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Chemistry. In the following article, which appeared in number 17, September 1, 1992, of *Proc. Natl. Acad. Sci. USA* (89, 7991–7995), several of the figures were poorly reproduced.

Evidence for helical structures in poly(1-olefin sulfone)s by transmission electron microscopy

[freeze-dried vertically Pt-C replicated/poly(1-tetradecene sulfone)/poly(cyclohexene sulfone)/single molecule imaging]

GEORGE C. RUBEN*[†] AND W. H. STOCKMAYER[‡]

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Contributed by W. H. Stockmayer, May 15, 1992

ABSTRACT Transmission electron microscope images were obtained of fractions of poly(1-tetradecene sulfone) and poly(cyclohexene sulfone) cast from very dilute solutions (0.007%, wt/vol) and rapidly freeze-dried on a mica surface. The samples were then vertically platinum-carbon (Pt-C) replicated with 9 ± 0.3 -Å Pt-C and held together with 128 Å of electron-transparent evaporated carbon. The Pt-C coating enlarges the molecular chain diameters by ≈ 5 Å, so that a single polysulfone chain has an apparent diameter of 9–12 Å in the transmission electron microscope. Poly(1-tetradecene sulfone) forms short helical regions that show irregular helical turns of pitch 7–18 Å, two to eight turns long with apparent helix diameters of 16–22 Å. The n -C₁₂H₂₅ side chains were not obvious on the helices, but a few were visible on extended chain sections. In contrast, poly(cyclohexene sulfone) appears as a collection of Pt-C-coated single chains 10–12 Å in diameter with no side-chain projections. The presence and absence of helical regions in these freeze-dried polysulfones thus reflects their solution conformations as long ago inferred on the basis of dielectric measurements.

Advances in the techniques of transmission electron microscopy, including the preparation of ultrathin vertically shadowed platinum-carbon (Pt-C) replicas (ref. 1 and references therein), have allowed the direct recognition of single-chain structural features, such as DNA or pectin helices and polysiloxane or resorcinol-formaldehyde polymers (2–4). Here we further illustrate the power of this technique by reporting some observations on the chain conformations of several poly(olefin sulfone)s, which are alternating copolymers of sulfur dioxide and an olefin (5). We find strong evidence for the presence of some helical conformations, which had been postulated over a decade ago on the basis of dielectric data but could not so far be established by other methods.

Unusual conformational behavior of poly(1-olefin sulfone)s, $[-CH_2-CHR-SO_2-]_n$, was recognized over 25 years ago in two different ways: (i) the “unperturbed” dimensions of poly(1-hexene sulfone), apparently a typical flexible-chain polymer, in two different θ solvents differed (6) by over 30% and (ii) dilute solutions of several poly(1-olefin sulfone)s in nonpolar solvents exhibited (7) unexpectedly strong low-frequency dielectric dispersion, with relaxation times typical of rigid tumbling of the whole chain or of the terminal Rouse-Zimm mode. In contrast, SO₂ copolymers from olefins with internal double bonds (e.g., 2-butene, cyclopentene, and cyclohexene) show no low-frequency response (8). Omitting much history [which is summarized elsewhere (9)] of attempts to explain these facts, we refer directly to the crucial experiments of Fawcett and Fee (10), who prepared terpolymers of 1-hexene, cyclohexene, and SO₂ and found that the

strength of the low-frequency dielectric relaxation process is a markedly nonlinear function of the 1-hexene content. Their result shows unequivocally that the low-frequency process is due to the existence of strongly correlated sequences of longitudinal repeat-unit dipole components. The only plausible rationalization of this behavior is a preference of the chain for helical conformations, and indeed this idea is supported by conformational energy calculations (11). It was until now not possible to demonstrate directly the existence of such helices, because the polymers do not crystallize (12) and have random tacticity (13). Also, a polysulfone prepared from an optically active 1-olefin [ref. 14; A. Samoć, unpublished work in this laboratory (Department of Chemistry)] did not furnish conclusive results.

All the poly(olefin sulfone)s, whether or not they exhibit the low-frequency dielectric relaxation, show a higher-frequency response (9) with a correlation time independent of molecular weight and similar in magnitude to that found by NMR spin-lattice relaxation measurements (9, 13). It is natural to attribute (9) the faster process to local segmental motions redirecting the transverse components of the sulfone dipoles in the nonhelical regions of the chains. However, since there is only a single observed NMR spin-lattice relaxation time for the entire polymer, the C—H bonds in the presumed helices are also quite mobile. Thus the helices must be far from uniform in pitch, and of course they will have a distribution of sequence lengths (10).

In the present work, transmission electron microscopy was used to study samples of poly(1-tetradecene sulfone), p-C₁₄, which displays the aforementioned low-frequency dielectric response, and of poly(cyclohexene sulfone), p-C₆, which (by virtue of its symmetric structure) does not. As described below, the results give rather direct evidence for the presence of helices in the former polymer.

METHODS AND MATERIALS

The olefin/SO₂ alternating copolymers were prepared in this laboratory by Keizo Matsuo (9) with standard free-radical recipes (15). The p-C₁₄ sample was a fraction of viscosity-average molecular weight about 5×10^6 . The p-C₆ sample was unfractionated, with a molecular weight above 2×10^5 .

The p-C₁₄ film was prepared by depositing 10–20 μ l of a very dilute solution [0.007% (wt/vol) in CCl₄] on a 13-mm mica disc, which was then plunged bottom-side first into liquid propane for rapid freezing. The disc was later replicated under the following conditions: 9.3-Å Pt-C (80° angle), followed by 128-Å carbon (100° angle). It should be emphasized that the specimens were cooled to -185°C prior to Pt-C deposition and were warmed to -100°C for rotary carbon deposition of ≈ 64 Å followed by a second film at 20°C of the same thickness. The p-C₆ film was prepared in the same

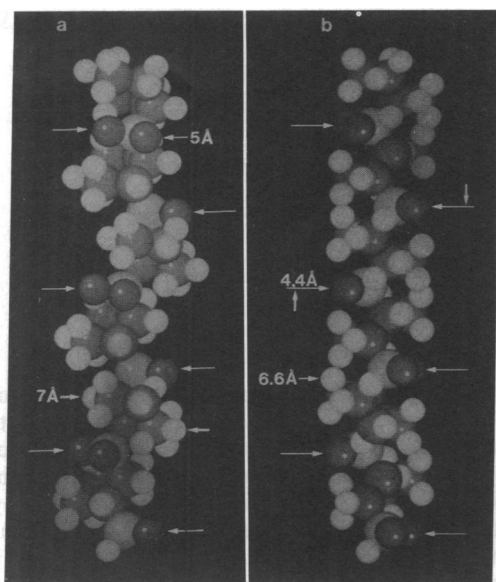


FIG. 1. (a) The extended syndiotactic p - cC_6 chain has a contour repeat distance of 4.4 Å. The diameter of the chain across the cyclohexene or the SO_2 group is 7 Å or 5 Å, respectively, which are the maximum and minimum chain diameters. (b) A 90° rotation of the model shows that the polymer chain appears cylindrical with a diameter of ≈ 6.6 Å.

way, except that the solvent was $CHCl_3$ and the Pt-C film thickness was 8.7 Å.

Observations were made with a JEM 100CX transmission electron microscope at 80 kV, with a resolution of 6.6 Å and a depth of field of 2600 Å (p - cC_6 and p - C_{14} samples), or with a JEM 2000FX transmission electron microscope at 80 kV, with a resolution of 4.8 Å and a depth of field of 500 Å (Pt-C

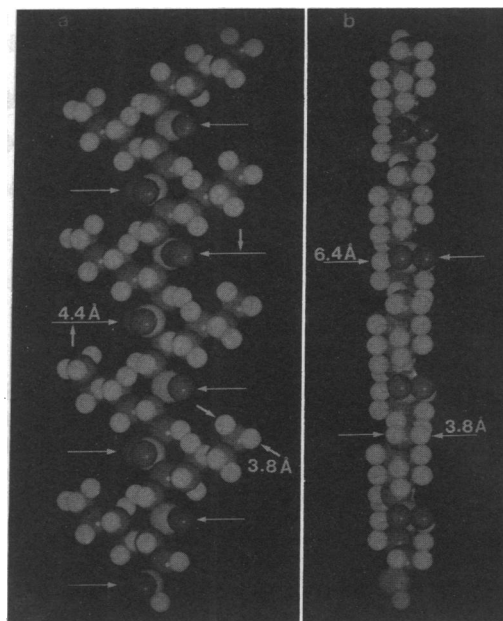


FIG. 2. (a) The extended syndiotactic poly(1-hexene sulfone) model shown here was substituted for p - C_{14} because it has shorter side chains. The side chains of 1-tetradecene are 3 times as long (≈ 17 Å fully extended), whereas both have side-chain diameters of ≈ 3.8 Å. Both polymers have a contour repeat distance of 4.4 Å. (b) A 90° rotation of the model shows that the maximum and minimum polymer chain diameters are 3.8 Å and 6.4 Å, respectively.

film on mica). The method for making micrograph reversals has been outlined (1) with one exception. The micrograph reversals were developed in full-strength D76 at 68°C for 3–4 min. The original micrographs were taken at $\times 100,000$ mag-

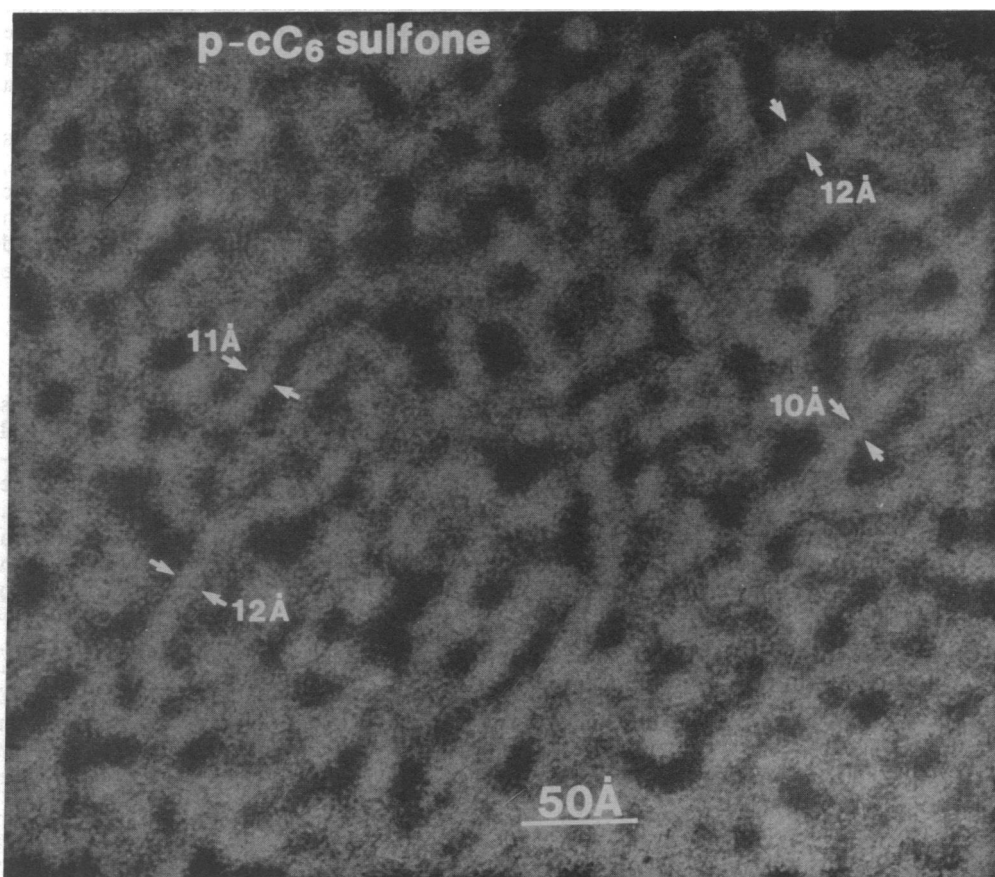


FIG. 3. No evidence of helical domains in p - cC_6 . Freeze-dried rapidly frozen solution of p - cC_6 [0.007% (wt/vol) in $CHCl_3$] was vertically replicated with 8.7-Å Pt-C and backed with 128 Å of evaporated carbon. This figure represents an area 342 Å wide by 324 Å high and contains ≈ 10 chains 70–160 Å long with many shorter chain sections. The measured chains have diameters of 9–12 Å when coated, corresponding with an uncoated diameter of 4.3–7 Å. It is often possible to distinguish whether a polymer chain crosses over or under another by observing the continuity and contrast at polymer chain edges. There were no helical chains detected in this preparation with the same extensive searching as that performed for p - C_{14} . ($\times 3,640,000$.)

nification. The reverse-contrast negatives were printed at $\times 250,000$ on Ilford Multigrade II fiber-based paper. These prints were used to find regions of interest, which were then enlarged $\times 20$ to a final magnification of $\times 2,000,000$ on a Durst Laborator 1200 enlarger. To develop contrast within the chains, the prints were developed in two consecutive developing solutions for a total of 4 min. The prints were developed ($\approx 65^\circ\text{C}$) first in Dektol (Kodak; diluted normally) for 15–45 sec and moved directly to a second tray of Selectol Soft (Kodak; diluted normally) for the rest of the time. The slightly higher contrast developer Selectol (Kodak; diluted 1 part to 2 parts of water) was used in place of Selectol Soft when the print contrast was too flat. Images (at $\times 2,000,000$) of interest were rephotographed on Ilford Pan F 35-mm film as described (1) and were further enlarged to approximately $\times 5,000,000$ magnification and printed with the same double-tray development procedure. The unusual double-developing method allows printing of the normal-contrast topographical features and the fine features to be distinguished by a layer of a few more or a few less platinum atoms from adjacent features, so that both contrast ranges can be visualized without losing one of them to over- or under-contrast in the same print.

RESULTS AND DISCUSSION

To estimate the diameter to be expected for single nonhelical chains, models were constructed with the Chem X program (Chemical Design, Oxford), which makes use of generally accepted bond lengths and bond angles. The available NMR evidence (13) indicates these polymers to be stereoirregular (atactic), but for simplicity we here display only small sections of syndiotactic chains in their fully extended all-trans conformations. In Fig. 1 the syndiotactic $p\text{-C}_6$ is displayed in two views differing by a 90° rotation. With the appropriate atomic van der Waals radii, the chain diameter ranges from 5 to 7 Å, and the repeat distance is 4.4 Å. These dimensions are unchanged in the isotactic or heterotactic stereoisomers of this polymer. In Fig. 2 we similarly display a model of the extended syndiotactic chain of poly(1-hexene sulfone) in two aspects. This chain was chosen in place of $p\text{-C}_{14}$ because the side chains are shorter and easier to visualize. The diameter of the model chain ranges from 3.8 to 6.4 Å, again with a repeat distance of 4.4 Å. The alkyl side chain has a diameter of 3.8 Å and an extended side chain in $p\text{-C}_{14}$ would measure 17 Å, or about 3 times longer than the side chains of the 1-hexene copolymer displayed in Fig. 2. The isotactic stereoisomer of this polymer has roughly the same diameter as

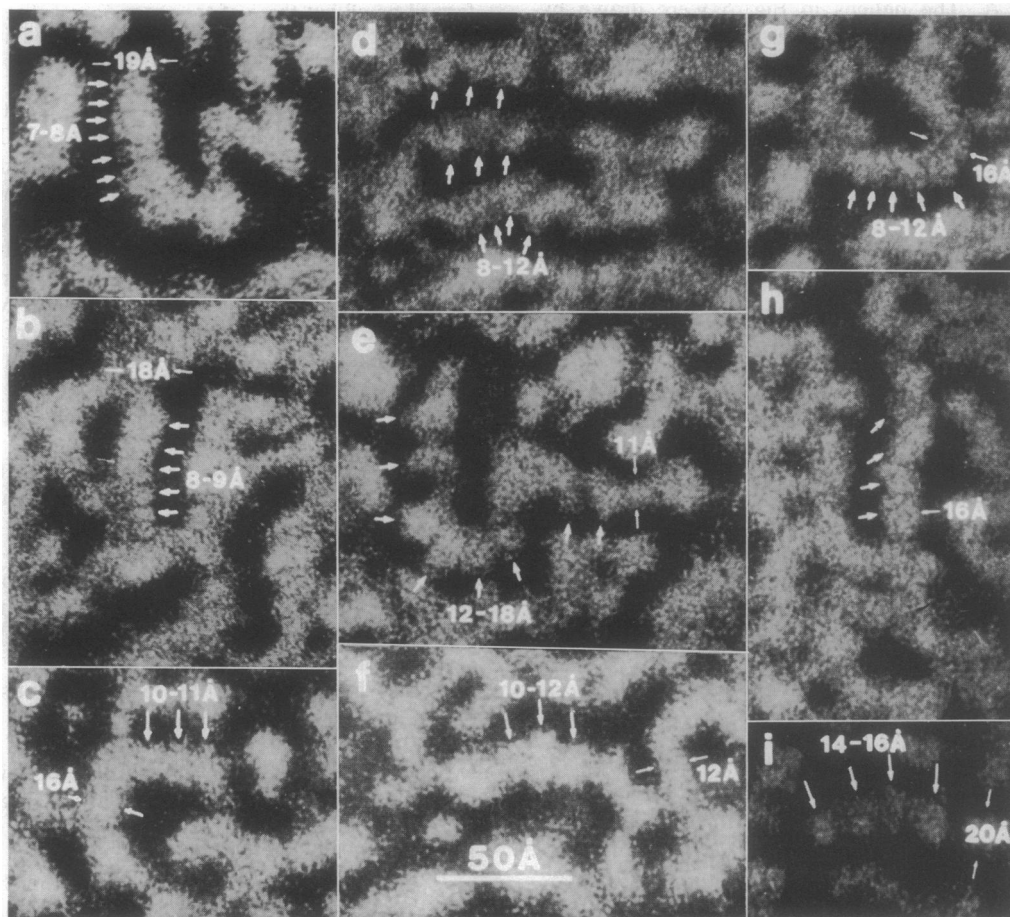


FIG. 4. Helical domains in $p\text{-C}_{14}$. Freeze-dried rapidly frozen solution of $p\text{-C}_{14}$ [0.007% (wt/vol) in CCl_4] was vertically replicated with 9.3-Å Pt-C and backed with 128 Å of evaporated carbon. The chain diameter of the uncoated polymer is 3.8–6.4 Å, and with the Pt-C coating the chain diameter is enlarged to 9–12 Å. Distances within the polymer are unchanged by replication. (a) Helical domain of seven to nine turns that are spaced 7–8 Å apart. The diameter of the helix is ≈ 14 Å (≈ 19 Å with a Pt-C coating of 5.3 Å). (b) Helical domain of five or six turns that are spaced 8–9 Å apart. The diameter of the helix is ≈ 13 Å (≈ 18 Å with a Pt-C coating of 5.3 Å). (c) Helical domain of three turns that are spaced 10–11 Å apart. The diameter of the helix is ≈ 11 Å. (d) Helical domain of three to four turns that are spaced 8–12 Å apart. The diameter of the three helices is ≈ 14 Å. (e) Helical domain of six and two turns that are spaced 12–18 Å apart. The diameter of the helix is ≈ 17 Å. To the right is the expected nonhelical chain diameter of 6 Å. (f) Helical domain of three to five turns that are spaced 10–12 Å apart. The diameters of the helical turns are 11, 13, and 19 Å. A nonhelical chain at the right is ≈ 6.7 Å (≈ 12 Å with a Pt-C coating of 5.3 Å). (g) Helical domain of five to eight turns that are spaced 8–12 Å apart. The diameter of the helix is ≈ 11 Å. (h) Helical domain of four turns with a helix diameter of ≈ 11 Å. (i) Helical domain of four turns that are spaced 14–16 Å apart. The diameter of the helix is ≈ 15 Å. ($\times 3,640,000$.)

in Fig. 2*b*, but the view similar to Fig. 2*a* shows periodic bumps along each side of the chain at 8.8-Å intervals. Otherwise the diameters are similar to those in Fig. 2*a*.

Polymer chain enlargement in vertically deposited Pt-C films has been empirically found (1, 4) to be 4 Å less than the Pt-C film thickness measured on a quartz crystal monitor. The chain diameter of p-C₆ would thus be enlarged to 10–12 Å by a vertically deposited 8.7-Å Pt-C film. Similarly, the chain diameter of p-C₁₄ would be enlarged to 9–12 Å with a vertically deposited 9.3-Å Pt-C film.

The p-C₆ film is shown in Fig. 3. The observed Pt-C-coated chains are quite featureless, with measured diameters of 10–12 Å, as expected. Since the diffraction limit of the objective aperture is 6.6 Å, the repeat unit of 4.4 Å indicated by the model in Fig. 1 is too small to be seen. No suggestions of helices or of side-chain projections are found in the p-C₆ film.

In contrast, the p-C₁₄ film of Fig. 4 shows a number of apparently helical domains. These domains were identified as stacks of separate bands, roughly crossing a single axis, which when measured had coated axial diameters of 16–22 Å (i.e., 11–17 Å uncoated). If the side chains were uniformly packed around the extended p-C₁₄ chain (a "degenerate helix"), this would form a cylinder with a Pt-C-coated diameter of 16 Å. The helices in Fig. 5 were drawn by observing a 35-mm slide of Fig. 4 on an M5 Wild microscope fitted with a Wild M5 drawing tube. The tracings were made from the 35-mm slide on white paper under the drawing tube at a magnification of about $\times 10$. Selected helical domains from Fig. 4 were digitized with a Newvicon camera (Dage-Mti model 66) and a densitometry scan parallel to each image's helical axis was performed (computer program "NIH Image 1.44, distributed by Wayne Rasband, Research Services Branch, National Institute of Mental Health). These densitometry traces confirmed the presence of stacks of bands and objectively located their centers. An example is shown in Fig. 6. We have also traced with a densitometer most of the other panels in Fig. 4 and found little difference with the measurements made with vernier calipers.

Table 1 summarizes the distances per helical turn and the total lengths (± 10 Å) of the helical domains shown in Fig. 4. As previously mentioned, the NMR data suggest that the helices must be quite irregular. The pitch of the most stable regular helices suggested by Mansfield's molecular mechanics calculations (11) is in the range 5.5–8.2 Å, although he favored 8.2 Å per turn as the most reasonable. The dilute-solution dielectric data combined with Mansfield's optimal helix lead to an estimated average helix domain length of ≈ 70

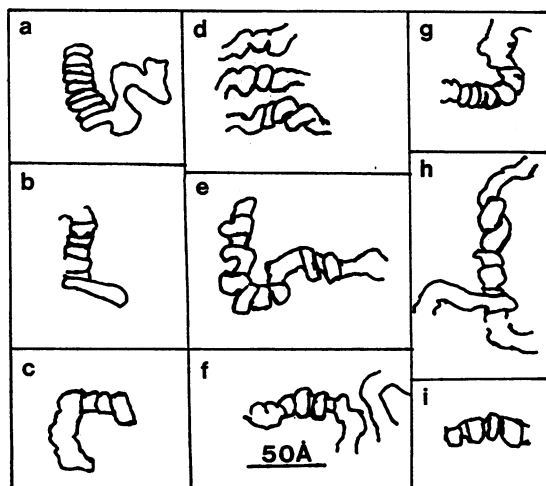


FIG. 5. Tracing of the helical domains in p-C₁₄ (see Fig. 4).

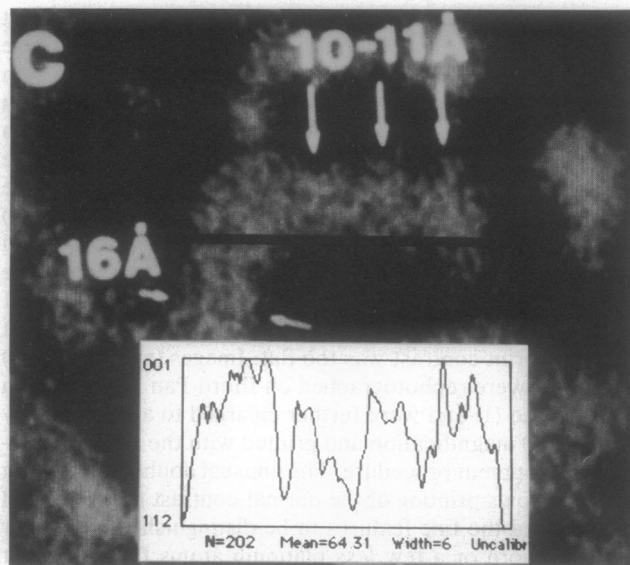


FIG. 6. Densitometry of Fig. 4*c*. This figure shows the line width and path of the densitometry measurement on the image and the corresponding transmittance trace below it. Densitometry was performed on all but three of the more open helices. Band positions estimated by this densitometric method differed little from the band positions measured with a vernier caliper.

Å (11). This solution average helix length is similar in magnitude to the helical domain lengths in Table 1.

The *n*-C₁₂H₂₅ side chains, with an uncoated diameter of 3.8 Å and with a length of ≈ 17 Å when fully extended, cannot be identified along p-C₁₄ helical regions. However, the side-chain projections are visible (Fig. 7*a* and *b*) along other regions of the p-C₁₄ polymer and two of them are as long as 13–14 Å with a coated diameter of 8–9 Å. Most of the side chains are not fully extended, or are entangled with an adjacent side chain. About 10 side chains out of a possible 25 can be identified in Fig. 7*b*. In Fig. 7*c* the extended p-C₆ polymer does not show evidence of any side-chain projections, as already seen in Fig. 3.

The surface of mica was replicated under the same conditions (Fig. 7*d*) to show that none of the structures in Figs. 3–7 could have been observed in the absence of the polymer samples. It should be emphasized that Pt-C-replicated samples without thoroughly degassed electron beam guns, with specimens $\approx 40^\circ\text{C}$ warmer than -185°C , at shadowing angles lower than 80°, with 40% thicker Pt-C (13 Å) or carbon (179 Å) films, or in a poorer vacuum than 5×10^{-8} torr (1 torr = 133 Pa) will not produce the results demonstrated here (1). Many conditions adversely increase Pt-C grain size, decrease resolution, or decrease contrast.

Thus, the vertical Pt-C replication technique, which appears to be a very powerful tool for visualizing polymer

Table 1. Length of p-C₁₄ helices in Fig. 4

| Panel | Distance per turn, Å | Total helix length,* Å |
|----------|----------------------|------------------------|
| <i>a</i> | 7–8 | 60 |
| <i>b</i> | 8–9 | 50 |
| <i>c</i> | 10–11 | 50 |
| <i>d</i> | 8–12 | 50, 40, 40 |
| <i>e</i> | 12–18 | 90, 20 |
| <i>f</i> | 10–12 | 50 |
| <i>g</i> | 8–12 | 70 |
| <i>h</i> | 13–17 | 60 |
| <i>i</i> | 14–22 | 70 |

* ± 10 Å.

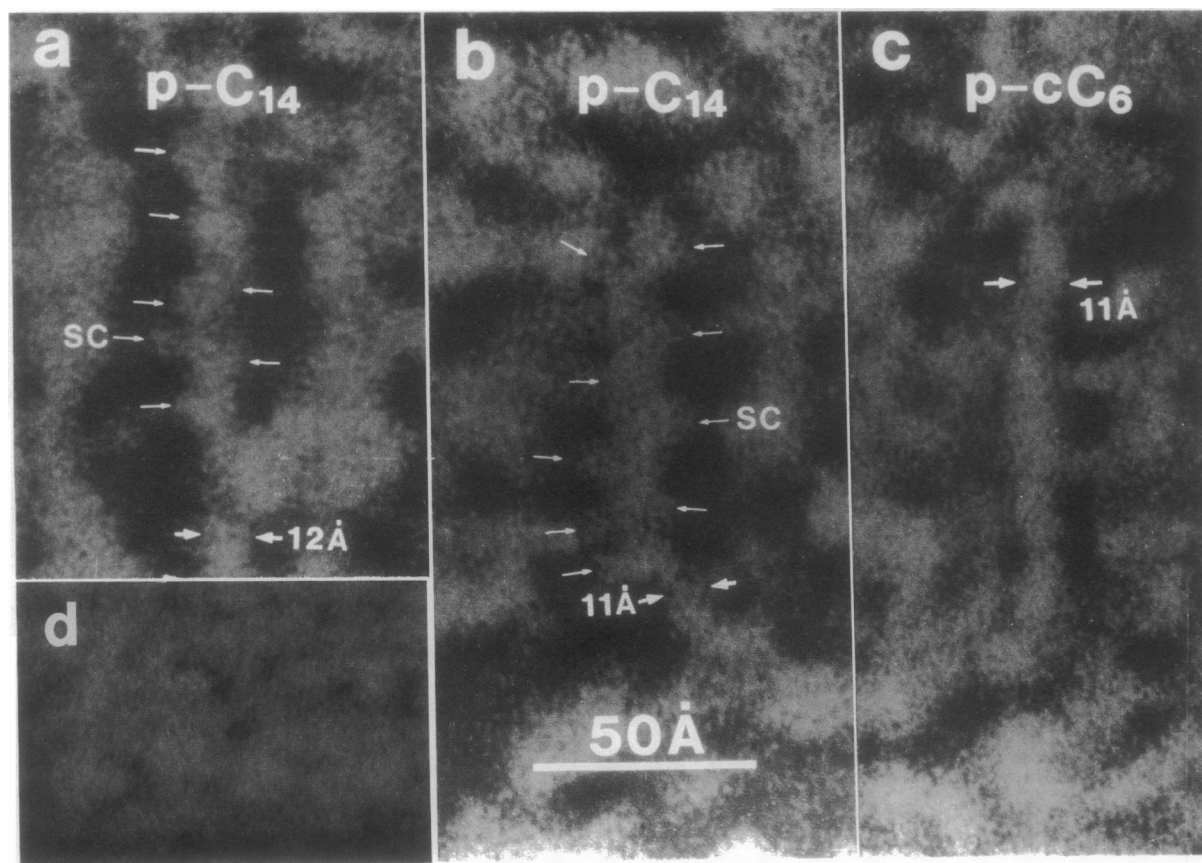


FIG. 7. Presence of side chains in extended p-C₁₄ and their absence in p-cC₆. These samples were prepared as described in Figs. 3 and 4. (a) An extended p-C₁₄ chain showing lateral projections, the longest of which is 10–15 Å, shorter than the fully extended length of ≈17 Å. Most of the projections suggest that the side chains are not fully extended. The arrows mark the centers of these projections, which are separated by multiples of ≈4.4 Å. n-C₁₂H₂₅ side chains 4.4 Å apart along the main chain could be discerned because the side chains extend outside the Airy disc diffraction limit of 6.6 Å. The diameter of the main chain is ≈6.4 Å (12 Å with a Pt-C coating of 5.3 Å). (b) The main chain of p-C₁₄ is ≈112 Å long in this image. Out of the 25 possible side chains, 9–10 side chains can be detected as side projections that are separated by multiples of ≈4.4 Å. Many of these side chains are either entangled with adjacent side chains or they are not fully extended. Two side chains were measured as long as 13–14 Å and were also estimated to be ≈3 Å in diameter (8 Å with 5.3 Å of added Pt-C), smaller than the expected ≈3.8 Å. The main-chain diameter was estimated to be ≈6 Å. (c) This p-cC₆ extends for ≈140 Å along the surface. The diameter of the p-cC₆ in the image varies from 4.3 to 7 Å (9 to 12 Å with 4.7 Å of added Pt-C) over this length. As in Fig. 3, there is no evidence of any projections or side chains on this polymer. (d) A 9.3-Å Pt-C film deposited on mica under the same conditions as in a and b. Pt-C filaments, when present, have diameters approximately the film thickness minus 4 Å, which is also the estimated diameter enlargement for a Pt-C-coated polymer chain if it were present (1). (×5,870,000.)

structures in gels (4), or on rough surfaces where the scanning probe technologies experience difficulties (16), here gives evidence altogether consistent with the presence and previously estimated average helical domain size in poly(1-olefin sulfone)s and their absence in p-cC₆.

G.C.R. wishes to thank GeoM Co. for financial support; the Dartmouth Rippel Electron Microscope facility for the use of its equipment; C. P. Daghlion for image processing assistance; and A. Olson for suggesting the suitable low-contrast print developers Selectol and Selectol Soft. We thank H. A. Trujillo for assistance in constructing Figs. 1 and 2, and Prof. Edwin L. Thomas of the Massachusetts Institute of Technology, for valuable criticism. This work was supported in part by the National Science Foundation under Grant DMR-86-08633 of the Polymers Program, Division of Materials Research.

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ABSTRACT Transmission electron microscope images were obtained of fractions of poly(1-tetradecene sulfone) and poly(cyclohexene sulfone) cast from very dilute solutions (0.007%, wt/vol) and rapidly freeze-dried on a mica surface. The samples were then vertically platinum–carbon (Pt–C) replicated with 9 ± 0.3 -Å Pt–C and held together with 128 Å of electron-transparent evaporated carbon. The Pt–C coating enlarges the molecular chain diameters by ≈ 5 Å, so that a single polysulfone chain has an apparent diameter of 9–12 Å in the transmission electron microscope. Poly(1-tetradecene sulfone) forms short helical regions that show irregular helical turns of pitch 7–18 Å, two to eight turns long with apparent helix diameters of 16–22 Å. The n -C₁₂H₂₅ side chains were not obvious on the helices, but a few were visible on extended chain sections. In contrast, poly(cyclohexene sulfone) appears as a collection of Pt–C-coated single chains 10–12 Å in diameter with no side-chain projections. The presence and absence of helical regions in these freeze-dried polysulfones thus reflects their solution conformations as long ago inferred on the basis of dielectric measurements.

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In the present work, transmission electron microscopy was used to study samples of poly(1-tetradecene sulfone), p-C₁₄, which displays the aforementioned low-frequency dielectric response, and of poly(cyclohexene sulfone), p-C₆, which (by virtue of its symmetric structure) does not. As described below, the results give rather direct evidence for the presence of helices in the former polymer.

METHODS AND MATERIALS

The olefin/SO₂ alternating copolymers were prepared in this laboratory by Keizo Matsuo (9) with standard free-radical recipes (15). The p-C₁₄ sample was a fraction of viscosity-average molecular weight about 5×10^6 . The p-C₆ sample was unfractionated, with a molecular weight above 2×10^5 .

The p-C₁₄ film was prepared by depositing 10–20 μ l of a very dilute solution [0.007% (wt/vol) in CCl₄] on a 13-mm mica disc, which was then plunged bottom-side first into liquid propane for rapid freezing. The disc was later replicated under the following conditions: 9.3-Å Pt–C (80° angle), followed by 128-Å carbon (100° angle). It should be emphasized that the specimens were cooled to -185°C prior to Pt–C deposition and were warmed to -100°C for rotary carbon deposition of ≈ 64 Å followed by a second film at 20°C of the same thickness. The p-C₆ film was prepared in the same

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Abbreviations: p-C₁₄, poly(1-tetradecene sulfone); p-C₆, poly(cyclohexene sulfone).

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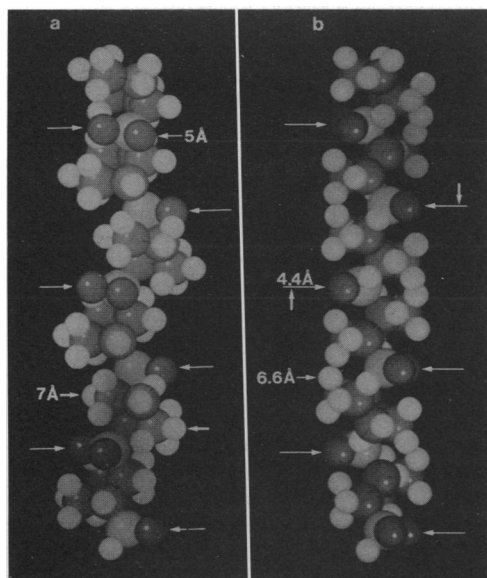


FIG. 1. (a) The extended syndiotactic p-cC₆ chain has a contour repeat distance of 4.4 Å. The diameter of the chain across the cyclohexene or the SO₂ group is 7 Å or 5 Å, respectively, which are the maximum and minimum chain diameters. (b) A 90° rotation of the model shows that the polymer chain appears cylindrical with a diameter of ≈ 6.6 Å.

way, except that the solvent was CHCl₃ and the Pt-C film thickness was 8.7 Å.

Observations were made with a JEM 100CX transmission electron microscope at 80 kV, with a resolution of 6.6 Å and a depth of field of 2600 Å (p-cC₆ and p-C₁₄ samples), or with a JEM 2000FX transmission electron microscope at 80 kV,

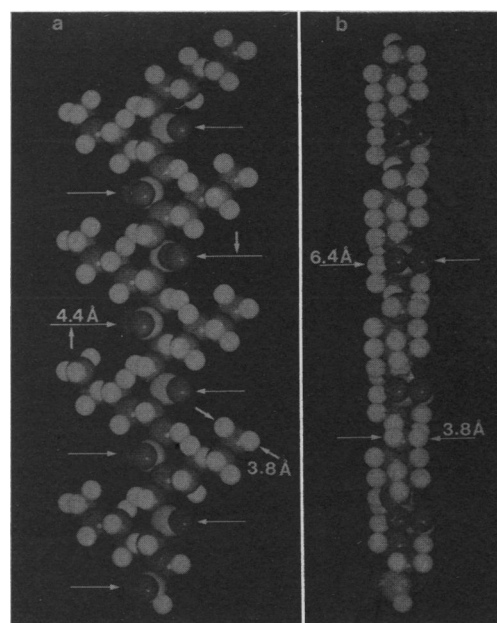


FIG. 2. (a) The extended syndiotactic poly(1-hexene sulfone) model shown here was substituted for p-C₁₄ because it has shorter side chains. The side chains of 1-tetradecene are 3 times as long (≈ 17 Å fully extended), whereas both have side-chain diameters of ≈ 3.8 Å. Both polymers have a contour repeat distance of 4.4 Å. (b) A 90° rotation of the model shows that the maximum and minimum polymer chain diameters are 3.8 Å and 6.4 Å, respectively.

with a resolution of 4.8 Å and a depth of field of 500 Å (Pt-C film on mica). The method for making micrograph reversals has been outlined (1) with one exception. The micrograph reversals were developed in full-strength D76 at 68°C for 3–4

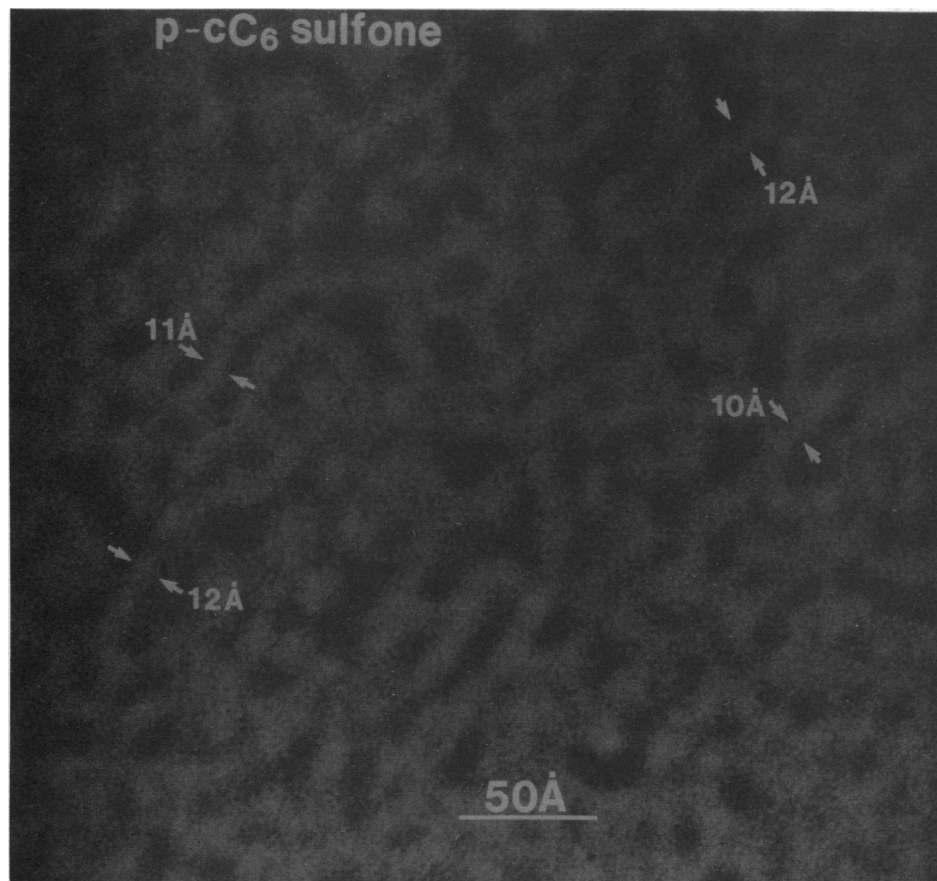


FIG. 3. No evidence of helical domains in p-cC₆. Freeze-dried rapidly frozen solution of p-cC₆ [0.007% (wt/vol) in CHCl₃] was vertically replicated with 8.7-Å Pt-C and backed with 128 Å of evaporated carbon. This figure represents an area 342 Å wide by 324 Å high and contains ≈ 10 chains 70–160 Å long with many shorter chain sections. The measured chains have diameters of 9–12 Å when coated, corresponding with an uncoated diameter of 4.3–7 Å. It is often possible to distinguish whether a polymer chain crosses over or under another by observing the continuity and contrast at polymer chain edges. There were no helical chains detected in this preparation with the same extensive searching as that performed for p-C₁₄. ($\times 3,640,000$.)

min. The original micrographs were taken at $\times 100,000$ magnification. The reverse-contrast negatives were printed at $\times 250,000$ on Ilford Multigrade II fiber-based paper. These prints were used to find regions of interest, which were then enlarged $\times 20$ to a final magnification of $\times 2,000,000$ on a Durst Laborator 1200 enlarger. To develop contrast within the chains, the prints were developed in two consecutive developing solutions for a total of 4 min. The prints were developed ($\approx 65^\circ\text{C}$) first in Dektol (Kodak; diluted normally) for 15–45 sec and moved directly to a second tray of Selectol Soft (Kodak; diluted normally) for the rest of the time. The slightly higher contrast developer Selectol (Kodak; diluted 1 part to 2 parts of water) was used in place of Selectol Soft when the print contrast was too flat. Images (at $\times 2,000,000$) of interest were rephotographed on Ilford Pan F 35-mm film as described (1) and were further enlarged to approximately $\times 5,000,000$ magnification and printed with the same double-tray development procedure. The unusual double-developing method allows printing of the normal-contrast topographical features and the fine features to be distinguished by a layer of a few more or a few less platinum atoms from adjacent features, so that both contrast ranges can be visualized

without losing one of them to over- or under-contrast in the same print.

RESULTS AND DISCUSSION

To estimate the diameter to be expected for single nonhelical chains, models were constructed with the Chem X program (Chemical Design, Oxford), which makes use of generally accepted bond lengths and bond angles. The available NMR evidence (13) indicates these polymers to be stereoirregular (atactic), but for simplicity we here display only small sections of syndiotactic chains in their fully extended all-trans conformations. In Fig. 1 the syndiotactic p-C₆ is displayed in two views differing by a 90° rotation. With the appropriate atomic van der Waals radii, the chain diameter ranges from 5 to 7 Å, and the repeat distance is 4.4 Å. These dimensions are unchanged in the isotactic or heterotactic stereoisomers of this polymer. In Fig. 2 we similarly display a model of the extended syndiotactic chain of poly(1-hexene sulfone) in two aspects. This chain was chosen in place of p-C₁₄ because the side chains are shorter and easier to visualize. The diameter of the model chain ranges from 3.8 to 6.4 Å, again with a repeat distance of 4.4 Å. The alkyl side chain has a diameter

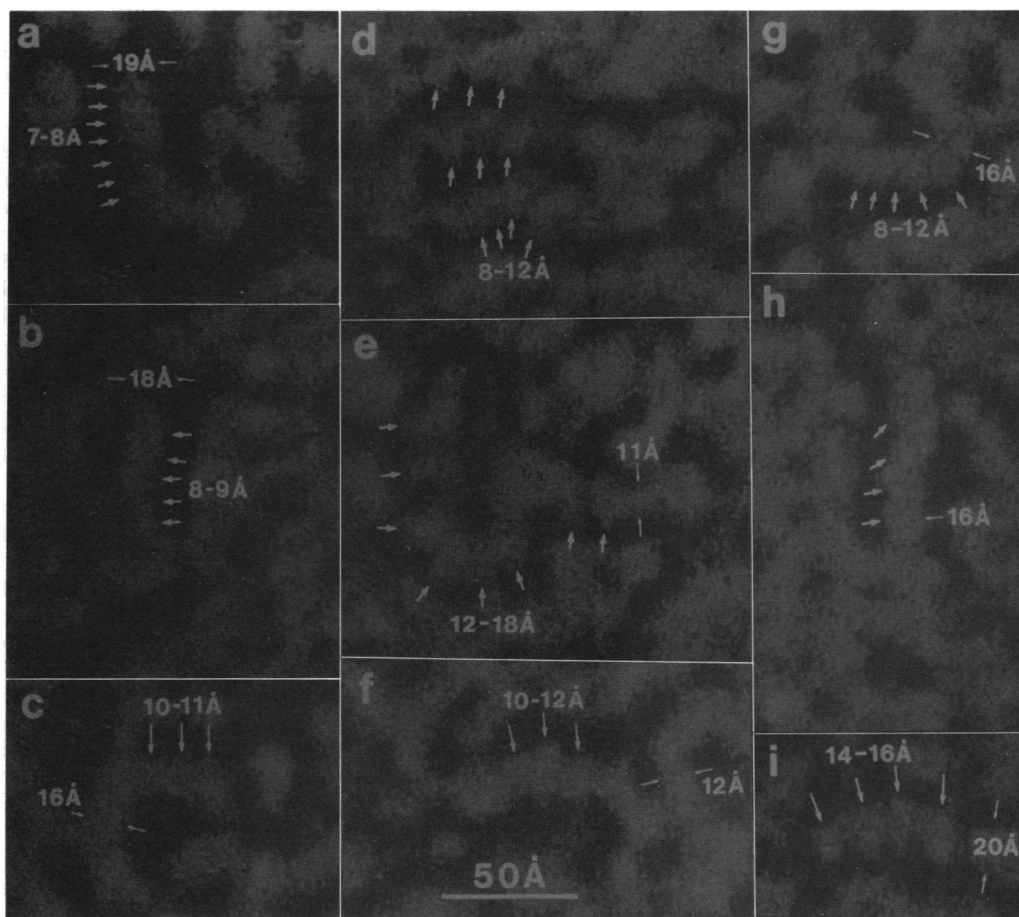


FIG. 4. Helical domains in p-C₁₄. Freeze-dried rapidly frozen solution of p-C₁₄ [0.007% (wt/vol) in CCl₄] was vertically replicated with 9.3-Å Pt-C and backed with 128 Å of evaporated carbon. The chain diameter of the uncoated polymer is 3.8–6.4 Å, and with the Pt-C coating the chain diameter is enlarged to 9–12 Å. Distances within the polymer are unchanged by replication. (a) Helical domain of seven to nine turns that are spaced 7–8 Å apart. The diameter of the helix is ≈ 14 Å (≈ 19 Å with a Pt-C coating of 5.3 Å). (b) Helical domain of five or six turns that are spaced 8–9 Å apart. The diameter of the helix is ≈ 13 Å (≈ 18 Å with a Pt-C coating of 5.3 Å). (c) Helical domain of three helices that are spaced 10–11 Å apart. The diameter of the helix is ≈ 14 Å. (d) Helical domain of three to four turns that are spaced 8–12 Å apart. The diameter of the helix is ≈ 14 Å. (e) Helical domain of six and two turns that are spaced 12–18 Å apart. The diameter of the helix is ≈ 17 Å. To the right is the expected nonhelical chain diameter of 6 Å. (f) Helical domain of three to five turns that are spaced 10–12 Å apart. The diameters of the helical turns are 11, 13, and 19 Å. A nonhelical chain at the right is ≈ 6.7 Å (≈ 12 Å with a Pt-C coating of 5.3 Å). (g) Helical domain of five to eight turns that are spaced 8–12 Å apart. The diameter of the helix is ≈ 11 Å. (h) Helical domain of four turns with a helix diameter of ≈ 11 Å. (i) Helical domain of four turns that are spaced 14–16 Å apart. The diameter of the helix is ≈ 15 Å. ($\times 3,640,000$.)

of 3.8 Å and an extended side chain in p-C₁₄ would measure 17 Å, or about 3 times longer than the side chains of the 1-hexene copolymer displayed in Fig. 2. The isotactic stereoisomer of this polymer has roughly the same diameter as in Fig. 2b, but the view similar to Fig. 2a shows periodic bumps along each side of the chain at 8.8-Å intervals. Otherwise the diameters are similar to those in Fig. 2a.

Polymer chain enlargement in vertically deposited Pt-C films has been empirically found (1, 4) to be 4 Å less than the Pt-C film thickness measured on a quartz crystal monitor. The chain diameter of p-cC₆ would thus be enlarged to 10–12 Å by a vertically deposited 8.7-Å Pt-C film. Similarly, the chain diameter of p-C₁₄ would be enlarged to 9–12 Å with a vertically deposited 9.3-Å Pt-C film.

The p-cC₆ film is shown in Fig. 3. The observed Pt-C-coated chains are quite featureless, with measured diameters of 10–12 Å, as expected. Since the diffraction limit of the objective aperture is 6.6 Å, the repeat unit of 4.4 Å indicated by the model in Fig. 1 is too small to be seen. No suggestions of helices or of side-chain projections are found in the p-cC₆ film.

In contrast, the p-C₁₄ film of Fig. 4 shows a number of apparently helical domains. These domains were identified as stacks of separate bands, roughly crossing a single axis, which when measured had coated axial diameters of 16–22 Å (i.e., 11–17 Å uncoated). If the side chains were uniformly packed around the extended p-C₁₄ chain (a “degenerate helix”), this would form a cylinder with a Pt-C-coated diameter of 16 Å. The helices in Fig. 5 were drawn by observing a 35-mm slide of Fig. 4 on an M5 Wild microscope fitted with a Wild M5 drawing tube. The tracings were made from the 35-mm slide on white paper under the drawing tube at a magnification of about $\times 10$. Selected helical domains from Fig. 4 were digitized with a Newvicon camera (Dage-Mti model 66) and a densitometry scan parallel to each image’s helical axis was performed (computer program “NIH Image 1.44, distributed by Wayne Rasband, Research Services Branch, National Institute of Mental Health). These densitometry traces confirmed the presence of stacks of bands and objectively located their centers. An example is shown in Fig. 6. We have also traced with a densitometer most of the other panels in Fig. 4 and found little difference with the measurements made with vernier calipers.

Table 1 summarizes the distances per helical turn and the total lengths (± 10 Å) of the helical domains shown in Fig. 4. As previously mentioned, the NMR data suggest that the helices must be quite irregular. The pitch of the most stable regular helices suggested by Mansfield’s molecular mechan-

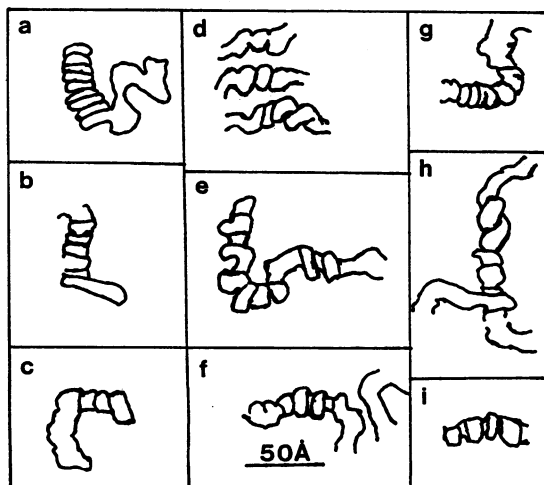


FIG. 5. Tracing of the helical domains in p-C₁₄ (see Fig. 4).

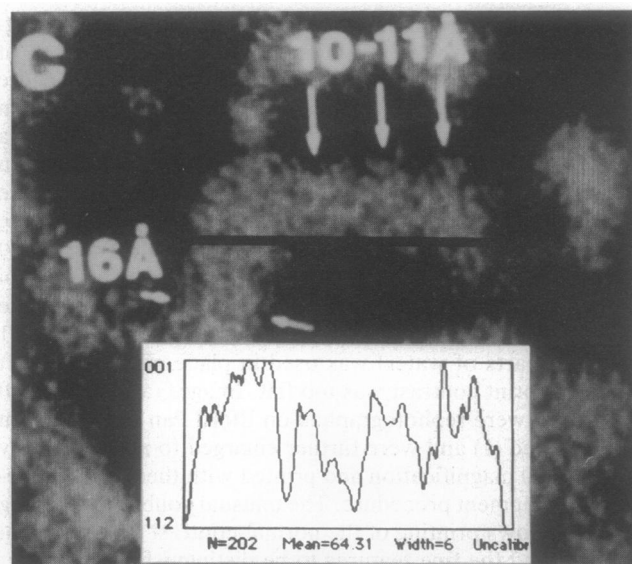


FIG. 6. Densitometry of Fig. 4c. This figure shows the line width and path of the densitometry measurement on the image and the corresponding transmittance trace below it. Densitometry was performed on all but three of the more open helices. Band positions estimated by this densitometric method differed little from the band positions measured with a vernier caliper.

ics calculations (11) is in the range 5.5–8.2 Å, although he favored 8.2 Å per turn as the most reasonable. The dilute-solution dielectric data combined with Mansfield’s optimal helix lead to an estimated average helix domain length of ≈ 70 Å (11). This solution average helix length is similar in magnitude to the helical domain lengths in Table 1.

The n -C₁₂H₂₅ side chains, with an uncoated diameter of 3.8 Å and with a length of ≈ 17 Å when fully extended, cannot be identified along p-C₁₄ helical regions. However, the side-chain projections are visible (Fig. 7a and b) along other regions of the p-C₁₄ polymer and two of them are as long as 13–14 Å with a coated diameter of 8–9 Å. Most of the side chains are not fully extended, or are entangled with an adjacent side chain. About 10 side chains out of a possible 25 can be identified in Fig. 7b. In Fig. 7c the extended p-cC₆ polymer does not show evidence of any side-chain projections, as already seen in Fig. 3.

The surface of mica was replicated under the same conditions (Fig. 7d) to show that none of the structures in Figs. 3–7 could have been observed in the absence of the polymer samples. It should be emphasized that Pt-C-replicated samples without thoroughly degassed electron beam guns, with specimens $\approx 40^\circ\text{C}$ warmer than -185°C , at shadowing angles lower than 80° , with 40% thicker Pt-C (13 Å) or carbon (179 Å) films, or in a poorer vacuum than 5×10^{-8} torr (1 torr = 133 Pa) will not produce the results demonstrated here (1).

Table 1. Length of p-C₁₄ helices in Fig. 4

| Panel | Distance per turn, Å | Total helix length, * Å |
|-------|----------------------|-------------------------|
| a | 7–8 | 60 |
| b | 8–9 | 50 |
| c | 10–11 | 50 |
| d | 8–12 | 50, 40, 40 |
| e | 12–18 | 90, 20 |
| f | 10–12 | 50 |
| g | 8–12 | 70 |
| h | 13–17 | 60 |
| i | 14–22 | 70 |

* ± 10 Å.

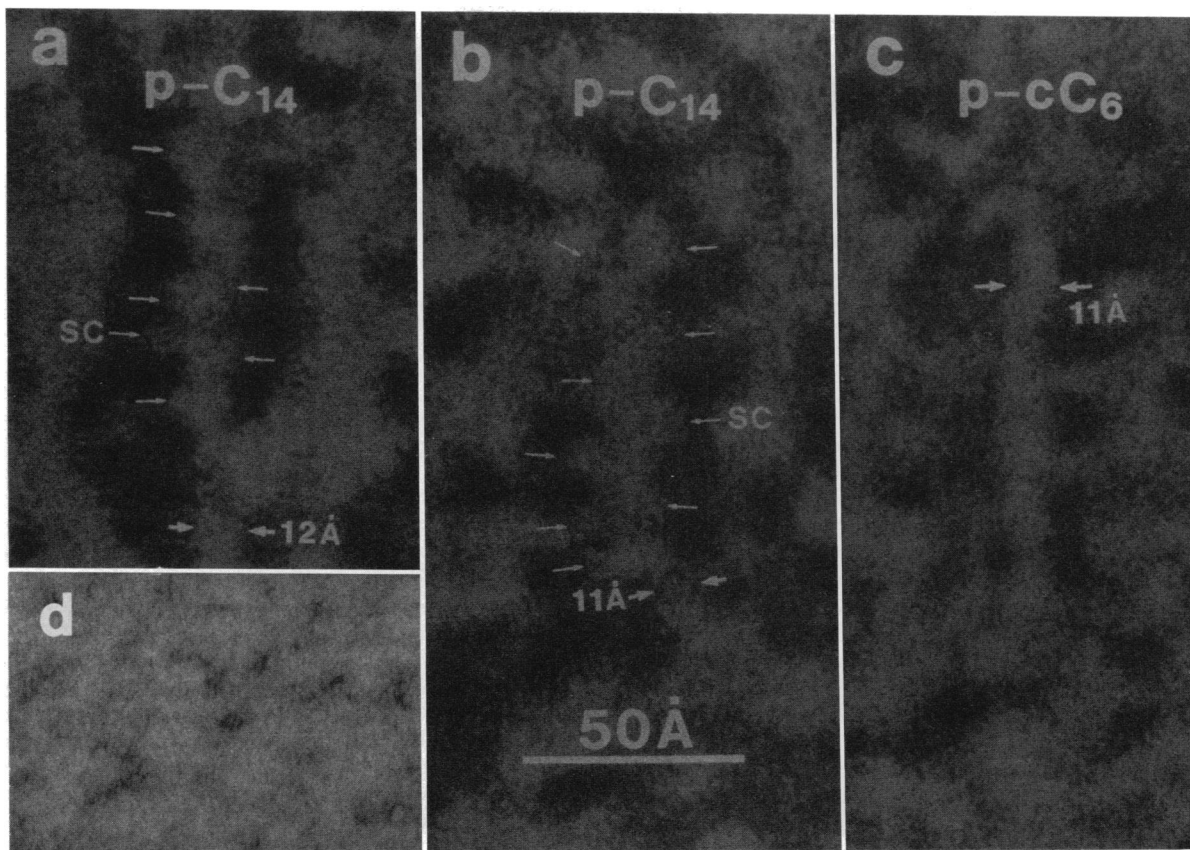


FIG. 7. Presence of side chains in extended p-C₁₄ and their absence in p-cC₆. These samples were prepared as described in Figs. 3 and 4. (a) An extended p-C₁₄ chain showing lateral projections, the longest of which is 10–15 Å, shorter than the fully extended length of ≈17 Å. Most of the projections suggest that the side chains are not fully extended. The arrows mark the centers of these projections, which are separated by multiples of ≈4.4 Å. n-C₁₂H₂₅ side chains 4.4 Å apart along the main chain could be discerned because the side chains extend outside the Airy disc diffraction limit of 6.6 Å. The diameter of the main chain is ≈6.4 Å (12 Å with a Pt–C coating of 5.3 Å). (b) The main chain of p-C₁₄ is ≈112 Å long in this image. Out of the 25 possible side chains, 9–10 side chains can be detected as side projections that are separated by multiples of ≈4.4 Å. Many of these side chains are either entangled with adjacent side chains or they are not fully extended. Two side chains were measured as long as 13–14 Å and were also estimated to be ≈3 Å in diameter (8 Å with 5.3 Å of added Pt–C), smaller than the expected ≈3.8 Å. The main-chain diameter was estimated to be ≈6 Å. (c) This p-cC₆ extends for ≈140 Å along the surface. The diameter of the p-cC₆ in the image varies from 4.3 to 7 Å (9 to 12 Å with 4.7 Å of added Pt–C) over this length. As in Fig. 3, there is no evidence of any projections or side chains on this polymer. (d) A 9.3-Å Pt–C film deposited on mica under the same conditions as in a and b. Pt–C filaments, when present, have diameters approximately the film thickness minus 4 Å, which is also the estimated diameter enlargement for a Pt–C-coated polymer chain if it were present (1). (×5,870,000.)

Many conditions adversely increase Pt–C grain size, decrease resolution, or decrease contrast.

Thus, the vertical Pt–C replication technique, which appears to be a very powerful tool for visualizing polymer structures in gels (4), or on rough surfaces where the scanning probe technologies experience difficulties (16), here gives evidence altogether consistent with the presence and previously estimated average helical domain size in poly(1-olefin sulfones) and their absence in p-cC₆.

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