

Propagation of Vinyl Polymers on Clay Surfaces.

I. Preparation, Structure, and Decomposition of Clay Initiators

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Synopsis

Bentonite and kaolin adsorb 2,2'-azobisisobutyramidine hydrochloride by means of an ion-exchange reaction. The rate of decomposition of the resulting azo-clays in water is about twice as fast as that of the azo compound itself. The use of those organoclays as initiators in vinyl polymerization makes it possible to propagate vinyl polymers from the clay surface and prepare polymer-clay composition.

INTRODUCTION

In order to enhance the usefulness of clays we developed a method whereby polymer chains become chemically attached to a clay surface. Polymer-clay compositions are unusual fillers in resins because of their compatibility with the resins. It has been reported,¹ for instance, that poly(methyl methacrylate) filled with a poly(methyl methacrylate)-silica graft has a glass transition temperature 19°C. higher than that of the same resin filled with unmodified silica. Also, the modulus of elasticity and hardness of the resin filled with polymer-silica are greater.

It is well known that many azo compounds are efficient initiators for vinyl polymerization. It is also a fact that many naturally occurring clay minerals will chemisorb organic cations by means of an ion-exchange reaction. If, therefore, we had an azo initiator which, in water, dissociates into azo-cations, the latter could be chemisorbed by clay. The resulting organoclay complex could initiate the polymerization of vinyl monomers. Propagation would occur at the clay surface, and polymer-clay compositions would result. The water-soluble azo compound used by us in the preparation of such compositions was 2,2'-azobisisobutyramidine hydrochloride. This material is easily synthesized, it dissociates into cations, and it is an initiator for the polymerization of ethylene and acrylonitrile.²

EXPERIMENTAL

Purified kaolin was prepared by dispersing 21 parts of a crude kaolin obtained from the Georgia Kaolin Company in a Waring Blendor with

480 parts of distilled water containing 0.03 part of Calgon. After allowing gangue to settle for 1 hr., the supernatant dispersion, containing about 66% of the clay, was supercentrifuged, and the solids thus obtained dried in an air current overnight. The solids were dispersed in the dry state in a Waring Blendor, air-dried for two more days, and stored in a jar. The weight loss after heating for 24 hr. at 110°C. was 0.345%.

The cation-exchange capacity of this purified kaolin was 2.07 meq./100 g. This value was calculated from the nitrogen content (Kjeldahl) in a portion of the sample which had been treated with ammonium acetate.

The bentonite used in our experiment was supercentrifuged, spray-dried Wyoming bentonite from the Baroid Division of National Lead Company. The material was used as received since it had already been beneficiated. Cation exchange capacity was 88 meq./100 g., and amount of bound water 7.0%.

Upson's method³ was used to synthesize 2,2'-azobisisobutyramidine hydrochloride (AIBA)* from 2,2'-azobisisobutyronitrile, anhydrous ethanol, anhydrous hydrogen chloride, and anhydrous ammonia.

Preparation of Activated Clays

AIBA-kaolin was prepared by adding AIBA to a dispersion of purified kaolin in water. The dispersion was filtered, and the clay adduct was washed with distilled water and air-dried. When excess AIBA was used, the per cent carbon in the air-dried AIBA-kaolin was 0.145.

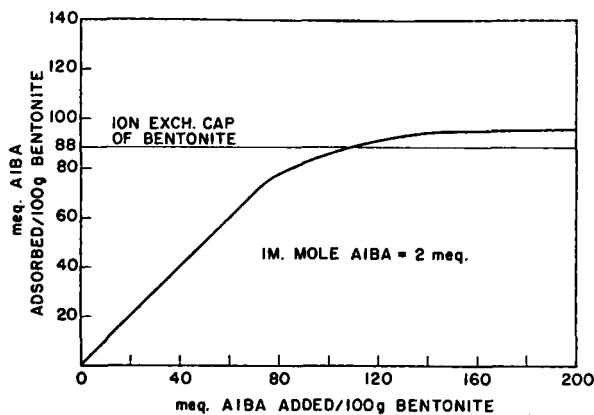


Fig. 1. Adsorption isotherm for AIBA on bentonite in 2:1 $\text{CH}_3\text{OH}-\text{H}_2\text{O}$.

AIBA-bentonite was prepared by adding AIBA to a dispersion of 10–20 g. bentonite in one liter of distilled water. The resulting material was rather viscous and difficult to filter. Addition of methanol aids in flocculating and isolating the organoclay. An alternate method which eliminated

* For simplicity, throughout the paper the symbol AIBA is used to identify both the hydrochloride salt and the cation form which is ionically attached to the clay.

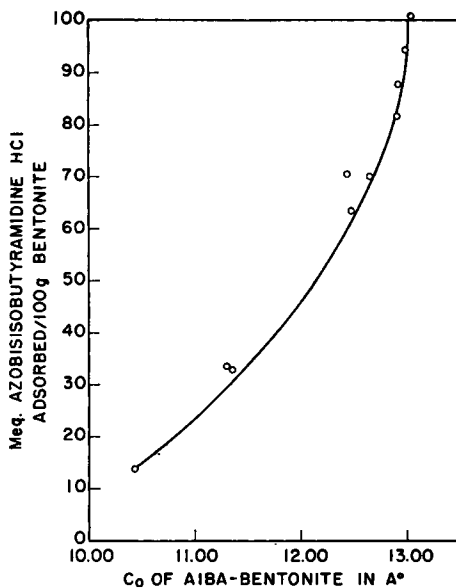


Fig. 2. Correlation of c_0 distance of AIBA-bentonites with milliequivalents of AIBA adsorbed/100 g. clay.

the swelling of the clay consisted of dispersing 10.0 g. of bentonite in a mixture of 34 cc. of methanol and 17 cc. of distilled water. To the non-swollen clay dispersion the AIBA was added. After stirring the clay for 1 hr. the AIBA-bentonite was easily recovered by filtration. This method was used to determine how much AIBA was absorbed by the bentonite and how the AIBA was positioned between the basal planes of the clay. The AIBA-bentonite was filtered, air-dried, and dried over P_2O_5 under high vacuum at room temperature. The amount of AIBA in the organoclay was determined from a measurement of the amount of unabsorbed AIBA in the filtrate by measuring the azo adsorption at 365 $m\mu$ in the ultraviolet. Figure 1 shows the relationship between milliequivalents AIBA added and milliequivalents AIBA adsorbed per 100 g. of clay. In Figure 2 the c_0 spacings for these different products are shown as a function of composition. A very similar adsorption isotherm was found when methanol was used as the sole dispersant and solvent for AIBA.

Kinetic Measurements

The rate of decomposition of AIBA, AIBA-kaolin, and AIBA-bentonite was determined by measuring the rate of nitrogen evolution of the above compounds in water. In the case of AIBA, the distilled water was heated to the desired temperature while being purged with argon, after which the AIBA was added. In the case of the AIBA-clay adducts, the clay-water dispersion was heated to the desired temperature and then the AIBA

added. The amount of AIBA was always less than the adsorption capacity of the clay for this compound. Timing began with the appearance of the first gas bubble.

RESULTS

We checked the accuracy of our apparatus by decomposing AIBA itself in aqueous solution. The values we found for the decomposition rate constant, k_d , $0.370 \times 10^{-4} \text{ sec.}^{-1}$ at 60°C. and $5.13 \times 10^{-4} \text{ sec.}^{-1}$ at 80°C. , agreed fairly well with those found by Dougherty⁴ ($0.41 \times 10^{-4} \text{ sec.}^{-1}$ at 60.20°C. and $5.01 \times 10^{-4} \text{ sec.}^{-1}$ at 80.0°C.). Dougherty calculated his rate constants by following the disappearance of the azo absorption in the ultraviolet at $365 \text{ m}\mu$ while decomposing the AIBA.

Table I summarizes the results obtained in our decomposition rate studies, and Figures 3, 4, and 5 show the results graphically.

TABLE I
Reaction Rate Constants

Temp., °C.	$k_d \times 10^4, \text{ sec.}^{-1}$				
	AIBA ^a	AIBA ^b	AIBA- kaolin ^c	AIBA- bentonite ^d	AIBA- bentonite ^e
50.0	—	—	0.137; 0.137	0.187; 0.173	0.194
50.05	0.097	—	—	—	—
55.0	—	—	—	0.401; 0.393	0.391
60.0	—	0.358; 0.381	0.666; 0.567	—	—
60.20	0.41	—	—	—	—
65.0	—	—	—	1.531; 1.527	1.58
70.0	—	1.41; 1.24	2.17; 2.39	3.33; 3.10	3.03
70.10	1.54	—	—	—	—
75.0	—	2.42; 2.74	—	—	—
80.0	—	5.01; 5.26	9.91; 9.14	10.13; 10.66	10.60
100.10	49.83	—	—	—	—

^a As reported by Dougherty,⁴ average of two runs.

^b Values found by us.

^c Adduct of kaolin and AIBA.

^d Adduct of bentonite and AIBA.

^e Values found by drawing straight line by using method of least squares and values of previous column.

The heat of activation, ΔH_a , was found in the usual way by plotting $\log k_d$ against the reciprocal of the absolute temperature. The slope of the line thus obtained equals $-\Delta H_a/2.303R$. The values for ΔH_a for the decomposition of AIBA-kaolin and AIBA-bentonite are summarized in Table II and shown graphically in Figure 6.

The entropy of activation, ΔS , was found by using the Eyring equation:

$$k_d = (k_b T/h) e^{\Delta S/R} e^{-\Delta H_a/RT} \quad (1)$$

where k_d = the decomposition rate constant, k_b = Boltzmann's constant (1.38×10^{-16} erg-deg. $^{-1}$), h = Planck's constant (6.625×10^{-27} erg-sec.), ΔS = entropy of activation, ΔH_a = heat of activation, R = the gas con-

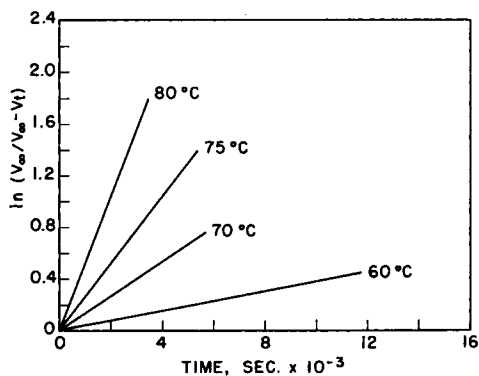


Fig. 3. Decomposition of AIBA in H₂O at various temperatures.

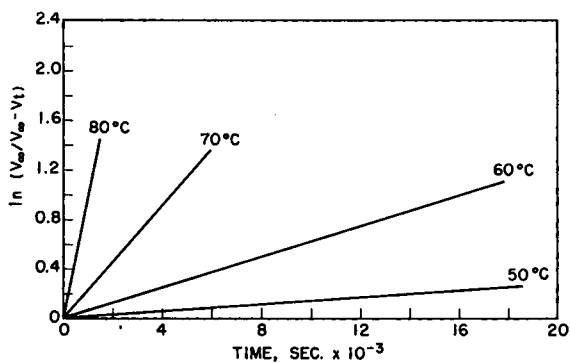


Fig. 4. Decomposition of AIBA-kaolin in H₂O at various temperatures.

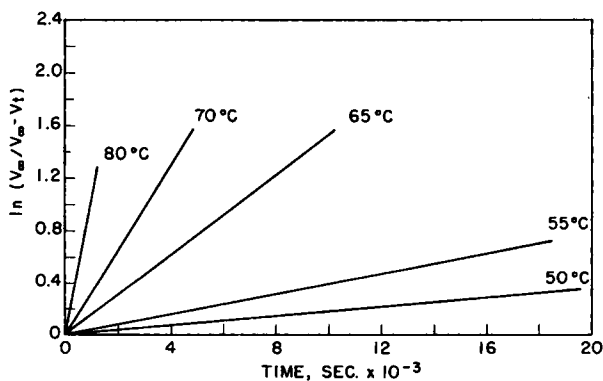


Fig. 5. Decomposition of AIBA-bentonite in H₂O at various temperatures.

TABLE II
Thermodynamic Parameters

	AIBA ^a	AIBA ^b	AIBA-kaolin	AIBA-bentonite
ΔH_{\ddagger} , kcal./mole	29.1; 29.9 ^c	30.765	32.048	30.227
ΔS_{\ddagger} , entropy units	+8.5 ^a	+13.1	+18.16	+13.20
s , sec. ⁻¹	1.632×10^{15a}	5.593×10^{15}	6.689×10^{15}	5.483×10^{15}
	4.863×10^{15c}			
$k = se^{-\Delta H_{\ddagger}/RT}$, sec. ⁻¹	$1.632 \times 10^{15e} - 29,100/1.987T^a$	$5.593 \times 10^{15e} - 30,765/1.987T$	$6.689 \times 10^{15e} - 32,048/1.987T$	$5.483 \times 10^{15e} - 30,227/1.987T$
	$4.863 \times 10^{15e} - 29,900/1.987T^c$			

^a As reported by Dougherty.⁴

^b Found from our experimental data.

^c As calculated by us from Dougherty's data.⁴

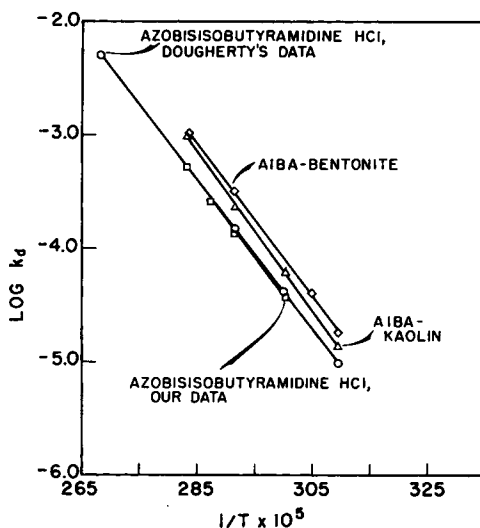


Fig. 6. Arrhenius plots for 2,2'-azobisisobutyramidine hydrochloride and its kaolin and bentonite adducts.

stant ($1.987 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$), and T = the absolute temperature. Values for ΔS are reported in Table II.

According to the Arrhenius equation:

$$k_d = se^{-\Delta H_a/RT} \quad (2)$$

where s is a constant, and other symbols are the same as above.

$$\log k_d = -\Delta H_a (1/2.303 RT) + \text{constant} (= \log s) \quad (3)$$

When $1/T = 0$, $k_d = s$, and, thus, from the data in Figure 6, the values of s may be found. These values are reported in Table II.

DISCUSSION

Nature of the Clays

The structure of kaolinite involves a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedrons and one of the layers of the octahedral sheet form a common layer (see Fig. 7).⁵ Broken bonds around the edges of the silica-alumina units give rise to unsatisfied charges which are balanced by adsorbed cations. In kaolinite, broken bonds are the major cause of cation-exchange capacity. The individual particles are quite flat and hexagonally shaped. The ion-exchange sites are found on the edges and corners of the particles.

Montmorillonite, according to Hofmann, Endel and Wilm,⁶ Marshall,⁷ and Hendricks,⁸ is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet (Fig. 8). The outstanding

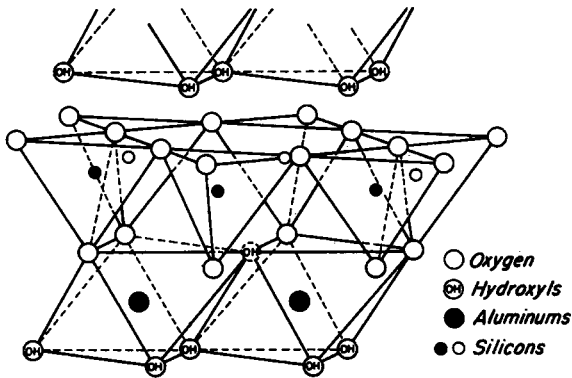
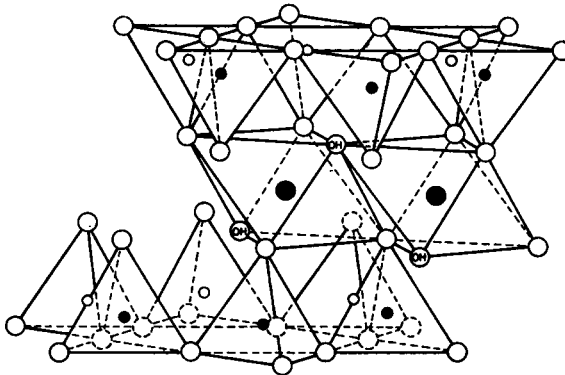


Fig. 7. Structure of kaolin.



Exchangeable Cations
 $n\text{H}_2\text{O}$

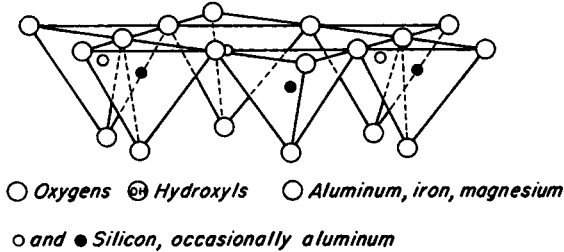


Fig. 8. Structure of montmorillonite.

feature of the montmorillonite structure is that water and other polar molecules can enter between the unit layers, causing the lattice to expand in the c direction. Ion exchange in montmorillonite is primarily due to substitutions within the lattice structure of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium, for trivalent aluminum in the octahedral sheet. The exchangeable cations resulting from lattice substitutions are found mainly

on cleavage surfaces, e.g., the basal cleavage surfaces of the layer clay minerals, and balance the charge deficiencies in the lattice layer of ions.

The amount of AIBA added to the clay dispersion in our kinetic studies had to be no more than the maximum amount of AIBA that could chemically be adsorbed by the two clays. Hence it was necessary to find experimentally how much AIBA could be adsorbed by each of the clays. This was described in the experimental section. It was also important to determine whether the AIBA was adsorbed as a monocation or a dication. It will become clear later why this is an important factor.

AIBA-Kaolin

The base-exchange capacity of the purified kaolin we used was 2.07 meq./100 g. If all the sites of the kaolin participated in the ion-exchange reaction and if all of the participating AIBA ions were adsorbed as monocations, the per cent carbon in the AIBA-kaolin would amount to 0.23%. When we added an excess of AIBA to the purified kaolin, we found only 0.145% carbon in the AIBA-kaolin. Either a sizeable fraction of the cations was adsorbed as dications or the exchange reaction was incomplete. We have found in previous experiments that a certain weight of hydrogen kaolin, that is, natural kaolin in which the exchangeable cations have been replaced by H^+ , adsorbed as many molecules of hexamethylenediamine as of *n*-hexylamine. On this basis, we believe that most of the AIBA cations are adsorbed as monocations.

AIBA-Bentonite

The cation-exchange capacity of the bentonite as determined by the ammonium acetate method was 88 meq./100 g. Hence 100 g. of the bentonite could adsorb 88 mmoles of AIBA if the cations were adsorbed as a monofunctional compound or 44 mmoles (= 88 meq.) if the cations were doubly adsorbed. From Figure 1, it appears that the AIBA cations are adsorbed mostly as dications. When a very large excess is used, especially when water is the sole dispersing medium, as much as 40% of the AIBA cations will become singly attached but we never used that much AIBA in our studies. This agrees with the work of other investigators such as Bradley,⁹ who have found that the number of organic cations adsorbed is inversely proportional to their functionality. About 80% of the exchange sites in bentonite are located on the basal planes,⁵ the remaining 20% are located on the outer surface of the clay particles. Many of the latter would adsorb the AIBA cations as monofunctional cations which on decomposition would give rise to one clay-attached free radical and one water-soluble unattached free radical, and only they can initiate the formation of homopolymer. We also wanted to determine whether a doubly adsorbed AIBA cation, sandwiched between the basal planes, is adsorbed on the same plane or on adjacent planes. Figure 2 indicates that the maximum *c* axis spacing of the dried AIBA-bentonite equals 13.0 Å. Since the *c* axis spacing of the clay without any adsorbed cations or water equals

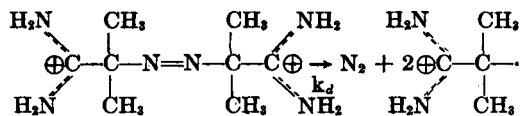
about 9.6 Å,⁵ the organic layer thickness would amount to about 3.4 Å. Because the thickness of a single layer of AIBA is of the order of 3.4 Å., we may conclude, therefore, that the dried AIBA-bentonite has a monomolecular layer of AIBA cations sandwiched between and parallel with the basal planes. If each AIBA cation were doubly adsorbed but on the same plane, we could expect a bimolecular layer of AIBA cations.

According to Weiss,¹⁰ alkylene α, ω -diammonium ions are adsorbed as dications on adjacent planes. The basal spacings of his dried clays also indicate a monomolecular layer of organic ions, which, in aqueous dispersion, assume a slanted position. Since adjacent planes are connected by the organic cations, the clay does not swell more than the length of the cation allows it to.

We made similar observations on our AIBA-bentonites. The basal spacing of water-swollen bentonite amounted to 45 Å., hence the layer of water in between the planes was 35.4 Å. thick. When AIBA was dispersed in this swollen clay, the basal spacing of the wet clay was reduced to 15 Å. Subtracting the *c*-axis spacing, the organic layer thickness of the AIBA cations amounted to 15 - 9.6 = 5.4 Å. This indicates a monomolecular layer of slanted AIBA cations and is in agreement with Weiss' observations.

Decomposition of the AIBA-Clay Adducts

The first step in the thermal decomposition of AIBA in aqueous solution yields nitrogen and two free radicals:



Figures 5 and 6 indicate that the decomposition of the AIBA-kaolin and AIBA-bentonite adducts is a first order reaction. A slight error was necessarily introduced in the determination of the rate constants of the decomposition of the above two clay adducts. If we add the azo compound to the clay dispersion at room temperature and then heat the AIBA-clay adduct to the desired temperature, some decomposition will occur before the desired temperature has been reached. If, on the other hand, we add the AIBA when the clay dispersion has been brought to the desired temperature, as we did, some of the azo compound will decompose before it has reacted with the clay. Thus, we would be measuring k_d for the AIBA decomposition rather than for the AIBA-clay. Fortunately the water-soluble azo cation is absorbed almost instantly by kaolin as well as by bentonite. Thus, our procedure should introduce only a very slight error.

In a future paper, we hope to show how these clay free radicals will initiate the polymerization of a series of vinyl monomers.

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Résumé

La bentonite et le kaolin adsorbent le chlorhydrate de 2,2'-azobisisobutyramidine au moyen d'une réaction d'échange d'ions. La vitesse de décomposition dans l'eau de l'azo-argile obtenu est environ double du composé azo lui-même. L'usage de ces organo-argiles comme initiateurs de la polymérisation vinylique rend possible la propagation de polymères vinyliques au départ de la surface argileuse et la préparation de mélanges polymère-argile.

Zusammenfassung

Bentonit und Kaolin adsorbieren 2,2'-Azobisisobutyroamidinhydrochlorid durch eine Ionenaustauschreaktion. Die Zersetzungsgeschwindigkeit des erhaltenen Azo-Tons in Wasser ist etwa doppelt so gross als diejenige der Azoverbindung selbst. Die Verbindung solcher Organo-Tone als Starter für die Vinylpolymerisation ergibt ein Wachstum der Vinylpolymeren von der Tonoberfläche und eine Darstellung von Polymer-Tonsystemen.

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