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Morphology

Fully Oriented Non-Fibrous Crystalline Polyacetylene

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SUMMARY

The preparation of fully oriented non-fibrous crystalline polyacetylene is demonstrated. Poly-7,8-bis-(trifluoromethyl)-tricyclo-[4.2.2.0]-deka-3,7,9-triene, poly-(BTFM-TCDT), is polymerized by a ring opening metathetical polymerization. Films cast from a solution of poly-(BTFM-TCDT) (precursor polymer) can be converted to polyacetylene by heating. During this conversion process an uniaxial stress is applied to the precursor polymer film which results in a high orientation of the polymer chains. SEM pictures show a compact and homogeneous morphology, whereas sharp and well defined electron diffraction (HEED) patterns indicate a fully oriented crystalline trans-polyacetylene material. Consequently we present polarized infrared spectra, expecially for the C-H out-of-plane deformation vibration (1010 cm^{-1}), which exhibit a tremendous dichroism for infrared radiation polarized parallel and perpendicular to the chain axis (c-axis, orientation direction).

INTRODUCTION

Recently it has been shown (LEISING 1984) that highly crystalline oriented single fiber polyacetylene can be produced by stress-orientation of a polymer which is converted to polyacetylene by heating under vacuum or inert atmosphere. In this paper we demonstrate the production of fully oriented non-fibrous crystalline polyacetylene films. A similar preparation procedure as for the single fiber synthesis was used. This synthesis follows a route first published by (EDWARDS and FEAST 1980). The precursor polymer poly-(BTFM-TCDT) is produced by a ring opening metathetical polymerization of the monomer BTFM-TCDT in solution with the catalyst system WCl_6 and $(CH_3)_4$ Sn. The precursor polymer is soluble in polar solvents and therefore it can be purified to a very high extent by conventional precipitation techniques. Films of different size and thickness were cast from a solution of the precursor polymer and converted to polyacetylene by applying an appropriate stress at temperatures up to 120 Centigrade. During the conversion an elongation of the polymer film (at the moment any desired value of l/l_0 up to 10) and a simultaneous alignment of the polymer chains take place. The width of the resulting polyacetylene films is up to 1 cm with a thickness varying from less than one micron up to 20 µm. By choosing the appropriate dimensions of the precursor polymer film and an appropriate stress it is possible to produce polyacetylene films of any desired shape. Investigations of these oriented polyacetylene films with SEM and TEM gave, what concerns the morphology, pictures of a very compact and homogeneous material, whereas the electron diffraction (HEED) patterns indicate a fully oriented crystalline trans-polyacetylene. Thus crystallographic data of trans-polyacetylene are available with a very high accuracy. Structural investigations by HEED and by X-ray diffraction will be published elsewhere. An extraordinary impression of the orientation of the polyacetylene chains comes from the dichroitic ratio of the C-H out-of-plane deformation vibration (at 1010 cm^{-1}) for infrared radiation polarized parallel and perpendicular to the c-axis i.e. the orientation direction. Thus for the first time it is possible to get reliable data on the anisotropic properties of polyacetylene in the insulating, semiconducting and metallic conduction regime, which are published elsewhere. In this view the different theoretical concepts (HEEGER and MACDIARMID) 1981) which were developed to explain the behavior of this so called synthetic metal can be carefully reviewed and applied to the non-fibrous polymer. Even technological applications of polyacetylene e.g. for solar cells thus have become more realistic possibilities.

EXPERIMENTAL

The monomer 7,8-bis-(trifluoromethyl)-tricyclo-[4.2.2.0]-deka-3,7,9-triene (BTFM-TCDT) is synthesized by a Diels-Alder reaction of hexafluoro-2-butene and cyclo-octatetraene. Purification and enrichment was done by fractional distillation. To chlorobenzene as the solvent the catalysts WCl_6 - $(CH_3)_4$ Sn and the monomer were introduced. After the polymerization reaction of BTFM-TCDT to poly-(BTFM-TCDT) has occured, the precursor polymer was precipitated by addition of methanol. The precursor polymer is then filtered from the solution by a glass filter, dried and dissolved in absolute acetone at low temperature (to prevent conversion to polyacetylene) and again precipitated and dried under vacuum.

This purification step is done two to four times and yields a precursor polymer with high purity what concerns catalyst residues (monitored by electron microprobe measurements). The precursor polymer is stored either at -40 Centigrade in the solid state sealed under vacuum for long time storage or at -27 Centigrade dissolved in acetone under inert gas atmosphere (argon) for short times. Films were cast from a saturated solution of the poly-(BTFM-TCDT) in acetone. The films were dried under argon gas flow and subsequently mounted in a stretching apparatus, where the conversion to polyacetylene and the elongation starts, when the film was heated up to 120 Centigrade. The apparatus was held at high temperature until the conversion reaction had completed. The extent of the elongation (l/l_0) depends on the weight used for stretching and was related to the cross section of the precursor-polymer film. The recommended strain for an elongation of 10 is about 20 kg/cm^2. The thickness of the polyacetylene films can be varied from less than one micron (for electron diffraction and optical investigations) presently up to 20 µm, although there is practically no limit from the preparative point of view. It is only a question of choosing suitable dimensions of the precursor polymer and an appropriate stress. The polyacetylene films were stored and handled under vacuum or inert gas atmosphere (highly purified argon glove box). The scanning electron microscopy (SEM) was done with a LEITZ 1000A. The transmission electron microscope used for electron diffraction experiments was a PHILIPS EM 420. The infrared spectra were recorded on a PERKIN ELMER 684 grating instrument equipped with a wire-grid polarizer.

RESULTS AND DISCUSSION

The above described preparation method allows to produce trans-polyacetylene films with a compact and homogeneous morphology and high quality surfaces (Fig.1).

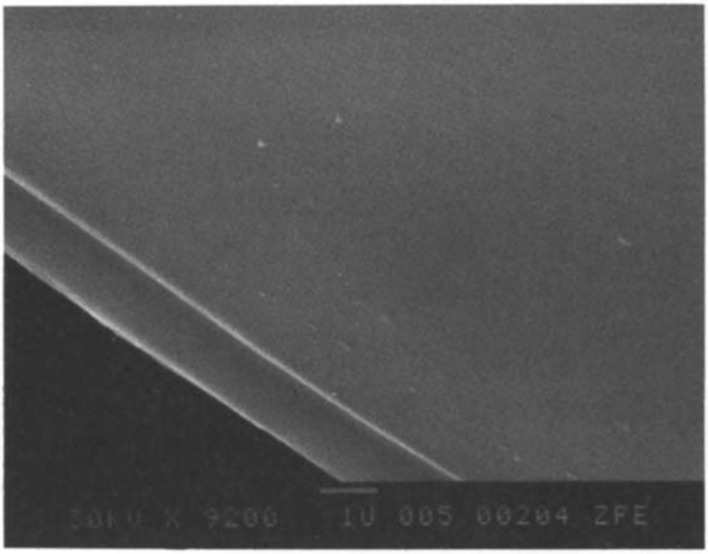

Figure 1. Scanning electron micrograph of a fully oriented non fibrous crystalline polyacetylene film (orientation direction parallel to the edge)

These polymer films exhibit a crystallinity with nearly full orientation of the polyacetylene backbone as one can see from the almost negligible off-equatorial extension of the hkO reflections in the electron diffraction pattern (Fig.2). Lattice parameter calculations of doped and undoped trans-polyacetylene based on these high quality electron diffraction results will be published elsewhere.

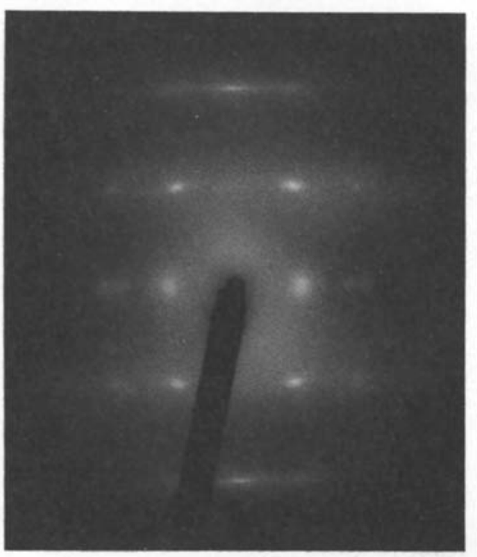

Figure 2. Electron diffraction pattern (U_0=120KV) of the polyacetylene film shown in figure 1.

The infrared spectrum of a 1000 % strech-oriented polyacetylene film show a total lack of the C-H out-of-plane deformation vibration (1010 cm^{-1}) for the electrical vector being polarized parallel to the polymer chain direction (c-axis, drawing direction). In contrast, for perpendicular polarization the deformation IR band developes rather strong (Fig.3).

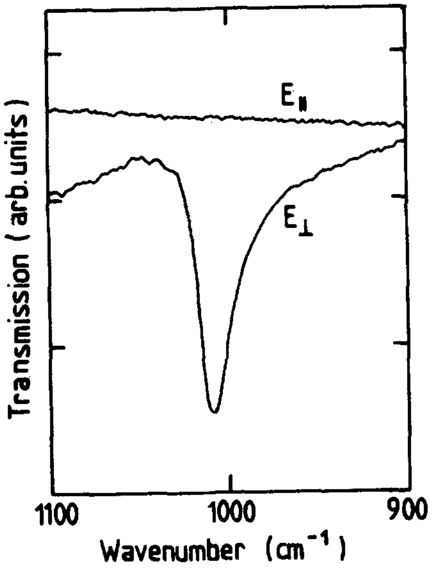

Figure 3. CH out-of-plane deformation vibration for infrared radiation polarized parallel ($E_\parallel$) and perpendicular ($E_\perp$) to the c-axis (orientation direction).

First experiments with doped fully oriented polyacetylene gave a comparable dramatic behavior of the doping induced bands for parallel and normal polarization. Interference features in the infrared spectra of films with an appropriate thickness also indicate the homogeneous morphology and the quality of the film surface.

CONCLUSION

A method for the preparation of fully oriented crystalline polyacetylene films is described, which for the first time provides material suitable for studying intrinsic, morphology independent anisotropic optical and transport properties of polyacetylene in the doped and undoped state. Infrared dichroism of the C-H out-of-plane deformation vibration of the so prepared trans-polyacetylene is more spectacular than in any other even highly crystalline polymer. Similar dramatic anisotropic behavior of transport and optical properties have already been observed and will be the subject of subsequent publications.

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