pyrolysis temperature must be over the boiling point of the N,N-dimethyl-1-amino-2-hydroxypropane (bp 126°) one would expect little or no reaction between the alcohol and isocyanate. Instead, the amino alcohol should flash off and leave free isocyanate groupings in the polymer. In the other case (copolymers of IV) the amino diol should not flash off (bp 109–111° at 15 mm) but should remain to react with the pendant isocyanate groups.

The infrared spectra of the various copolymers, pyrolyzed at 160–180°, showed that the reasoning above, with modification, was correct. Strong isocyanate absorption at about 2250 cm^{-1} was present, as expected, after pyrolysis of the copolymers of III. Contrary to expectation, however, the pyrolyzed copolymers of IV exhibited both a strong isocyanate absorption band at 2250 cm^{-1} and a weak band at 1710 cm^{-1}, indicative of a urethane grouping. In the case of the copolymers of IV, the presence of the isocyanate absorption can be explained by the low reactivity of the tertiary aliphatic isocyanate group.

Properties of the pyrolyzed and unpyrolyzed films of the copolymers of I, III, and IV with methyl methacrylate were compared along with unmodified methyl methacrylate polymer. The results are shown in Table III. The Sward hardness values of all of the polymers increase upon pyrolysis. The modified methacrylates seem to be slightly harder than the base polymer. This could be due to enhanced van der Waals bonding because of the highly polar aminimide grouping before pyrolysis and isocyanate or urethane grouping after pyrolysis. The most remarkable difference between the base polymer and those modified with aminimides is in adhesion. Here the modified methacrylates show greatly enhanced adhesion after pyrolysis. This may be due to the isocyanate groupings generated by the pyrolysis. These isocyanate groups probably both react chemically with active hydrogen atoms on the substrate surface and interact physically with the surface through van der Waals bonding. The polymer modified with IV was the only one that showed reasonable adhesion to glass, both before and after pyrolysis. This is perhaps due to hydrogen bonding of the larger number of OH groups to the hydrated glass surface. One should also note the enhanced adhesion of the polymer modified with I to aluminum and steel prior to pyrolysis. No explanation is offered.

From the data presented, indications are that the monomers described possess great potential as modifiers of base vinyl polymers, especially in increasing their hardness and their adhesion to varied substrates.

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Colloidal Properties of Styrene–Butadiene Block Copolymers[1]

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ABSTRACT: Styrene–butadiene block copolymers form micelles in selective and in nonselective solvents because of interactions of the different polymer sequences with the solvent or with each other. The formation of micelles has been studied by electron microscopy. The compatibility of random, block, or graft copolymers with the corresponding homopolymers is discussed.

Block and graft copolymers have sequences of different homopolymers in the same molecule. Selective solvents can often be found which are good with respect to one of the homopolymer sequences, but are poor with respect to the other types of sequences. As with soaps and nonionic surfactants, block and graft copolymers are nonuniformly soluble in selective solvents and can show a variety of colloidal properties. They can emulsify oil–water systems,[2] and they can form micelles[3-4] and stabilize organic lattices[5] in which an organic solvent rather than water is the continuous phase. In analogy to conventional surfactants, the colloidal properties of block and graft copolymers in selective solvents have been explained on the basis of their nonuniform solubility,[2-4] *i.e.*, on the basis of polymer–solvent interactions.

Previous work[6,7] has demonstrated that block and graft copolymers can stabilize emulsions of the oil-in-oil type, which consist of phases of immiscible polymer solutions. Such emulsions are obtained by dissolving two chemically different homopolymers and the corresponding block or graft copolymer in a mutual solvent. Since all components are required to be soluble, a nonselective solvent is usually chosen, *i.e.*, a good solvent for both types of polymer chains present in the system. The stability of the resulting "polymeric

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oil-in-oil emulsions" has been attributed to interactions between the branches of the emulsifying block or graft copolymers and the homopolymers dissolved in the two oil phases.[7] Since the highest emulsion stability is attained in truly mutual solvents, it appears that block and graft copolymers show at least some of the colloidal properties found in selective solvents also in nonselective solvents, but in the latter case based on polymer–polymer interactions rather then on polymer–solvent interactions. Such polymer–polymer interaction should be repulsive in character, because polymers of chemically different structure are generally incompatible,[8] and should give rise to a certain segregation of chemically different sequences within the block or graft copolymer molecules.[7–15] Thus, phenomena like micelle formation, which have been found in nonselective solvents and have there been attributed to polymer–solvent interactions, can also be expected to occur in nonselective solvents, but as a result of polymer–polymer interactions. In the present paper, micelle formation of styrene–butadiene block copolymers is shown to occur under certain conditions. These studies shed some light on the problem of compatibility of block copolymers with the corresponding homopolymers.

Selective Solvents. Merrett[16] has shown that two modifications, a "hard form" and a "soft form," can be prepared from the same sample of a graft copolymer of natural rubber and polymethyl methacrylate. He dissolved the graft copolymer and precipitated it from solution choosing the solvent–nonsolvent system so that either the rubber chains or the polymethyl methacrylate chains collapse first, when the nonsolvent is added. In order to explain the observed behavior, Merrett postulated the formation of micelles during the precipitation. The cores of the micelles would be formed by those polymer chains that collapse first in the precipitation process. The opposite polymer chains, which are still soluble at that point, would form the shells of the micelles and would fuse together forming a continuous phase, when all of the graft copolymer has been precipitated. This continuous phase determines the overall appearance of the formed modification, which is either hard and rigid or soft and rubbery, when an elastomer is involved.

Merrett[3a,16] and other authors[3b,4] demonstrated the micelle formation of block or graft copolymers in selective solvents by physical–chemical methods, particularly by viscosity measurements. A morphological study of micelle formation is presented here using electron microscopy and the osmium tetroxide staining method recently published by Kato.[17] This method has been used for staining of the rubber in rubber-modified polymers and, accordingly, can be used to stain selectively the rubbery portions in micelles of block copolymers of butadiene or isoprene.

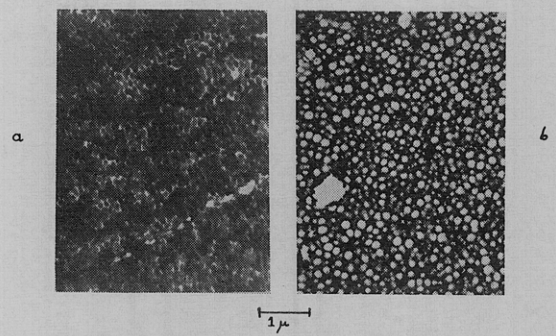

Figure 1. Hard form (a) and soft form (b) of a styrene–butadiene block copolymer.

The present studies are based on anionically prepared two-block copolymers of styrene and butadiene, containing 70 wt % styrene and 30 wt % butadiene and having number average molecular weights in the range of 150,000–250,000. In analogy to Merrett's experiments,[16] solutions of the block copolymers in nonselective solvents were prepared, from which colloidal sols of the block copolymers were formed by addition of selective nonsolvents which precipitated portions of the molecules. Depending on the nonsolvent added, micelles can thus be formed which have cores of either butadiene or styrene units. The hard or soft modifications of the solid block copolymers can be obtained by casting films from the colloidal sols. Figure 1 shows electron photomicrographs of the hard and the soft modifications of the styrene–butadiene block copolymers. The hard form (Figure 1a) was prepared from a colloidal sol containing methylene chloride as a solvent and a mixture of equal volumes of methyl ethyl ketone and acetone as a selective nonsolvent for the butadiene portions. The soft form (Figure 1b) was prepared from a colloidal sol obtained by adding *n*-hexane as a selective nonsolvent for the styrene portions to a second aliquot of the block copolymer solution in methylene chloride.

All electron photomicrographs shown were prepared from osmium tetroxide stained samples. In these pictures, the butadiene portions appear black and the styrene portions appear white. Figure 1a shows black micellar cores of butadiene sequences in a white continuous phase of the micellar shells of the styrene sequences. Figure 1b shows the opposite micelle structure, namely, white micellar cores of styrene sequences in a black continuous phase of shells of butadiene sequences. Thus, the microstructure of the two modifications of the styrene–butadiene block copolymers is in agreement with the microstructure postulated by Merrett[16] for the corresponding modifications of natural rubber–methyl methacrylate graft copolymers.

Nonselective Solvents. The influence of polymer–polymer interactions on the colloidal behavior of block copolymers can be studied without excessive interference from polymer–solvent interactions, if polymers and solvents are chosen so that the solvents are good with respect to both types of polymer sequences.

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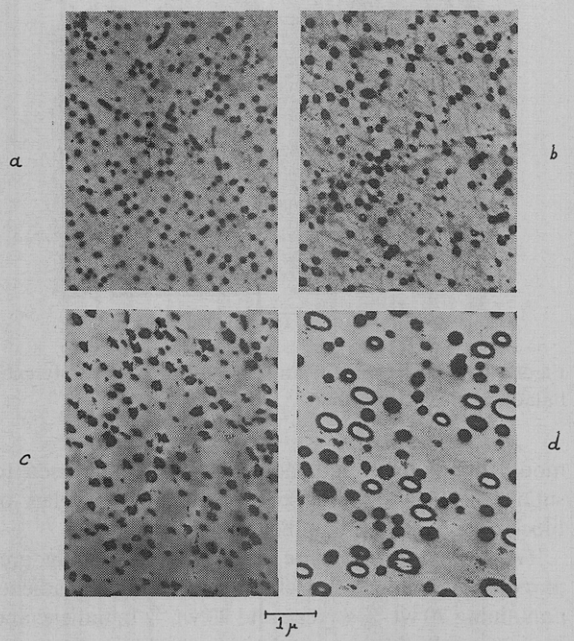

Figure 2. Styrene–butadiene block copolymer micelles embedded in a polystyrene matrix. The system contains (a) 0%, (b) 2.5%, (c) 5%, (d) 7.5% polybutadiene (see Table I).

Polymer–polymer interactions between chemically different sequences of sufficient length would be repulsive in character[7–15] and can be expected to give rise to various forms of orientation in block and graft copolymers, either in solution or in the solid state. In solution, the formation of spherical micelles has been suggested.[7] Spherical micelles could form by segregation of different polymer sequences in such a manner that all sequences of one type accumulate in the cores of the micelles while the other type sequences form the micellar shells. Vanzo[18] and Sadron[19] reported orientation of block copolymers of styrene and butadiene or isoprene, respectively, in solution as indicated by intense iridescence similar to the iridescence of cholesteric liquid crystals. In the solid state, Henderson, Grundig, and Fischer[20] demonstrated by stress birefringence measurements that the styrene and butadiene sequences occupy different domains in styrene–butadiene block copolymers. Vanzo,[18] Hendus, Illers, and Ropte[21] and Bradford and Vanzo[22] have studied styrene–butadiene block copolymers, and Kohler[23] has studied styrene–isoprene block copolymers in the solid state by electron microscopy. The styrene sequences in all block copolymers were segregated from the butadiene or isoprene sequences, respectively.

The structure of block copolymers in solution is not amenable to electron microscopic investigation, unless the solutions can be transformed into equivalent solid samples which can be prepared for the electron microscopy by the usual methods, such as thin slicing and staining or etching. In the ideal case, the solutions would have to be solidified without any changes in the structure of the solutes, but useful information can still be obtained from samples in which structural changes have occurred during the solidification process, if these changes proceed in a predictable and controllable manner. In the present study, styrene–butadiene block copolymers are dissolved in styrene as a nonselective solvent. Solidification of the solutions is brought about simply by polymerization of the styrene, which is carried out as described elsewhere.[6]

When some of the styrene has been polymerized, the block copolymer molecules dissolved in the styrene–polystyrene medium are in a situation similar to that of soap molecules dissolved in water, because portions of the molecules are incompatible with their environment. The butadiene sequences in the block copolymer molecules are incompatible with the polystyrene homopolymer being formed, just like the hydrocarbon tails of soap molecules are insoluble in water. In analogy to the formation of micelles by soap molecules in water, block copolymer molecules should form micelles in solutions containing one of the corresponding homopolymers. Possible forms of such micelles are the spherical oriented structures suggested in a previous paper.[7] If this type of orientation prevails in the present systems, spherical micelles representing only one of the two suggested types of orientation would be formed, namely, the type in which the butadiene sequences are coiled up in the center of the micelles, while the polystyrene sequences form the micellar shells. In this type of arrangement, the butadiene sequences would be least exposed to the surrounding polystyrene medium. Solid samples prepared by complete polymerization of a solution of a styrene–butadiene block copolymer in styrene would then contain micellar cores embedded in a polystyrene matrix. These cores would appear as black particles in the electron microscope when the osmium tetroxide staining technique is used.

Figure 2 shows electron photomicrographs of samples prepared in the manner described above. Thin slices of the samples were stained with osmium tetroxide so that the butadiene sequences appear black in the photomicrographs. The sample in Figure 2a has been prepared by dissolving 10% (by weight) of the 70/30 styrene–butadiene block copolymer in 90% styrene and polymerizing to completion. The picture shows black dots in a white background. The black dots are interpreted as being the butadiene cores of spherical micelles. The samples in Figures 2b, c, and d have been prepared following the same procedure, but increasing portions of the block copolymer have been replaced by polybutadiene homopolymer while the matrix has been kept constant at 90% (by weight) polystyrene. The compositions of the samples and the resulting micellar core diameters are listed in Table I.

In analogy to the well-known phenomenon of solubilization of solvents by soap micelles in water, the polybutadiene homopolymer seems to be "solubilized" in the block copolymer micelles. The micelles increase in size as more and more homopolymer is introduced into the system. Since the polybutadiene homo-

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polymer is added at the expense of the block copolymer, the total number of micelles in the system decreases as their size increases. The sum of block copolymer and added polybutadiene homopolymer has been kept constant at 10% by weight of the total system in order to maintain the viscosity of the solution at about the same level in all samples. The addition of still larger amounts of polybutadiene homopolymer leads, again in analogy to solubilization of oils in aqueous soap micelle solutions, to an expansion of the micelles to form droplets of a polymeric *oil-in-oil emulsion.*[6] For as yet unexplained reasons, many of the micelles change from a spherical to an elliptical structure (Figure 2d) as more and more polybutadiene homopolymer is added. The white center of the ellipses in Figure 2d is apparently occluded polystyrene. To some extent, white occlusions are visible also in Figure 2c. The wall thickness of the elliptical structures in Figure 2d is of about the same order of magnitude as the cores of the spherical micelles in Figure 2a. The ellipses could be cross sections of cylinders similar to those described by Skoulios[24] and coworkers for block copolymers of styrene and ethylene oxide dissolved in selective solvents.

Figure 3 illustrates the effect of varying the concentration of the block copolymer in the original solution. As might be expected, the number of micelles decreases as the block copolymer concentration decreases from 15% by weight (Figure 3a) to 5% by weight (Figure 3c), but the size of the micelles is relatively unaffected. The block copolymer used for the samples in Figure 3 contained some homopolymer which might be the reason for the appearance of elliptical structures in all samples prepared with this particular block copolymer. Figure 3c contains some linear structures of the same thickness as the walls of the elliptical structures. Close inspection of these linear structures gives the impression that they are linear aggregates of spheres similar to pearls on a string. The diameters of these alleged spheres are again of the same order of magnitude as the spherical micelles in Figure 2a.

The solutions of the block copolymer in styrene were stirred during the initial period of the polymerization. Figure 4 shows samples at 10 and at 1% (by weight) concentration of the block copolymer which have been prepared by polymerization without stirring. The pictures show that the morphology of the samples is greatly influenced by the mechanical treatment during the polymerization. Both pictures in Figure 4 are taken at lower magnification than the pictures in Figure 2 in order to show a larger cross section of the samples. The thickness of the black stripes is of the same order of magnitude as the diameter of the spherical micelles in Figure 2a and the wall thickness of the ellipses in Figure 2d.

Compatibility of Block Copolymers with the Corresponding Homopolymers. Electron-microscopic studies of the morphology of mixtures of block copolymers with the corresponding homopolymers are not only of interest with respect to the colloidal behavior of block copolymers, but also provide new insights into the general problem of polymer compatibility.

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TABLE I
MICELLAR CORE DIAMETERS AT VARIOUS LEVELS OF "SOLUBILIZED" POLYBUTADIENE

S/B block, %	PB, %	PS, %	Core diameters, Å
10.0	0	90	750–1100
7.5	2.5	90	1300–1700
5.0	5.0	90	1700–2100
2.5	7.5	90	2100–4000

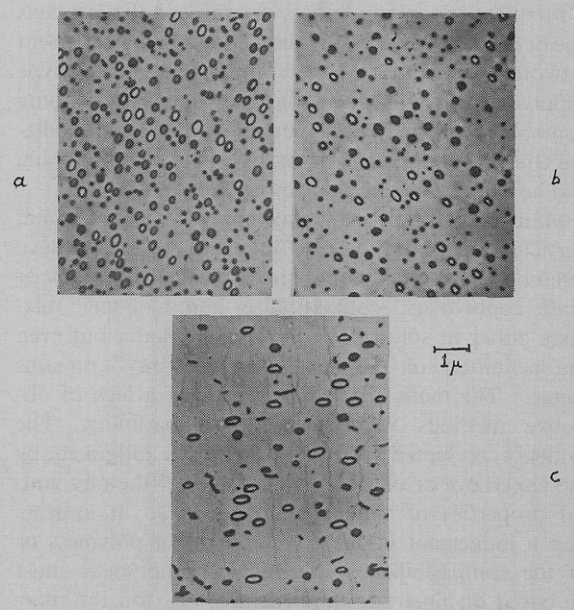

Figure 3. Styrene–butadiene block copolymer micelles embedded in polystyrene at (a) 15%, (b) 10%, (c) 5% by weight of the block copolymer.

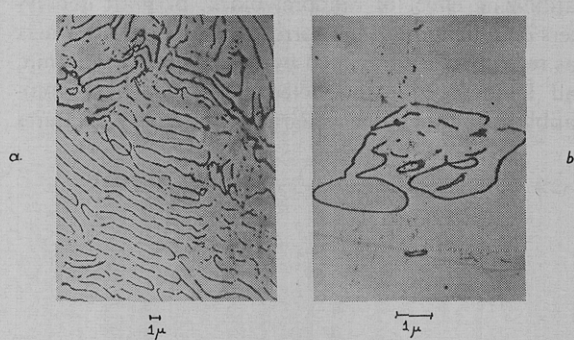

Figure 4. Styrene–butadiene block copolymer embedded in polystyrene without stirring during the polymerization, at (a) 10% and (b) 1% block copolymer.

Figures 1–4 show that the butadiene sequences are always segregated from the styrene sequences, regardless of the morphology of the system or of the composition, *i.e.*, regardless of whether the system contains block copolymers alone or in a mixture with one or both of the corresponding homopolymers. It seems to be immaterial in this case whether polymeric sequences in styrene–butadiene block copolymers are part of the same block copolymer molecule, or whether they belong to different homo- or block copolymer molecules. If long sequences are chemically different, they are incompatible.

Dobry and Boyer-Kawenoki[8] have studied a large number of mixtures of homopolymers and have come

to the conclusion that incompatibility of different homopolymers is the rule, and compatibility is a rare exception. Studies on various heterogeneous polymer systems presented in previous papers[6,25] showed that even such closely related polymers as polystyrene, polyvinyltoluene, and poly-*t*-butylstyrene are incompatible. It was further found that phase separation occurs even between random copolymers of the same comonomers, but of different composition, if the composition difference exceeds a certain critical value.

Mixtures of random, block, or graft copolymers with one or both of the corresponding homopolymers present a twofold problem: (1) the compatibility of any type copolymer with any one or both of the corresponding homopolymers, and (2) the possibility of a compatibilizing effect of copolymers in ternary mixtures containing two homopolymers and one copolymer.

Many speculations on the second point can be found, particularly in the patent literature. Claims have often been made that copolymers, particularly block or graft copolymers, compatibilize homopolymer mixtures either in solution or in the solid state, but even the definition of the term "compatibility" remains vague. The main problem seems to be a lack of objective methods for measuring compatibility. The evidence presented is usually based on judgment by the naked eye or on observed changes of the mechanical properties of the polymer mixtures. It appears that a judgement of the compatibility of polymers or of the compatibilizing influence of copolymers must be based on finer structural details, *e.g.*, on the morphology of a system as seen in the phase microscope or in the electron microscope.

A systematic approach to the problem of a compatibilizing effect of random, block, or graft copolymers on a mixture of the corresponding homopolymers has recently been presented by Riess, Kohler, Tournut, and Banderet,[26,27] who determined regions of compatibility in triangular diagrams of ternary mixtures of polystyrene and polymethyl methacrylate or polyisoprene, respectively, with the corresponding random, block, or graft copolymers. The criterion of compatibility was the clarity of films cast from solutions of the ternary mixtures, as judged by direct observation or by phase contrast microscopy. The study resulted in the conclusion that only block copolymers of certain intermediate compositions have a compatibilizing effect if the molecular weights of the homopolymers are lower than those of the block copolymers used. Graft and random copolymers had no effect on compatibility.

The present studies of block copolymer micelles embedded in a matrix of one of the corresponding homopolymers and the observed "solubilization" of the other homopolymer in the cores of the micelles as well as the studies on block copolymer morphology recently presented by other authors[21-23,26,27] necessitate a redefinition of the problem of copolymer compatibility. It appears that the question of the compatibility of a copolymer with the corresponding homopolymers is legitimate only in the case of random copolymers. Block copolymers are neither compatible nor incompatible with the corresponding homopolymers. On a molecular scale, they behave like mixtures of homopolymers, even though the mobility of the homopolymer sequences is restricted by chemical bonds. Any of the corresponding homopolymers blends into the phase of its own kind, which already exists in the block copolymer, thus altering the size but not the nature of this phase. On this basis, there can be no truly compatibilizing effect of a block copolymer on a mixture of homopolymers. The effect of the block or graft copolymer is of a colloidal nature—it results in finer and finer dispersions of one phase in the other.

Acknowledgment. The authors are obliged to H. M. Baker and P. A. Traylor for the preparation of the electron photomicrographs.

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