TABLE I
Clay Minerals Identified in Various Samples

Clay	Clay minerals
Kendposi and Bhonda	Mixtures of poorly crystallized kaolinite, montmorillonite, talc and muscovite
Appenhalli	Poorly crystallized kaolinite (about 70%), admixed with talc and illite
Nandihalli	Poorly crystallized kaolinite, traces of talc
Rairangpur	Dickite admixed with muscovite (about 15%) and traces of talc
Thirthahalli, Palyangadi, and Kannapuram	Well crystallized kaolinite

The clay minerals identified in these eight samples are given in Table I.

These clays were later compounded in natural rubber, and the properties of the rubber stocks were studied. The results indicate that Thirthahalli, Palyangadi, and Kannapuram clays exhibit superior compounding properties as compared to the rest, confirming the importance of the mineralogical status of rubber-grade china clays.

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Note on Colloidal Dispersions from Block Copolymers

Controlled addition of a selective nonsolvent to the solution of a block copolymer results in the "precipitation" of one of the components of the copolymer.[1] Aggregate formation is expected and has been reported in such instances. It seems reasonable to assume that clustering of like segments occurs, and that the resulting aggregate is maintained dispersed by the blocks still soluble in the solvent–nonsolvent mixture.

If the aggregate formed is constrained to contain primarily one kind of block, then the colloidal particle should possess a limiting size. Subsequent removal of solvent will cause collapse of the other block component to form a shell around the original aggregate core.

Addition of acetonitrile to benzene solutions of polystyrene–poly(methyl methacrylate) (PS–PMMA) block copolymers causes formation of such colloidal dispersions. When the copolymer composition is roughly 1:1, a highly turbid solution develops at a solvent composition corresponding to about 55% acetonitrile. The intrinsic viscosity exhibits a pronounced decrease at this solvent composition as is shown in Figure 1. The same level of acetonitrile when added to benzene solutions of PS homopolymer causes polymer precipitation. These experiments indicate that the addition of acetonitrile causes collapse of the PS chains which may be accompanied by micelle formation. Solubility of the PMMA chains in the solvent-nonsolvent mixture prevents phase separation.

Dilution of an (80:20) acetonitrile–benzene mixture at constant solvent composition followed by evaporation to produce specimens suitable for viewing by electron microscopy yields colloidal particles of spherical shape as demonstrated by Figure 2. The diameter of these particles varies with the molecular size of the copolymer (See Table I).

TABLE I
Particle Sizes of Some Colloidal Dispersions

Copolymer preparation	How dispersion formed	$\bar{M}_{total}$	$\bar{M}_{PS\ block}$	Chrome shadowed	Diameter, A.
1	Direct in CH_3CN	169,000	76,000	No	550
2	Direct in CH_3CN	(350,000)	(175,000)	Yes	1230
2a	Pption from C_6H_6 with CH_3CN	"	"	Yes	1050
2b	"	"	"	No	735

With PS–PMMA block copolymers, dispersions may also be produced by direct peptization of the dried polymer in acetonitrile, followed by dilution and evaporation as above. The particles thus formed were found to be similar in size to those formed by selective precipitation (see entries 2 and 2a in Table I); small differences are probably due to variations in the amount of chrome shadowing.

Since the acetonitrile is a nonsolvent for PS and a poor solvent for PMMA, it appears that dispersions formed either by precipitation, involving collapse of the PS component first, or by direct dispersion should produce a colloidal aggregate of many chains with the PMMA on the surface and the PS at the core.
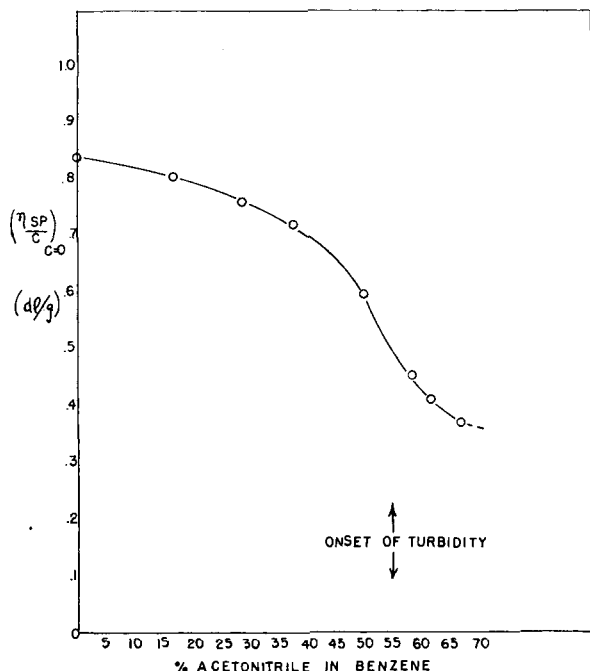
Fig. 1. Intrinsic viscosity vs. solvent composition for a PS–PMMA block copolymer.

Fig. 2. Electron micrograph of spherical colloidal aggregate particles from a PS–PMMA block copolymer, chrome shadowed. ×12,300.

An attempt has been made to rationalize the particle diameter in the following manner: Consider a block copolymer of the type $A_m - B_n - A_m$; then, on addition of a precipitant for B, let B collapse and aggregate while A remains solvated. If this aggregate core is to contain B units (and unavoidably some A) then its radius, r_B, will exceed the root-mean-square end-to-end length of the B block. If the unperturbed root-mean-square chain displacement, $(\bar{R}_0{}^2)^{1/2}$, is taken as a satisfactory approximation to the length of the B block, then $2r_B \geqslant (\bar{R}_0{}^2)_B{}^{1/2}$. The volume of the core, V_B, then becomes $\geqslant (\pi/6)(\bar{R}_0{}^2)_B{}^{3/2}$. The minimum number of B chains in the core will equal $(V_B d_B)/\bar{M}_B$ where d refers to density and $\bar{M}_B$ to the molecular weight of the B block.

On subsequent precipitation of the A units onto the surface of the core, the volume of the particle becomes $(\pi/6)(\bar{R}_0{}^2)_B{}^{3/2}[1 + (2\bar{M}_A d_B)/(\bar{M}_B d_A)]$, since there are two A blocks per B block and $\bar{M}_A$ refers to each of the two A chains.

The diameter of the resulting particles now becomes $(\bar{R}_0{}^2)_B{}^{1/2} [1 + (2\bar{M}_A d_B/\bar{M}_B d_A)]^{1/3}$. Utilizing the relation given by Krigbaum[2] and Thurmond and Zimm[3] $(\bar{R}_0{}^2)^{1/2} = 70M^{1/2}$, leads to values of about 200 A. and 300 A. for the unperturbed root-mean-square end-to-end dimensions of the PS chains in preparations 1 and 2b, respectively, of Table I.

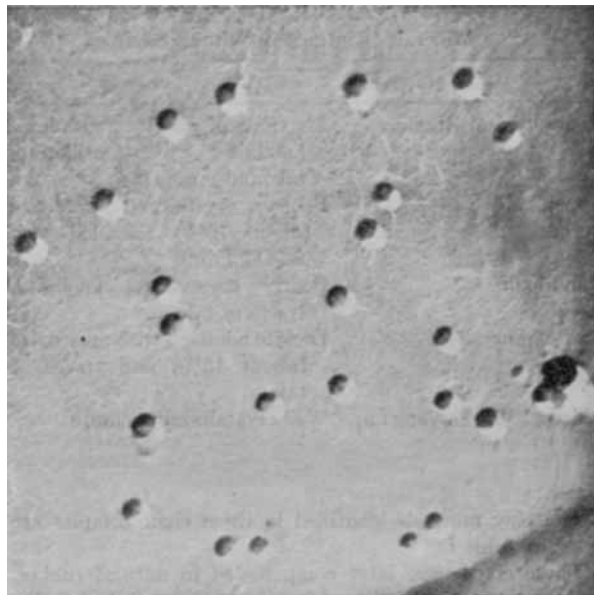If it is assumed that there are no voids and that the densities of the core and shell are near unity, then from the above, diameters of about 250 A. and 380 A. are calculated, respectively, for preparations 1 and 2b in Table I. These are about half the observed values of 550 A. and 735 A., a not unsatisfactory comparison considering the simplicity of the model.

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