in CCl_4 at a slower rate than the 8.60×10^5 sample in benzene. It has been observed that CCl_4 is a noneluting solvent for polystyrene on silica gel.[2a] From this it is tempting to relate chromatographic mobility directly to desorption rate. This is an obvious oversimplification, because all the fractions studied here elute completely with benzene (R_f = 1.0) despite marked differences in their desorption rates in the static solvent.

Stirring tremendously enhances desorption rates. In stirred benzene the 1.60×10^5 sample is lost more rapidly than the 1.98×10^4 polymer in the same static solvent. In addition, it was possible to establish that the residue was displaced significantly (several millimeters in some cases) from its original position. The cause of enhanced desorption may arise from increased concentration gradients above the adsorbed layer as the flowing liquid removes desorbed molecules. Momentum transfer between the flowing solvent and partially desorbed molecules may also be significant. The appearance of material on substrates remote from the initial coverage is indicative of rapid readsorption of displaced polymer. While quite remote, it is not impossible that the adsorbed macromolecules have been displaced without desorption. One can picture an isolated molecule acting somewhat like a tumbleweed, moving even though a number of segments are always in contact with the substrate. In actual chromatographic experiments, it is doubtful whether momentum transfer could be significant because of low solvent velocities. However, the transport of desorbed species is a well-known feature in tlc for conventional molecules.

Several important conclusions may be drawn from these results. The desorption of polymer from tlc substrates is rapid enough and sensitive enough to molecular weight to play a major part in the fractionation observed in tlc of polymers. The reason for rapid desorption in these experiments remains a matter of conjecture. At the present time, our hypothesis is that the method of applying the material, *i.e.*, spotting and drying, results in a decreased number of solute–substrate attachments per molecule compared to conventional adsorption.

Acknowledgment. The authors wish to thank T. K. Kwei and R. J. Roe for several helpful discussions.

Communications to the Editor

A New Kind of Polymeric Material Obtained by the Rigidification of Heterophase Block Copolymer–Solvent Systems

In this communication we describe a new class of rigid polymeric materials which, although they appear homogeneous on visual inspection, reveal *periodic* microstructure when examined by the low-angle X-ray technique or by electron microscopy. It is hoped that many of these novel materials will have practical value, and work aimed at their utilization is being carried out in this laboratory.

The technique developed by Szwarc[1] for preparation of living polymers permits the synthesis of block polymers having structures such as A–B or A–B–A, in which A and B denote the sequences of monomers a and b, respectively. This method also allows one to vary the size of individual blocks.[2] Using this approach, we prepared many block polymers and thoroughly examined their behavior in solvents, S, which preferentially dissolve one of the component blocks. It has been demonstrated[3–7] that a system may acquire various structures, depending on temperature; on the size, composition, and nature of the block polymer; and on the choice of solvent, as indicated by the phase diagram shown in Figure 1.[8] At very low concentration, the block polymer dissolves in S and a conventional solution of A–B in S is then formed. Irregularly located aggregates of A–B appear in the solution when the concentration of the block polymer increases to a few per cent. The insoluble blocks, B, then form cores surrounded by soluble chains of A. At still higher concentrations (20–30%), the aggregates coalesce into regular and periodic structures. Three types of structures have been revealed by low-angle X-ray diffraction, namely lamellae, hexagonally packed cylinders, and, less frequently, cubically packed spheres. The "insoluble" blocks form the "solid" phase, while the soluble blocks are mixed with the solvent, as shown in Figure 2.

The structural parameters, obtained from X-ray analysis, depend on the nature and sizes of the blocks as well as on the nature and proportion of the solvent. For example, the thickness of the layers may vary from 200 to 800 Å, the diameters of cylinders may be 80–400 Å, and the distance between their axes may range from 200 to 700 Å. Although many systems were examined and some empirical rules were established, a comprehensive theory of these systems is not yet available in spite of several attempts[9,10] to develop one.

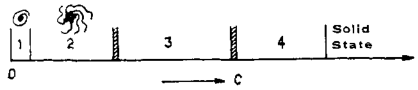

Figure 1. A schematic phase diagram as generally observed in (A–B)S systems, at growing concentrtaions of copolymer: (1) pure solution (monomolecular micelle); (2) aggregates (polymolecular micelle); (3–5) successive regular and periodic structures (*i.e.*, spheres, cylinders, lamellaes).

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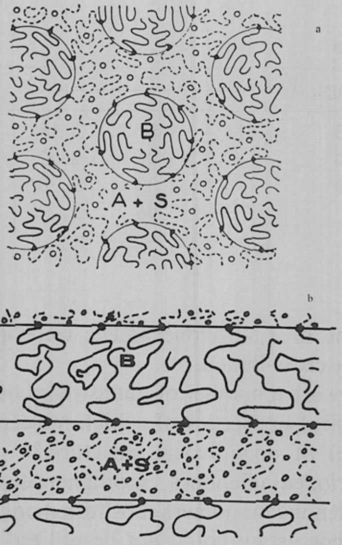

Figure 2. (a) Sections of a hexagonal packing of cylinders normal to the plane of the figure. (b) Section of lamellae structure normal to the plane of the figure.

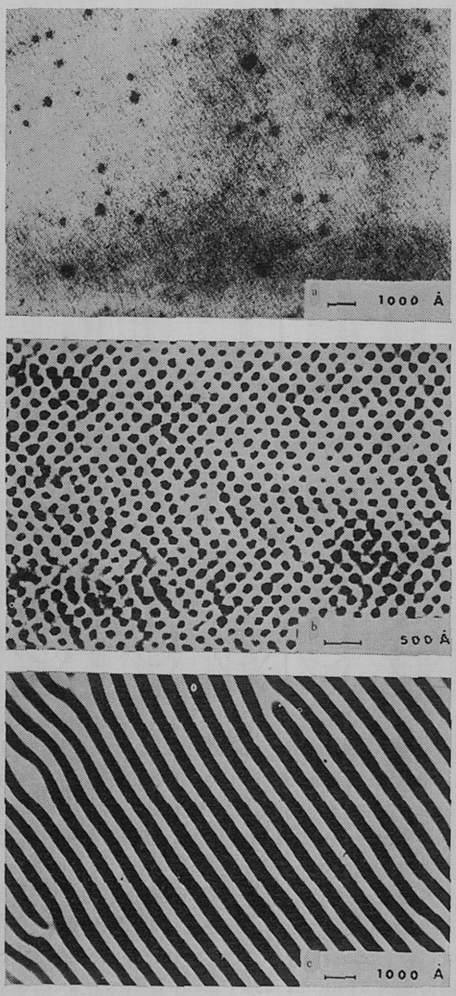

Figure 3. Electron micrographs of three types of structures: (a) (A–B)S, where A is polyisoprene ($M = 24{,}500$), B is poly(vinylpyridine) ($M = 40{,}500$), S is 99% poly(methyl methacrylate) (pmma) (the black spots are formed by isoprene aggregates in the pmma matrix); (b) (A–B)S, where A is polystyrene ($M = 49{,}000$), B is polybutadiene ($M = 12{,}400$), S is 30% pmma (the black spots are the perpendicular sections of a hexagonal packing of polybutadiene cylinders); (c) (A–B)S, where A is polyisoprene ($M = 55{,}000$), B is poly(vinyl-2-pyridine) ($M = 45{,}000$), S is 21% poly(vinyl acetate) (the black stripes are the sections, normal to their planes, of the parallel layers formed by polyisoprene).

All of these materials are viscous fluids which are difficult to handle and presumably of little practical interest. However, their properties can be drastically changed by using liquid monomer as a solvent which is polymerized eventually,[3,11] *e.g.*, by uv irradiation. Thus, by this method, one obtains a *rigid* material which retains the periodic structure of the original liquid, as may be seen from the electron microscope photographs (Figure 3)[12] obtained from thin cuttings (500 Å) stained with osmium tetroxide.

As shown by low-angle X-ray diffraction, the polymerization technique changes the structural parameters of the original gel only slightly. In addition, this procedure permits us to see by electron microscopy the aggregates which cannot be investigated by X-ray diffraction (see Figure 3a).

Two final remarks may be of some interest. (1) It is possible to use as a solvent S the same monomer which produces the soluble block sequences. We then obtain a material containing only two kinds of polymers, A and B. (2) In the limiting case, when the concentration of S approaches zero, we have the pure organized copolymer that we have described above. It has been studied by other authors.[9–13]

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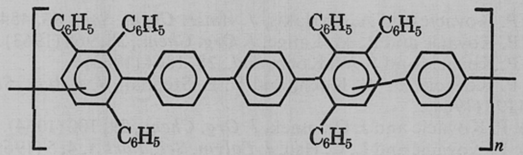
Poly(*p*-phenylene)

High-molecular-weight phenylated polyphenylenes obtained from the 1,4-cycloaddition reaction of biscyclopentadienones or bispyrones with bisacetylenes[1–5] have properties which are quite different from those of unsubstituted polyphenylenes prepared by other methods. The phenylated polyphenylene **1**, in which the phenylated rings have a 1:1 para to meta catenation ratio and have number-average molecular weights of 40,000–100,000, are light yellow, amorphous, and completely soluble in common organic solvents (benzene, chloroform, etc.) in concentrations of up to 10 wt %.



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By contrast, those polyphenylenes prepared either from benzene by a Friedel–Crafts reaction under oxidative condi-

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