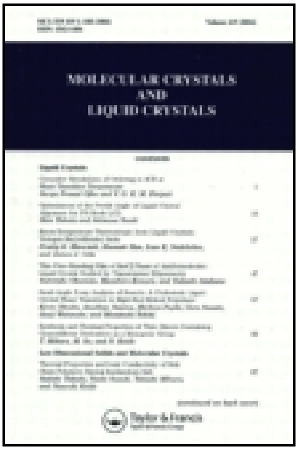

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Polyacetylene: Structure Synthesis Relationships

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POLYACETYLENE: STRUCTURE-SYNTHESIS RELATIONSHIPS

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Abstract. Owing to its extreme intractability, the structure and morphology of polyacetylene is fixed at the time of synthesis. By altering the standard procedures for acetylene polymerization, polyacetylene with different structures and morphologies have been synthesized. Among the products are single fibrils of *trans*-polyacetylene, and also *trans*-polyacetylene which contains few neutral defects. The synthesis of block/graft copolymers offers a particularly attractive method by which the structure and morphology of polyacetylene may be modified. Copolymers were formed with phases ranging from amorphous aggregates to single crystals to sheet-like phases.

Due to its extreme intractability, the structure and morphology of polyacetylene is established at the time of synthesis. Although minor morphological changes can be effected by such techniques as stretch alignment, the most significant post synthetic structural change available remains the thermal isomerization of *cis*-polyacetylene to the trans isomer.

Variations in polymerization catalysts and synthetic procedures can lead to dramatically varying physical forms of polyacetylene. Previous work by Shirakawa and Ikeda[1] has demonstrated that changes in catalyst concentration leads to polyacetylene samples ranging from silvery films (catalyst concentration ~ $10^{-1}M$), to a foam product ($10^{-2}M$), to a black powder ($10^{-6}M$). In each case a characteristic fibrous microstructure was obtained.

We have prepared polyacetylene at room temperature using catalyst concentrations considerably more dilute ($10^{-6}M$) than those previously reported.

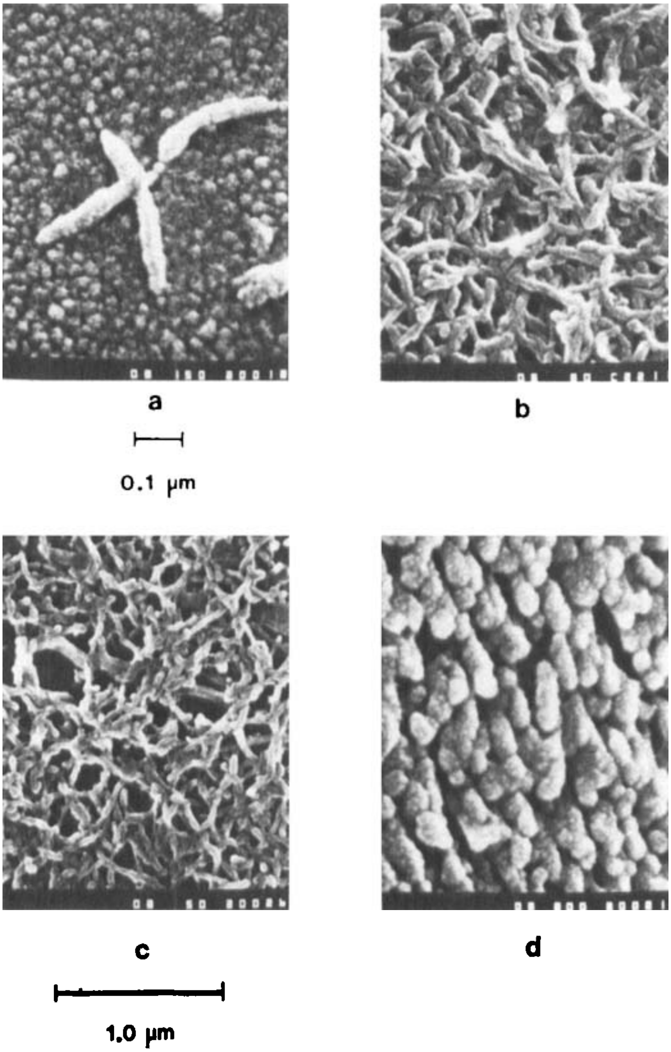

Figure 1. SEM micrographs of polyacetylene single fibrils. **a**, isolated fibrils; **b**, mat of fibrils obtained by solvent evaporation; **c**, mat obtained by filtration of a suspension of fibrils; **d**, ordered structure obtained by evaporation of a concentrated suspension of fibrils onto a gold coated microscope grid.

Polymerizations at these extremely dilute catalyst concentrations are quite susceptible to trace impurities, and can vary considerably between preparations. By conducting the polymerization in a 10% solution of polyisoprene in toluene, the product obtained did not consist of the typical tangled mat of fibrils, but rather was composed of individual fibrils of *trans*-polyacetylene (Fig. 1). The fibrils, typically 3000Å in length and 400Å in diameter, were concentrated by either evaporation or filtration to yield mats of fibrils which are remarkably similar to the typical product of a Shirakawa polymerization. The most striking result was obtained when a concentrated suspension of these fibrils was evaporated onto a gold coated microscope grid. The fibrils, nearly uniform in size, adsorbed strongly to the surface, forming a packed array resembling packed cylinders.

We have found that block and graft copolymerization of polyacetylene represents a more direct method of modifying the structure and morphology of polyacetylene than that described above. Several routes to these materials have been explored.[2–9] Our work[2–5] has concentrated on preparing block copolymers *via* termination reactions. In these polymerizations, the growing polyacetylene chains are intercepted by graft sites such as aldehydes, ketones, or expoxides, thus terminating the polyene chain growth and chemically binding the polyene chain to a carrier polymer such as polyisoprene or polystyrene. This procedure has two important advantages: the chemical and electronic structure of the polyacetylene chain remains unaltered, and more importantly, the procedure provides for the control of the polyacetylene block molecular weight.

Variations in the polyacetylene block molecular weight are obtained by varying the ratio of monomer to graft sites in the polymerization. At low ratios of monomer to graft site, the UV/vis spectra of the products (Fig. 2) resemble those of low molecular weight polyenes.[10] (The carrier polymer is transparent in the spectral region being examined). As the ratio is increased, the absorption maximum for the product shifts to lower energies, indicative of the increased conjugation length. Finally, spectra typical of *trans*-polyacetylene are obtained at the highest level of monomer to graft site.

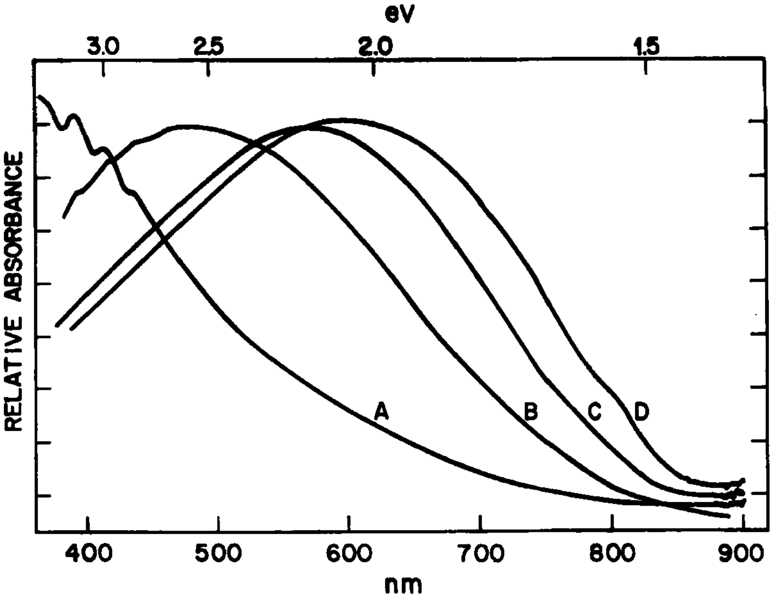

Figure 2. UV/vis spectra of polyacetylene/polystyrene block copolymers. The ratio of acetylene to graft sites was increased from A to D. (From reference 5).

Samples of solubilized graft copolymer containing polyacetylene compositions below a critical value are easily handled in solution. They are stable in the absence of air for many months in solvents such as toluene, hexane, and carbon tetrachloride, and can easily be filtered to give solutions suitable for light scattering. A recent light scattering study[11] of one of these copolymers revealed that these macromolecules tend to aggregate in solution, forming micellular domains containing a polyacetylene core. The radius of gyration for the polyacetylene portion of the micelle was measured to be 350 ± 70Å and the overall size of the micelle was found to be 1050 ± 200Å

If the polyacetylene chain length in a graft copolymer is increased beyond a critical value, crystalline products are obtained from the polymerization. Previously

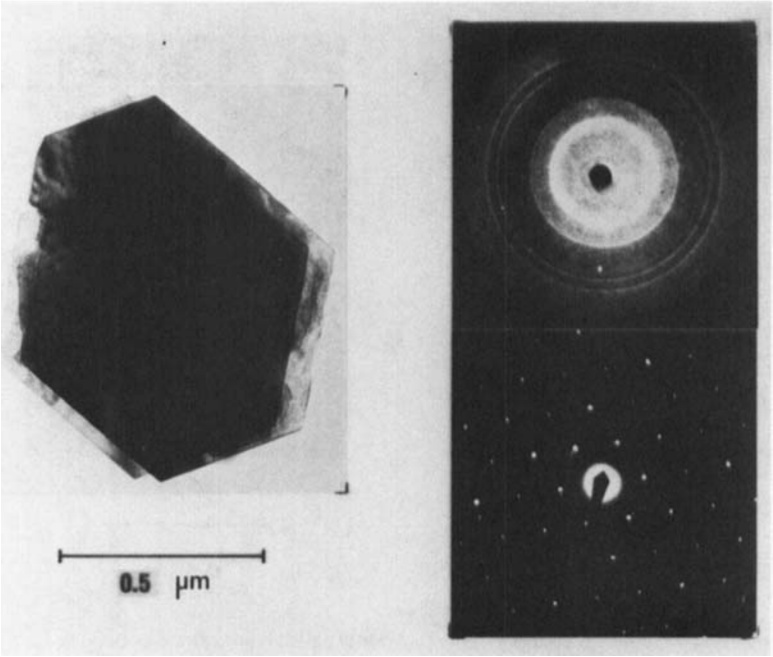

Figure 3. Transmission electron microscopy micrograph of single crystals of polyacetylene. The corresponding X-ray and electron diffraction patterns appear at right, and are consistent with a cis, cisoid structure for polyacetylene.

we reported[4] that a graft polymerization carried out at low temperatures yielded lamellar single crystals of *cis*-polyacetylene surrounded by the carrier polymer to which it is chemically bound (Fig. 3). Both the X-ray and electron diffraction results from these crystals were inconsistent with the normal cis, transoid structure for polyacetylene, but were best explained by a cis, cisoid chain conformation.

In general, we have found that a graft polymerization which results in crystallization produces a *distribution* of polyene chain lengths, and a mixture of products. The corresponding mixture of structures has proven difficult to characterize and interpret. An example of this situation is shown in Figure 4. These micrographs depict the product of a polymerization carried out to an acetylene composition sufficient to cause the copolymer to precipitate from solution.

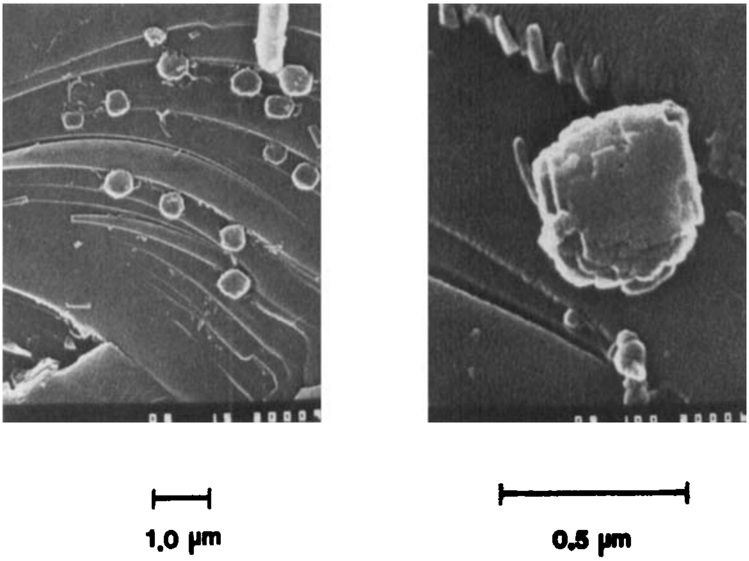

Figure 4. Lamellar phase of a polyacetylene/polystyrene block copolymer. Note the mixture of products.

The left panel shows a fractured lamellar phase of the copolymer. Selected area diffraction from intact portions of the sheet reveals a radiation stable trans, transoid structure. However, the small rectangular structures lying on the sheet were unstable in the electron beam, producing a transient diffraction pattern which was different from that of conventional *trans*-polyacetylene. Obviously this mixture of structures complicates any interpretation of X-ray scattering measurements.

Further increases in the polyacetylene block length leads to a return of the fibrous morphology typical of homopolyacetylene. This change occurs at polyacetylene contents as low as 50% when polystyrene or polyisoprene are used as the carrier polymer.

In graft copolymerizations, it is preferable to alter the polymerization conditions from that typically used to prepare thin films of polyacetylene. Best results are obtained when the catalyst is prepared *in situ*, in the presence of the monomer, graft sites, and carrier polymer. When the same procedure is applied to acetylene homopolymerizations, *trans*-polyacetylene can also be prepared at room temperature. The product is obtained as a fine suspension of polyacetylene which can be concentrated by evaporation to give thin silvery films suitable for spectroscopic measurements.

The most significant property of this material is that it contains a very low level of neutral defects. During the thermal isomerization of *cis*-polyacetylene, numerous free spins (~ 1/3000 C atoms) are generated.[12] Typical *trans*-polyacetylene samples prepared at room temperature contain an order of magnitude fewer spins (1/47,000 C atoms), and are characterized by a broad 5G linewidth. Thermal treatment of the samples results in small increases in the number of spins and a sharpening of the ESR linewidth to 3.8G. Previous ESR measurements on solubilized polyacetylene block copolymers[5] provided similar results, e.g. a low level of neutral defects (1/300,000 C atoms) and a 5G linewidth.

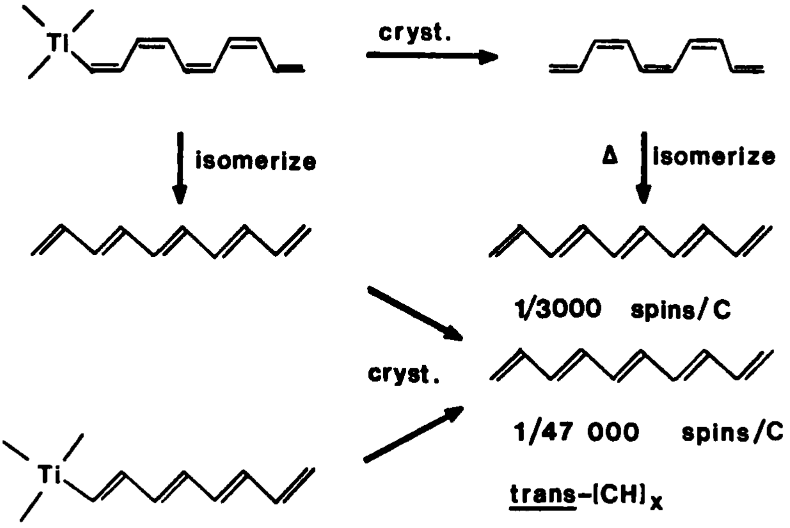

Figure 5. Simple mechanisms for the production of low spin *trans*-polyacetylene.

Since the rate of cis-trans isomerization for polyacetylene is slow in the solid state, it is clear that the trans isomer must be generated prior to crystallization (Fig. 5). Two simple mechanisms can be proposed. In the first, the normal cis insertion mechanism generates *cis*-polyacetylene; however prior to crystallization, the isomerization step occurs. Since the isomerization takes place in solution, fewer defects are expected. Alternatively it is possible that by preparing the catalyst *in situ*, a chemically different catalyst is formed which yields the trans isomer directly.

By understanding the fundamentals of catalyst chemistry, it is possible to augment our control over polymerization processes. This must be coupled with an understanding of the physical properties of the resulting polymers in order to obtain the product in its desired form. This is particularly true for intractable polymers such as polyacetylene. We anticipate that further work on polymerization methods and catalysts should provide the mechanism for obtaining new and interesting structural forms of these materials.

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