PREPARATION AND PROPERTIES OF SOME POLYMER-CLAY COMPOUNDS*

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ABSTRACT

Novel polymer-clay compositions were synthesized by neutralizing hydrogen montmorillonite and hydrogen kaolinite with amine-terminated polystyrene. The latter was obtained by the amide ion-initiated polymerization of styrene in liquid ammonia at −33°C. The neutralization reactions were carried out in methyl ethyl ketone, acetone, N,N-dimethylformamide and their aqueous solutions. As a result of their chemical modifications, the clays change from hydrophilic to hydrophobic, organophilic substances. Polystyrene–montmorillonite compositions containing about 50 per cent by weight of combined polymer formed dispersions in hydrocarbon oils which were similar to high temperature lubricating greases. The basal spacings of the organo-montmorillonites indicate the deposition of a polymer layer one molecule thick.

INTRODUCTION

SANDERSON and Hauser (1949) as well as Evans, Higginson and Wooding (1949, 1952) polymerized styrene in liquid ammonia in the presence of sodium amide and potassium amide. Higginson and Wooding (1952) postulated the following mechanism for the process:

$$NaNH_2 \rightleftarrows Na^+ + NH^-_2$$

initiation:

$$CH_2 = CH - C_6H_5 + NH^-_2 \rightarrow NH_2 - CH_2 - \bar{C}H - C_6H_5$$

propagation:

$$NH_2 - CH_2 - \bar{C}H - C_6H_5 + n\,CH_2 = CH - C_6H_5 \rightarrow NH_2 - (CH_2 - \underset{\displaystyle C_6H_5}{\underset{|}{CH}})_n\,CH_2 - \bar{C}H\,C_6H_5$$

termination:

$$NH_2 - (CH_2 - \underset{\displaystyle C_6H_5}{\underset{|}{CH}})_n\,CH_2 - \bar{C}H - C_6H_5 + NH_3 \rightarrow NH_2(CH_2 - \underset{\displaystyle C_6H_5}{\underset{|}{CH}})_n - CH_2 - CH_2 - C_6H_5 + NH^-_2$$

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Thus we obtain a high molecular weight primary amine which is capable of reacting with acids such as the acid clays used in the present study.

The nature of hydrogen kaolinite (H-Kaol.) and hydrogen montmorillonite (H-Mont.) has been treated in standard references such as Grim (1953) and is more recently reviewed in detail by van Olphen (1963).

For present purposes it seems adequate to note that more nearly equant dimensions of kaolinite crystals result in a greater importance in reactions of edge surfaces as compared with layer surfaces than is true for montmorillonite.

The outstanding 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 and affording enormous exposure of layer surfaces in the dispersed state without any great change in edge exposures. 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 layers of ions.

The possibility that the balancing ions be protons exists, but it has been shown by Paver and Marshall (1934), Chatterjee and Paul (1942), Muckherjee and others (1942) that H-Mont. and H-Kaol. are in reality hydrogen–aluminum systems. It is substantially impossible to prepare a clay in which all the exchange positions are occupied by H^+, since Al^{+3} moves from the lattice to exchange positions before saturation with H^+ becomes complete.

Because of this problem, an abundance of literature exists concerning the synthesis of organo-clays by means of a cation exchange reaction between an organic ammonium salt and montmorillonite, or kaolinite, but there are only a few descriptions (Servais, Fripiat, and Leonard, 1962; Sieskind and Wey, 1957) of how such organo-clays could be made by means of an acid–base reaction between the acid clay and an amine. The two reactions may be represented as follows:

$$\overset{+}{M}\ \overset{-}{\text{Clay}} + \overset{+}{RNH_3}\ \overset{-}{X} \rightarrow \overset{+}{M}\ \overset{-}{Cl} + \overset{+}{RNH_3}\ \overset{-}{\text{Clay}} \qquad (1)$$

$$\overset{+}{H}\ \overset{-}{\text{Clay}} + RNH_2 \rightarrow \overset{+}{RNH_3}\ \overset{-}{\text{Clay}} \qquad (2)$$

Both reactions take place. When we attempted to prepare polystyrene–montmorillonite by preparing the hydrochloride of amine-terminated polystyrene and reacting this with montmorillonite, we found that less polystyrene was attached to clay than was attached by reaction (2). We directed most of our study to the second type of reaction.

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Chemical combinations of polymers and clays have been described by Gluesenkamp (1957) and Ruehrwein (1957) who reacted montmorillonite with high molecular weight polycations. The latter were prepared by copolymerizing a basic monomer such as 4-vinylpyridine with one or more non-basic monomers. Since such copolymers contain a "plurality of recurring nitrogen-containing basic groups in the molecule" each polymer molecule can "effectively bind two clay surfaces together to give a semi-cross-linked system". This system is less free to swell in non-polar organic liquids than clays treated with simple amines. We have circumvented this disadvantage by preparing high molecular weight primary mono-amines.

EXPERIMENTAL AND RESULTS

Materials

(1) Styrene monomer was purified by drying over $CaCl_2$ and distilling at reduced pressure over sulphur. (2) Methacrylonitrile, Eastman Kodak, was distilled at atmospheric pressure; we used the fraction B.P. 89.5° — 90.0°C, which was stored over anhydrous magnesium sulphate. (3) Anhydrous liquid ammonia was obtained by distilling liquefied ammonia from sodium metal into a resin flask cooled by a dry ice–acetone mixture. (4) Sodium amide was obtained from Fisher Scientific Company. (5) Kaolin was obtained from the Georgia Kaolin Company and purified by discarding the fraction (about 1/3) that settled within 1 hr from a 10 per cent aqueous dispersion. (6) Bentonite,* from the Baroid Division, National Lead Co., was purified by discarding the silt that settled from a 2 per cent water suspension standing overnight.

Procedure

Preparation of amine-terminated polymer.—In a typical experiment 1 g of sodium amide was dissolved in 1800 cc of anhydrous liquid ammonia after which 250 cc of purified monomer was added. The reactants were stirred while the liquid ammonia was allowed to reflux. Excess $NaNH_2$ was destroyed by adding some NH_4Cl at the end of the reaction. The polymer precipitated as it was formed and was recovered by allowing the ammonia to evaporate and washing the residue in water and methanol. The solid polymer was dried *in vacuo* at 60°C under a nitrogen atmosphere. Its number average molecular weight, M_n, was determined by analysis of its basic nitrogen content and, assuming one amine group per polymer chain, M_n was generally between 9000 and 25,000.

Preparation of acid clays.—(a) Hydrogen montmorillonite (H-Mont.)

*Impure montmorillonite.

was prepared from a 2 per cent* aqueous dispersion of bentonite, allowing sand and silt to settle and pumping the supernatant dispersion successively through an ammonium Amberlite 1R–120 exchange column, an Amberlite 1RA–410 anion exchange column and an Amberlite 1R–120 hydrogen ion exchange column. The solid content† of the resulting H-Mont. dispersion was usually about 1.6 per cent and its pH generally 2.6. (b) Hydrogen kaolinite (H-Kaol.) was prepared by dispersing 100 parts of kaolin in 1000 parts of distilled water containing 0.2 g of Calgon. After allowing gangue to settle for 1 hr, the supernatant material was pumped through the same ion exchange columns described under (a). The resulting H-Kaol. dispersion, pH 3.5, usually had a solid content of 67 g/l. and was either used as it came from the columns or spray dried for later use.

Preparation of Polymer-Clays

Polystyrene-kaolinite (PST–NH_3 Kaol.).—Fifty grams of spray-dried H-Kaol. was dispersed in 1 l. of acetone–water (50-50) solution and stirred in a Waring blender while adding a solution of 10 g of PST–NH_2 (0.49 meq amine) in 500 cc of acetone. The pH increased from 3.90 to 4.30. In the absence of H-Kaol. the pH would have been 7.67. An additional 10 g of PST–NH_2 caused the pH to increase to 4.65. The reaction mass was filtered, the filter cake washed with methanol and then dried at 60°C *in vacuo*. Seven grams of the crude product (containing 5.0 g of kaolinite) dispersed in 100 cc of distilled water gave a pH of 6.4. The pH of 5.0 g of H-Kaol. in the same amount of water was 4.0.

To isolate the unreacted polystyrene, 10.00 g of the crude product was shaken with 100 cc of chloroform and allowed to stand for 1 hr. Since practically all of the insoluble fraction remained suspended, the suspension was centrifuged, and the solids were washed three times with chloroform. Thus, 3.5 g of PST–NH_2 was extracted. The chloroform-insoluble material contains 2.1 per cent polystyrene.‡ This PST–NH_3 Kaol. is a hydrophobic, organophilic powder. Table 1 illustrates how H-Kaol. has become organophilic by reacting it with amine-terminated polystyrene. Sample 1 contains 1.00 g of the crude product described under 3a. Sample 2 contains a mixture of amine-terminated polystyrene and H-Kaol., and sample 3 contains a mixture of "free radical"¶ polystyrene and H-Kaol. All samples contain the same amount of kaolinite and polystyrene.

Polystyrene-montmorillonite (PST–NH_3 Mont.).—The process is briefly as follows: 50 g of PST–NH_2 is dissolved in 1 l. of a water-miscible solvent, our choice being N,H-dimethylformamide (DMF), and the solution is stirred for 1 hr in a Waring blender with 1 l. of a 2 per cent aqueous

*All clay weights are based on materials as received.

†Determined by evaporating an aliquot and heating 24 hr at 110°C.

‡Based on C analysis.

¶Polystyrene prepared by polymerizing styrene by means of a free radical initiator.

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TABLE 1.—STABILITY OF VARIOUS KAOLINS IN CHLOROFORM

Sample	$PST-NH_2$[1] grams	PST-FR[2] grams	PST-K[3] grams	H-Kaol. grams	$CHCl_3$ cc	Hours of settling	Volume of precipitate cc	Appearance of supernatant liquid
1	0.272	0	0.728	0	10	0.25	0.02	milky
						1.25	0.02	milky
						6.75	0.02	milky
						24.0	0.02	milky
						72.0	0.02	milky
						168.0	0.02	milky
						504.0	0.02	milky
2	0.28	0	0	0.72	10	0.25	0.25	milky
						1.25	0.65	milky
						6.75	0.75	milky
						24.0	—	clear
						72.0	1.52	clear
						168.0	1.4	clear
						504.0	1.3	clear
3	0	0.2	0	0.72	10	0.25	5.0	clear
						1.25	5.0	clear
						6.75	4.8	clear
						24.0	4.5	clear
						72.0	4.5	clear
						168.0	4.2	clear
						504.0	3.5	clear

[1] Amine-terminated polystyrene, 4.8 meq amine/100 g.
[2] Polystyrene prepared by polymerizing styrene in presence of a free radical initiator.
[3] Polystyrene ammonium kaolin, containing 2 per cent polystyrene.

TABLE 2.—POLYSTYRENE AMMONIUM MONTMORILLONITES

Reference	PST–NH_2 g	M_n[1] PST–NH_2	Amine used per 100 g HM meq	Vol PST–NH_2 solution in DFM, cc	H-Mont.[2] g	H-Mont. dispersion cc	H-Mont. dispersion pH	Hr stirred	PST[3] in PST–M, %	C* period of PST–M, Å	Basic nitrogen in PST–M%
L0347	25	9556	26	1000	10[4]	1000	—	1	45.6		<0.003
L1751	50	9556	26	1000	19.63[4]	1000	3.00	1	40.35	13.25	<0.008
L1781	25	16,092	17	500	9[4]	500	—	1	49.7	13.1	<0.001
L1795	200	7335	13.0	2000	100[4]	5000	2.82	0.25	46.2	—	—
			14.3								
L3752	160	7200	8.5	5000	96[5]	5000	—	0.16	29.8	14.0	—
			13.6								
L3758	100	9220	11.7	5000	91.30[6]	5000	3.47	1	37.7	13.0	—
L3759	100	8852	8.5	5000	133[6]	4800	2.9	1	17.21	14.9	—
L3763	10	13,333	3.5	1000	21.16[6]	1000	3.35	1	20.35	13.6	—
	20	13,333	7.0	1000	21.16[6]	1000	3.35	1	34.50	13.4	—
	30	13,333	10.5	1000	21.16[6]	1000	3.35	1	18.3	13.1	—
	50	13,333	17.5	1000	21.16[6]	1000	3.35	1	30.25	13.5	—
L6052[8]	50	9210	27	1000	19.8[7]	1000	2.4	1	Very little coagulation		—

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TABLE 2. (*cont.*)

L6067	50	21,212	13	1000	23.0[9]	1000 2.6	1	46.5	—	—
L6074	303	16,115	17	5000	113	5000 2.7	1	42		—
L6084	50	12,300	29	1000	14[10]	1000 2.45	1	52		—
L6086	200	12,000	28	4000	60.7[10]	4000 2.4	1	48	12.90	—
L6090	250	12,000	26	5000	82.2[10]	5000 2.48	1	52.4	12.99	—
L6100	250	14,007	20	5000	90[10]	5000 2.44	1	59.0	—	—
L8011	250	11,200	22	5000	100[10]	5000 2.3	1	49.1	—	—
L8016	50	5800	51	1000	16.8[10]	1000 2.35	1	48.4	—	—

[1] M_n = Number average molecular weight. Calculated from per cent basic nitrogen and assuming one primary amine per polymer chain.

[2] Based on solids remaining after drying aqueous dispersion at 60°C *in vacuo*.

[3] Refers to benzene insoluble residue. Per cent PST calulated from per cent C.

[4] Baroid Blended Aquagel from Baroid. Rec'd. 4–2–1956.

[5] Prepared from Baroid Bentonite, Grade B–1–44. Nat. Standard Dust Bag Material. Approx. 1–10μ particle size. Reg. No. 30629.

[6] Baroid Aquagel–200 mesh—rec'd. 6–20–61.

[7] Prepared from 1948 batch of Baroid Bentonite (Aquagel).

[8] H-Mont. dispersion was added to the PST solution in 10 min.

[9] Prepared from 1948 Aquagel. Instead of passing the ammonium Mont. through a column filled with H-ion exchange resin, the ammonium Mont. was stirred with the resin and the latter filtered off.

[10] Prepared from National Lead Company's super centrifuged, spray dried Wyoming Bentonite passed through the three ion exchange columns.

dispersion of H-Mont. The resulting mass is poured into methanol, the solids filtered, dried at 60°C *in vacuo* and extracted with benzene to remove unreacted polymer. The benzene insoluble fraction, a grease-like material, was dispersed in methanol, and the resulting precipitate filtered and dried. The conditions under which various batches of PST–NH_3-Mont. were made and some of its properties are compiled in Table 2.

Polymethacrylonitrile-montmorillonite.—To a solution of 50 g of amine-terminated polymethacrylonitrile (η* = 0.380 at 25°C in DMF) in 1 l. of DMF was added 20 g of dry H-Mont. To this dispersion we gradually added 2 l. of distilled water. The acetone-insoluble fraction contains 17 per cent polymethacrylonitrile† and has a basal spacing of 13.95 Å.

Polystyrene-montmorillonite by ion-exchange reaction.—To a solution of 32 g of PST–NH_2(M_n = 7,671) dissolved in 1 l. DMF we slowly added the stoichiometric amount (= 4.17 meq) of 1 N HCl. The polystyrene ammonium chloride solution was added to a dispersion of 23.87 g of montmorillonite in 1 l. of distilled water, and the mixture was blended for 10 min. The solids were isolated in the usual way and extracted with benzene to remove unreacted polymer. The benzene-insoluble residue contained 14.5 per cent polystyrene‡

Preparation and Properties of Greases Based on PST–NH_3–Mont.

A mixture of five parts of solvent-treated lubricating oil base stock (1.1 stokes at 100°F), one part PST–NH_3–Mont. and 0.2 part of acetone was mixed and heated on a steambath until the odor of acetone was no longer noticeable. The resulting paste was cooled, milled five times on a three-roll paint mill and spread on a 300°–350°F hot plate After cooling the grease, it was again milled five times after which it was subjected to the following tests: consistency, Shell roll test, oxidation stability, wheelbearing test and high temperature beater test. The results are tabulated in Table 3. From the table it appears that the PST–NH_3–Mont.-based greases are reversible, and have excellent oxidation stability. One per cent PST–NH_3–Mont. added to an oil base paint makes it gel and confers thixotropic properties to that paint.

X-ray Diffraction Studies

Measurements of the layer thickness periodicities were made from X-ray diffraction patterns recorded either by a 114.59 mm diameter powder camera, or by a diffractometer with the sample pressed to a 1-in. disc

*n = intrinsic viscosity.
†Based on C analysis.
‡Based on C analysis.

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TABLE 3.—SOME PROPERTIES OF POLYSTYRENE-MONTMORILLONITE GREASES

Sample	L–6092	L–6084	L–6100	L–8006[7]	L–8011	L–8016
Penetration, ASTM[1] Penetration, Micro[2]	332 180	254 —	376 297 —	343 292 — —	285 — —	288 —
Oxidation stab, pressure drop after 100 hr, psi[3]	2					
Softening in Shell Roll Test, pen. units[4]	Too soft to test	—	—	Softens — 65 pts	Softens 73 pts	Softens 93 pts
PST in PST–NH_3–M, %	50	52	59 59	53.2	49.1	
Oil	500 SDS[6]	500 SDS[6]	500 460 SDS[6] Oil	500 460 SDS[6] Oil	500 SDS[6]	500 SDS[6]
Concentration thickener	16.6%	16.6%	16.6%	16.6%	16.6%	16.6%
High Temp. Beater 250–260°F, 7 hr	After 2 hr still greaselike. Cooled sample has good consistency. After 7 hr good body.81/290[5] 81 unworked/ 290 milled micropen	—	—	—	—	—
Wheelbearing Test ASTM D1263–53T beat 130 g pack, 2 hr at 220°F	9.7 g leakage, about 1 g oil. Rollers moderately oily. No slumping from hub. No seepage. Rating good. 51/182[5] micropen	—	—	—	—	—

[1] ASTM D217–60T—worked by spatula on workbench.
[2] Shell Micropenetration—ditto
[3] ASTM D942–50.
[4] UTM 135–60.
[5] Millec 5 times.
[6] 500 second Duo Sol Oil (1.1 Strokes at 100°F).
[7] This is L–6100 but re-extracted with benzene.

at 80,000–100.000 lb/in.* The radiation was nickel–filtered CuKα or, less frequently iron–filtered CuKα. The difficulty of determining the exact position of the broad asymmetric *001* peak together with possible variations from the different diffraction techniques employed is believed to lead to intercomparison uncertainties of about 0.5 Å in layer thicknesses.

DISCUSSION

The reaction between H-Mont., or H-Kaol., and amine-terminated polymers, i.e., high molecular weight amines, is one of neutralization. We have the following evidence that the amine-terminated polystyrene has reacted with the acid clays: (a) On adding the amine we notice an increase in pH. (b) If the PST–NH_2 reacts with H-Mont. to form a salt, we would expect the benzene-insoluble fraction to be devoid of primary amine groups, and this is indeed the case. (c) A certain fraction of the polystyrene remains attached to the clay after repeated solvent extractions. There are certain instances where the physical attraction between an organic molecule and the clay surface is so strong that the former cannot be leached from the clay surface. For instance, Brindley and Rustom (1958) found that montmorillonite treated with an aqueous solution of "Nonisol 250"† retains, after repeated water washings, a monomolecular interlaminar layer of the ester. Polystyrene has no polar groups responsible for hydrogen bonding, and we would not expect an irreversible adsorption unless the terminal amine group reacted with the acid clay.

When H-Mont. and Styron‡ are brought together under the same conditions, the benzene insolubles contain only 4.4 per cent carbon instead of about 44 per cent and do not form a gel in benzene.

CONFIGURATION OF THE POLYMER CHAIN

From the C* periods found by X-ray diffraction we estimate that we have deposited a monomolecular layer of polystyrene between the basal planes of the montmorillonite. Whereas the polycation-montmorillonite compositions described by Gluesenkamp (1957) and Ruehrwein (1957) do not exhibit good swelling properties in non-polar substances because of the multiplicity of chemical bonds between each chain and opposing clay surface, our polystyrene–montmorillonite samples do swell in benzene since there is only one point of attachment per chain. Thus a 1-g sample of

*All clay weights are based on materials as received.

†$HO-CH_2-CH_2-(O-CH_2-CH_2)_nO-CH_2-CH_2-O-C(=O)-(CH_2)_7CH=CH-(CH_2)_7CH_3$.

‡Dow Chemical Company's "free radical" polystyrene.

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benzene-extracted polystyrene–montmorillonite containing 50 per cent polystyrene has a gel volume of 9.2 cc in benzene. There is also a difference in the degree of coverage between our organo-clays and those of Gluesenkamp, as evidenced by the benzidine color test. Gluesenkamp states, "The benzidine color reaction also gives evidence for disorder in these systems. Benzidine, and other aromatic amines, form intensely colored complexes with montmorillonite surfaces. The intensity of color when organobentonites are treated with benzidine would be a measure of the amount of clay surface not covered by organic material. Simple alkyl ammonium bentonites give only faint colors when the alkyl radical covers essentially all of the surface. However, all of the polycation-bentonites, even those where the computed area per ion is more than enough to cover the clay surface completely, gives relatively intense color with benzidine. This can be taken to mean that, while a stable polymer-clay complex from which free polymer cannot be extracted can be prepared by reacting the clay with a polycation, orderly and complete coverage of the clay surface is not attained." Our polystyrene–montmorillonite complexes give only the faintest color with benzidine and, according to the foregoing criterion, the basal planes should be completely covered.

Jordan's (1949) work on the reaction between n-alkylammonium salt and montmorillonite is quite interesting in that it shows that as the length of the alkyl group increases, we get a non-continuous stepwise separation of the platelets. Table 4 shows this relationship.

TABLE 4.—SPATIAL RELATION FOR HOMOLOGOUS ALKYL AMMONIUM BENTONITES[1]

No. carbon atoms	001 spacings Å	Separation of clay platelet, Å	Layers of amine
0	9.6	0	0
3	13.5	3.9	1
4	13.4	3.8	1
8	13.3	3.7	1
10	13.6	4.0	1
12	17.4	7.8	2
14	17.4	7.8	2
16	17.5	7.9	2
18	17.6	8.0	2
26	18.6	9.0	2
38[2]	24.7[3], 23.2[4]	15.1	4

[1] Jordan, J. W. (1949), *J. Phys. and Colloid Chem.*, v.56, pp.294-306.
[2] National Lead Company's Bentone–34 (dimethyl dioctadecyl ammonium Bentonite
[3] This study.
[4] Barrer, R. M., and Kelsey, K. E. (1961), *Trans. Faraday Soc.* v.57, pp.625–640.

According to Jordan, as soon as the area of the alkylamine exceeds 50 per cent of the surface area per exchange site (161 $Å^2$) adjacent laminae are unable to approach more closely than 8 Å, which is the thickness of two methylene chains. Offhand one might conclude that when an amine, many times larger than the dimethyl dioctadecyl ammonium cation, reacts with montmorillonite, the resulting plane separation would be well in excess of 23.2 Å. Yet, this is not the case with the high molecular weight polystyrene amines. We suspect that whereas in the case of alkylammonium cations a large number of rapidly diffusing small molecules compete simultaneously for exchange sites on the clay basal planes, the larger polystyrene molecules diffuse much more slowly and there is probably a gradual coverage of acid sites, one chain covering a large number of sites.

Dyal and Hendricks (1950) determined experimentally that 1 g of hydrogen montmorillonite adsorbs 0.25 g of ethylene glycol, and calculated from the unit cell dimensions the total surface area, external (Makower, Shaw, and Alexander, 1937) (43.9 m^2/g) + internal, or montmorillonite as 810 m^2/g. They reasoned that, on that basis, the contact area per ethylene glycol molecule would be 33 $Å^2$. (There are two layers of ethylene glycol between each pair of opposite basal planes.) Hence the molecule must lie with a long axis parallel to the clay surface. (We calculated from a molecular model that the contact area under these restrictions would be 21 $Å^2$.) We have used this approach on a typical polystyrene–montmorillonite sample containing 50 per cent by weight of attached polystyrene. Two grams of this material contain 1 g of montmorillonite with a surface area of 8.1×10^{22} $Å^2$ and 1 g of polystyrene containing $6.023 \times 10^{23}/104$ mers ($CH_2 - CH(C_6H_5)$), consequently the contact area between each mer and one of the two basal planes between which it is "sandwiched" would be $0.5 \times 8.1 \times 10^{22}/6.023 \times 10^{23} \times 1/104 = 7$ $Å^2$, provided all of the polystyrene is spread out in a monomolecular layer* and does not protrude. When we examine a molecular model of polystyrene, it becomes obvious that this contact would be at least 8.7 $Å^2$; this is the case where the benzene rings are all in a plane vertical to the basal clay plane. This is sterically impossible and would require an organic layer thickness of about 4.5 Å instead of the observed 3.4 Å. Apparently a significant portion of the polystyrene protrudes from the basal planes. We can reach the same conclusion by assuming that all of the polystyrene is located between the basal planes. The layer thickness for our sample would then be: volume of 1 g polystyrene ($Å^3$)/1/2 internal surface area of 1 g montmorillonite ($Å^2$) Œ $(1/1.054 \times 10^{24}) : (810–44/2 \times 10^{20})$Å = 24.8 Å instead of 3.4 Å as found by X-ray diffraction.

According to Table 2 there is no correlation between the c_0 distance

*According to X-ray diffraction measurements the layer is 3.4 Å thick.

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and the percent polystyrene combined with the clay. Apparently the proportion of polymer protruding from the basal planes is not constant for each sample.

SUMMARY

1. Amine-terminated polystyrene, polymethacrylonitrile, hydrogen kaolinite and hydrogen montmorillonite have been prepared.
2. Acid clays were neutralized by the basic polymers to yield novel polymer-clay combinations.
3. Most of the polystyrene protrudes from the basal planes of the montmorillonite, which seems to be completely covered by a monomolecular layer of polystyrene.
4. When polystyrene–montmorillonite is added to a mineral oil, such as a solvent-treated lubricating oil base stock, a reversible grease results which has good oxidation stability.
5. Polystyrene–montmorillonite exhibits good swelling properties in aromatic hydrocarbons as well as in polar solvents.

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