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Structure analysis of conductive polymer systems: Poly-4-vinylpyridine and poly(butadiene-b-4-vinylpyridine) with 7,7′,8,8′-tetracyanoquinodimethane

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SUMMARY

The structure analysis of two conductive polymer systems - poly-4-vinylpyridine and poly(butadiene-b-4-vinylpyridine) with 7,7',8,8'-tetracyanoquinodimethane (TCNQ) - was done by X-ray diffraction, scanning tunneling microscopy (STM) and FTIR. The charge transfer complex formed between the pyridine group and the known electron acceptor, TCNQ, is supposed to be the conductive element in these systems. In order to understand the structure of this complex, a model compound, the complex of 4-ethylpyridine (4EP) with TCNQ, 4EP/TCNQ$_2$, was studied by the mentioned methods. It appears that there are two crystalline modifications of the model compound with different type of stacks of the TCNQ molecules. In polymer systems only one type of the complex is dominant as revealed by joint analysis of X - ray diffraction diagrams, STM and FTIR data. In the STM image of the polymer surface one can distinguish that molecular stacks with periodicities of 4.1 Å in a row are separated (12.5 Å) from each other. Such organization is similiar to the one observed in conductive charge transfer complexes such as tetrathiofulvalene (TTF) with TCNQ. The ordered molecular domains are scattered on the polymer surface and take part in the formation of the conductive network.

INTRODUCTION

One possibility to prepare conductive polymer systems is the formation of conductive charge transfer complexes. This situation can be realized by addition of the well known electron acceptor TCNQ to polymers with electron donor groups. The analysis of the crystalline structure of such a complex as well as the morphology is important for the understanding and optimization of the conductive properties of these materials. Among the conductive polymer systems are poly-4-vinylpyridine 1) and poly(butadiene-b-4-vinylpyridine) with TCNQ 2). The mainly amorphous structure of these polymers restricts the number of methods suitable for structure characterization. Transmission electron microscopy studies of the blockcopolymer have de-

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**To whom offprint requests should be sent monstrated that a percolative crystalline network exists in this material [2]. The basis of the conductive network is supposed to be the charge transfer complex between TCNQ and the pyridine group of the polymer. The elucidation of the molecular structure of the conductive complex is the subject of this communication. In addition to traditional methods of structure analysis, X-ray diffraction and FTIR, a new microscopical technique - scanning tunneling microscopy (STM) was applied. In this method a sharp metallic tip travels a few Ångstrom above the conductive or semiconductive surface at a constant tunneling current level. The resulting map of the local surface charge distribution with a spatial resolution of atomic scale in many cases gives a unique structural information. Despite its short history STM nowadays is widely used for surface studies of conductive and semiconductive materials. Conductive charge transfer systems are among the organic materials suitable for STM analysis. The first organic charge transfer complex studied by STM was the complex of the TCNQ with TTF [3]. The visualization of stacks of TCNQ molecules in the STM images well correspond to the atomic arrangement on the crystallographic a,b plane of this complex. The observed periodicities along the stack (4 Å) and perpendicular (12 Å) are in good agreement with the crystallographic data. Our experience accumulated during STM studies of this and several other TCNQ complexes [4-6] can be summarized as follows. There exists a definite correspondence between the atomic distribution on the surface, derived from crystallographic data, and the STM patterns. This correspondence is well established at the level of unit cell parameters and can be the main argument for the STM validity for structure examination of organic compounds. More difficult is the installation of the correlation between atomic distribution and details of the STM image inside the unit cell. The problems are connected with tip effects (changes of geometry, possible mechanical interactions with surface atoms, influence of adsorbates) and elucidation of a mechanism involved in formation of surface charge distributions.

EXPERIMENTAL

The monocrystals of the organic charge transfer complex 4EP/$TCNQ_2$ were prepared by precipitation from acetonitrile solution. The individual compounds were purchased from Aldrich Chemical Company and used after recrystallizing twice. The preparation of conductive polymer samples was described earlier [2]. The monocrystals and polymer samples were fixed on a metallic support by silver glue and these samples were used in STM experiments.

The X-ray powder diffraction diagrams of the monocrystals and the polymer samples were obtained at ambient temperature with a STADI P (STOE, Darmstadt, FRG) powder diffractometer. Ge monochromatized $CuK\alpha_1$ radiation, $\lambda = 1.5405$ Å was used. The samples were prepared in glass capillaries, d=0.3 mm, for Debye Scherrer geometry or as discs for reflection geometry. Data collection was performed with a computer operated scintillation counter, typical parameters for step width and counting time were 0.04^o and 20 sec/step. For data processing STOE software [7] was used.

For STM experiments at ambient conditions the commercial microscope Nanoscope

II (Digital Instruments, Inc., USA) was used. The piezohead (type "A") allows a maximal scanning area of 380 · 380 nm^2. The quality of the mechanically cut tips (Pt(70)/Ir(30)) was checked on monocrystals of highly oriented pyrolitic graphite. Current imaging mode was used in all experiments. The STM images are usually presented as topview pictures in which the bright patterns correspond to a more remote position of the tip with respect to the sample surface in z direction. More details of STM measurements are published elsewhere 6).

The FTIR measurements of monocrystals and thin slices of polymers were done with the Bruker IFS-88 Fourier Transform Infrared Spectrometer, equiped by an IR microscope. The samples were placed on a KBr support, situated on the microscope stage. Among the monocrystals one can find thin sections or thin monocrystals suitable for transmission measurements. Areas bigger than 20 · 20 μm^2 are usefull for FTIR microscopic measurements. The treatment of transmission measurements is simpler than of reflection data, which are usually used for studies of charge transfer complexes 8). For accumulation of FTIR data 400 scans were collected at a spectral resolution of 4 cm^{-1}. The IR spectra were converted into absorbance scale. The spectrum of the KBr support was used as reference.

RESULTS

In order to provide the basis for the structure studies in the polymer systems we have studied the model compound $4EP/TCNQ_2$. It was found that this compound exists in two crystallographic modifications. Compact monocrystals in the shape of brickets can easily be distinguished from needle-shaped crystals. Detailed crystallographic, STM and FTIR studies of these complexes were performed for structure analysis of these modifications. Detailed results are presented in a subsequent communication 6). Below we will use these results in comparison with the data obtained for the polymer systems.

The results of X - ray crystallographic studies are presented in Figs. 1A-1D. The powder diagrams 1A and 1B were obtained for monocrystals of the different modifications of $4EP/TCNQ_2$. Both compounds crystallize in the triclinic crystal system with following lattice parameters: bricket shaped monocrystal - $a = 7.112_2$ Å, $b = 7.862_7$ Å, $c = 13.954_4$ Å, $\alpha = 72.95_4^{\circ}$, $\beta = 94.12_3^{\circ}$, $\gamma = 106.80_8^{\circ}$; needle shaped monocrystal - $a = 3.865_2$ Å, $b = 6.658_9^{\circ}$, $c = 26.386_7$ Å, $\alpha = 92.63_3^{\circ}$, $\beta = 94.12_3^{\circ}$, $\gamma = 106.80_8^{\circ}$.

The complete single crystal X-ray structure determination was performed for a bricket type monocrystal 6). The poor quality of the needle type monocrystals permits only the determination of the lattice parameters. The powder diagrams of the polymer samples, homopolymer (1C) and blockcopolymer (1D), show some differences regarding the relative intensities. These effects could be partly due to texture effects. The diagram of the copolymeric sample had to be done from a platelet in reflection geometry, while the others were taken from powders in Debye Scherrer geometry. The comparison of the d-values of the polymeric samples with those of the model compound shows some similarities. The prominent peaks at 3.31 Å and 3.11 Å in the bricket modification of the model compound represent crystallographic planes which

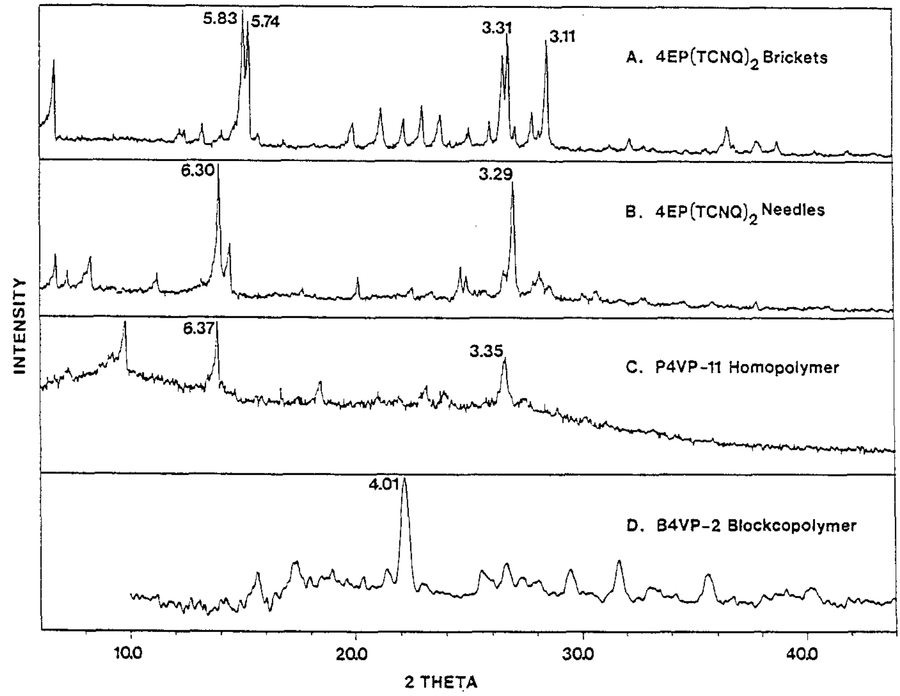
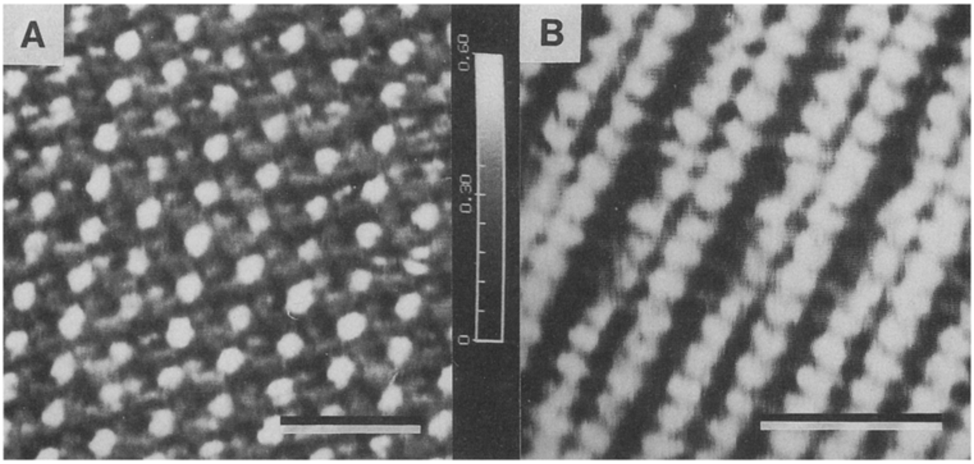


Figure 1: X-ray diffraction patterns of TCNQ salts

run almost parallel to the TCNQ ring planes. The planes which belong to the peaks at 5.83 Å and 5.74 Å are nearly parallel to the direction of the stacks. The exact crystallographic structure of this monocrystal with its diadic stacks of TCNQ molecules in the diagonal direction of the unit cell has been discussed in detail [6]. The main spacings found in X-ray diagrams of the polymeric sample P4VP-11 (3.35 Å and 6.37 Å) are similiar to those observed for the needle type modification of 4EP/TCNQ$_2$ (3.29 Å and 6.30 Å). It means that the ordered molecular structures existing in polymers look like the ones of the needle type monocrystal. The TCNQ rows are probably less densely packed in the polymers because the corresponding d-values of the planes are larger by approximatelly 0.6 Å. The size of the crystallites in the polymer has been estimated by use of the Scherrer equation: $I = k \cdot \lambda \cdot \beta^{-1} \cdot \cos\theta^{-1}$, with I = edgelength of the particle, λ = wavelength of X-ray, λ = 1.5405 Å, k = constant = 0.9, β = FWHM of the peak at d = 13.894 Å of the needle type monocrystal. The resulting values are $0.04 \cdot 10^{-6}$ m and $0.1 \cdot 10^{-6}$ m for blockcopolymer and homopolymer, respectively.

The STM investigations of the polymeric systems were more difficult than in case of the monocrystals of the conductive charge transfer complexes. The main problem, to our mind, is the heterogenious distribution of conductive and non-conductive regions on the surface of the polymeric sample. This means that for a successful STM observation the tip should be positioned in a conductive region. Better STM images were obtained for the blockcopolymer system, the morphology of which shows a conductive network 2). In Figs. 2A-2C the STM images of the model compound are presented together with the image of the surface of the blockcopolymer sample. The STM images of the bricket type and the needle type monocrystals are quite different. The patterns of the first image are well correlated with the atomic distribution in the crystallographic a,b plane 6). The molecular monadic stacks are the characteristic feature of the structure of the needle type monocrystals. This structure is similiar to that of the well studied TTF/TCNQ complex. Different stacks of a zig-zag type with diadic unit cells were found for the bricket-like modification. Though, due to experimental difficulties (small size of crystals) the conductivity of the monocrystals was not measured, one can assume that higher conductivity can be expected in the case of needle-like crystals because of close similarity of this compound to the conductive complex of TTF/TCNQ.



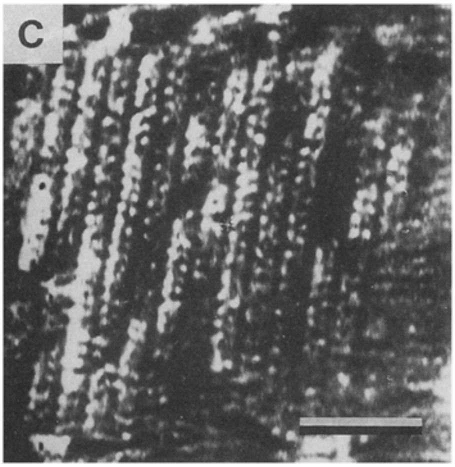


Figure 2: STM topview images of the surfaces of

- A - bricket-shaped 4EP(TCNQ)$_2$ monocrystal
- B - needle-shaped 4EP(TCNQ)$_2$ monocrystal
- C - B4VP-2 blockcopolymer film surface

Bars correspond to 2 nm (A,B) and 5 nm (C). Tunneling conditions: $I_{tun.}$ = 2 nA, $V_{bias.}$ = 35 mV. The grey scale vertical bar describes the corrugation of the STM patterns in the direction perpendicular to the surface.

The STM image of the blockcopolymer (Fig.2C) shows a highly ordered molecular array on the sample surface. In other STM images randomly distributed smaller ordered regions with similiar structure have been detected. The existence of molecular stacks on the blockcopolymer surface is clearly seen in the STM image. The molecular stacks can be characterized by repeat distances inside the chains and between them. The averaged values are 4.1 Å and 12.5 Å, respectively. These parameters as well as the type of stacking are analogous to those distinguished in STM images of the needle-like crystalline modification of 4EP/TCNQ$_2$. It should be mentioned that the accuracy of the determination of the molecular parameters with STM is not better than 5%. Thus STM results, as well as X-ray powder diagrams confirm the similarity of the structures of the crystalline parts of the polymers and the needle-like model com-

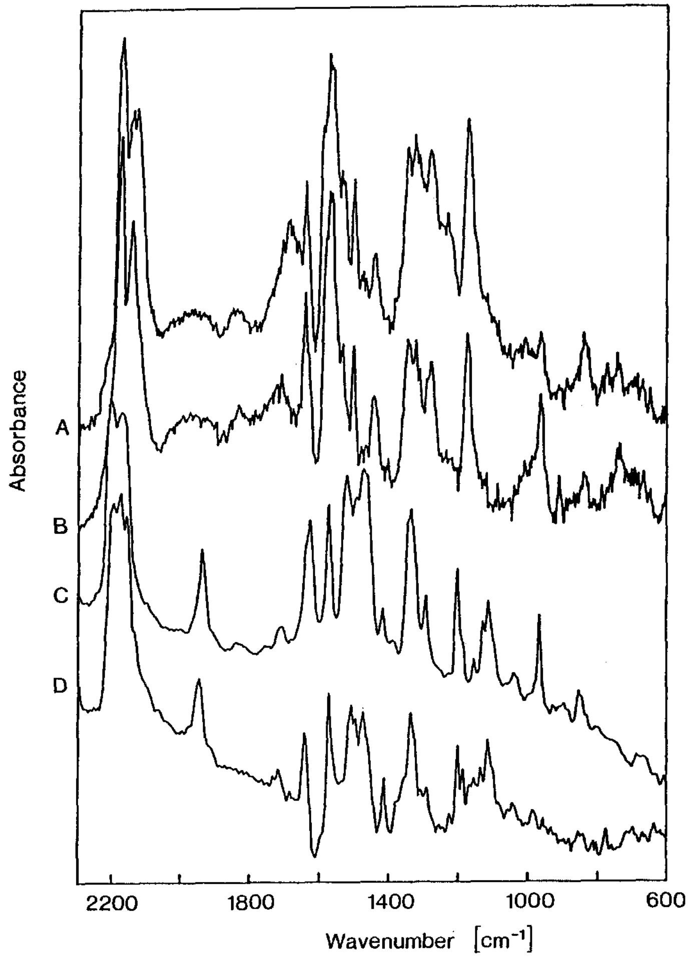


Figure 3: FTIR spectra of the two modifications of 4EP(TCNQ)$_2$ and the polymers:
- A - blockcopolymer B4VP-2 - B - homopolymer P4VP-12
- C - 4EP(TCNQ)$_2$ needles - D - 4EP(TCNQ)$_2$ brickets

pound. The discrepancy between the periodicity constants found in STM images (4.1 Å) and those obtained from X-ray data (3.2 Å) can be explained as follows. Usually the molecules of the stacks in TCNQ-based charge transfer complexes are inclined with respect to the main crystallographic planes. Therefore the periodicity in a stack measured by STM on a surface, which corresponds to the crystallographic plane, is larger than the interplanar distance between neighbouring molecules obtained from X-ray powder diagrams.

Generally this new microscopic technique appeared to be usefull for structure determination in organic charge transfer systems and can also provide information about morphology. For example, the size of largest ordered molecular array on the polymer surface was found to be 15 · 15 nm^2. In addition to the structural aspect of the STM application information about surface electronic structures can also be obtained. The comparison of details of well resolved atomic scale STM images of several charge transfer complexes with the atomic arrangement helps to distinguish the electronic contribution to the images. The analysis of electronic peculiarities is under way and it is hoped, that this important information can be clearified in future.

The FTIR spectra of the two modifications of the 4EP/TCNQ$_2$ complex and the polymer systems are presented in Fig. 3. IR spectroscopy is widely used for structure analysis of similiar charge transfer systems, and for many compounds the band assignment is known 9). In our case we have concentrated on the determination of spectral differences for the two crystal modifications having the idea to use them for structure investigations in related polymers. The comparison of the IR spectra of the different crystal modifications shows that there are bands which can be used as indication of the needle type modification. Such bands appear at 1200 and 868 cm^{-1}. The last band is practically absent in the spectrum of the bricket type monocrystal. The observed differences in the spectra of the two crystal modifications of 4EP/TCNQ$_2$ are more pronounced in comparison with the differences in the IR spectra of the two different modifications of the Rb/TCNQ complex 10). The IR bands mentioned indicators of the needle type modification are present in the IR spectra of the polymer systems. Thus from the IR data we also have the confirmation that in the polymer the crystalline structure of the needle type modification prevails.

DISCUSSION

Two aspects of the obtained results may be discussed:

1. The joint application of X-ray diffraction, FTIR, and STM for the structure application in ill ordered conductive polymer systems.
2. Clarification of the nature of molecular stacks found in the polymeric system as performed by parallel STM studies on this system as well as on its low molecular mass analogue.

To 1. We succeeded to establish the molecular structure of the ordered domains which form the conductive paths. The STM appears to be a new important instrument for this kind of investigations.

To 2. In the case of the low molecular weight charge transfer complex 4EP/TCNQ$_2$ -

needle shape crystal modification - the crystalline structure is composed of alternating stacks of donors and acceptors, analogous to the well-studied TTF/TCNQ complex. This means that the stabilization of TCNQ stacks is achieved by regular packing of pyridine groups forming the neighbouring stack. Such a situation is hard to imagine in macromolecular systems. The probability of stacking of pyridine groups situated in different chains is not very high. The formation of stacks with periodicities near 4 Å from pyridine groups of the same chain is also improbable because of stereochemical difficulties. Thus, the question of the origin of TCNQ stacking is still open in the studied polymer systems. The situation is not unique, however: Similar columnar structures were observed in discotic LC-polymers [11]. It has been mentioned that columnar structures can be achieved also by donor-acceptor interactions.

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