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Communications to the Editor

Polyacetylene Single Crystals

Polyacetylene is a semiconducting organic polymer that can be brought to near-metallic conductivity by reaction with a wide range of oxidative or reductive doping agents. The discovery of doping-induced conductivity in 1977[1] triggered an enormous increase in polyacetylene research, whereby today polyacetylene is the most widely studied of the conducting polymers. Past investigations have focused primarily on silvery, free-standing films prepared by polymerizing gaseous acetylene on a layer of concentrated Ziegler–Natta catalyst solution, as reported by Shirakawa et al.[2] in 1971. Such polyacetylene films consist of a mat of tangled semicrystalline fibers, typically 10–30 nm in diameter, which provide an overall film density of about 0.4 g/cm^3. It is the inhomogeneous, insoluble, and poorly characterized nature of this material that has presented the major impediment to understanding the fundamental electrical and electronic properties of pristine and doped polyacetylene. We have attempted to rectify these shortcomings by developing methods for preparing well-defined forms of polyacetylene. In a recent communication[7] we reported the synthesis of soluble polyacetylene graft copolymers. In solution, these polymers provide a unique opportunity to study the single-chain properties of polyacetylene. We presently report on another form of polyacetylene, single crystals, which have been prepared from a solution of polyacetylene block copolymer.

Diblock copolymer of atactic polystyrene ($M_n = 1 \times 10^5$, $M_w/M_n < 1.06$) and polyacetylene, designated PS$_{100}$–PA, was prepared by the previously reported polyacetylene grafting reaction.[7] Acetylene was polymerized at −78 °C in toluene with a $Ti(OC_4H_9)_4/Al(C_2H_5)_3$ catalyst in the presence of polystyrene carrier polymer. Each carrier polymer chain contained a single terminal methyl ketone functionality. Grafting is effected by the nucleophilic attack of a growing polyacetylene molecule on the electrophilic ketone of the carrier polymer. Following reaction, the PS$_{100}$–PA solution was kept at low temperature for about 1 h and subsequently stored at room temperature.

Figure 1A illustrates the visible absorption spectrum obtained from PS$_{100}$–PA immediately after reaction (solid curve). The observed spectrum is consistent with that reported for *cis*-polyacetylene[8] and shows little evidence of the trans isomer. Over a period of 2 days the trans content increased to a constant value, as also shown in Figure 1A (dashed line). Such room-temperature isomerization has also been reported for thin-film polyacetylene.[9]

Homopolystyrene was extracted from sample PS$_{100}$–PA, and the purified and dried diblock copolymer was examined by infrared spectroscopy and wide-angle X-ray scattering. IR spectra of polystyrene, PS$_{100}$–PA, and polyacetylene film prepared at −78 °C by the method of Shirakawa are presented in Figure 1B. The agreement in relative band intensities between the polyacetylene in PS$_{100}$–PA and the thin film reflects a similarity in cis content between these samples. On the basis of the infrared results and the knowledge of the carrier-polymer molecular weight, the polyacetylene number-average molecular weight in PS$_{100}$–PA was estimated to be $M_n \simeq 6 \times 10^4$. This is consistent with our previously reported values for soluble polyacetylene graft copolymers.[7]

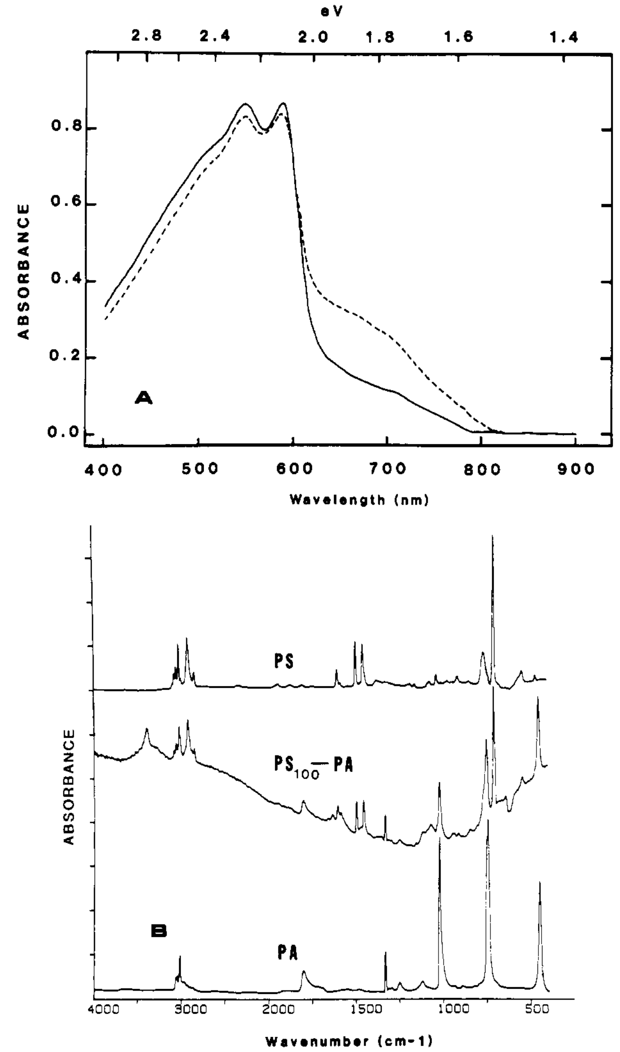

Figure 1. (A) Visible absorption spectrum of a suspension of PS$_{100}$–PA in toluene immediately following preparation at −78 °C (solid curve) and following 2 days at 25 °C (dashed curve). The shoulder at high wavelengths in the latter spectrum results from a partial trans isomerization of the initially *all-cis*-polyacetylene. (B) Infrared absorption spectra of polystyrene (PS), PS$_{100}$–PA diblock copolymer, and polyacetylene film (PA) prepared by the method of Shirakawa et al.[2-4] at −78 °C and stored at room temperature.

The crystalline structure and properties of PS$_{100}$–PA were examined by X-ray and electron diffraction and transmission electron microscopy. Figure 2A illustrates the X-ray diffraction powder pattern obtained from this diblock copolymer. The lattice spacings associated with the Debye rings are listed in Table I. Two electron micrographs of *cis*-polyacetylene single crystals characteristic of PS$_{100}$–PA (containing homopolystyrene) are presented in Figure 3. An electron diffraction pattern was taken from the area defined by the selected area diffraction aperture and is shown in Figure 2B; the electron diffraction spacings are also given in Table I.

The results presented in Figures 1–3 and Table I clearly demonstrate that sample PS$_{100}$–PA is composed of polystyrene and 0.1–1-μm size single crystals of polyacetylene. In the remainder of this report we will briefly discuss the molecular parameters involved in producing polyacetylene

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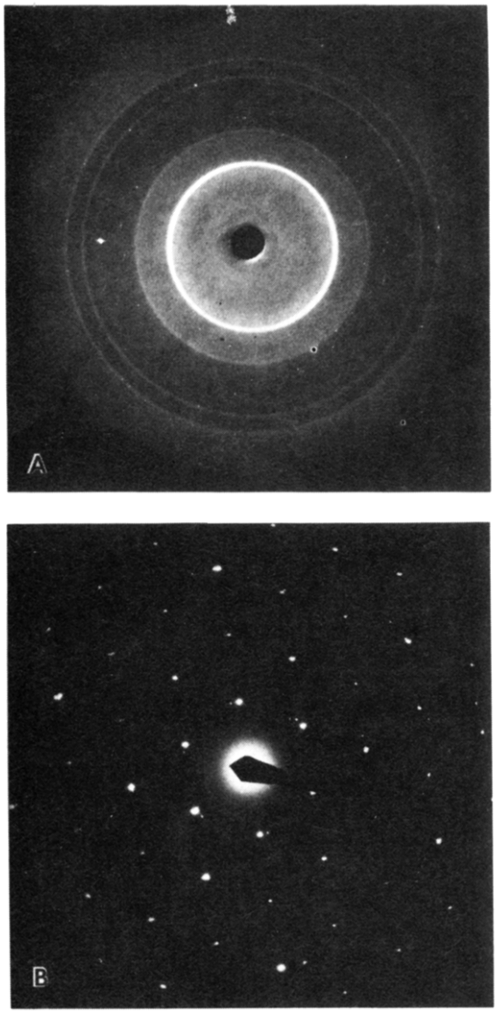

Figure 2. (A) X-ray powder pattern taken from PS_{100}–PA diblock copolymer following extraction with methanol/HCl. (B) Polyacetylene single-crystal electron diffraction pattern obtained from the specimen indicated in Figure 3. Diffraction spacings are listed in Table I.

Table I
Measured and Calculated Lattice Spacings

d, Å			
ED	X-ray	calcd [a]	(*hkl*)
4.44	4.42	4.43	(100)
	3.27	3.27	(101)
2.56	(2.57) [b]	2.56	(110)
	2.43	2.42	(002)
	2.27	2.26	(111)
2.23		2.22	(200)
	2.01	2.02	(201)
1.69		1.68	(210)
1.48		1.48	(300)

[a] Hexagonal lattice with $a = 5.12$ and $c = 4.84$ Å.
[b] Weak reflection.

single crystals of the type depicted in Figure 3 along with a preliminary analysis of their crystal structure.

The morphologies of block and graft copolymers have been extensively studied for over 2 decades. Representative experimental studies of these systems can be found in ref 10–13. Helfand[14] and Leibler[15] among others have provided a clear picture of the molecular interactions reponsible for the unique phase diagram that characterizes this class of polymers. Unlike homopolymer blends, block copolymer phase separation is restricted to a microscale, due to the covalent bond between adjacent blocks. This necessitates placement of the block–block junction at the phase boundary while maintaining uniform phase densities and low free energy molecular conformations.[14] In general, block molecular weights determine domain sizes while the overall block copolymer composition establishes the phase geometry. Although the principles underlying block copolymer microphase separation in solution are similar to those for the bulk case, the influence of solvents on such phase diagrams has only recently received attention.[13,16]

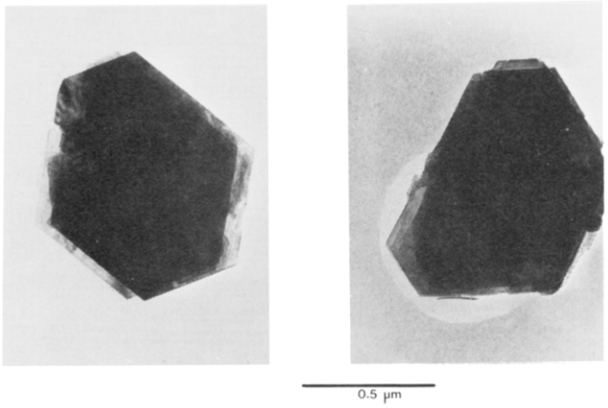

Figure 3. Representative transmission electron micrographs of PS_{100}–PA, containing excess polystyrene carrier homopolymer. The polyacetylene single crystals were very lightly stained with OsO_4 in order to enhance the phase contrast. A diffraction pattern was obtained from the area delineated by the selected area diffraction aperture and is presented in Figure 2B.

We have attempted to exploit the morphological control afforded by block and graft copolymers in manipulating the structure of what has invariably been reported as an intractable polymer. In our previous report[7] it was demonstrated that a graft-block copolymer containing 15–20% by weight polyacetylene contained amorphous microdomains which dissolved upon the addition of a suitable solvent. We have presently shown that a diblock copolymer containing 35–40% by weight polyacetylene undergoes phase separation from solution to produce lamellar single crystals (see below). Reducing the weight fraction of carrier polymer reduces the interfacial surface area required to satisfy the packing constraints outlined above, which allows the formation of the observed crystalline phase. These results are consistent with the upper critical solution temperature (UCST) phase behavior exhibited by block copolymers characterized by van der Waals interactions.[14,15]

The diffraction results obtained from PS_{100}–PA can be described by a hexagonal lattice with $a = 5.12$ and $c = 4.84$ Å. As listed in Table I, all the electron and X-ray reflections are accounted for with this structure. *cis*-Polyacetylene has been reported previously to crystallize in a cis-transoid conformation in an orthorhombic unit cell with $\rho = 1.16$ g/cm^3.[17–19] The placement of cis-transoid chains in the hexagonal lattice assigned here would result in an unreasonably low crystal density of 0.79 g/cm^3. Instead, we suggest that these crystals contain distorted cis-cisoid polyacetylene in a 2* 3/1 helical conformation[20] (see below), which would result in a calculated crystal density of 1.18 g/cm^3. A more detailed crystallographic analysis will be presented elsewhere.

Hashimoto et al.[12] have experimentally determined the interfacial area occupied by a polystyrene chain (S/N) of a diblock copolymer containing a lamellar microstructure and have found that for $M_n = 1 \times 10^5$, $S/N \approx 800$ Å^2. Therefore, in order to obtain the lozenge-shaped crystals of PS_{100}–PA depicted in Figure 3, the polyacetylene must chain fold, since S/N for a single unit cell is only 22.7 Å^2. On the basis of a molecular weight of 6×10^4, distributed over an average of 35 folds, the fold length can be estimated to be $\sim$100 Å, which is consistent with the transmission electron micrographs. These findings are not surprising since polymers generally crystallize from solution by chain folding with a characteristic fold length of $\sim$100 Å.[21,22] It should be noted that Lieser et al.[18] have previously proposed the concept of chain folding with respect to polyacetylene. Such a crystal structure may also explain the room-temperature isomerization reflected in Figure 1; that is, it derives from amorphous material present at the fold surfaces.

Many polymers are known to crystallize in helical conformations, including the polydienes,[23] which are structurally related to polyacetylene, and Natta and Corradini[24] have empirically derived a set of principles concerning the crystallization of such macromolecules. In particular, they have shown that the conformation in a crystal approaches that corresponding to the minimum potential energy of the isolated helical chain. Recently, Cernia and D'Ilario[25] have made potential energy calculations for isolated *cis*-polyacetylene chains and concluded that this molecule should assume a distorted cis-cisoid helical conformation, similar to the one we have assigned to our crystals. We suggest that prior to crystalization the *cis*-polyacetylene in PS$_{100}$–PA existed in solution as such a helix.

What then accounts for the dramatic difference between the previously reported crystal structure of *cis*-polyacetylene[17-19] and that described above? We propose the following explanation.

Although both crystal packing modes exhibit nearly the same density (see above), the hexagonal structure contains 36% more (00l) surface area per unit cell than those previously published. Chain folding also increases the effective (00l) crystal surface area per molecule so that decreasing the fold length results in an increase in the interfacial surface area per polyacetylene chain. It is this (00l) crystal plane that must accommodate the polystyrene blocks, and we believe that the cis-transoid crystal structure cannot provide a sufficient (00l) surface area to permit the formation of a stable crystalline phase in sample PS$_{100}$–PA. For the same reasons PS$_{200}$–PA and PI$_{200}$–PA, which contained twice the carrier polymer molecular weight, were found to be soluble. As stated, it is our contention that the equilibrium conformation of isolated *cis*-polyacetylene is a distorted cis-cisoid helix and not planar cis-transoid, although it is the latter form that appears to be produced by Ziegler–Natta polymerization.

In the case of the Shirakawa synthesis, polymerization is followed by immediate crystallization which dictates a crystal structure based upon the planar cis-transoid conformation. On the other hand, crystallization of initially formed PS$_{100}$–PA is inhibited by packing restrictions associated with the carrier block and this, we believe, allows the polyacetylene block to attain an equilibrium helical conformation in solution. Crystallization can then occur with a hexagonal crystal structure because this permits accommodation of the carrier polystyrene.

In conclusion, we have demonstrated for the first time a method of preparing single crystals of polyacetylene. In particular, the *cis*-polyacetylene moiety of a polyacetylene–polystyrene diblock copolymer has been shown to crystallize from solution by chain folding into a hexagonal structure. We propose that these crystals consist of helical polyacetylene chains in a distorted cis-cisoid conformation and that this reflects an equilibrium helical conformation in solution.

Forthcoming reports will address the properties of single-crystalline *cis*- and *trans*-polyacetylene in more detail.

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Registry No. Acetylene–styrene copolymer, 84824-32-8.

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Do Scaling Laws Apply in Moderately Concentrated Polymer Solutions?†

In spite of an enormous amount of experimental work on semidilute polymer solutions, no critical experiment has been performed that can differentiate between competing

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