edge to surface area than does kaolin.¹

The comparative effectiveness of the minerals in inhibiting the free-radical polymerizations is also of significance; the aluminosilicates* (kaolin, attapulgite, montmorillonite) are more effective inhibitors than magnesium silicate (talc). This observation taken in conjunction with the reduced inhibiting effect of the mineral when the crystal edge is masked by a polyphosphate, suggests that aluminum in octahedral coordination and situated at the crystal edge is responsible for a considerable percentage of the inhibiting action shown by the mineral.

The clay minerals are therefore influencing the free-radical polymerizations by virtue of their Lewis acidity, and in agreement with this suggestion it is noted that the ability of a mineral to inhibit polymerization (attapulgite > kaolin > montmorillonite > talc) is comparable to the order found by acidity measurements with Hammett indicators.⁷⁻⁹ Two likely mechanisms by which weak Lewis acids such as the clay minerals could inhibit free-radical reactions, involve preferential adsorption by the Lewis acid of the initiating or propagating free radical, and then either termination by dimerization or disproportionation, or electron transfer from the radical to the Lewis site and the formation of a carbonium ion.

In the particular case of methyl methacrylate, the cation is not a propagating species and adds preferentially to the carbonyl double bond of the monomer.¹⁰

Support for the electron-transfer mechanism comes from a study of the action of clay minerals on stable organic free radicals and on simple compounds. The triphenylmethyl radical is converted to a triphenylmethyl

* The structures of the minerals used in this study have been discussed previously in Part I.¹

carbonium ion by aluminosilicates (attapulgite, kaolin, montmorillonite) but not by talc. This reaction is readily followed by ESR and by visual spectroscopy. The triphenylmethyl carbonium ion eventually forms triphenylcarbinol by abstracting a hydroxyl ion from the mineral surface.

Under the conditions used in our experiments, the formation of the triphenylcarbonium ion was not a secondary reaction product of the triphenylcarbinol or of triphenylmethane which may have formed by alternative mechanisms, such as those proposed for silica-alumina catalysts under more drastic conditions.¹¹

Polyphosphate treatment of the mineral significantly reduces or destroys the ability of the mineral to convert the triphenylmethyl radical to the cation. These experiments demonstrate that the majority of the electron-accepting sites of significance to inhibition of polymerization by the mineral are located at crystal edges, and that free radicals can be oxidized to carbonium ions by these sites. The electron-accepting properties of aluminosilicates can also be demonstrated by the conversion of neutral organic compounds to radical cations; benzidine readily forms the blue radical-cation.

Once again, this reaction proceeds at the crystal edge as shown by the reduced reaction with the polyphosphate-treated clay. Some oxidation also takes place along the planar surfaces where transition metals present in the lattice act as electron acceptors in this reaction. The mechanism suggested for the polymerization of styrene on clay minerals also requires the crystal edge to act as an electron acceptor, but in this case from the styrene molecule¹ rather than a free-radical intermediate.

Although the evidence tends to favor electron transfer as the mechanism responsible for the inhibition of free-radical polymerizations the alternative of enhanced chain termination cannot be eliminated. The possibility of enhancing the interaction of two radicals is supported by the work of Hall,¹² who has shown that the thermal decomposition of benzoyl peroxide in the presence of an electron acceptor gives increased yields of diphenyl as a result of combination of phenyl radicals.

Compounds with a stronger Lewis acidity than the clay minerals have been shown previously to exert a variety of effects on free-radical reactions. Haas and Karlin^{13,14} noted that aluminum chloride, when present in large quantities, inhibited polymerization of acrylonitrile initiated by azoisobutyronitrile. On the other hand, in copolymerization reactions at low concentrations of aluminum chloride, the Lewis acid appears to influence the copolymer composition by preferentially promoting the incorporation of one monomer species.^{13,14} Brief reports also suggest that some Lewis acids may exhibit chain-transfer characteristics.¹⁵ The manner in which Lewis acids affect free-radical polymerization reactions can be related to a number of factors which include the concentration of Lewis acid, the ability to complex preferentially with the monomer or monomer radical, the specific adsorption of the undissociated initiator, the enhanced adsorption of reactive intermediates, and the ability to transfer chain activity.

The theory developed above for the manner in which clay minerals affect free-radical reactions has been applied successfully to polymer-filler systems of commercial interest. The vulcanization of a rubber-kaolin system proceeds more readily if the filler is treated with a polyphosphate, and similar results are obtained in the crosslinking of an unsaturated polyester system.

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Résumé

L'influence des aluminosilicates et des silicates de magnésium sur la polymérisation radicalaire du méthacrylate de méthyle est discutée ici. La relation entre la structure du minéral et son aptitude à inhiber les réactions radicalaires a été considérée et on en a conclu que la coordination octaédrique de l'aluminium est principalement responsable de cette inhibition. Des mécanismes qui rendent compte de la réaction de terminaison sont proposés et confirmés par des études de la réaction des radicaux libres stables avec les minéraux.

Zusammenfassung

Der Einfluss von Aluminumsilikaten und Magnesiumsilikaten auf die radikalische Polymerisation von Methylmethacrylat wird diskutiert. Die Beziehung zwischen der Struktur des Minerals und seiner Fähigkeit Radikalreaktionen zu inhibieren wird erörtert und der Schluss gezogen, dass oktaedrische koordiniertes Aluminium hauptsächlich für die Inhibierung verantwortlich ist. Mechanismen für die Abbruchsreaktion werden vorgeschlagen und durch Untersuchung der Reaktion stabiler freier Radikale mit den Mineralen gestützt.

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