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SYNTHESIS AND PROPERTIES OF (CH)$_x$- FILMS PREPARED BY POLYMERIZATION OF BTFM-TCDT

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Résumé - Des films de (CH)$_x$ ont été obtenus par une polymérisation métathétique avec ouverture de cycle de 7,8-bis-(trifluorométhyle)-tricyclo[4,2,2,0]$^{3,7,9}$ triene (BTFM-TCDT). Des films 100% trans ont été obtenus, ayant une densité bien supérieure à celle des échantillons obtenus avec la technique de Shirakawa. Nous présentons une étude de la morphologie, de la transmission infrarouge, de la conductivité avant et après diverses procédures de dopage, et comparons ces résultats avec les propriétés de films préparés avec la méthode de Shirakawa.

Abstract - (CH)$_x$-films were prepared by a ring-opening meta-thetical polymerization of 7,8-bis-(trifluoromethyl)-tricyclo[4,2,2,0]$^{3,7,9}$ triene (BTFM-TCDT). 100% trans-(CH)$_x$-films were obtained having a density considerably higher than the films prepared by the Shirakawa-technique. We present a study of the morphology by scanning-electron microscopy, of the infrared transmission, and of the conductivity before and after various doping procedures, and compare these results with properties of (CH)$_x$-films prepared by the Shirakawa-technique.

1. INTRODUCTION

Samples for the investigation of the properties of (CH)$_x$ almost exclusively have been prepared in the past by the so called Shirakawa-technique /1/. Since such samples exhibit a large scattering of even such basic properties as their density, we have been looking for alternative preparation procedures. The work by Edwards and Feast /2/ was a first important step in this direction. Starting with the same monomer, we used a modification of their method for the preparation of nearly amorphous (CH)$_x$-films with reproducible morphology and a bulk density comparable to that of the fibers of Shirakawa-(CH)$_x$.

2. EXPERIMENTAL

The monomer BTFM-TCDT can be polymerized using a catalyst system like WCl$_6$ and Sn(CH$_3$)$_4$ and then be converted to (CH)$_x$ at higher temperatures and dynamic vacuum. The reaction mechanism is shown below:

![Reaction mechanism diagram]

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This two-step preparation procedure follows the method first described by Edwards and Feast /2/. For our work we developed a modified procedure, which proceeds in one step from stage 1) to stage 3) in the following manner:

To chlorobenzene as the solvent 0.09 ml of a 0.15 molar WCl₆ solution and 1.15 ml of a 0.2 molar Sn(CH₃)₄ solution were added and stirred for 5 min at room temperature. Then the solvent was removed by applying dynamic vacuum resulting in the formation of a solid layer of active catalyst on the walls of the vessel. Subsequently, 0.3 ml (1.5 mmole) of the monomer were introduced into this vessel. After heating this liquid layer up to about 100°C, the reaction started immediately, forming a silvery film at the walls and some foam with metallic luster plus a colorless liquid at the bottom of the vessel. Thus, the polymerization of the monomer 1)→2) and the splitting off the 1,2 bis-(trifluoromethyl)-benzene 2)→3) took place at the same time. The films were dried by pumping off the aromatic compound and cleaned by washing them in toluene under application of an ultrasonic cleaner. All reactions were carried out under high vacuum or under pure argon atmosphere.

3. RESULTS AND DISCUSSION

The (CH)ₓ we obtained by this preparation procedure was a flexible film with metallic luster. The bulk density has a value of 1.1 g/cm³ which is very close to the flotation density of Shirakawa-(CH)ₓ and about a factor of three higher than the density of (CH)ₓ-films prepared by the Shirakawa-method.

These (CH)ₓ-films appear to have no fibrous morphology, as one can see from the scanning-electron micrographs in Fig. 1, which show a comparison of the morphology of the surface and the bulk for our material (left hand side) and the material prepared by the Shirakawa-method (right hand side). Investigations of the structure of our material by X-ray diffraction and HEED show amorphous rings only, which indicate a mean spacing of 10 Å. Even with large magnification and small diffraction areas no patterns produced by crystalline parts of the polymer could be detected. The modification of this type of (CH)ₓ is 100% trans, as one can see from a typical IR-spectrum in Fig.2, which exhibits only the features of the trans-isomer and of residual 1,2 bis-(trifluoromethyl)-benzene. Additional evidence for the pure trans-form of our samples can be seen in the DSC-spectrum shown in Fig.3, where the cis-trans isomerization peak between 100°C and 200°C is completely absent.

We have tried different doping procedures to increase the conductivity of our material. The conductivity of the undoped samples is of the order of 10⁻⁸ Ω⁻¹cm⁻¹ and thus considerably lower than all reported values for trans-(CH)ₓ prepared by the Shirakawa-technique. Attempts to dope our samples with iodine or bromine in the vapour phase did not result in high conductivity values, presumably because of the high density of the material. Applying the technique of doping in a solution of low dopant concentration resulted in maximum conductivity values of about 200 Ω⁻¹cm⁻¹ for the case of iodine and 10 Ω⁻¹cm⁻¹ for the case of bromine. The value for the iodine doped samples is comparable to the result reported by Rolland et al./3/ for optimally isomerized iodine doped trans-(CH)ₓ prepared by the Shirakawa technique.
Fig. 1: SEM-micrographs of the surface [(a) and (c)] and the bulk [(b) and (d)] of samples obtained by the present method [(a) and (b)] and by the Shirakawa method [(c) and (d)].

Fig. 2: IR-transmission spectrum of the present (CH)$_x$-samples.

Fig. 3: DSC-spectrum of the present (CH)$_x$-samples (----) and of Shirakawa-(CH)$_x$ (---).
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