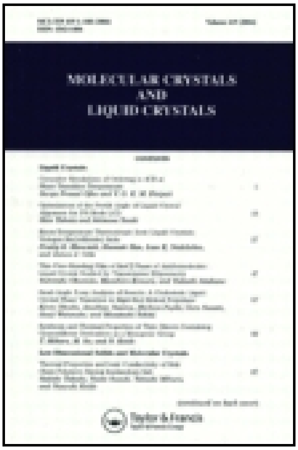

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Morphology of Pristine Poly (Acetylene) Obtained by Luttinger's Catalyst

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MORPHOLOGY OF PRISTINE POLY(ACETYLENE) OBTAINED BY LUTTINGER'S CATALYST

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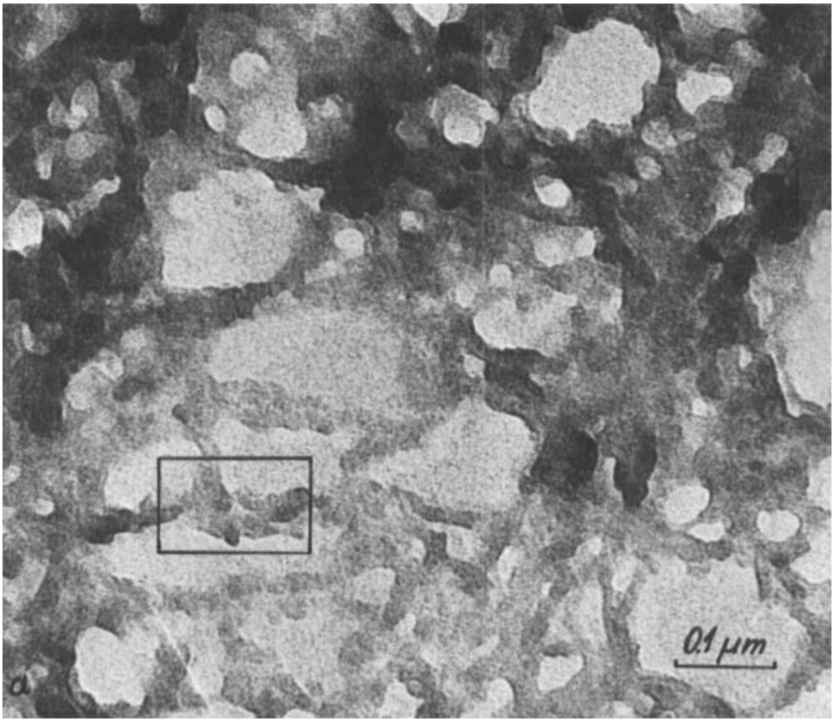
Poly(acetylene) was prepared as freestanding mechanically stable film using Luttinger's catalyst. The cis isomer formed initially is stable during storage at room temperature over many days. Electron micrographs show a loose conglomerate of irregularly shaped platelets with a diameter of several ten nanometers and a thickness of less than 10 nm. Electron diffraction on the cis form shows the chain axes perpendicular to the lamella surface. Annealing converts the polymer into the trans isomer. Morphological changes are not observed. The chains however tilt in the course of the phase transition associated with the isomerization. Films of the material obtained by Luttinger's catalyst show essentially the same electrical and mechanical behavior as the ones prepared by the Shirakawa-technique.

The majority of investigations on poly(acetylene) reported in literature is performed with a polymer prepared by blowing acetylene gas onto a surface of toluene solution of a Ziegler catalyst. This method was first described by Shirakawa[1] and has in the meantime almost become standard. Other ways of chemical synthesis of poly(acetylene) seem scarcely to find interest. Therefore we studied morphology and structure of poly(acetylene) polymerized by means of catalysts due to Luttinger[2] in comparison to the polymer prepared by Shirakawa's method.

Concerning the polymerization and also the purification of the polymer it is worth to mention that the use of Luttinger's catalyst has some advantages. For our investigations we selected the catalyst complex of $Co(NO_3)_2$ and $NaBH_4$. Both compounds were dissolved separately in ethanol. After the solutions were poored together a stable bright red complex is formed at temperatures lower than -30°C. Exposure of this solution to acetylene gas yields immediately the polymer as the cis isomer. For electron microscopical investigations we prepared poly(acetylene) both as suspensions or films. In the first case we get an intensely red very fine dispersed precipitate which after a few minutes coagulates to black flakes. The flakes sediment but can be redispersed by ultrasonic treatment of the suspension even after storage at room temperature over more than two weeks. By visual inspection the redispersed suspension cannot be distinguished from a red solution, indicating that no irreversibel aggregation of individual particels has taken place. Also no color change of the suspension is observed after the two weeks period. Although the catalyst has not been removed from the suspension the complex is inactivated due to the temperature rise from at least -30°C to room temperature. Under the same conditions a poly(acetylene) suspension obtained by a Ziegler catalyst converts to the trans isomer to such an extent that already after a shorter storage the color of a redispersed suspension has definitely changed to violet.

Poly(acetylene) films are made by performing the reaction in thin laminar films of catalyst solution spread out onto a glass substrate or by deposition of a suspension on a flat substrate. After drying these films have a remarkably high strength and are easy to handle during electon microscopical preparation. For the purpose of morphological studies the film thickness is aimed to be in the region of 50 nm. Those films also are intensely red colored and become dark blue after annealing at temperatures higher than 110°C, indicating the formation of the trans isomer. For most of our observations on trans films the exact annealing conditions were 150°C for 2h.

Figure 1a shows a transmission electron micrograph of a thin film of poly(acetylene) obtained by Luttinger's catalyst. We never could observe the slightest difference of appearance between films of the cis and the trans isomer for both the Luttinger and the Ziegler catalysed polymer. The image shows a conglomeration of lamellae which in some areas by chance form ribbons. The original polymer as long as solvent is still present has the form of a sponge which afterwards collapses during evaporation of the solvent. To illustrate this kind of morphology, in Figure 1b a drawing of a small area is excerpted from Figure 1a.



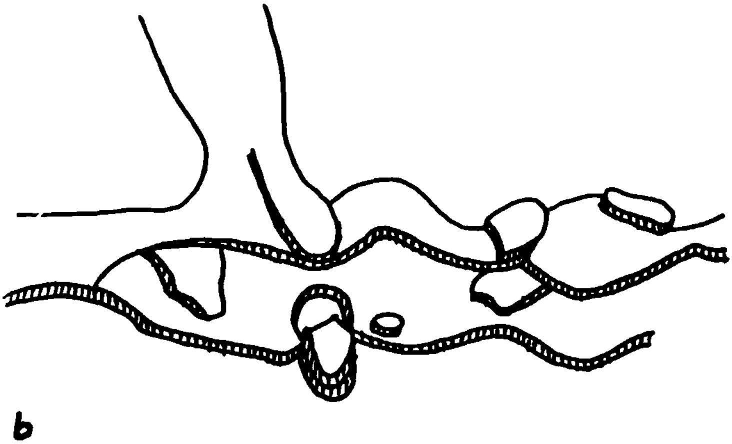


FIGURE 1 a. Transmission electron micrograph of a thin film of poly(acetylene) obtained by Luttinger's catalyst
b. Drawing of a small area depicted from Figure 1a

The same type of morphology occurs in Ziegler catalysed polymer too, as demonstrated in Figure 2. In the transmission electron micrograph the ribbon is clearly resolved as an aggregation of single lamellae. It differs clearly from the morphology of a polymer fiber.

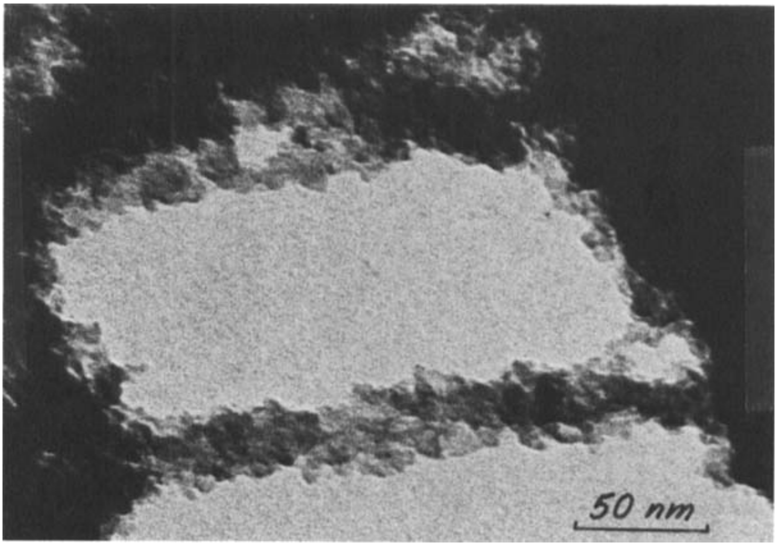


FIGURE 2 Transmission electron micrograph of a ribbon consisting of aggregated single lamellae in poly(acetylene) obtained by Shirakawa's technique

For the final decision whether such strings as shown in Figures 1 and 2 are are fibers or not, it is necessary to know the chain direction with respect to the morphology. The best experimental proof for this question is to carry out electron diffraction from small specimen areas. Figure 3 illustrates expectations for such experiments with fibers, isolated polymer single crystals and their agglomerations, when their orientational distribution is at random round an axis perpendicular to a flat substrate.

The most important feature of a fiber diagram are layer lines,the distance of them representing the length of the chain repeat. For a single crystal in which the polymer chains generally are oriented perpendicular to the lamella surface a point diagram is expected, all reflections of it belonging to only one crystallographic zone (when the crystallographic c-axis is assigned to the chain direction, the diffraction pattern shows the hk0 reflections). If instead of an individual crystal, an ensemble of them distributed round the c-axis is exposed to the electron beam, each hk0 reflection degenerates to a circle. The diffraction pattern looks similar to a powder pattern, but in contrast to it, hkl reflections with l ≠ 0 are missing.

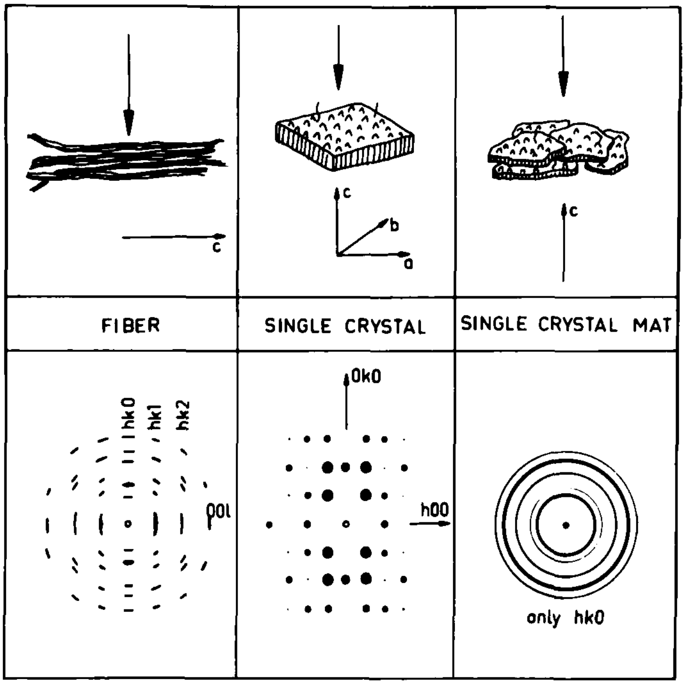


FIGURE 3 Schematic drawing of electron diffraction patterns for different polymer morphology

For cis poly(acetylene) an electron diffraction pattern always is of the latter type, even if a sample area of only 100 nm in diameter is depicted (Figure 4). All the reflections can be indexed as hk0. From this and other diffraction patterns[3] not presented here, an orthorhombic unit cell is derived with parameters similar to a set reported from x-ray measurements in literature[4]. More important than the coincidence of x-ray and electron diffraction data is the occurance of a hk0 pattern under the usual conditions of electron diffraction. Therefore only a perpendicular orientation of the chains with respect to the lamella surface is compatible with the experimental findings.

From the point of view of polymer morphology in general poly(acetylene) too behaves quite similar to other polymers where lamella like morphology with the chains perpendicular to the surface is predominant. The small size of the crystallites (5 to 10 nm in thickness and a few 10 nm in lateral extension) is mainly due to the fast polymerization reaction and the insolubility of the polymer. For example a similar morphology is observed for polyethylene, as-polymerized with Ziegler catalyst from the gas phase[5]. In addition to the similar morphology, chainfolding is present in poly(acetylene) as well. The average chain length exceeds the lamella thickness by a factor of roughly 5, so that the same chain has to run several times through one crystallite[8]. Some chains also may connect different crystallites as so called "tie-molecules". A chain fold has to have cis configuration and cannot change configuration during isomerization.

Isomerization of pristine poly(acetylene) obtained by Luttinger's catalyst requires annealing of the sample at temperatures above 110°C, as mentioned earlier, and is always associated with a crystallographic phase transition[6].

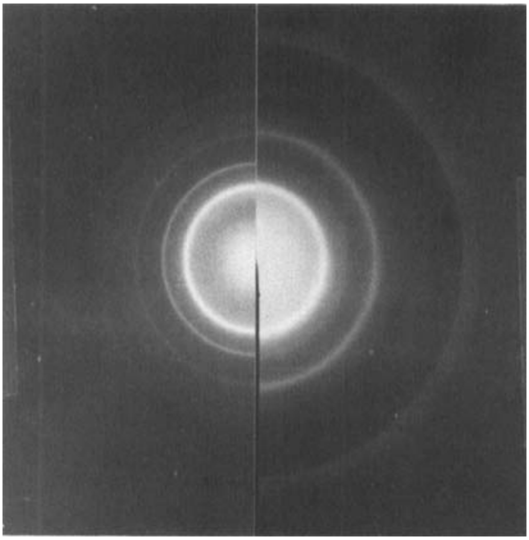


FIGURE 4 Electron diffraction patterns of cis- (left) and trans- (right) poly(acetylene) at beam incidence normal to the specimen

Electron diffraction patterns of the new phase show broadening of the reflections, small shifts of their positions and intensity changes. In addition, a new reflection appears, which can be indexed as a 002 reflection corresponding to the trans chain repeat. The reflection broadening indicates a decrease of coherently scattering areas within individual crystallites and the new 001 reflection is indicative of a chain tilt within the crystalline lamellae. In an earlier paper[6] we derived from our diffraction data a monoclinic primitive unit cell for the trans isomer which in the meantime is supported by packing calculations[7]

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