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, especially 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 WC₁₆ and (CH₃)₄Sn. 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 1/₁₀ 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]dek-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 WCl₆ - (CH₃)₄ Sn and the monomer were introduced. After the polymerization reaction of BTFM-TCDT to poly-(BTFM-TCDT) has occurred, 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/l₀) 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 l₀ is about 20 kg/cm². The thickness of the polyacetylene films can be varied from less than one micron (for electron diffraction and optical