Reactions Catalyzed by Minerals.   Part I.
Polymerization of Styrene

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Synopsis

The polymerization of styrene on neutral mineral surfaces has been studied. It has been shown that the polymerization has characteristics expected for both a radical and cationic reaction, and a mechanism involving a radical-carbonium ion is proposed to explain this evidence. A range of mineral catalysts have been investigated and a tentative theory proposed to relate the variation in activity with catalyst structure. Experiments have also been carried out to define the specific portion of the mineral surface responsible for the catalyst activity.

INTRODUCTION

Synthetic and naturally occurring minerals are used in a number of widely diversified roles in the chemical industry, and these include "carriers" for catalyst systems,[1] depolymerization or cracking catalysts,[2] alkylating[3] and isomerization[4] catalysts, decolorizing agents,[5] and polymerization catalysts[6] (often only dimer or trimer formation). In the vast majority of the applications involving polymerization or depolymerization, the mineral is first treated by acid and it is generally accepted that the activity is related to the minerals' ability to promote carbonium ion reactions,[7] usually by the donation of a proton.

Studies of polymerization on the neutral or nonacidic (in the Brønsted sense) minerals, are comparatively few. Hauser and Kollman[8] have shown that certain conjugated dienes are slowly converted to a monolayer of polymer on some clay minerals, while Friedlander[9] has noted a similar conversion of butadiene and cis-butene-2 on sodium montmorillonite (a layer silicate structure). Friedlander[9] has also briefly noted the vigorous exothermic polymerization of styrene on sodium montmorillonite, and this report contrasts with Blumstein's[10] inability to polymerize styrene on this mineral.

The present paper, which is the first of a series dealing with the reaction of polymerizable monomers on a mineral surface, discusses the polymerization of styrene on certain mineral surfaces and proposes a mechanism to account for this reaction.

EXPERIMENTAL AND RESULTS

Reagents

Styrene and methyl methacrylate were washed free of inhibitor with $1N$ sodium hydroxide, then washed with water, dried, and distilled under reduced pressure and an atmosphere of nitrogen.

Benzene, toluene, carbon tetrachloride, and ethyl acetate were analytical reagent quality and were distilled and the middle fraction collected. Acetone was distilled from potassium permanganate, while dioxane was purified by distillation from sodium. Analytical grade chloroform was washed with water to remove alcohol, dried, and distilled.

The minerals were ground in a mortar and pestle and micronized, if necessary, to give a particle size of approximately 2 μ.

Cobalt and calcium montmorillonite were prepared by shaking sodium montmorillonite with a $1N$ solution of the appropriate chloride until saturation was achieved, washing the mineral with water until chloride-free, and drying. Cobalt attapulgite and cobalt vermiculite were prepared in a similar manner.

Polymer Preparation, Isolation, and Characterization

Two methods of polymerizing the styrene with the mineral (sodium montmorillonite and attapulgite) were studied.

(a)   The mineral (0.5 g.) was dried in a muffle at the required temperature and time and then transferred to a vacuum desiccator containing P_2O_5. After cooling to room temperature under vacuum, the mineral was added to the styrene (25 g.) or styrene (25 g.)–solvent (25 g.) mixture and the polymerization allowed to proceed for 30 min. An aliquot of the reaction mixture was then taken in such manner as to exclude any clay mineral and slowly added to methanol with stirring. The polymer precipitate was filtered off and dried at 35–40°C. under vacuum and weighed. The polymers were redissolved in benzene and precipitated into methanol for molecular weight measurement. The relative viscosity was determined in an Ostwald tube at 25°C. using a solution of 0.5% polymer in methyl ethyl ketone. Molecular weight was calculated by using the constants of Outer et al.[11] The methanol solution was evaporated with the use of a rotary vacuum evaporator and the residue weighed. The methanol soluble fraction from the styrene–attapulgite system was distilled under reduced pressure and three fractions isolated. Molecular weights determined in a vapor osmometer corresponded to the dimer, trimer, and tetramer of styrene. During the distillation, further polymerization occurred and resulted in considerable nondistillable residue. Results on the effect of solvent are given in Table I.

(b)   The undried mineral (0.5 g.) was heated under reflux with the styrene (25 g.) or styrene (25 g.)–solvent (25 g.) mixture with the use of either a Dean and Stark or, where necessary, a crankcase dilution apparatus to

TABLE I
Effect of Solvents on the Polymerization of Styrene[a]

Mineral	Method of activation[b]	Solvent	Polystyrene, %	Molecular weight	Methanol-soluble fraction, %	Conversion of styrene, %
Attapulgite	1	—	29	6,400	71	100
Attapulgite	2	—	27	9,500	73	100
Attapulgite	1	Benzene	49	2,000	51	100
Attapulgite	2	Benzene	63	5,300	37	100
Attapulgite	1	Carbon tetrachloride	51	5,600	49	100
Attapulgite	2	Carbon tetrachloride	39	1,100	61	100
Montmorillonite	1	—	1.9	—	0.7	2.6
Montmorillonite	2	—	30	19,600	58	88
Montmorillonite	1	Benzene	0.6	—	0.3	0.9
Montmorillonite	2	Benzene	5.6	10,000	9.0	14.6
Montmorillonite	1	Carbon tetrachloride	0.4	—	0.2	0.6
Montmorillonite	2	Carbon tetrachloride	12	4,400	18	30

[a] In the presence of ethyl alcohol, dioxane, ethyl acetate, and methyl methacrylate, using mineral activated by preheating, no polymer formed after 30 min. Some polymer was formed after 14 days and this reaction will be reported in more detail later.

[b] Method 1: mineral heated for 1 hr. at 300°C.; method 2: mineral, solvent, and styrene heated under reflux for 30 min.

separate water removed by azeotropic distillation. Heating was continued for 30 min. and the reaction mixture isolated and characterized as above. Results are in Table I.

Catalyst Type and Activation Conditions

The effect of activation time at 300°C. on the catalyst was studied by using sodium montmorillonite (1 g.), and the catalyst activity judged by the yield of polymer from styrene (20 g.) in 30 min. Results are recorded in Table II.

TABLE II
Effect of Time on Activity of Sodium Montmorillonite at 300°C.

Time, hr.	Polystyrene, %	Molecular weight	Methanol-soluble fraction, %
0.5	6.9	20,000	1.0
1	5.2	33,300	0.7
3	5.9	14,000	0.5
16.5	5.6	14,900	0.5
66	4.7	22,000	0.5

The effect of the temperature of activation is shown in Table III for sodium montmorillonite (1 g.) using a standard time of 1 hr. at the specified temperature and styrene (20 g.)

TABLE III
Effect of Activation Temperature on Sodium Montmorillonite after 1 Hr.

Temperature, °C.	Polystyrene, %	Molecular weight	Methanol-soluble fraction, %
80	Trace	—	Trace
130	2.4	94,600	0.4
300	5.2	33,300	0.7
500	4.2	49,200	1.0
680	1.2	120,000	1
1050	Trace	—	Trace

The activity of the cobalt minerals was assessed by comparing the yield of polystyrene obtained after activation of the mineral by heating for 1 hr. at 300°C. Results for sodium and cobalt montmorillonite are shown in Table IV.

TABLE IV
Activating Effect of Co on Montmorillonite

	Polystyrene, %	Molecular weight	Methanol-soluble fraction, %	Total conversion, %
Cobalt montmorillonite	60	3,000	18	78
Sodium montmorillonite	3.2	9,600	1.6	4.8

An even more striking example of the activating effect of cobaltous ions is shown with vermiculite. Whereas the sodium derivative gives no polymer, the cobaltous mineral is comparable to cobalt montmorillonite and yields approximately 70% polystyrene.

To determine whether the heat activation process involved any oxidation of the mineral, attapulgite was dried for 1 hr. at 300°C. under a hydrogen atmosphere. Polymer yield and molecular weight were comparable to those obtained in the normal drying treatment.

A series of minerals belonging to the same general class as sodium montmorillonite and attapulgite was studied in order to relate catalyst composition to activity. The important structural differences between the minerals and the activity in polymerizing styrene are shown in Table V.

To determine the portion of the surface responsible for catalytic activity, the following experiments were carried out. (a) Sodium montmorillonite was washed with methanol (three times) and then styrene in an attempt

TABLE V

Comparison of Mineral Structure and Catalytic Activity

Mineral	Formula[a]	Layer charge, meq./100 g.	Efficiency in polymerizing styrene[b]
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	0	1
Talc	$Mg_3Si_4O_{10}(OH)_2$	0	0
Montmorillonite	$(Al_{2-x}Mg_x)Si_4O_{10}(OH)_2$	90–100	3
Hectorite	$(Mg_{3-x}Li)Si_4O_{10}(OH)_2$	80	1
Vermiculite	$(Mg_{3-x}Fe_x)Si_3Al \cdot O_{10}(OH)_2$	120–200	0
Muscovite	$Al_2Si_3Al \cdot O_{10}(OH)_2$	250	1
Illite	$Al_2Si_3Al \cdot O_{10}(OH)_2$	200	3
Kaolinite	$Al_4Si_4O_{10}(OH)_8$	3–15	5
Gibbsite	$Al(OH)_3$	0	0
Alumina	Al_2O_3	0	0
Attapulgite	$(Si_{3.9}Al_{0.1})(Al_{0.68}FeMg_{1.22})O_{1.05}$	20–30	5

[a] For detailed formulae refer to references quoted.[12–14]

[b] The minerals have been given a rating based on yield of polystyrene: O, represents no polymerization while 5 is quantitative conversion.

to form an interlayer complex.[13b] X-ray diffraction showed no evidence of an interlayer complex. (b) Both sodium montmorillonite and attapulgite were treated with a 1% aqueous solution of a polyphosphate (Calgon, marketed by I.C.I., Ltd.) for 4 hr., the mineral was removed by filtration, washed with water, and activated by heating for 1 hr. at 300°C. Greatly reduced activity as judged by the exotherm and polymer yield (trace only) was shown by the treated minerals.

Effect of Reaction Conditions

To gather evidence relating to the mechanism of styrene polymerization the following experiments were carried out. (a) A solution of diphenyl, picryl hydrazyl (0.5 mg.) in styrene (5 g.) was added to the activated mineral. The purple color was rapidly discharged. A blank experiment using the same concentration of diphenyl picryl hydrazyl in benzene was also discolored by the mineral but very much more slowly than the system with styrene. (b) The activated attapulgite was added to styrene containing benzoquinone (0.2%). The rate of reaction was greatly reduced and a yield of 11% polystyrene, molecular weight 1200, and 7% methanol-soluble product (total yield 18%) was obtained. (c) The temperature of reaction was lowered and it was found that the polymerization rate decreased with temperature and that no polymerization occurred at −10°C. after 30 min.

Attempts to determine the presence of free radicals by ESR were not successful even at temperatures where polymerization was slow.

DISCUSSION

The polymerization of styrene by sodium montmorillonite and attapulgite (the structures of these minerals are discussed below) shows the characteristics of both a radical and an ionic mechanism. The activating effect of cobaltous ions associated with the mineral would suggest a radical or one-electron transfer type of mechanism presumably assisted by the ability of cobaltous ions to form cobaltic ions and electrons. Also, we have shown that the established one electron transfer oxidation of benzidine to benzidine blue takes place more readily on cobalt clays than on the corresponding sodium clay. Similarly, the inhibition or retardation of the reaction by benzoquinone, the decolorization of diphenyl picryl hydrazyl (DPPH), and the dependence of reaction rate of temperature are all typical of a radical mechanism. The interpretation of these results, however, is not as clear-cut as one would desire, since the DPPH is decolorized in benzene solution by the activated mineral, although the rate is very much slower than in the additional presence of styrene, and the inhibiting effect of benzoquinone could be related to adsorption on active sites of the mineral.

Comparison of benzene and carbon tetrachloride as solvents for the polymerization should give an indication of the mechanism operating since the dielectric constants and boiling points are comparable,[15] and hence, little difference should occur in ionic polymerization, whereas the chain transfer coefficients in radical polymerization are in the approximate ratio of 1:5000 (benzene:carbon tetrachloride).[16] Carbon tetrachloride should, therefore, substantially lower the molecular weight and introduce chlorine into the polymer chain if a radical mechanism operates. The results in Table I suggest that a radical mechanism is not operating, since the molecular weights of polymers formed in the presence of benzene and carbon tetrachloride are comparable, and no chlorine was detected in either the polystyrene or methanol-soluble fraction. The relatively low molecular weight of the polymer and the high yield of dimer, trimer, etc., are also more in conformity with an ionic polymerization. Attempts to establish the mechanism of the propagation step by examining the copolymer composition from a methyl methacrylate–styrene monomer system[17] were unsuccessful since the methacrylate inhibited polymerization. This effect, which was also exhibited by other oxygenated solvents, is discussed below.

We believe that a radical-ion mechanism satisfactorily explains the above results. In view of the known electron-accepting properties of the minerals[18] used, we propose the formation of a radical-carbonium ion as the initiating step, followed by a rapid dimerization and then cationic propagation. Termination could then proceed by proton transfer, if necessary to monomer, and this could result in the initiation of some polymerization by a conventional cationic mechanism. Evidence to support termination by proton transfer comes from the presence of approximately two double bonds for every three styrene units in the methanol soluble product. No evidence for stereospecificity was found by NMR or x-ray diffraction tech-

niques. The structure of the radical ion can be formally written as either I or II.

$$\overset{\cdot}{CH}-\overset{+}{CH_2} \qquad\qquad \overset{+}{CH}-\overset{\cdot}{CH_2}$$

I   II
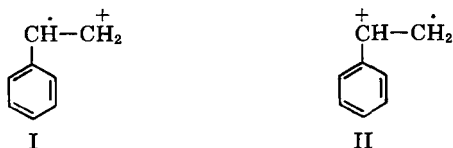
It is hoped that a further study of the structure of the low molecular weight methanol-soluble fraction will give more information on the structure of the radical-ion since the dimeric products will have either a 2,3 or 1,4 arrangement of the phenyl groups. At this stage, however, structure II would be favored, since on dimerization this yields the more stable dicarbonium ion.

Attempts to detect the presence of the styrene radical-ion by ESR were not successful, probably because of the low concentration and short life of such an entity. Similar difficulties have been encountered previously in the detection of radical polymerization.[19]
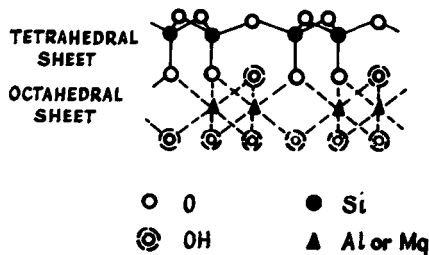

Fig. 1. Base structure of a two-sheet mineral (schematic).

The proposed radical-ion mechanism, which as far as we can ascertain, has not been invoked previously to explain a styrene polymerization, involves an initiation step similar to that proposed by Bawn and Sharp[20] to account for the oxidation of styrene by cobaltic salts in dilute acid solution. Similar radical-carbonium ions have been shown to result from hydrocarbons during color changes on aluminum silicates of comparable structure to the minerals used to polymerize styrene. For example, Rooney and Pink[21] have shown that 1,1'-diphenylethylene and anthracene form stable radical-carbonium ions by electron transfer to the mineral.

From a study of a range of minerals, it has been possible to deduce qualitatively some of the structural aspects necessary for the mineral to catalyze styrene polymerization.

The minerals studied belong to the general class of layer silicates. Basically, these minerals consist of a sheet of silicon-oxygen tetrahedra in conjunction with an octahedral sheet containing aluminum or magnesium (Fig. 1). Three of the oxygen atoms of the tetrahedron involving silicon are shared with other neighboring tetrahedra, while the fourth oxygen is
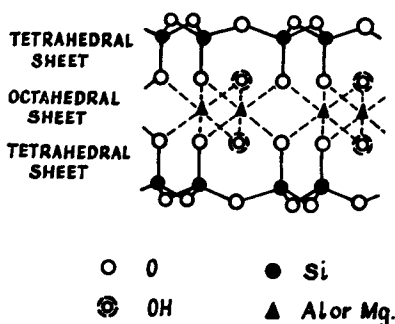
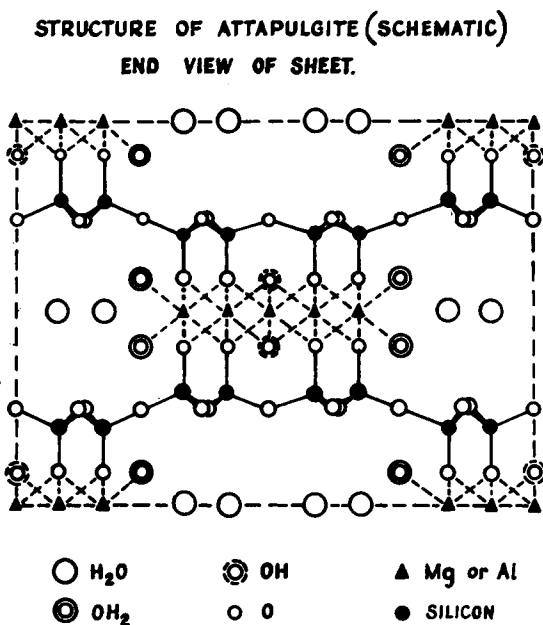Fig. 2. Base structure of a three-sheet mineral (schematic)-

Fig. 3. Structure of attapulgite (schematic). End view of sheet.

shared with the octahedral sheet. In some minerals, an additional silicon–oxygen sheet is present on the other side of the octahedral sheet (Fig. 2). The stacking of these sheetlike structures, one on top of the other, results in the formation of the layer silicate. Isomorphous substitution is possible in either the tetrahedral or octahedral sheet, and this gives rise to a negatively charged silicate layer and the presence of a compensating number of associated cations external to the silicate layer. Some distortion of bond angles results and the presence of an exchangeable cation can, therefore, be taken as an indication of distorted structures.
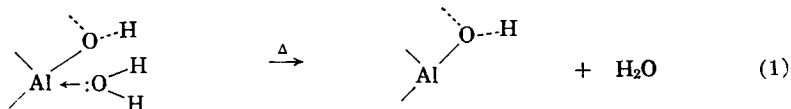
As can be seen from the results in Table V, activity can be related to the presence of aluminum in octahedral coordination. For example, pyro-

phyllite is active whereas talc* is not, while montmorillonite is more active than hectorite. However, the presence of aluminum in octahedral coordination does not necessarily result in catalytic activity as shown by the failure of gibbsite, essentially an aluminum hydroxide consisting of octahedral sheets only, to yield polystyrene. The strong activity shown by kaolin, a two-sheet structure, suggests that the reactivity of the aluminum sheet is affected by the presence of the silicate sheet, particularly at the crystal edges. This postulate agrees with the findings of Benesi,[22] who has shown that the amine adsorption by the mineral edges varies with structure in a similar manner to that proposed here.

Activation time and temperature of the mineral are also important, and from the results in Tables II and III for sodium montmorillonite we have chosen 1 hr. at 300°C. as basis of comparing the range of minerals.

It is well established that certain organic molecules can penetrate the silicate layers and form interlayer complexes.[13b] However, attempts to form such complexes with styrene were not successful, a result in agreement with the findings of Blumstein,[10] and the catalytic sites are not, therefore, between the silicate sheets. The greater activity shown by attapulgite (Fig. 3) over sodium montmorillonite would suggest that crystal edges are involved in the catalysis, since attapulgite has a much greater edge-to-surface area ratio due to its structure. Support for this theory comes from the loss of activity following treatment of the mineral with a polyphosphate which is known to coat crystal edges.[13c]

We, therefore, suggest that the catalytic activity is related to aluminum in octahedral coordination and situated at crystal edges. Activation by heating would result in removal of coordinated water molecules with the generation of electron-accepting Lewis acid sites [eq. (1)].

$$\text{Al} \xleftarrow{} :O \begin{array}{c} O\text{---H} \\ \diagdown \\ H \\ H \end{array} \quad \xrightarrow{\Delta} \quad \text{Al} \begin{array}{c} O\text{---H} \\ \diagup \end{array} \quad + \quad H_2O \qquad (1)$$

The inhibiting action of polar oxygenated solvents and methyl methacrylate is also readily explained by this hypothesis, since these would be expected to satisfy the Lewis acid requirements by donation of an electron pair from the oxygen and, in the case of the methacrylate, the double bond would not adsorb in a favorable manner for activation. Similar explanations have been invoked to explain other electron-accepting reactions of these minerals.[21]

CONCLUSIONS

The mechanism of the polymerization of styrene on heat-activated neutral minerals has been studied. The proposed mechanism invokes initia-

* No polymer forms until after 14 days. This polymerization, which differs from the one under discussion, will be discussed in a later communication.

tion by one-electron transfer to the mineral resulting in the formation of a styrene radical-carbonium ion which then rapidly dimerizes. Propagation and termination then take place by a conventional cationic mechanism. Termination by proton transfer to monomer could initiate concurrent polymerization by a purely cationic mechanism.

The activity of the mineral is connected with Lewis acid sites resulting from the presence of aluminum at crystal edges.

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Résumé

On a étudié la polymérisation du styrène sur des surfaces minérales neutres. On a montré que la polymérisation avait les caractéristiques d'une réaction radicalaire et cationique; pour expliquer ces observations on a proposé un mécanisme qui introduit un radical-ion carbonium. On a passé en revue toute une série de catalyseurs minéraux et on a tenté d'expliquer théoriquement la variation d'activité avec la structure du catalyseur. On a aussi effectué des expériences pour définir la portion spécifique de la surface minérale, responsable de l'activité catalytique.

Zusammenfassung

Die Polymerisation von Styrol an neutralen mineralischen Oberflächen wurde untersucht. Die Polymerisation besitzt charakteristische Eigenschaften, die sowohl für eine radikalische, als auch eine kationische Reaktion erwartet werden können; ein Mechanismus unter Beteiligung eines Carboniumionnenradikals wird zur Erklärung dieses Verhaltens vorgeschlagen. Eine Reihe mineralischer Katalysatoren wurde untersucht und versuchsweise eine Theorie zur Erklärung der Abhängigkeit der Aktivität von der Katalysatorstruktur vorgeschlagen. Weiters wurden Experimente zur Festlegung des spezifischen, für die katalytische Aktivität verantwortlichen Anteils der mineralischen Oberfläche ausgeführt.