Morphology of Polymer Films and Single Molecules

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Synopsis

Seven polymeric substances were examined by high-resolution transmission electron microscopy. Features on the scale of the diameter of single molecular chains were observed. Polymers examined include (1) linear polyethylene (M_w = 52,000), (2) linear polyethylene (M_w approximately 5,000,000), (3) poly(*cis*-1,4-butadiene), (4) poly-γ-benzyl-L-glutamate, (5) poly(etheretherketone) (PEEK), (6) deuterated polystyrene-poly(methylmethacrylate) (PMMA) block copolymer, and (7) a polydiacetylene, poly(1,12-di(butoxy-carbonylmethylurethanyl)-5,8-dodecadiyne), also called poly-4BCMU. A variety of methods were used to prepare dispersed single molecules and very thin films, some of which had regions with strands containing only a few molecules. Staining with RuO_4 revealed structures near the surface of the films that were reproducible and characteristic of each polymer.

INTRODUCTION

Direct examination of polymer molecular structure to produce detailed structural information never before available is possible with transmission electron microscopes that have atomic-scale resolving power. Although chemical changes produced by the electron beam remain a serious problem, staining with electron-dense atoms such as ruthenium permit high-resolution images of molecular scale features to be made.

A primary goal of this work was to develop techniques for producing very thin polymer samples on conducting substrates of carbon, graphite, or metal. Layers only one molecule thick or discontinuous layers composed of a random network of very small fibers or even single chains were sought. Such samples would then be candidates for examination using scanning tunneling microscopy.[1,2]

A number of techniques described below were tested with polyethylene. The technique of broadest applicability was that of spreading a dilute solution of the polymer on the surface of a liquid that was immiscible with the polymer solvent, and this technique was used to investigate all the other polymers.

Results reported here include examination by transmission electron microscopy of nine polymers. Polymers examined are listed in Table I.

HIGH-RESOLUTION ELECTRON MICROSCOPY OF POLYMERS

Until recently, typical transmission electron microscope investigations of polymers concentrated on features an order of magnitude or more larger than

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TABLE I
Experimental Materials*

Linear low-density polyethylene, NBS SRM 1475, M_w = 52,000, M_w/M_n = 2.9 (M_w is the weight average and M_n is the number average molecular weight)

Ultrahigh molecular weight polyethylene, medical grade, M_w = 5,000,000, Hercules Chemical Co., #99974

Polystyrene, NBS SRM 705, M_w = 179,300, M_w/M_n = 1.07

Polystyrene, NBS SRM 1479, atactic, M_w = 1,050,000

Polystyrene, isotactic, M_w = 1,440,000, M_w/M_n = 2.0, fraction F3BR, obtained from McKenna and Guenet[3]

Poly(etheretherketone), Victrex, Imperial Chemical Industries

Polystyrene-poly(methyl methacrylate) block copolymer, with deuterated polystyrene; PS, M_n = 83,000, M_w/M_n = 1.25, 43%; PMMA, M_n = 110,000, M_w/M_n = 1.25, 57%

Poly(cis-1,4-butadiene), M_w = 400,000–450,000, dispersion = 4–4.5, Polysciences, catalog #0750

Poly-γ-benzyl-L-glutamate, M_w = 15,000–30,000, Sigma Chemical Co., catalog #P 5261

Poly-4BCMU, specifically, poly(1,12-di(butoxycarbonyl-methylurethanyl)-5,8-dodecadiyne) obtained from Art Snow of the Naval Research Laboratory; prepared following the method of Patel[4]

* To describe the procedures adequately, it is occasionally helpful to identify commercial products and equipment. In no case does such identification imply NIST recommendation or endorsement, nor does it imply that the item identified is necessarily the best available for the purpose.

those presented in here. An early report of molecular scale resolution of an electron-beam sensitive polymer was made by Dobb et al.[5] in 1975 who published a micrograph of polyaramid exhibiting 0.433 nm lattice fringes. In 1981, Read and Young[6] obtained direct lattice resolution of a polydiacetylene, poly(1,6-di(N-carbazolyl)-2,4-hexadiyne) (pDCHD), and further investigations of pDCHD were reported by Young and Yeung[7] in 1985 who obtained images of the diacetylene molecules viewed end on. Shimamura et al.[8] produced lattice images of poly(p-phenylene benzobisthiazole) fibers. Tsuji et al.[9-11] obtained lattice images of poly(p-xylylene). Chanzy and co-workers reported lattice images of polytetrafluoroethylene.[12,13] Lattice images of cellulose were published by Kuga and Brown.[14]

Polyethylene crystal morphology has been studied intensively by electron microscopy, and this work was reviewed by Bassett.[15] The diffraction pattern of polyethylene crystals changes during exposure to the electron beam and is destroyed after an exposure not much greater than that required to focus and expose a plate. Giorgio and Kern[16] examined polyethylene crystals with dimensions between 20 and 150 nm, which were surprisingly resistant to radiation damage, at magnifications of 300,000–750,000. These investigators observed 0.41 nm lattice fringes parallel to the (110) planes. Revol and St. John Manley[17] obtained lattice images from corrugated polyethylene crystals that showed the normal high sensitivity to radiation damage. Montezinos, et al.[18] stained polyethylene with RuO_4 and examined it under the electron microscope. Features approximately 5 nm in size are resolved in their micrographs. Iwatsuki[19] showed lattice images of polyethylene and poly(4-methyl-1-pentene) obtained by Tsuji.

The work reported here is aimed at resolution of molecular scale features that do not necessarily show the cooperative scattering expected from lattice planes. Staining, or decoration, of the polymer molecules with a heavy metal (ruthenium) is used to provide contrast.

EXPERIMENTAL METHODS

Preparation of Polymer Samples

For polyethylene, a variety of special methods described below were used to produce samples containing isolated molecules, lamellar crystals, and other structures. The most generally applicable method was the spreading of a thin film of polymer solution on the surface of an immiscible liquid. This method was used for polyethylene and for the other polymers examined. The thickness of the films produced in this way was estimated from the amount of polymer solution spread on a known area of liquid surface, to be no greater than 10 nm.

Thinned Support Films

Evaporated carbon films on microscope grids were thinned in an oxygen plasma (0.27–0.4 Pascals) until holes and cracks were formed in most of the grid squares. This required a few minutes with the low-power radio frequency supply used to generate the plasma. These very thin substrates were then used to collect polymer samples spread from solution onto the surface of water or other immiscible liquids.

Staining with RuO_4

Ruthenium tetraoxide stains many polymers,[20] including polyethylene, although compounds containing double bonds are stained more readily. RuO_4 staining is essential for observing the smallest features reported here. Higher resolution is obtained with this technique than with C—Pt shadowing.

The thin films, on the thinned carbon support films, were exposed to RuO_4 vapor at room temperature for times of around 15 min. The vapor had access to only the top surface of the film except in the few instances in which the film was stretched across a small crack. The amount of detail seen in the images suggest that the ruthenium moieties that attached to the polymer actually penetrated only one or two molecular thicknesses. The persistence of characteristic morphological features at the molecular scale during long exposures to the intense electron beam needed for high magnification suggest that the RuO_4 treatment stabilized the structure of these layers.

Electron Microscopy

A Philips 400 transmission electron microscope operated at 120 kV was used for most of the observations reported here. A few of the samples were examined with a Philips 430 operated at 300 kV. Total electron and optical magnification of six million times showed the molecular scale features at a useful size. The resolution of the microscope was demonstrated by recording the planes of graphite.

Special precautions were taken to insure that features seen on the micrographs were indeed produced by the polymer. Astigmatism was checked regularly and kept to a minimum. Blank carbon films exposed to ruthenium tetraoxide were examined for comparison purposes. Conventional through-focus series were made on these as well as on the polymer samples collected on carbon films. The amount of defocusing and astigmatism present on a micrograph plate was checked by optical diffraction. Plates showing resolved linear features of molecular scale best were approximately 50 nm under focus.

Tilting the sample by 20–40 degrees inside the electron microscope provides different levels of focus from one side of the image to the other. Figure 1 is an example. In this image, the tilt axis runs from upper left to lower right. On a
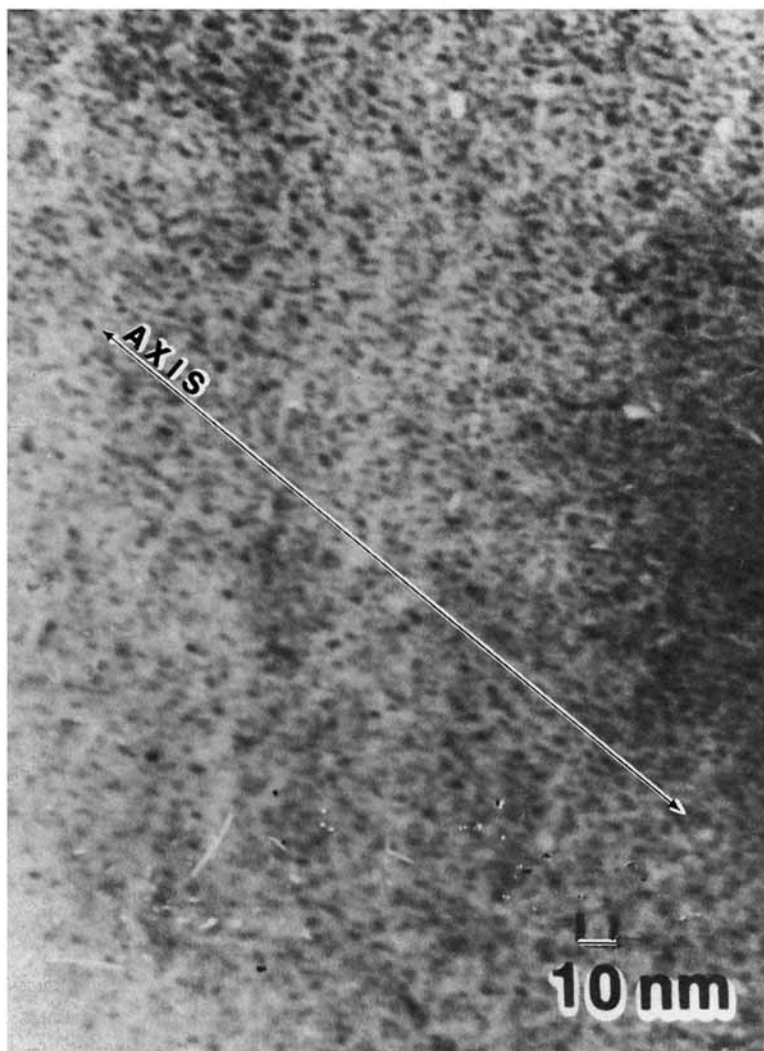

Fig. 1. Polyethylene of 5 million molecular weight. The sample was tilted in the microscope by an angle of 40° about an axis running from upper left to lower right so that the amount of defocus varies along a line perpendicular to that axis.

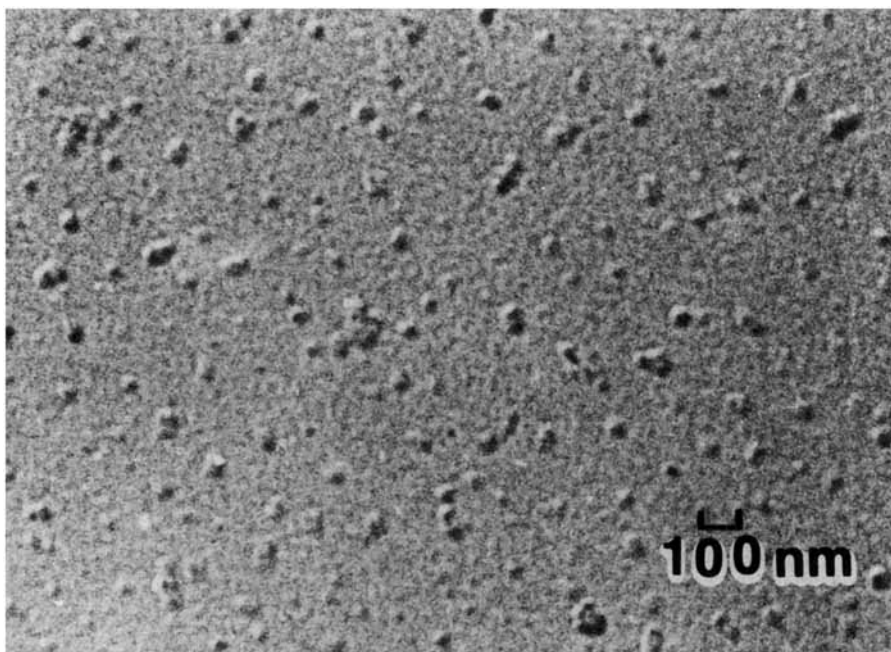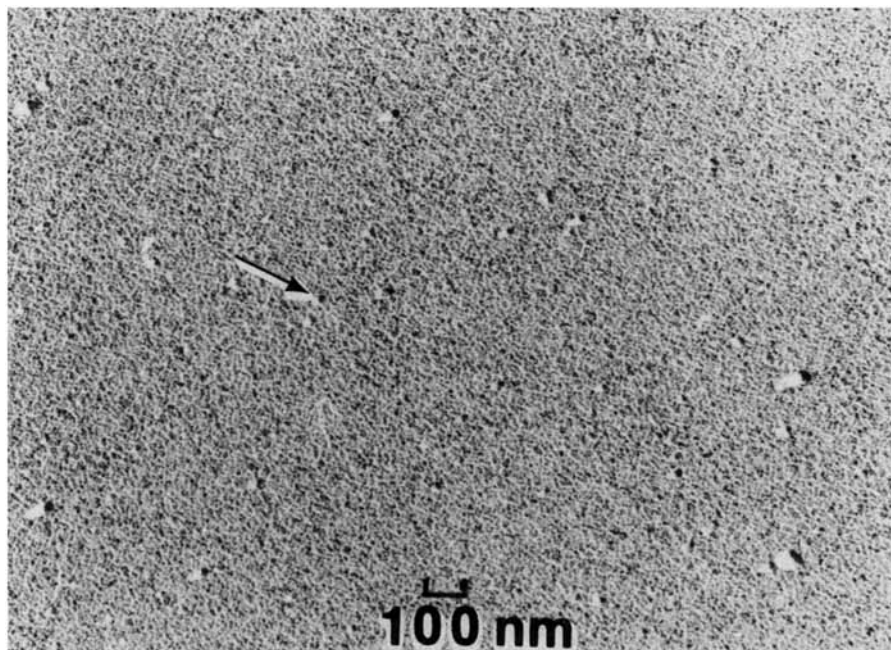Fig. 2.   (a) Polyethylene precipitated onto mica from a rapidly cooled, dilute solution in xylene. $M_w = 52,000$; concentration $= 10^{-5}$ g/mL. Shadowed from the upper right. (b) Ultrahigh molecular weight polyethylene prepared in the same way as (a). $M_w = 5,000,000$.
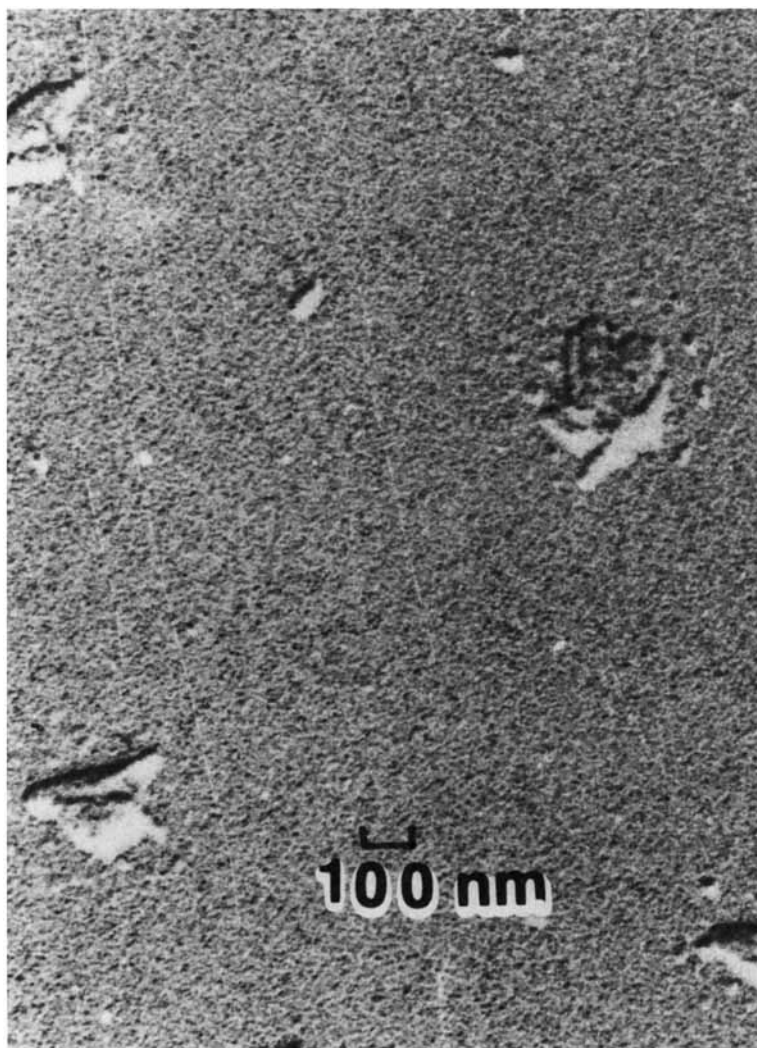
Fig. 3.   (a) Same as Figure 2(a), except concentration = 10^{-3} g/mL, with structures containing from one to a few hundred molecules. (b) Same as Figure 2(b), except concentration = 10^{-3} g/mL, with elongated connected rod structures.

line perpendicular to the tilt axis, the amount of defocus varies from approximately -150 to $+150$ nm at a magnification of 220,000. The tilting technique provides a useful alternative to the more cumbersome through-focus procedure for samples such as these in which the same features are uniformly distributed across the sample. Examination of micrographs of tilted samples was helpful in eliminating artifacts since the complete range of defocus images were recorded on a single plate.

For some samples, electron micrographs of the same area were recorded at two magnifications. Prints of the two plates were optically enlarged so that the total magnification produced from each plate was the same. One print was
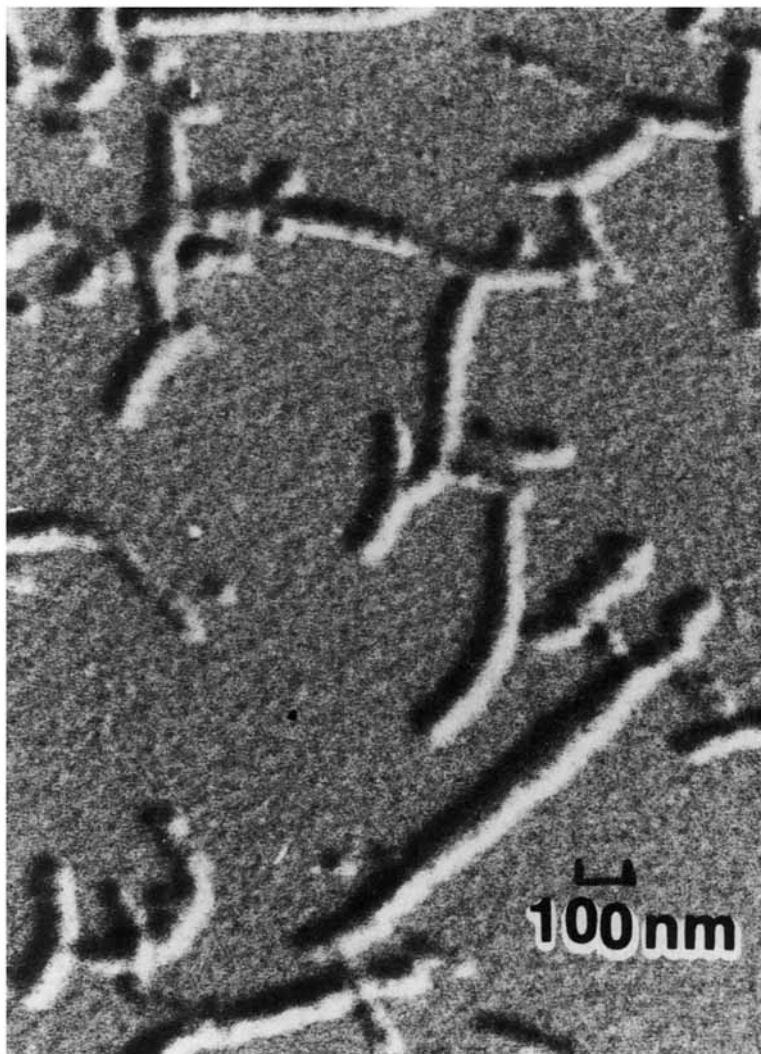
Fig. 3. (*Continued from the previous page.*)

made as a transparency and used as an overlay to facilitate comparison of the two prints. Features identical on both prints were taken to be most significant.

Computed simulations of polymer micrographs that demonstrate the effect of objective aperture size, and level of defocus, as well as the influence of electron microscope spherical aberration on the polymer image were performed for polyethylene using software called the ASU Multislice Program, developed at the Arizona State University.

The following practices were used routinely to minimize electron-beam damage to the sample: (1) High-energy electrons (120 keV or higher) were employed because these interact less with the sample than those of lower energy. (2) Very thin polymer films were employed, since thin polymer films are less affected by an electron beam than are thicker samples. (3) Electron doses were kept
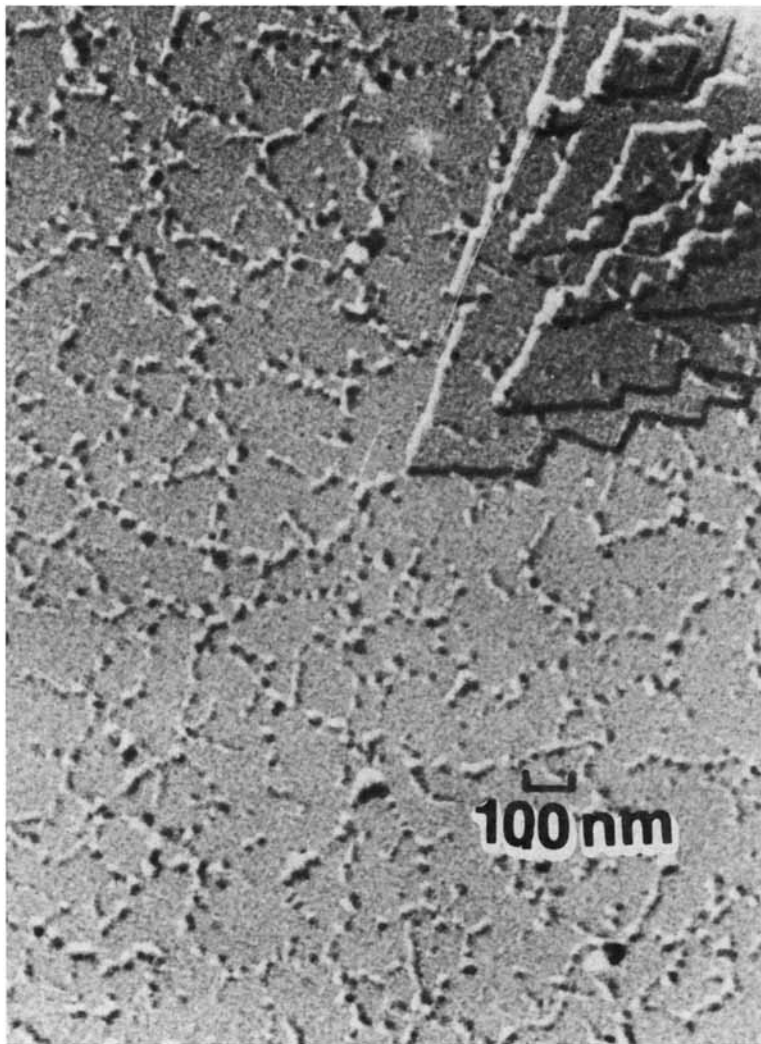
Fig. 4.   (a) Same as Figure 3(a), except concentration = 10^{-2} g/mL. (b) Same as Figure 3(b), showing relationship of elongated structures and lamellar crystals. Concentration = 10^{-3} g/mL.

low by spreading the beam and shifting to nearby but previously unexposed areas after focusing.

RESULTS

Polyethylene

Polyethylene samples prepared from solution were studied first since much is already known about the behavior of this polymer. It is known from previous work[21] that in very dilute solutions the molecules do not overlap and can be precipitated in the form of separated particles, which are roughly spherical at
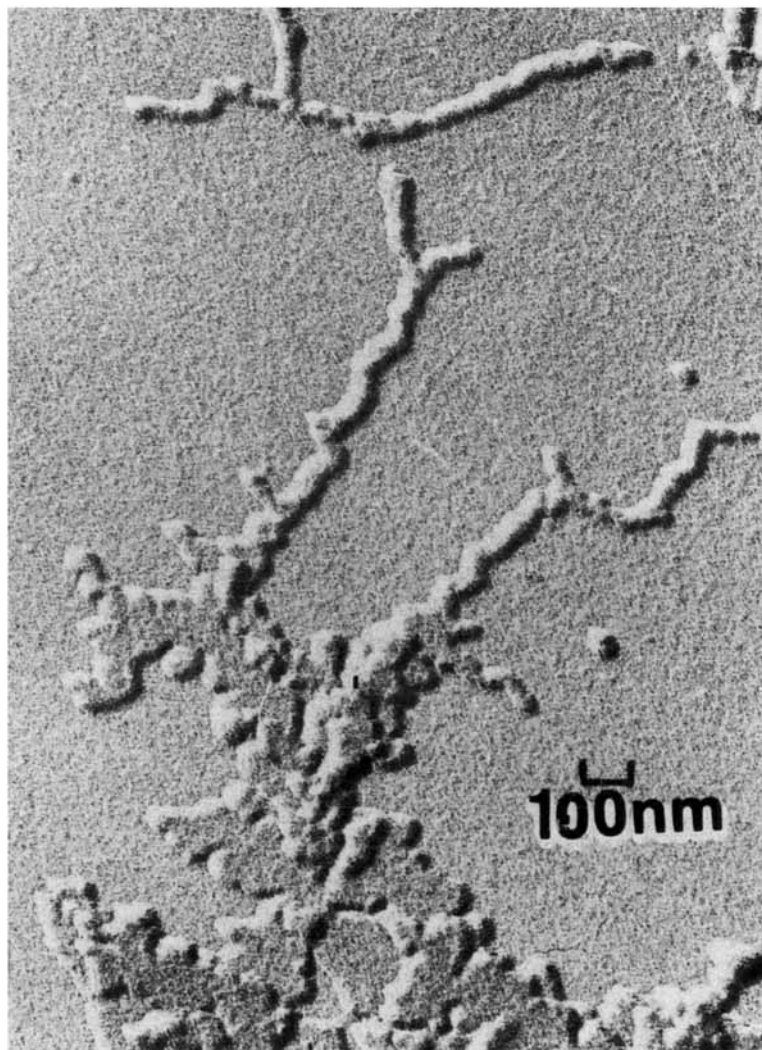
Fig. 4.   (*Continued from the previous page.*)

the resolution obtainable with shadowed samples. At higher concentrations, the molecules begin to overlap, so that two or more may be incorporated into each particle. As the concentration is increased further, the molecules become more intertwined with each other, so that when a thin layer of the solution is cooled to precipitate the material, and the solvent is evaporated, a network of fibers with some crystalline overgrowth is created. At still higher concentrations, the more familiar morphological features of shish kabobs and folded chain lamellar crystals are observed.

Collection of the polyethylene particles is difficult because of a tendency for the surface tension of the evaporating liquid to clump the polymer particles. One technique successfully used to avoid clumping was to precipitate polyethylene from a thin layer of solution trapped between pieces of freshly cleaved
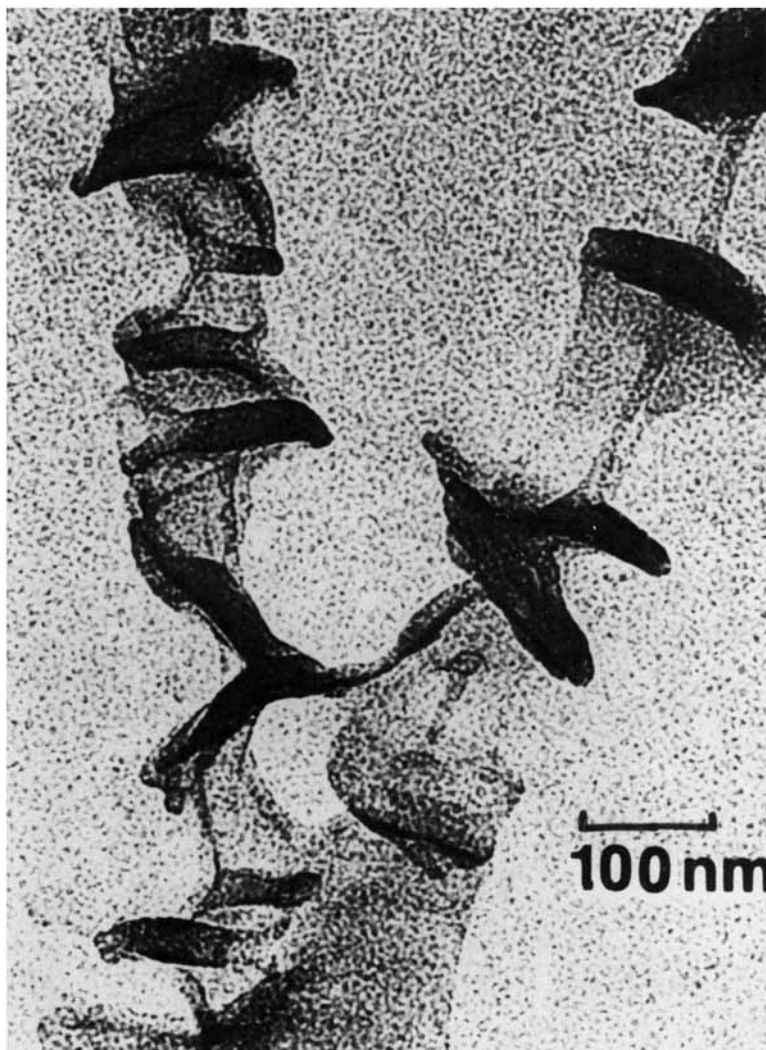
Fig. 5.   Small polyethylene shish kabobs. The smallest fibers contained as few as 40 chains.

mica.[22] The mica with the trapped layer of xylene was withdrawn from a solution at approximately 120°C with a concentration of 10^{-4}–10^{-5} g/mL of polymer. The polymer precipitated rapidly, and after evaporation of the solvent layer,

TABLE II
Overlap Concentration

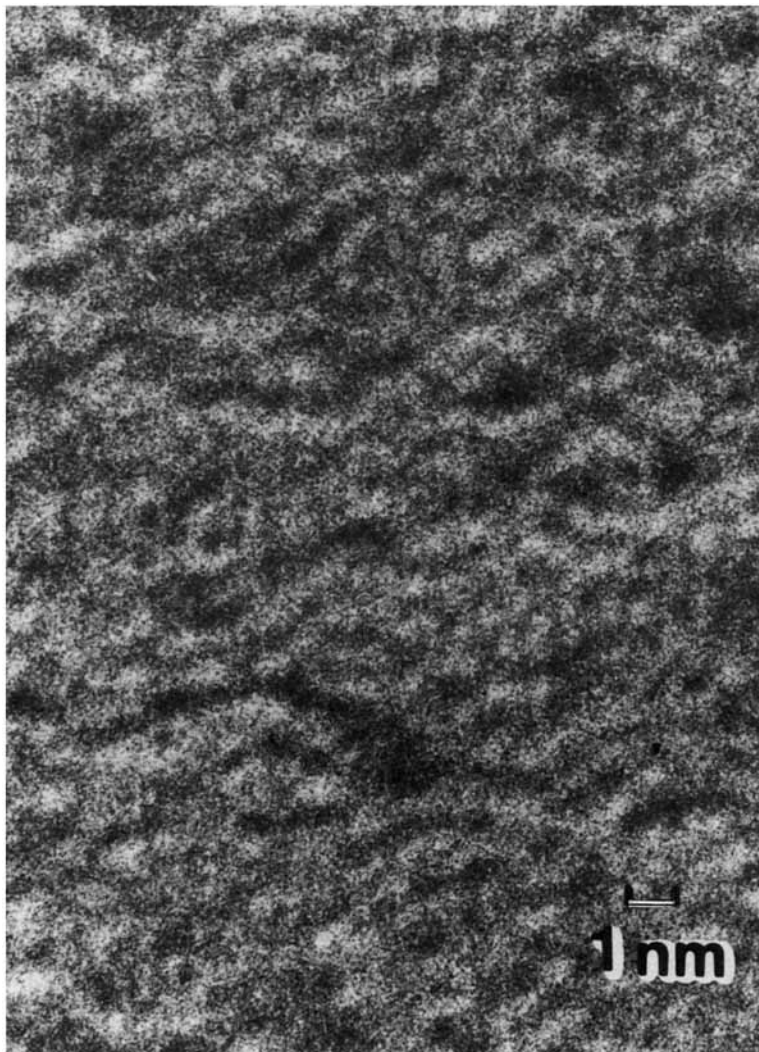| M_w of polymer	Concentration in g/mL	
	Experimental	Theoretical
52,000	10^{-3}	0.09
5,000,000	3×10^{-5}	0.009

Fig. 6. Polyethylene, 5 million molecular weight from a hot solution in xylene, that was dropped onto a cold water surface. The concentration of the polyethylene solution was 10^{-4} g/mL. The polyethylene is stained with RuO_4.

the mica surfaces to which the polyethylene particles were attached were shadowed with Pt—C.

Shadowed particles were of the size (around 10 nm), and distribution of sizes, expected for the 52,000 molecular weight SRM 1475 polyethylene. For the five million molecular weight polyethylene, particles containing a single molecule were sometimes acicular and had roughly 10 times the diameter (1000 times the volume) of those seen for polyethylene with molecular weight 52,000. This size relationship is evident in comparison of Figure 2(a) (PE, $M_w = 52,000$, single molecules indicated by arrow) and Figure 2(b) (PE, $M_w = 5,000,000$).

When more concentrated solutions (10^{-4}–10^{-3} g/mL) of polyethylene were used, fibers and structures containing many molecules were seen [Fig. 3(a)
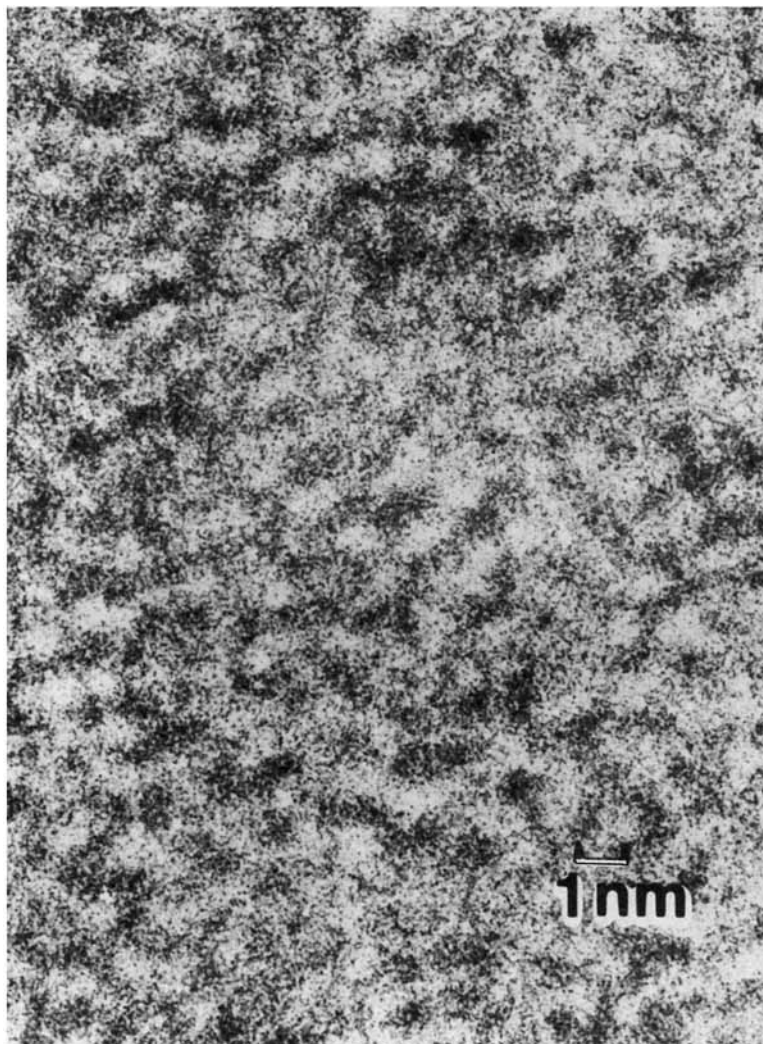
Fig. 7. Poly(*cis*-1,4-butadiene) film from a 10^{-4} g/mL solution in xylene, dropped on water. Stained with RuO_4.

and (b)]. These are much smaller objects than were the lamellar crystals produced from more concentrated solutions by slower cooling.

Solutions even more concentrated than these (10^{-3} g/mL and above) produced lamellar morphologies [Fig. 4(a) and (b)], along with beaded networks and elongated structures. The rod structures appear to be a variation of the more familiar lamellar morphology.

Polyethylene samples also yielded shish kabobs when the mica pieces were forced together in a xylene solution of SRM 1475 polyethylene at a temperature of approximately 105°C (Fig. 5). Small crystals grew on fibers formed as the crystallizing solution flowed from between the mica sheets. These are commonly called shish kabobs.
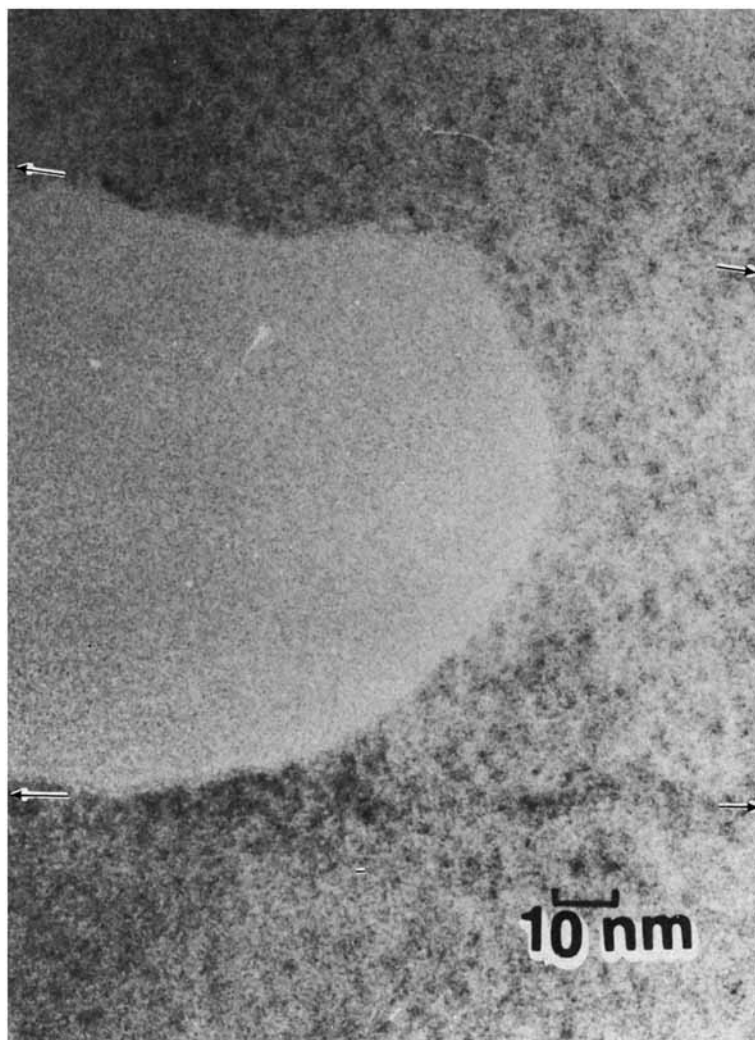
Fig. 8.   Same as Figure 7. The edge of a thin polymer film is stretched across a crack in the carbon substrate. The crack is horizontal, and the film of interest is at the right side of the Figure.

Morphologies seen in Figures 2–4 can be used to find the concentration of polyethylene at which the polymer molecules are significantly intertwined in solution. This value can be compared with calculated values for c^*, the critical overlap concentration. This is the concentration at which spheres with radii equal to the radius of the polymer molecules would touch and is proportional to the molecular weight divided by the cube of the radius of gyration (R_g). Other measures of c^* are described by Odell et al.[23] For PE, the value of c^* is 0.09 g/mL for a molecular weight of 52,000 and 9×10^{-3} g/mL for a molecular weight of 5 million, taking the density of both the polymer and solvent as one. For 52,000 molecular weight polyethylene, features containing more than one molecule, which indicate intertwining, appeared when the concentration reached
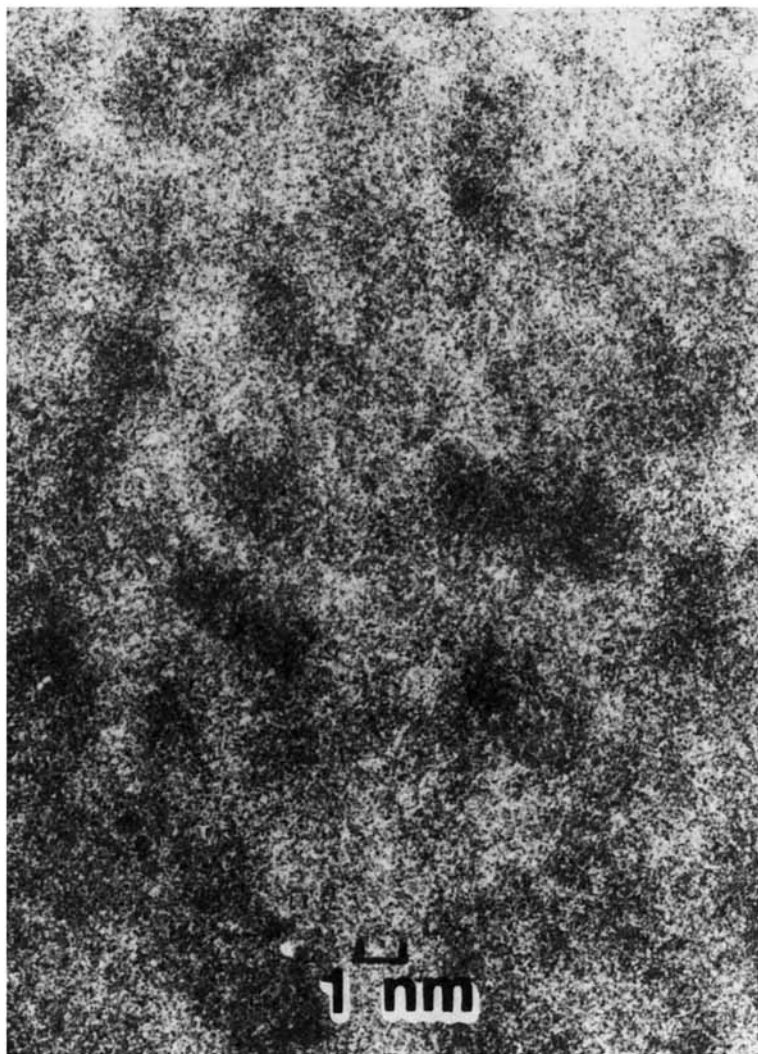
Fig. 9. PEEK, from a 50% saturated solution in α-chloronaphthalene solution, dropped on water. Stained with RuO_4.

10^{-3} g/mL, whereas for high molecular weight polyethylene, overlap occurred at 3×10^{-5} g/mL. Results are summarized in Table II.

These morphological observations show that the molecules are intertwined in a mechanically effective way at concentrations more than an order of magnitude smaller than the critical concentrations. It is interesting to note that observations of elongational flow in polymer solutions by Odell et al.[23] that were cited earlier also lead to the conclusion that effective, time-dependent intertwining of the molecules in solution occurs at concentrations well below c^*.

When hot xylene solutions of polyethylene were dropped on water, the resulting film stained with RuO_4; examined under the electron microscope (Fig. 6),[24] an imperfect grid of lines crossing at angles near 70° was visible on the

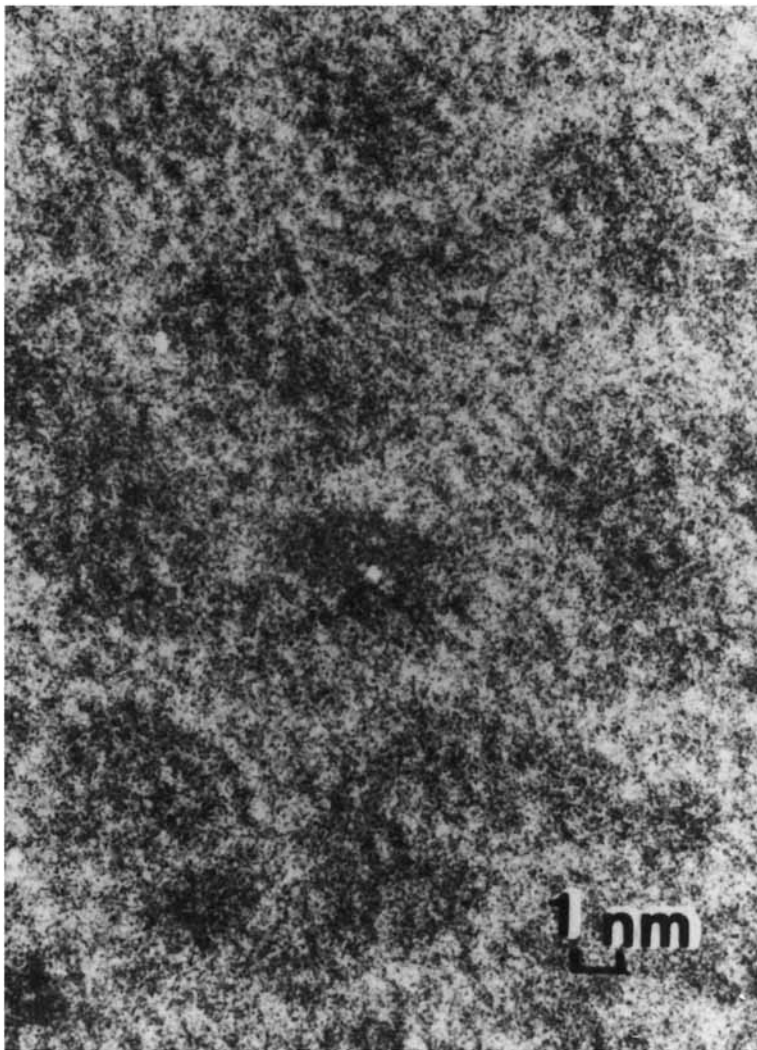Fig. 10.   Poly-γ-benzyl-L-glutamate, saturated solution in methylene chloride, dropped on water. Stained with RuO₄.

original prints. The smallest spacings between these lines is about 0.8 nm, which is about twice the spacing of the (110) planes of polyethylene crystals, which also intersect at an angle near 70°.

Optical diffraction measurements were performed on a micrograph of ultra-high molecular weight polyethylene shown in Figure 6. The optical diffraction pattern had four broad radial streaks or lobes. Axes drawn through opposite pairs of lobes cross at an angle of approximately 70°. Weak intensity maxima along these axes correspond to a spacing of 0.43 nm. This would be expected if the lines in the micrograph are associated with (110) lattice planes, the planes in which the polyethylene molecules often fold when they crystallize into lamellar crystals. This optical diffraction pattern suggests a tendency for the a and b crystal axes to lie in the plane of the polymer film, although no
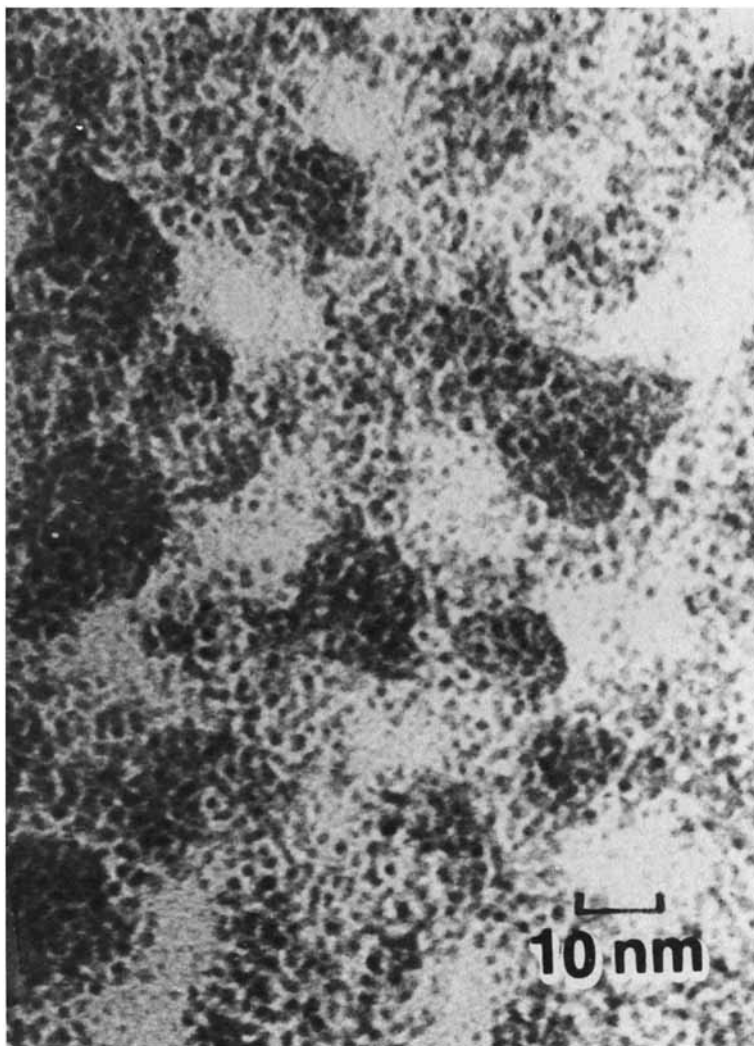
Fig. 11. Block copolymer of deuterated polystyrene and poly(methyl methacrylate) from a 10^{-3} g/mL solution in methylene chloride, dropped on water.

optical diffraction intensity maxima were found at angles corresponding to the expected positions for a or b planes.

The observations lead to the conclusion that polyethylene films prepared by the highly nonequilibrium process of spreading a hot solution on room temperature water produces a film with a very imperfect crystalline structure, which incorporates a reduced ruthenium moiety from ruthenium tetraoxide in a way that provides information about the somewhat irregular surface layers of such a film.

Thin Films of Other Polymers

Poly(cis-1,4-butadiene) samples, because of the double bonds, reacted more strongly with ruthenium tetraoxide than did polyethylene. This polymer had
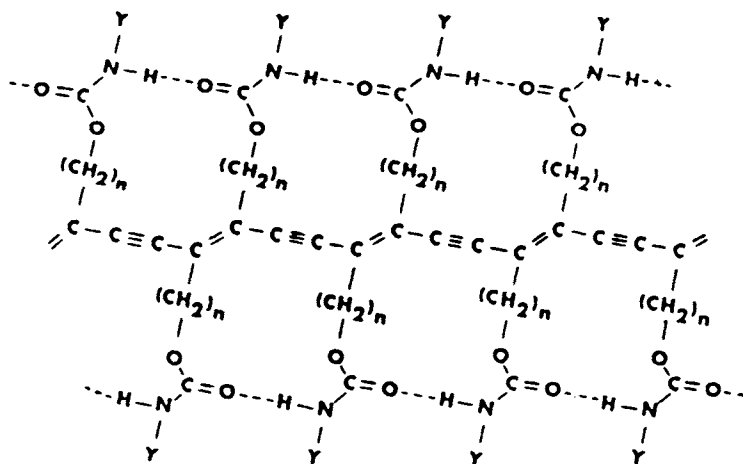
Fig. 12.   Chemical structure of poly(1,12-di(butoxy-carbonylmethylurethanyl)-5,8-dideca-diyne), called poly-4BCMU. The value of n is 4.

the appearance (Fig. 7) of the surface of a tangled pile of beaded chains. A poly-*cis*-butadiene film stretched across a carbon film crack was observed, as shown in Figure 8. Where the film crosses the crack in the carbon substrate, only the stained polymer was present, although both the top and bottom layers of the unsupported areas are stained. Also, shrinkage caused by the electron beam may have stretched the unsupported area. The similarity of the image over the crack with that over the substrate is evidence that carbon-supported polymer film micrographs presented here exhibit features characteristic of the
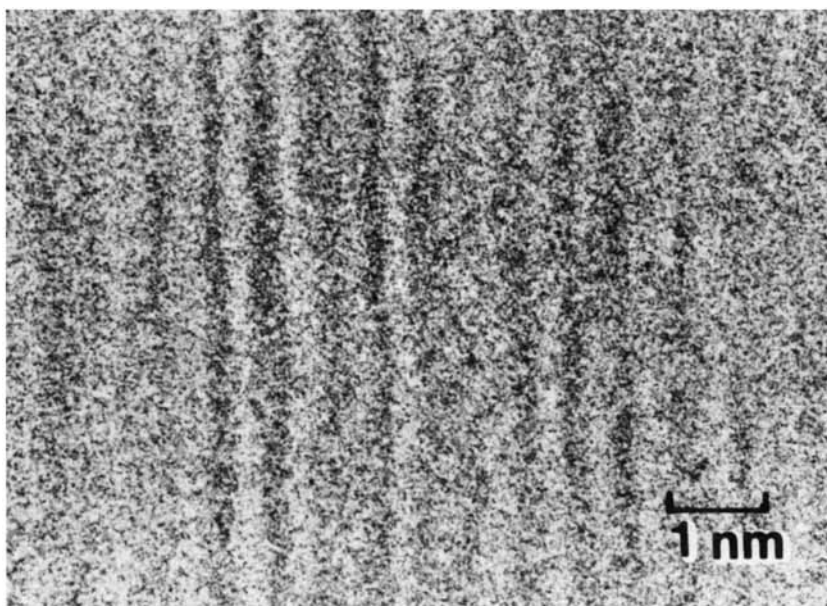

Fig. 13.   Poly-4BCMU from a 10^{-4} g/mL solution in chloroform, dropped on water.

ruthenium tetraoxide-stained polymer being examined. Examples of other polymers stretched across cracks, in which the structure observed in unsupported and carbon film supported areas were similar, were also found.

The structure of poly(etheretherketone) (PEEK) crystallized at different temperatures[25] was studied by electron microscopy in 1983 by Cogswell[25] who observed features as small as 0.1 μm. A study of PEEK by electron microscopy, optical microscopy, and small angle light scattering was made by Kumar et al.[26] in 1986. The crystal structure and unit cell spacings were reported. Electron microscopy and diffraction of PEEK crystallized from solution was reported by Lovinger and Davis in 1986.[27] Features less than 1 μm in scale were observed, and the crystallographic structure was determined.

In this work, PEEK film samples were prepared by dropping alpha-chloronaphthalene solution on water. Carbon-coated grids on which sample was collected were stained with RuO_4 and examined under the electron microscope. These images contained dark patches 2 or 3 nm across separated by irregular lighter regions on the same scale (Fig. 9). The lighter regions were crossed with faint dark lines less than 0.5 nm wide, which may be traces of single molecules.

Poly-γ-benzyl-L-glutamate was dissolved in methylene chloride and floated on water. Samples were collected by lifting carbon-coated grids through the polymer film floating on the water surface. The polymer on the grids was stained with RuO_4. The micrographs (Fig. 10) show a tangled mass of linear features with a transverse dimension of 0.5 nm on a background of 4.0-nm-diameter dark patches. The existence of a general vertical direction of the linear feature near the left side of the figure is consistent with the tendency of this molecule to form lyotropic liquid crystals or, when the solvent is completely removed, to crystallize.

Differential staining of block copolymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) by RuO_4 was demonstrated by Trent et al.[28] who found that polystyrene is stained much more intensely than is poly(methyl methacrylate). Phase separation of this block copolymer with deuterated polystyrene (M_n = 83,000) and PMMA (M_n = 110,000) was investigated by neutron scattering,[29] which indicated no formation of a phase-separated layered structure. Instead, a correlation distance between the PS and PMMA blocks of 6.3 nm was observed. In the electron micrographs, heavily and lightly stained regions about 15 nm in diameter were observed (Fig. 11).

The dimensions of the stained and unstained areas are in the range of the diameters of molecular blocks collapsed into balls. This indicates that the sample contained an intimate mixture of PS and PMMA separated into volumes appropriate for single block segments. The more lightly stained PMMA blocks of Figure 11 show linear features approximately 0.4 nm wide, the size expected for individual polymer chains. Spots around 1 nm in diameter that were often arranged in rows were seen in the darker regions, which suggest decoration of segments of the polystyrene molecules by the RuO_4.

Poly-4BCMU, a polymer of interest because it is the basis for a family of polymers with nonlinear optical properties, has the structure shown in Fig. 12. Samples were prepared by dropping a chloroform solution of this polymer on water. These samples showed parallel linear features, with spacings of 0.6 ± 0.1 nm (Fig. 13). In one conformation, the molecules pack as ribbons stacked into

a sheet with the side chains at the surfaces of the sheet. The thickness of each ribbon in this arrangement is 0.6 nm. Such an arrangement, viewed from a direction perpendicular to the sheet, would produce a micrograph like that shown in Figure 12. Hydrogen bonding is an important factor in holding the ribbons together.

CONCLUSIONS

These experiments show, most importantly, that features characteristic of a given polymer can be observed at the molecular scale. The meaning of particular characteristic features in the micrographs is not well understood, but it is reasonable to expect that current advances in microscopy and more observations can resolve many of these ambiguities.

Some of the polymers studied here do not crystallize. Information that is available about their molecular scale structure comes from averages over large volumes and contains little detail about how the molecular segments pack together in the amorphous solid. These micrographs show that electron microscopy provides molecular scale information about the structure of particular amorphous samples.

This paper concentrates on sample preparation methods involving both temperature and concentration changes at a high rate that may not give the polymer time to reach its most highly ordered state. Other ways of preparing films of these polymers would be expected to produce different structures. In these samples, the distance a particular molecular scale feature could be followed, a few hundred angstroms at best, was only a small fraction of the length of a typical molecule.

High-resolution electron microscopy of samples stained with RuO_4 makes it possible to observe interesting characteristic molecular-scale features of polymer molecules in thin films. These include irregular lattice features in polyethylene, molecular bundles in PEEK, individual block segments of a block copolymer (PS/PMMA), and regular arrangements of poly-4BCMU. Ruthenium tetraoxide reveals very small structural features that could not be seen with other techniques currently in use.

Networks with a myriad of single-molecule strands connecting the nodes are interesting candidates for examination by scanning tunneling microscopy.[30] Networks with strands containing some tens of molecules were produced from both polyethylene and polystyrene by varying the sample preparation conditions. It seems likely that networks containing strands with less than 10 molecules can be produced.

Electron microscopy, used in conjunction with computer imaging, and scanning tunneling microscopy make more structural detail available than ever before. Studies such as this will make possible improved correlations of structure to important molecular properties such as wear resistance, melting point, and solubility and may suggest chemical structures for polymers that can be synthesized to have improved properties.

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