reactions are uncorrelated, in the sense discussed above in connection with eq 9.

A system to which our new results are relevant is that studied experimentally by Worsfold.[7] He gives data for concentrated solutions of nitrophenol-capped polystyrenes, dissolved in diethylbenzene with a tertiary amine as linking agent. (Similar measurements on polymers end capped with carboxylic acid groups are currently in progress.[16]) For chains in the fully entangled regime (his polymer PS-S), Worsfold gives q values in the range 0.3-0.5. The measured viscosities are of order $\eta/\eta_0 \simeq 1.21$-1.35; while there is considerable scatter, these results appear to be broadly consistent with eq 13. The indication is that, in this particular system, the dissociation time of a dimer may be very short compared to the disengagement time of a chain ($\alpha < 0.02$). If so, the observed viscosity enhancement can be attributed solely to the shift in the curvilinear diffusion constant D_c, as described by eq 10. It is interesting to find a rheological experiment in which the chain-length dependence of D_c is, apparently, manifested in isolation from the other factors that determine the viscosity.

More generally, one can expect to find other systems for which the calculated curves of Figure 2 will yield semiquantitative estimates for α, rather than just a bound as in this particular example. Certainly there are ion-containing polymers which undergo rather long-lived pairwise associations;[8] moreover the shear-rate-dependent rheological activity of other associating polymers[2-4] is an indication that the time scales for rearrangement of the associations, and for stress relaxation, are comparable in many cases of interest.

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Electron Microscopy Studies of the Cofacial Phthalocyanine Polymers $(AlPcF)_n$ and $(SiPcO)_n$

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ABSTRACT: $(AlPcF)_n$ and $(SiPcO)_n$ (Pc = phthalocyanine ligand), both of which are cofacial polymers, have been studied by electron microscopy. $(AlPcF)_n$ has been examined after being sublimed onto glass or KCl. $(SiPcO)_n$ has been examined as synthesized. Films formed by heating $(SiPcO)_n$ and condensing the resulting vapors on KCl have also been studied. It is concluded that some of the molecules in $(AlPcF)_n$ have molecular weights in the range 18 000-23 000 and that the rings in the molecules are eclipsed. It is also concluded that the molecules in $(SiPcO)_n$ have quite variable molecular weights. Electron diffraction data indicate that the $(AlPcF)_n$ crystallites from both types of sublimations are tetragonal with $a = b = 13.37$ Å and $c = 3.6$ Å.

Introduction

The first linear, cofacial phthalocyanine polymer reported was $(GePcO)_n$[1] (Pc = phthalocyanine ligand). Others that have been reported since are $(SiPcO)_n$,[2] $(SnPcO)_n$,[3] $(AlPcF)_n$,[4,5] $(GaPcF)_n$,[5] $(CrPcF)_n$,[6] and $(GePcS)_n$[7] (Figure 1).

A number of studies have been done on members of this family. A study of $(AlPcF)_n$ based on X-ray powder and other techniques[5] has led to the conclusion that its chains are packed parallel to each other and has yielded interring spacing data for it.[8] Results from an electron microscopy study of $(AlPcF)_n$[9] have been interpreted as providing data on the lengths of the chains. A single-crystal X-ray study of $(GaPcF)_n$[10] has shown that its chains are truly linear and its rings are eclipsed. It also has provided confirmation of the conclusion, derived in an earlier study based partly on powder data,[5] that its chains are packed parallel to each other. In addition, it has provided confirmation for and refinement of interring spacing data from the earlier study.[5] A powder study of $(SiPcO)_n$, $(GePcO)_n$, and

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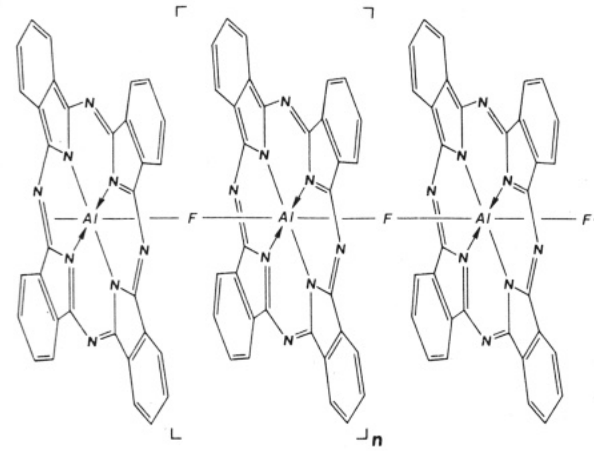

Figure 1. Structure of $(AlPcF)_n$.

$(SnPcO)_n$[11] has led to the conclusion that the chains in these polymers are also truly linear and that they pack parallel to each other.[12] This study has also confirmed interring spacing data from an earlier powder study.[3] An electron microscopy study of $(GePcO)_n$[15] has confirmed the parallel packing of the chains in $(GePcO)_n$. From an extension of this study,[16] data have been obtained suggesting that $(GePcO)_n$ can be produced by a topotatic polymerization reaction. A powder study of $(CrPcF)_n$ has yielded interring spacing data for it.[6]

From conductivity studies, it has been learned that $(AlPcF)_n$, $(GaPcF)_n$, $(SiPcO)_n$, and $(GePcO)_n$ are good conductors when suitably fractionally oxidized,[17,18] e.g., $[AlPcF(I)_{3.3}]_n$ has a pressed-disk conductivity of 5 Ω^{-1} cm^{-1}.[17] Other studies have demonstrated that $(AlPcF)_n$ and $(SiPcO)_n$ are quite stable. Thus, for example, $(SiPcO)_n$ resists pyrolysis under vacuum at 520 °C[2] and solvolysis in concentrated H_2SO_4 at room temperature.[2,19]

Because of their properties, these polymers are of considerable interest. The present report discusses results of a new high-resolution electron microscopy study of two of these polymers, $(AlPcF)_n$ and $(SiPcO)_n$.[20]

Experimental Section

Synthesis. **$(AlPcF)_n$.** With Linsky's work as a model,[5] $AlPcOH\cdot xH_2O$ was treated with aqueous HF and the resulting solid was heated under vacuum. The crude product was sublimed onto glass.

$(SiPcO)_n$. In accordance with the procedure described by Joyner,[2] $SiPc(OH)_2$ was heated under vacuum.

Specimen Preparation. **$(AlPcF)_n$.** In one procedure, the sublimed $(AlPcF)_n$ was suspended in isopropyl alcohol and the suspension was sprayed onto carbon-coated grids. In a second procedure, the sublimed polymer was resublimed onto heated (~230 °C), fresh, (100) KCl crystal faces. The resulting films were coated with carbon, floated off on water, and picked up on grids. The upper surfaces of the films used in the high-resolution work were coated with a second layer of carbon (so as to encapsulate the crystallites[23]). (No residue was left in the sublimation boat at the end of the sublimations.)

$(SiPcO)_n$. The vacuum-synthesized $(SiPcO)_n$ was suspended in isopropyl alcohol and the suspension was sprayed on carbon-coated grids.

Product from Heated $(SiPcO)_n$. The vacuum synthesized $(SiPcO)_n$ was heated under vacuum, and the easily condensable vapors were collected on heated (~230 °C), fresh, (100) KCl crystal faces. The resulting condensates were treated in the same fashion as the analogous $(AlPcF)_n$ sublimates. (A carbonized residue was left in the boat at the end of the heating procedures.)

Instrumentation. Most of the microscopy was done with a JEOL 1200EX 120-KeV electron microscope (Japan Electron Optics Laboratory, Tokyo, Japan) equipped with a Mullard Badger image intensifier (Mullard Ltd., London, Great Britain). The images were recorded at a magnification of 120000× under minimal exposure conditions on Kodak X-ray film (Eastman Kodak Co., Rochester, NY). The remainder of the microscopy was done with the 600-KeV Cambridge University High-Resolution Electron Microscope (constructed in house).

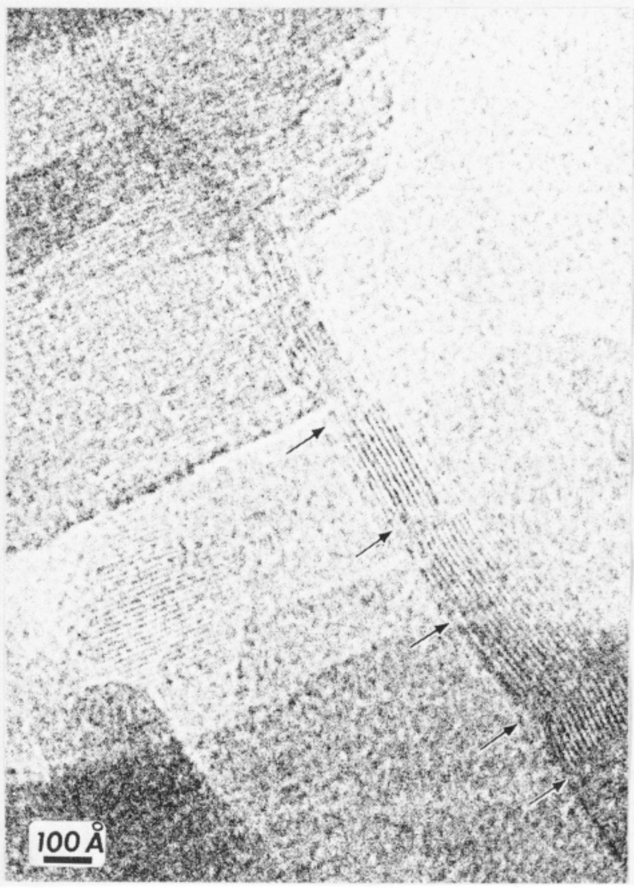

Figure 2. Image of normally sublimed $(AlPcF)_n$ crystallites showing the lengths of the unbroken lattices.

Results and Discussion

$(AlPcF)_n$. On the basis of several kinds of data, it was concluded earlier that normally sublimed $(AlPcF)_n$ is made up of acicular crystallites and that the molecular chains in these crystallites are parallel to the needle axes of the crystallites.[5] Thus, as expected, images of the preparations of the normally sublimed $(AlPcF)_n$ show that the needle axes of some of the crystallites in these preparations are horizontal (i.e., in the film plane) and that the molecules in the crystallites are parallel (Figure 2).

In several cases, the fringes in the images have discontinuities or breaks of about 120–150 Å or multiples of this interval (Figure 2). These breaks indicate in accordance with the conclusion drawn from earlier work[9] that at least some of the chains are 120–150 Å long. Since the interring spacing in $(AlPcF)_n$ is 3.66 Å,[5] these lengths indicate that the chains contain about 33–41 rings and have molecular weights of about 18000–23000.

Images of the films formed by depositing $(AlPcF)_n$ on KCl, when observed in the usual (nontilted) orientation, show that they consist of platy crystallites lying horizontally. They further show that the molecules in these crystallites are parallel to each other and are oriented vertically (i.e., perpendicular to the film plane) (Figure 3). Because the individual molecular columns are well defined, it is apparent that the phthalocyanine rings are perpendicular to the Al–F backbones. The disorder within the crystalline islands is attributable to the nonpolar, rigid, essentially cylindrical nature of the molecules. The relatively great uniformity of contrast in the images indicates

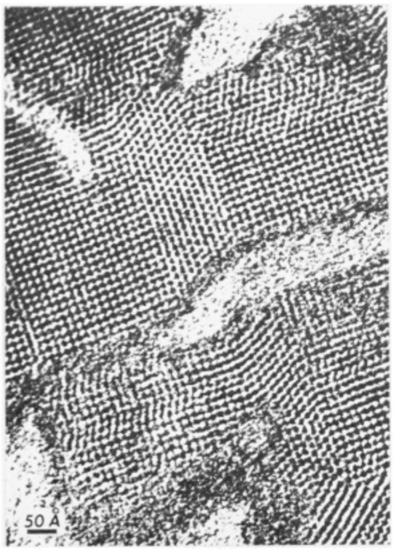

Figure 3. Image of epitaxally grown $(AlPcF)_n$ crystallites giving evidence of the vertical orientation of the molecules.

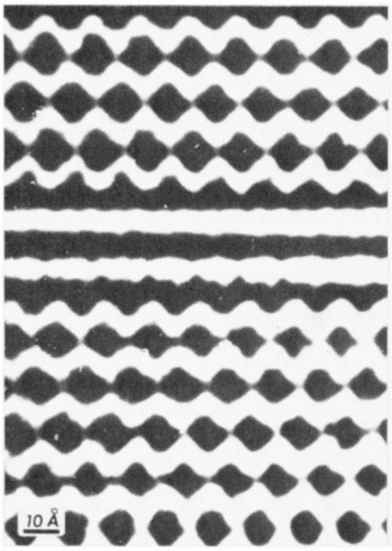

Figure 4. Photographically averaged image of an epitaxially grown crystallite of $(AlPcF)_n$ showing partially developed quatrefoils.

that the lengths of the molecular chains are fairly constant. In view of the 120–150-Å chain length found in the nonepitaxial crystallites and the density of the crystallite portions of the images, it is likely that the molecules are about 120 Å long.

A photographically averaged high-resolution image of an epitaxial crystallite (and thus an epitaxial crystallite image of very high resolution) shows rows of shapes that can be interpreted as being partially developed quatrefoils (Figure 4). Since the phthalocyanine ring has a quatrefoil outline (because of its four benzo rings), it is apparent that the rings are eclipsed.[24] This eclipsed conformation is not surprising because the interring spacing in $(AlPcF)_n$, 3.66 Å, is greater than the minimum value thought necessary for an eclipsed conformation in cofacial phthalocyanine polymers, ~3.5 Å.[10] Further, as already noted, the rings in $(GaPcF)_n$ are eclipsed.[10]

Electron diffraction data for the normally sublimed crystallites show that their unit cell is tetragonal with $a = b = 13.37$ Å and $c = 3.6$ Å. Diffraction data for the epitaxial crystallites show that they have the same a and b cell constants and it is concluded that the normal and epitaxial growth processes yield the same type of crystal.

Figure 5. Image of vacuum-synthesized $(SiPcO)_n$ crystallites showing the diversity of lengths of the unbroken lattices.

These diffraction data indicate that the c-axis of the crystallites is parallel to the long axis of the polymer molecules and provide further support for concluding that the rings of the molecules are eclipsed.

The process by which $(AlPcF)_n$ sublimes is unknown. It could entail sublimation of entire polymer chains, i.e., chains of 30–40 rings. Alternatively, as suggested earlier,[5] it could involve depolymerization of the chains to short oligomers or the monomer, sublimation of the species formed, and, finally, repolymerization of these species.

$(SiPcO)_n$. From earlier data,[13] it is apparent that vacuum-synthesized $(SiPcO)_n$ is composed of nonacicular crystallites and, as stated above, that the molecules in these crystallites are parallel. Consistent with this, images of the preparations of the vacuum-synthesized $(SiPcO)_n$ show that some of the crystallites in these preparations lie with their molecules in a horizontal orientation and also that the molecules in the crystallites are parallel. In addition, the images show that some of the crystallites are agglomerated (Figure 5).

The diversity in the lengths of the unbroken lattices in these images indicates that the lengths and hence molecular weights of the chains vary considerably. Since no other structural differences in the crystallites are apparent, it is concluded that they are chemically homogeneous.

Images of the films formed by heating $(SiPcO)_n$ show that they are composed of platy crystallites lying horizontally. Further, they indicate that the crystallites contain phthalocyanine rings that are arranged in vertical stacks and that the rings are parallel to the film plane (Figure 6). The low contrast in these images suggests that the ring stacks are short. It is estimated that they contain about 10 rings and that the variation in the number of rings per stack is not more than four. The unit cell of these crystallites appears to be tetragonal.

While it is not certain, it may be that these films are composed of $(SiPcO)_n$ crystallites in which the molecules are vertically oriented. If so, the fact that they are tetragonal is not surprising because bulk $(SiPcO)_n$ that has been fractionally oxidized and then reduced, is tetragonal.[25]

If these films consist of $(SiPcO)_n$ crystallites, the process by which they are formed is of interest. It could entail, as with $(AlPcF)_n$, sublimation of entire polymer chains, i.e., chains of about 10 ± 4 rings. Alternatively, it could entail hydrolytic depolymerization of the chains to short hydroxy-capped oligomers or the hydroxy-capped monomer

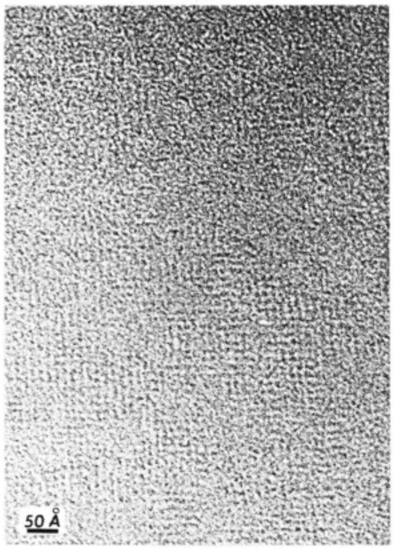

Figure 6. Image of crystallites formed by heating (SiPcO)$_n$.

(HO(SiPcO)$_n$H or SiPc(OH)$_2$), sublimation of the species formed, and, finally, repolymerization of the sublimed species. It could also involve the thermal depolymerization of the chains to SiPc=O and sublimation and repolymerization of this species. If one or more processes like these are involved, the low efficiency of the film formation process and the thinness of the films are understandable.

Additional Studies. Preliminary work has yielded images of films formed by heating the cofacial naphthalocyanine polymer (SiNcO)$_n$[26] and collecting the condensable vapors on KCl. These images show that the films are composed of platy crystallites lying horizontally. They indicate that the crystallites contain vertical ring stacks and that the rings are parallel to the film plane. The unit cell of the crystallites is apparently tetragonal. On the basis of the data available, it is thought that these films may be composed of crystallites of (SiNcO)$_n$ in which the molecules are oriented vertically.

Summary. Images of films of (AlPcF)$_n$ formed by vapor deposition on KCl show crystallites in which the molecules are oriented vertically. A photographically averaged image of one of the crystallites shows that its rings are eclipsed.

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Registry No. (AlPcF)$_n$, 74018-71-6; (SiPcO)$_n$, 39114-20-0.

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Notes

Crystallization in Polyproline and Gelatin Blends by X-ray Diffraction of Stretched Films

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Introduction

From X-ray diffraction two solid-state conformations I and II have been found for polyproline. Form I[1] is a right-handed helix having $3^{1}/_{3}$ residues per turn with all cis peptide bonds while form II[2,3] is a left-handed 3-fold helix with all trans peptide bonds.

Gelatins may be regarded as water-soluble denaturation products from collagen.[4] The native collagen molecule contains three polypeptide α-chains each about 1000 amino acids long and with a triplet repeat scheme of [glycine-X-Y]$_n$ where X is frequently proline and Y hydroxyproline.[5] The three α-chains are thought to have a conformation based on the polyproline II structure but are further coiled into a right-handed triple-helix structure.[6] A given gelatin contains a characterizing spectrum of collagen molecule parts which may include whole α-chains (α-gelatin), co-