Propagation of Vinyl Polymers on Clay Surfaces.
II. Polymerization of Monomers Initiated by
Free Radicals Attached to Clay

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Synopsis

The adduct of kaolin and 2,2′-azobisisobutyramidine hydrochloride has been used to initiate the polymerization of methyl methacrylate, styrene, styrene–butadiene, vinyl acetate, chloroprene, acrylamide, and acrylonitrile. Both extractable and nonextractable polymers are obtained. The adduct of bentonite and 2,2′-azobisisobutyramidine hydrochloride will initiate the polymerization of methyl methacrylate, acrylamide, vinyl acetate, 4-vinylpyridine, and styrene. Both extractable and nonextractable polymers are formed. When the bentonite or the hectorite adducts are more than 99% decomposed prior to the addition of methyl methacrylate, essentially no extractable polymer is formed, but an increased quantity of nonextractable polymer is produced. This is probably due to an increased accessibility of the monomer to the clay's interior surface and a decrease in the rate of chain termination. As is the case of the kaolin adduct, the clay surface of bentonite appears to accelerate the chain growth considerably.

INTRODUCTION

In order to change the chemical and physical properties of clays and thus to increase their usefulness, polymer–clay compounds have been prepared. Two general methods have been used in the past to make such compounds. One method consists of reacting clays and certain polymers which contain active groups capable of forming a bond between the clay and the polymer. Gluesenkamp,[1] for instance, prepared quaternary ammonium salts of copolymers containing basic groups and reacted such polyfunctional polymers with bentonite by means of an ion-exchange reaction. The x-ray diffraction data indicated that a monomolecular layer of the polymer was intercalated between the basal planes of the clay. The other general method consists of polymerizing vinyl monomers in the presence of natural, acidic, or otherwise modified clays. Te Grotenhuis[2] first reacted vinyl isocyanate with silica (presumably the silica's OH groups reacted with the isocyanate) and then polymerized a vinyl monomer in the presence of this vinyl silica using benzoyl peroxide as an initiator.

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The investigator claims that a bond is formed between the polymer and the silica.

Hauser[3,4] attached vinyl groups onto bentonite by means of an ion-exchange reaction between the clay and a salt of polymerizable olefinic carboxylic acid such as lead acrylate. Thus he obtained $(CH_2\!=\!CH\!-\!COOPb)_m$-bentonite which he used as a comonomer. Hauser[5] also found that conjugated dienes such as butadiene, chloroprene, and isoprene will polymerize in the presence of naturally occurring acid clays. After extracting the reaction products with a solvent for the polymer, the insoluble fraction still contained some polymer. Freidlin[6] studied the transformation of individual stereoisomers of 1,3-pentadiene and of their mixtures in the presence of acid-type catalysts, such as silica–alumina, aluminum oxide, and calcium phosphate. He showed that the *cis–trans* isomerization is accompanied by polymerization. The former reaction occurs at a slower rate than the latter one. The *cis*-1,3-pentadiene polymerizes more rapidly than the *trans* form.

Wheeler[7] found that tetrafluoroethylene polymerizes in the presence of preheated silica. According to this investigator, heating the silica creates free radicals on its surface. Whether the polymer is bonded to the silica is not reported. Recently, Friedlander[8–10] polymerized butadiene and *cis*- and *trans*-butene-2 on acid as well as on neutral sodium bentonite. The polymer was formed in only 1% yield and the product was partly extractable. The author suggests a cationic mechanism for the polymerization.[10] Friedlander and Frink also reported the "spontaneous" polymerization of 4-vinylpyridine [9,11] and acrylamide[11] on sodium bentonite. From the x-ray measurements of the clay, it was concluded that a monomolecular layer of poly-4-vinylpyridine or polyacrylamide became intercalated between the basal planes of the clay.

Uskov[12] reported that vibration disintegration of air-dried sodium bentonite in methyl methacrylate leads to polymerization of the monomer and grafting of the polymer onto the clay particles. No homopolymer is formed. With benzoyl peroxide as initiator, he observed both homopolymer and grafted polymer. An excess of bentonite, however, leads to almost complete inhibition of the polymerization.

Russian investigators[13] also found that vinyl-substituted silica, when present during the polymerization of methyl methacrylate, becomes attached to the polymer, which appears to be crosslinked. They observed that the glass transition temperature of the resulting product was 12 and 19°C. higher than that of pure polymer and polymer filled with unmodified silica, respectively. Furthermore, there was a change in the modulus of elasticity, probably due to the stiffening caused by the crosslinking of the polymer.

A very interesting observation was made by Blumstein,[14] who polymerized methyl methacrylate in the presence of bentonite using a free-radical initiator. The fraction of the polymer which could not be extracted by

solvents for linear poly(methyl methacrylate) was liberated from the clay by digesting with hydrofluoric acid and was found to be branched.

It is apparent that considerable work has been done on the preparation of polymer–clay compositions.   Yet, as far as can be ascertained, no general method has been reported for the preparation of such potentially useful and interesting materials.   In this paper, a method is described whereby such materials may be synthesized by employing, as the initiator, the adduct produced by reaction of a water-soluble cationic azo compound and clays having cation exchange capacity.   The synthesis, structure, and rate of decomposition of such "azo-clays" has been described in the first paper of this series.[15]

EXPERIMENTAL AND RESULTS

Materials

Monomers

Methyl methacrylate as supplied by the Rohm and Haas Company was freed of inhibitor by extracting with 10% aqueous NaOH.   The inhibitor-free monomer was extracted with distilled water, dried over $CaCl_2$, and distilled.   Styrene supplied by Matheson, Coleman and Bell was similarly treated.

Acrylamide supplied by American Cyanamid was used as received, as was butadiene (rubber grade) from Phillips 66.

Acrylonitrile and vinyl acetate were distilled immediately before use, as was 4-vinylpyridine.

Clay Minerals

The bentonite was spray-dried, supercentrifuged Wyoming bentonite from the National Lead Company.   It was used as received.

The kaolin was supplied by the Georgia Kaolin Company and was purified by discarding the fraction settling from an aqueous dispersion in 1 hr.

The attapulgite came from Gadsden County, Florida (API H-43), and was used as received.

The hectorite was supplied by the Inerto Company, Las Vegas, Nevada; and by the Baroid Division, National Lead Company.   It was used without purification.

The initiator, 2,2'-azobisisobutyramidine HCL (AIBA) was synthesized according to Upson's method.[16]

Triton X-155, an alkylaryl polyether alcohol, was supplied by the Rohm and Haas Company.

Igepal CO-630, a nonylphenoxypoly(ethylene oxy)ethanol, was supplied by Antara Chemicals.

The Calgon used was a commercial sample of sodium hexametaphosphate.

Poly(methyl Methacrylate)-Bentonite

Initiation by AIBA-Bentonite

Bentonite (10 g.) was dispersed in 400 ml. of distilled water by using a Waring Blendor. The dispersion was poured into a 1-liter reaction flask equipped with a mechanical stirrer, thermometer, reflux condenser with bubble cap on top, and a gas inlet. The flask was heated in a constant temperature bath kept at 60°C. (±0.1°C.). The blendor was rinsed with 60 ml. of distilled water which was added to the reaction flask. The clay dispersion was stirred and allowed to reach bath temperature while being purged with argon. Then a solution of 0.2500 g. of AIBA in 22.5 ml. of water was added. After 2 min., a mixture of 1 ml. of Triton X-155 detergent and 25.00 g. of distilled methyl methacrylate was added. Since the reaction is exothermic at first, the reaction temperature was kept at 60°C. by adding ice to the bath. After a given interval, ranging from 0.5 to 6 hr., the reaction mixture was poured into 2 liters of methanol, the solids allowed to settle, filtered off, slurried into 1 liter of methanol, filtered, and dried during 16 hr. under atmospheric conditions. The powder was dried at 100°C. for 24 hr. *in vacuo.*

The dry products were transferred to a vacuum desiccator, allowed to cool to room temperature, and weighed.

When a blank (mixture of 205 ml. water, 5.0 g. of bentonite, and 17 g. of methyl methacrylate and 1 drop Igepal CO-630) was kept at 80°C. for 2 hr., no polymerization took place.

In order to extract as much homopolymer as possible, the crude powdered product was stirred at room temperature in a 3:1 benzene–N,N-dimethylformamide mixture. The colloidal solids were allowed to settle overnight, and the supernatant liquids centrifuged. This procedure was repeated until no more polymer was found in the supernatant liquids. The polymer solution was poured into n-heptane to recover the homopolymer. The solvent-extracted clay was washed with methanol and dried as before. From the weight of the crude product and the per cent carbon in the extracted clay, the composition of the crude product and the per cent conversion of monomer to extractable and nonextractable polymer could be calculated. The data are graphically represented in Figure 1 and tabulated in Table I. The intrinsic viscosity of the extractable polymer was determined at 25°C. in benzene. When the above procedure was repeated in the absence of monomer, 9.1712 g. of clay, (C = 2.91%, c_0 = 12.7 A.) was isolated. One run was made in the absence of clay and 25-ml. aliquots were withdrawn after 0.5, 1.0, and 2.0 hr. The polymer contents were determined by precipitation in acidified methanol. The results from this run are shown in Table I and Figure 1.

The following two experiments show not only that vinyl monomers may be polymerized in bulk with the AIBA–bentonite but also that more graft polymer is formed when the initiator is absorbed by the substrate than when it is uniformly distributed throughout the reactants.

TABLE I

Emulsion Polymerization of Methyl Methacrylate over AIBA–Bentonite and AIBA at 60°C.

Run no.	Time, hr.	Wt. product, g.	Grafted polymer		Homopolymer			PMMA–clay
			Wt., g.	Conversion, %	Wt., g.	Conversion, %	$[\eta]^a$	c_0, A.
1	0.5	26.89	6.35	25.38	11.37	45.48	5.0	15.8
2	0.5	26.98	5.95	23.78	11.86	47.44	4.8	16.2
3	1.0	29.95	6.42	25.71	14.35	57.40	4.8	16.4
4	1.0	29.19	6.18	24.72	13.84	55.36	5.3	16.4
5	3.0	32.05	6.42	25.70	16.45	65.80	4.7	17.0
6	3.0	31.80	6.69	26.75	15.94	63.74	5.2	17.4
7	6.0	32.06	8.00	32.00	14.89	59.56	3.3	18.5
8	6.0	32.18	6.31	25.24	16.70	66.80	5.0	17.2
9[b]	6.0	9.22	0	0	0	0	0	12.6
10[b]	6.0	9.12	0	0	0	0	0	12.7
11[c]	0.5	0.85	—	—		3.41	—	—
12[c]	1.0	3.79	—	—		15.17	—	—
13[c]	2.0	23.5	—	—		94.0	1.5	—

[a] At 25°C. in benzene.
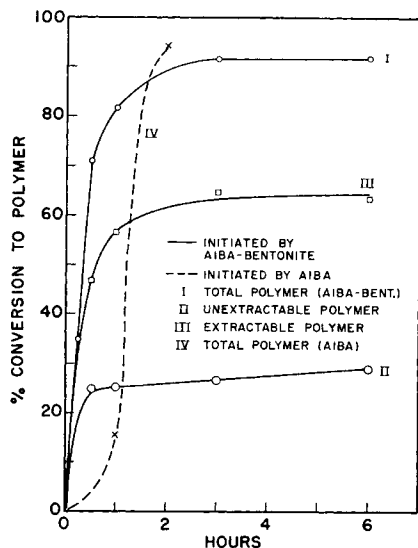[b] In the absence of monomer.
[c] In the absence of clay.

Fig. 1. Emulsion polymerization of methyl methacrylate over AIBA–bentonite and AIBA at 60°C.

Bulk Polymerization of Methyl Methacrylate with the Use of Clay Plus Benzoyl Peroxide.   A mixture of 4.000 g. of bentonite and 10.0 g. of methyl methacrylate containing 0.080 g. of benzoyl peroxide was maintained at 60°C. for 21 hr.   The polymer in the solid product (13.3 g.) amounted to 71%.   After extracting the solids with chloroform followed by acetone, the insoluble residue contained 36% polymer.   The crude material, therefore, contained 4.0 g. of clay, 2.25 g. of unextractable polymer, and 7.1 g. of extractable polymer.   In the absence of clay, 9.1 g. of polymer was obtained.

Bulk Polymerization of Methyl Methacrylate with the Use of AIBA–Clay.   AIBA–bentonite was prepared by adding 100 g. bentonite to a mixture of 666 ml. methanol, 333 ml. distilled water, and 2.000 g. of AIBA. After stirring of the reactants for 1 hr., the clay was filtered, slurried with methanol, filtered, and dried under vacuum over Drierite.   The preceding polymerization experiment was repeated but the 0.080 g. of benzoyl peroxide was replaced by 0.080 g. of AIBA in the form of 4.000 g. of the above-prepared AIBA–bentonite.   The crude product contained 4.0 g. clay, 5.2 g. of unextractable polymer, and 3.2 g. of extractable polymer. The c_0 spacing of the extracted product was 16.1 A.

In addition to methyl methacrylate, styrene, vinyl acetate, and 4-vinylpyridine were polymerized in emulsion by using the AIBA–bentonite initiator.   Acrylamide was polymerized in solution with the above initiator.

In a previous publication,[15] evidence was presented that showed most of the AIBA cations are absorbed on bentonite as dications and that they are intercalated between the basal planes of the bentonite.   The situation is graphically represented in Figure 2, which shows one intercalated AIBA
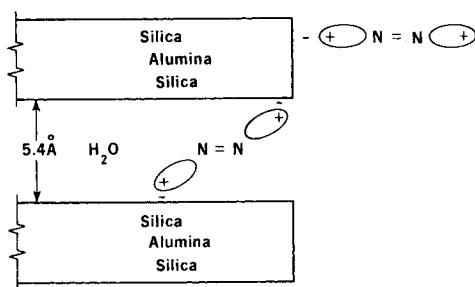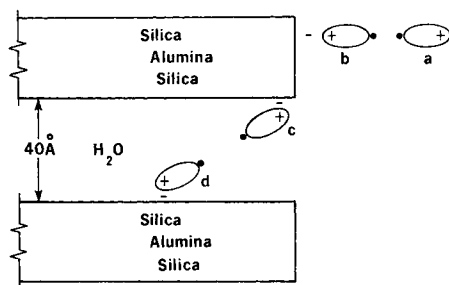
Figure 2.

Figure 3.

cation in its slanted position and one externally absorbed AIBA cation. In addition, some AIBA cations may function as a bridge between two clay particles. In heating, free radicals will be formed, all of which will remain attached to the clay surface except for type a (Fig. 3). In the presence of a monomer, free radical a will yield homopolymer which may become attached to the clay surface by means of an ion exchange reaction. We have found that poly(methyl methacrylate) prepared by initiation with AIBA cations and hence terminated in a cationic group will become attached to bentonite. Free radical b would give rise to clay-attached non-intercalated polymer. Free radicals c and d will form intercalated clay-attached polymer. It is this polymer which accounts for the increased c_0 spacing.

Since about 80% of the exchange sites are located on the interior surfaces of the clay, it is estimated that the ratio of intercalated AIBA cations to exterior AIBA cations equals $2:1$ and hence only 1 out of 6 free radicals is of type a. Yet, from Figure 1 (curves II and III) it is apparent that during the first $1/2$ hr. when 70% of the monomer polymerizes, the rate of homopolymer propagation, R_{PH} is almost twice that of the rate of graft polymer propagation, R_{PG}. The latter amounts to about 0.65×10^{-4} mole^{-1} sec.$^{-1}$. The molecular weight of the homopolymer is in the range of several million and remains fairly constant throughout the polymerization. Apparently, the ratio R_{PH}/R_{PG} is not solely dependent on the number of free radicals which could give rise to homopolymer and graft polymer, probably because

the two types of polymerization occur under different circumstances. The propagating graft polymer is restricted to what amounts to a two-dimensional field, covering up and making inaccessible future radicals of type c and d. The rate of diffusion of monomer and hence its concentration between the basal planes of the clay would strongly affect R_{PG}. Most likely there are two polymerizations occurring simultaneously in different environments with different rate constants.

From curves I and IV (Fig. 1) it appears that the retarder present in the clay free emulsion has been absorbed by the clay.

It is harder to explain why free radicals of type a which initiate homopolymer formation are far more productive than the average AIBA derived free radical. Comparing curves III and IV of Figure 1 we notice that the rates (ignoring the first hour of curve IV) are not too different. Yet the ratio of type a free radicals to AIBA-derived free radicals in the clay free system is about 1:6. In other words, type a radical propagates about 6 times as fast as does the ordinary AIBA-derived radical. We shall notice the same phenomena in polymerizations initiated by AIBA–kaolin.

Initiation by Decomposed AIBA–Bentonite

The ratio of extractable/unextractable poly(methyl methacrylate) can be significantly reduced while increasing the amount of unextractable polymer by heating the AIBA–bentonite dispersion prior to the addition of the monomer.

Example 1. To an argon-purged dispersion of 20.0 g. of bentonite in 1 liter of distilled water, a solution of 0.500 g. of AIBA in 50 cc. of distilled water was added. The dispersion was heated from 26 to 99°C. in 44 min., then cooled to 78°C. in 10 min. Then 50 g. of methyl methacrylate and 2 drops of Igepal CO-630 were added and the reactants stirred at 76°C. for 1 hr. The product was isolated by precipitation in methanol. Homopolymer was removed by exhaustive acetone and benzene extractions at room temperature. The residual gellike material was dried. The experiment was repeated without preheating the AIBA–bentonite. The results are tabulated in Table II. The c_0 spacing of the PMMA–bentonite was 16.1 A. for the preheated run and 14.4 A. for the nonpreheated run.

TABLE II
Effect of Preheating AIBA–Bentonite on Grafting Efficiency of MMA

	Preheated	Not preheated
Extractable PMMA formed, g.	6.0	28.0
Unextractable PMMA formed, g.	30.0	17.7
Total PMMA formed, g.	36.0	45.7
PMMA in PMMA–bentonite, %	60.0	47.0
Ratio of extractable/unextractable PMMA	0.2	1.6

Example 2.   A dispersion of 20.0 g. of bentonite, 0.5000 g. of AIBA, and 1050 ml. of water was heated under argon from 29 to 98.8°C. in 46 min. The dispersion was cooled to 78°C., and 50 g. of methyl methacrylate was added with a few drops of Igepal CO-630.   After 2 hr. at 77°C. we obtained 55.1 g. of a product containing 65% polymer.   No homopolymer was extracted by boiling benzene and acetone.

Example 3.   The above experiment was repeated except that the AIBA–bentonite complex was formed in methanol in place of water.   A 20-g. portion of bentonite was dispersed in 300 ml. of methanol and 0.5000 g. of AIBA was added.   After 1 hr., the clay was filtered off and dispersed in 1050 ml. of water.   The thin dispersion was heated to 95°C. in 40 min., cooled to 78°C. in 14 min., then 50 g. of methyl methacrylate was added plus 2 drops of Igepal CO-630.   After 1 hr. at 77°C., no polymer was formed.

Example 4.   In another experiment, 20 g. of bentonite was dispersed in 800 ml. of water.   The resulting dispersion was heated under argon to 70.0°C., then 0.9005 g. of AIBA was added.   The rate of nitrogen evolution was followed and from its rate of appearance the value for the velocity constant of decomposition was determined: $k_d = 3.33 \times 10^{-4}$ sec.$^{-1}$. This procedure was described in a previous paper.[15]   After the dispersion had been kept at 70°C. for 257 min. and the initiator was calculated to be 99.41% decomposed, 100 ml. of the hot dispersion was removed, and to it was added 5.0 g. of methyl methacrylate and 1 ml. Igepal CO-630.   This emulsion was kept for 1 hr. at 70°C. and the solids were recovered, dried, weighed, and extracted with acetone.   We obtained 0.34 g. extractable and 1.26 g. homopolymer.   After 23 hr. another 100 ml. sample of the decomposed AIBA–bentonite dispersion, which had been maintained at 70°C., was removed, and the polymerization experiment was repeated.   No polymer was obtained.

Example 5.   AIBA was 99.41% decomposed by heating a solution of 0.2000 g. of AIBA in 250 ml. of water for 170 min. at 80°C. under argon. After cooling to 72°C., 10.0 g. of methyl methacrylate was added with 2 drops of Igepal CO-630.   No polymer was formed after 1 hr. at 70°C. Since hectorite is structurally quite similar to bentonite, we expected to be able to obtain results similar to those described for the AIBA–bentonite and MMA system.   This proved to be the case.

Initiation by Decomposed AIBA–Hectorite

An experiment analogous to that described for decomposed bentonite was run using the clay mineral hectorite which is very similar to bentonite. An argon-purged dispersion of 20.0 g. of hectorite, 0.5000 g. of AIBA and 1050 ml. of distilled water was heated from 30 to 99°C. in 52 min.   It was cooled to 78°C. in 10 min. and a mixture of 10 drops of Triton X-155 and 43.6 g. of methyl methacrylate were added.   After 1 hr. at 76°C., the reactants were poured into methanol and treated as in the preceding experiment.   The experiment was repeated without first decomposing the

TABLE III
Effect of Preheating AIBA–Hectorite on Grafting Efficiency of MMA

	Preheated	Not preheated
Extractable PMMA formed, g.	0	23
Unextractable PMMA formed, g.	24	19
Total PMMA formed, g.	24	42
PMMA in PMMA–hectorite, %	55	50
Ratio of extractable/unextractable PMMA	∞	1.2

clay initiator. The c_0 distances of the PMMA-hectorites are 14.8 and 13.6 A. for the preheated and nonpreheated run, respectively. The results are shown in Table III.

X-Ray Examination of AIBA–Bentonite

A 10-g. portion of bentonite was dispersed in 300 ml. of distilled water. A small sample of the viscous dispersion was withdrawn and examined at once. The basal spacing was 45 A., and hence the thickness of the water layer was $45.0 - 9.6 = 35.4$ A.

To a dispersion of 10 g. bentonite in 250 ml. of water was added a solution of 0.5000 g. of AIBA in 50 ml. water. A sample of the viscous dispersion was examined by x-ray diffraction and showed only a weak peak at 15 A. Hence, the thickness of the organic layer was $15.0 - 9.6$ A. = 5.4 A.

When the above dispersion was kept in a closed container on a steambath for $1\frac{1}{2}$ hr., the dispersion becomes less viscous and shows two peaks, one at 55 A. and one at 43 A.

A dispersion of 10.0 g. of bentonite, 300 ml. of absolute methanol, and 0.5000 g. of AIBA was stirred for 1 hr. The solids were filtered off and dispersed in 300 ml. water. The clay did not swell (when the AIBA is omitted, it does swell) and even settles out. Two peaks were obtained by x-ray examination of the wet clay: one at 15 A. and one at 50 A.; the latter disappears on drying.

One-half of this aqueous dispersion was kept at 60°C. for 24 hr. but no swelling was observed. The other half was mixed with 15 g. of methyl methacrylate and 2 drops of Igepal CO-630 emulsifier. After 6 hr. at 60°C., 17 g. of solids (C, 44.6%; $c_0 = 17.9$ A.) were obtained. After extracting with 3:1 DMF–benzene: these values were C 30.8%; $c_0 = 17.3$ A.; $[\eta]$ of the homopolymer was 4.2.

It was shown above how the formation of homopolymer may be greatly decreased while the formation of graft polymer is increased by decomposing the AIBA–bentonite or the AIBA–hectorite prior to addition of monomer (Tables II and III).

Of the three types of free radicals formed during the decomposition of the AIBA-clay, only type a (Fig. 3) can form homopolymer, and type a radicals are free to be deactivated by recombining with type b free radicals.

There is no reason to believe that an active intermediate is formed which would decompose at a slower rate as has been observed, for instance, in the case of 2,2-azobisisobutyronitrile which, although fully decomposed, will still yield polymer due to the formation of a ketene-imine.[17]   Dougherty[18] pointed out that this is unlikely in the case of AIBA as was also demonstrated above (Example 5).

From our x-ray studies we concluded that type c and d radicals do not recombine but move apart due to the driving force of the water.   Once separated by some 30 A. they can initiate polymerization.   Thus, we can have graft polymer formation even though the initiator has decomposed. The reason more graft polymer is formed by decomposed AIBA–bentonite is because more monomer (thickness of MMA molecule about 3.8 A.) can now penetrate between the basal planes than while they were linked together and 5.4 A. apart.   Furthermore, we would expect termination between two chains growing along the clay surface and separated by some 30 A. to be quite low.   We have also demonstrated that when methanol is surrounding the intercalated free radicals instead of water, no graft polymer is formed since the free radicals are not being pushed apart.

That the free radicals, even though separated, have a limited life span was shown in experiment 4.   We assume that free radicals of type c or d recombine with their own type as a result of diffusion on the same basal plane or perhaps react slowly with impurities.   If there were a high concentration of free radicals on the basal planes, chances of termination would be quite high and not much polymer would be formed.

Poly(methyl Methacrylate)–Kaolin

An emulsion containing 232 ml. of distilled water, 50 g. of methyl methacrylate, 2 drops of Igepal CO-630, and 50 g. of AIBA–kaolin (0.3% AIBA) was stirred at 25°C. under argon for 4 hr.   Extraction of the product yielded 1.3 g. of homopolymer and the benzene-insoluble residue contained 2% polymer.   When the experiment was repeated with the use of 0.15 g. of AIBA instead of the AIBA–kaolin, no polymer was found in a 5-cc. aliquot.   When 50 g. of kaolin was added to the balance of the emulsion and stirred for 2 hr. at 25°C., 1.6 g. of homopolymer and an acetone-insoluble residue containing 1% polymer were obtained.

In a previous article,[15] it was demonstrated that most of the AIBA cations are absorbed as monocations on the kaolin surface.   Thermal decomposition of AIBA–kaolin will produce two free radicals: the one not attached to the clay surface produces homopolymer; the other, held to the clay surface by Coulomb forces, produces graft polymer.   An interesting feature of the preceding experiment is the relatively high propagation rate in the presence of AIBA–kaolin at 25°C.   Arnett[19] has demonstrated that the rate of polymerization of methyl methacrylate with the use of different aliphatic azobisnitriles at the same concentration and temperature is proportional to the square root of the decomposition rate constants k_d over a hundredfold range in the latter.

For the AIBA,[1] $k_d = 1.469 \times 10^{-7}$ sec.$^{-1}$ at 25°C., and for AIBA–kaolin, $k_d = 6.689 \times 10^{16}e^{-32,048/1.987T}$ (This was derived experimentally[16]); hence, at 25°C., $k_d = 2.023 \times 10^{-7}$ sec.$^{-1}$.

Consequently, since R_p for the AIBA–kaolin-initiated polymerization averaged 0.53×10^{-5} mole/l.-sec. during the first 4 hr., the AIBA-initiated polymerization should have an R_p of 0.45×10^{-5} mole/l.-sec. and should have produced 2 g. of polymer. The molecular weight of the polymer produced in the AIBA–kaolin should be high. In 4 hr. at 25°C., only 0.004% of the initiator had decomposed, yielding a maximum of 2.77×10^{16} productive free radicals. Since 2.3 g. of polymer was produced, the average molecular weight would be at the very least 5.20×10^7 unless chain transfer with the monomer took place.

We believe that the high yield of polymer produced by the AIBA–kaolin is due to a very low rate of termination caused by propagation of both the "anchored" and the "loose" polymer chains on the clay surface. The high yield of polymer produced by the AIBA–kaolin must be due to a very low rate of termination. This becomes plausible when we consider that propagation of most chains, derived from either the absorbed free radical or the nonabsorbed free radical, will occur on the clay surface.

The productivity of the clay attached free radical is almost the same as that of the loose free radical. In the case of bentonite, however, the productivity of the a type free radical was considerably higher than that of the b type. The reason for this is not quite clear.

Methyl methacrylate may also be polymerized in bulk by using dry AIBA–kaolin. When a mixture of 100 g. methyl methacrylate and 100 g. of AIBA–kaolin (0.3% AIBA) were kept for 4 hr. at 60°C. followed by 16 hr. at 78°C., we obtained 58 g. of extractable polymer and a benzene-insoluble fraction containing 23% polymer.

GR–S–Kaolin

An emulsion consisting of 120 ml. of water, 50.0 g. of AIBA–kaolin, 16.0 g. of styrene, 80 ml. of butadiene and 3 drops of Igepal CO-630 was stirred and kept at 50°C. for 24 hr. The product consisted of 0.55 g. of a carbon tetrachloride-soluble fraction and an insoluble residue containing 5.1% polystyrene and 5.7% polybutadiene as determined by infrared spectroscopy. The modified kaolin was hydrophobic.

The following monomers were emulsion polymerized at 60°C. by using AIBA–kaolin (The content) of nonextractable polymer is given in parentheses): vinyl acetate (6.6%), chloroprene (6.6%), styrene (4.0%), and acrylamide (1.9%).

CONCLUSIONS

Since methyl methacrylate does not "spontaneously" polymerize in an aqueous dispersion of bentonite or kaolin, it is concluded that the polymerization of methyl methacrylate in an aqueous dispersion of AIBA–clay is initiated by free radicals originating from the AIBA.

When a series of monomers is polymerized by means of AIBA–clay free radicals, both extractable and nonextractable polymer is found.

Complete decomposition of AIBA–bentonite or AIBA–hectorite as measured by nitrogen evolution, prior to addition of the monomer practically eliminates the formation of extractable polymer but increases the formation of nonextractable polymer.

The rate of decomposition of the AIBA–bentonite or AIBA–kaolin is not nearly fast enough to account for the remarkably high propagation rate of methyl methacrylate initiated by an aqueous dispersion of these activated clays. Apparently, the termination rate is quite low.

On the basis of x-ray diffraction studies, it was concluded that adjacent planes of AIBA–bentonite dispersed in water are connected by the AIBA–cations which undergo homolytic fission on heating to form free radicals. These free radicals remain attached to the adjacent planes which move away from each other allowing more water to penetrate.

Electron spin resonance data seem to indicate that the steady-state free-radical concentration of decomposed AIBA–bentonite is $<10^{-7}M$. If this is correct, recombination of most of the free radicals must occur by diffusion on the same plane or the free radicals are deactivated by impurities and the remarkable productivity of the surviving free radicals must be due to an extremely low rate of termination. This may also account for the high radical productivity of AIBA–kaolin.

The polymer–bentonite compositions swell and form gels in solvents which would dissolve the polymer itself. The polymer–kaolin compositions are more stable in solvents which would dissolve the polymer itself.

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Résumé

On a utilisé le produit d'addition du kaolin avec le chlorhydrate de 2,2′-azobisiso-butyramidine en vue d'initier la polymérisation du méthacrylate de méthyle, du styrène, du mélange styrène-butadiène, de l'acétate de vinyle, du chloroprène, de l'acrylamide et de l'acrylonitrile. On obtient à la fois des polymères qui peuvent être extraits, et d'autres qui ne peuvent pas l'être. Le produit d'addition de la bentonite au chlor-hydrate de 2,2′-azobisisobutyramidine initie la polymérisation du méthacrylate de méthyle, de l'acrylamide, de l'acétate de vinyle, de la 4-vinylpyridine et du styrène. On obtient des polymères extractibles et non-extractibles. Lorsque les combinaisons bentonite-azo ou hectorite-azo sont décomposés à plus de 99% avant l'addition de méthacrylate de méthyle, on obtient essentiellement un polymère non-extractible mais en quantité plus importante. Ceci est probablement dû à une accessibilité accrue du monomère a la surface interne de l'argile et à une diminution de vitesse de terminaison de chaîne. De même que dans le cas de la combinaison avec le kaolin, la surface argil-euse de la bentonite accélère considérablement la croissance de la chaîne.

Zusammenfassung

Das Addukt von Kaolin und 2,2′-Azobisisobutyramidinhydrochlorid wurde zum Start der Polymerisation von Methylmethacrylat, Styrol, Styrol–butadien, Vinyl-acetat, Chloropren, Acrylamid und Acrylnitril verwendet. Es wurden extrahierbare und nichtextrahierbare Polymere erhalten. Das Addukt von Bentonit und 2,2′-Azobisisobutyramidinhydrochlorid startet die Polymerisation von Methylmethacrylat, Acrylamid, Vinylacetat, 4-Vinylpyridin und Styrol. Es werden extrahierbare und nichtextrahierbare Polymere gebildet. Bei einer Zersetzung der Bentonit–Azo- oder Hectorit–Azoaddukte zu mehr als 99% vor dem Zusatz von Methylmethacrylat, wird im wesentlichen kein extrahierbares sondern in erhöhter Menge nichtextrahierbares Polymeres gebildet. Wahrscheinlich ist das einer erhöhten Zugänglichkeit der inneren Oberfläche des Tonmaterials für das Monomere sowie einer Abnahme der Abbruchs-geschwindigkeit zuzuschreiben. So wie im Falle des Kaolinaddukts scheint auch die Bentonittonoberfläche das Kettenwachstum beträchtlich zu beschleunigen.