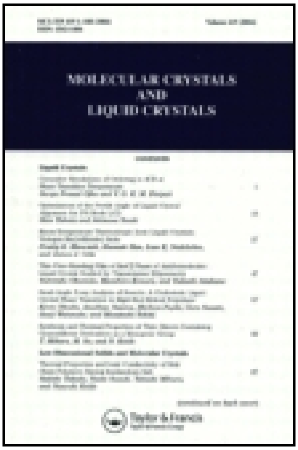

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Properties of $(CH)_X$-Fibers and Films Prepared from 3TFM-TCDT

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PROPERTIES OF $(CH)_x$-FIBERS AND FILMS PREPARED FROM BTFM-TCDT

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Abstract The preparation of $(CH)_x$ starting from bis-(trifluoromethyl)-tricyclo-deca-triene (BTFM-TCDT) allows to produce amorphous films, crystalline single fibers, and fully oriented non-fibrous crystalline films, depending on the preparation conditions. We describe the experimental methods to produce these three types of trans-polyacetylene samples. For a characterization of the material we present X-ray and HEED-patterns, and IR-spectroscopical data. In particular, the fully oriented crystalline films for the first time permit a detailed study of the polarization behavior of the IR-active modes of trans-$(CH)_x$. Our transport studies comprise measurements of the anisotropy of the DC-conductivity in doped and undoped samples and the temperature dependence of the conductivity. The transport behavior and the optical data in our opinion reflect intrinsic properties of crystalline polyacetylene not obscured by the fibrous morphology of previous investigated material.

1.PREPARATION AND MORPHOLOGY

The monomer 7,8-bis-(trifluoromethyl)-tricyclo-[4,2,2,0]-deca-3,7,9-triene (BTFM-TCDT) is prepared by a Diels-Alder reaction of hexafluorobut-2-yne and cyclooctotetraene. This monomer can be polymerized to poly-(BTFM-TCDT) (precursor polymer) using a metathesis catalyst prepared from tetramethyltin and tungsten hexachloride. It is furtheron converted to polyacetylene by a simple thermal treatment[1]. This general preparation route allows a variety of procedures for the synthesis of polyacetylene. The three ways of polyacetylene synthesis we carried out are outlined in Fig.1. If the precursor polymer is converted to polyacetylene under mild conditions (process in first line of Fig.1) over a long period of time (days) we obtain amorphous polyacetylene powder or films depending on the state of the precursor polymer. Films of this kind have been investigated by X-ray diffraction and the results are discussed in detail below.

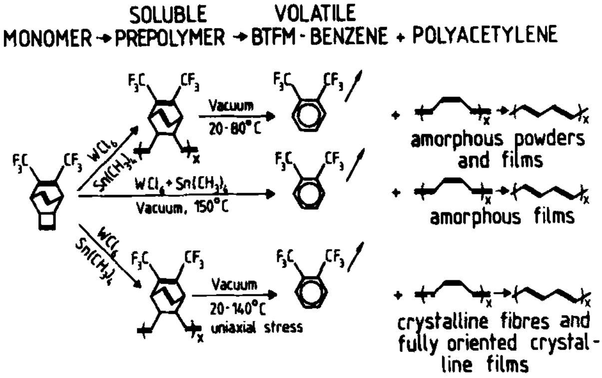

Fig.1 Processes for the synthesis of polyacetylene

Amorphous polyacetylene films can also be prepared by a one step method (process in second line of Fig.1), which proceeds by the polymerization of the monomer and the elimination of hexafluoroxylene in one step[2]. However, the purity of this one step polyacetylene is lower compared to the other two methods (processes in first and third line of Fig.1), as far as residues of the catalyst are concerned. The reason for this is that purification techniques applicable in the other two procedures can not be used in this case.

The conversion of the precursor polymer to polyacetylene is accompanied by a large decrease in volume of the polymer. This results in strong deformations inside the sample, when the conversion is carried out at elevated temperatures. The resulting stress leads to the formation of fibrillar structures in the previously homogeneous precursor polymer film (Fig.2).

Fig.2 SEM picture of stress cracked fibers of polyacetylene

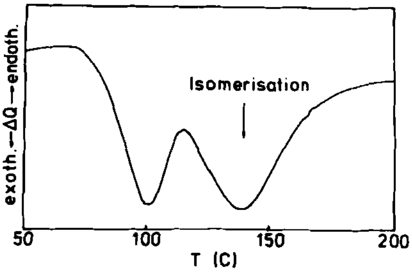

Fig.3 DSC trace of the precursor polymer; heating rate: 40 K/min

High-energy electron-diffraction (HEED) on these fibers document their high crystallinity and a very good orientation of the polyacetylene chains. Based on this observation of stress induced crystallization we produced single fiber polyacetylene[3] as well as fully oriented non fibrous crystalline polyacetylene[4] by applying uniaxial stress onto the precursor polymer fibers or films during the conversion reaction. The elimination of the hexafluoroxylene from the poly-(BTFM-TCDT) leaves the created carbon-carbon double bonds in the cis-form, which are consecutively isomerized to trans at the elevated temperature of the conversion process. We have studied these two processes by Differential Scanning Calorimetry (DSC). A DSC trace for a heating rate of

40 K/min is shown in Fig.3, where the exothermic peak for the elimination of hexafluoroxylene (at 100°C) and the peak originating from the isomerization (at 140°C) are clearly visible. The peak temperatures of these two reactions exhibit a rather strong dependence on the heating rate; both peak temperatures decrease with decreasing heating rate. This variation of the peak location can be used to calculate the respective kinetic parameters of the two reactions. As we know from SEM studies, polyacetylene samples synthesized by the preparation routes described above, have of a homogeneous and compact morphology [2,3,4,9,10].

2.STRUCTURE

Investigations on the structure of fully oriented crystalline and amorphous trans-$(CH)_x$ films were carried out by X-ray and electron diffraction experiments. Films obtained by the procedure described in Fig.1 (process in third line of Fig.1) exhibit a fully oriented highly crystalline arrangement of the polyacetylene chains.

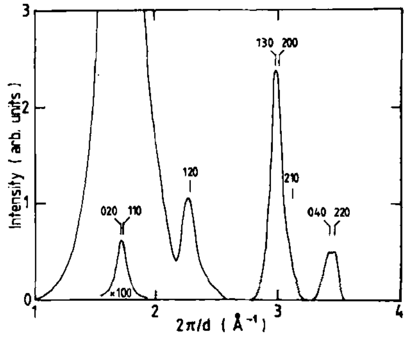

Fig.4 X-ray scan of oriented crystalline trans-$(CH)_x$ in a plane perpendicular to the stretching direction

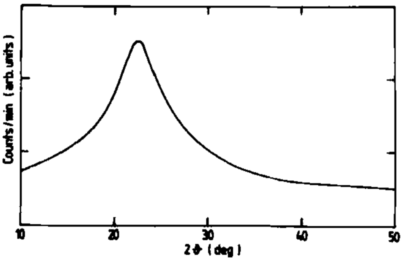

Fig.5 X-ray scan of the amorphous trans-$(CH)_x$

Fig.4 exhibits an X-ray scan in a plane perpendicular to the direction of orientation performed with copper $K\alpha$ radiation ($\lambda = 1.54178$ Å). There is negligible amorphous background scattering indicating the very high degree of crystallinity. Compared to previous results obtained by X-ray diffraction experiments on stretch oriented Shirakawa type polyacetylene[5], the amount of the crystalline portion in our samples is evidently much higher. The dominant reflection with its position at $2\theta = 24.4°$ is composed of the 020 and 110 intensities. It shows a full width at half maximum (FWHM) of 1.65°, which indicates an average crystallite diameter of more than 60 Å. This crystallite size is obtained from the Scherrer equation neglecting the fact of a composed peak. The individual crystallites are precisely aligned with their c-axis parallel to the direction of stretching. In contrast the a and b axis are randomly distributed in the a-b plane. Combined evaluation of the HEED and X-ray measurements[6] gives the following structural parameters assuming a monoclinic unit cell: $a = 4.18(1)$ Å, $b = 7.34(0)$ Å, $c = 2.42(9)$ Å and $\beta = 90.5°$ .A definite decision about the space group can only be made by reliable measurements of the X-ray intensities, especially of the 001 reflections. These kind of studies are currently in progress.

The result of an X-ray scan on an amorphous trans-$(CH)_x$ film produced by the upper most route in Fig.1 exhibit just one broad maximum (FWHM = 6.5°) in the vicinity of the strongest reflection of the crystalline material (see Fig.5). The position of the amorphous halo at $2\theta = 22.3°$, about two degrees below the crystalline 020-110 peak, is predominantly determined by intermolecular distances. Using the Bragg-equation for the angle at the scattering maximum we calculated an average intermolecular spacing of 4 Å. Nevertheless, the values of intermolecular distances and packing densities derived this way should be considered with extreme care, since intramolecular distances will also contribute to the halo.

3. OPTICAL AND TRANSPORT PROPERTIES

The infrared spectrum of pure trans-$(CH)_x$ is dominated by two absorption bands, one at 3011 cm^{-1} which arises from the C-H stretching vibration and the other at 1010 cm^{-1} which is due to the out-of plane C-H deformation vibration. Polarized infrared reflection and transmission spectra of a fully oriented crystalline trans-$(CH)_x$ film are shown in Fig.6 and 7, for parallel and perpendicular polarization of the electric vector with respect to the stretching direction.

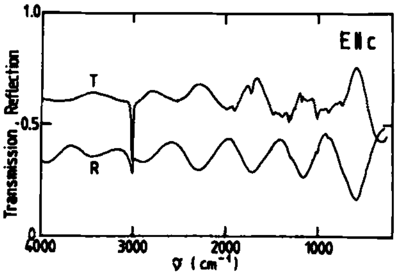

Fig.6 Infrared spectra for polarization parallel to the c-axis

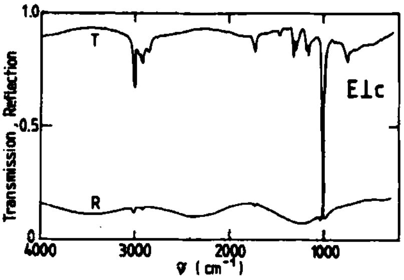

Fig.7 Infrared spectra for polarization perpendicular to the c-axis

The C-H deformation vibration is polarized perpendicular to the chain axis; our best samples showed no absorption in the parallel direction indicating again the precise alignment of the $(CH)_x$-chains. For the C-H stretching vibration one would also expect the absorption only at perpendicular polarization, whereas the infrared transmission data show a slightly higher absorption at parallel polarization. Studies to explain this behavior are in progress. The average infrared absorption is higher for polarization parallel to the orientation direction. From the Fabry-Perot interferences we deduced the refractive indices $n_{\parallel} = 2.66$ and $n_{\perp} = 1.33$. The weak infrared bands above and below 1000 cm^{-1} arise from hexafluoroxylene residues, which can be removed by further heating the sample in high vacuum.

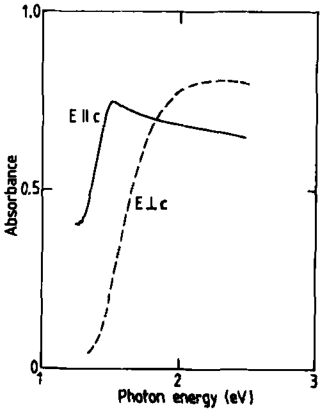

Fig.8 Polarized optical absorption spectra of pure trans-$(CH)_x$ in the visible range

Optical transmission spectra of the fully oriented trans-$(CH)_x$ in the visible range show extremly anisotropic behavior. The transmission minimum due to π-π^* transitions appears at 2.1 eV for parallel polarization[7,8]. For the amorphous trans-$(CH)_x$ the minimum occurs at 2.3 eV and indicates a somewhat smaller length of uninterrupted conjugated sequences compared to the oriented material. However, for the calculation of the true absorption spectra it is necessary to take the reflectivity into account. From optical transmission and reflectivity measurements of very thin films (a few hundred nanometers), in the range from 200 to 1000 nm, we have calculated the absorption spectra for both polarization directions (see Fig.8). The maximum of absorption is now located at about 1.5 eV.

The anisotropic behavior of the fully oriented trans-$(CH)_x$ is also revealed by the DC-conductivity[7,8]. The conductivity measurements were performed on samples cut either parallel or perpendicular to the orientation direction using the four probe technique. For the electric field oriented parallel to the chains we observe an activated conductivity with an activation energy of 0.26 eV and a value of $\sigma = 6.10^{-5}\ (\Omega\mathrm{cm})^{-1}$ at room temperature. In the perpendicular direction the conductivity at room temperature is about two orders of magnitude lower and exhibits an activation energy of 0.17 eV. The ratio of the anisotropy decreases with decreasing temperature. Doping of polyacetylene samples prepared by the methods described above appears to be very difficult, since the diffusion of the dopant is determined by the compact morphology. Oriented trans-$(CH)_x$ films doped with iodine (9 mol %) showed a room temperature conductivity of $\sigma = 33\ (\Omega\,\mathrm{cm})^{-1}$. The anisotropy ratio, however, is again of the order of 100 at room temperature and remains approximately constant down to 10 K. The temperature dependence of the doped samples cannot be explained by an activated behavior.

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