Physical properties of highly oriented polyacetylene films

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This paper is devoted to the characterization of highly oriented $(CH)_x$ films synthesized onto liquid crystal oriented by a strong magnetic field. The morphology of the films is studied by SEM and TEM. The fibril orientation and crystallinity are investigated by X-ray and electron diffraction. The anisotropic characteristics are measured by optical and transport measurements on undoped and iodine-doped samples. A longitudinal d.c. conductivity as high as $20\,000\,\Omega^{-1}\,cm^{-1}$ was obtained.

(Keywords: oriented polyacetylene; morphology; diffraction; Raman; infra-red; conductivity)

INTRODUCTION

During the last three years, several syntheses of highly oriented polyacetylene[1–3] led to a large renewal of interest in the study of anisotropic properties of this linear conjugated polymer. In this paper we report the morphology of oriented polyacetylene synthesized by Akagi's method[3] using the nematic phase of a liquid crystal as the solvent of the catalyst. Anisotroic behaviour has been studied by several techniques: electron and X-ray diffraction, Raman and i.r. spectroscopy and electrical conductivity.

EXPERIMENTAL

Sample preparation

Following Akagi's procedure, $Ti(OBu)_4$ and $AlEt_3$ with the ratio $Al/Ti=3$ formed the catalyst system. The liquid crystal solvent was an equimolar mixture of 4(*trans*-4n-polylcyclohexyl) ethoxybenzene and 4(*trans*-4n-propylcyclohexyl) butoxybenzene. The concentration of $Ti(OBu)_4$ was $0.015\,mol\,l^{-1}$ in the solvent. The catalyst solution was aged for 45 min at room temperature, and the synthesis was performed at 10°C.

To orientate the liquid crystal we used in the same experiment gravitational flow and vertical magnetic field (47 kG)[4]. This provided large areas of highly oriented films with thicknesses of a few microns. These samples are suitable for optical and transport studies.

For transmission electron microscopy (TEM) and electron diffraction we needed thin films (less than 1000 Å) directly deposited onto metallic grids. In this case the synthesis was performed onto grids wetted by the catalyst solution oriented by a 20 kG horizontal magnetic field. Gold grids were used to prepare samples which could be iodine doped. Copper grids were used for pristine $(CH)_x$.

All the as grown samples are partially *cis* (60%) and partially *trans* (40%) due to the temperature of the synthesis.

RESULTS

Scanning and transmission electron microscopy

After sputtering a 80 Å thick gold layer, the undoped $(CH)_x$ was observed with a Jeol JSM 35″ microscope. *Figures 1a* and *b* show, respectively, the gas and glass sides of the film. Both are oriented, and in both cases the film densities are higher than those obtained for films prepared by the usual Shirakawa method. *Figure 1c* is a low magnification view exhibiting very long fibrils ($>100\,\mu m$).

Figure 1d shows the detail of a highly oriented region. The diameter of the fibrils is about 1000 Å.

Thus the application of a strong magnetic field (47 kG) leads not only to highly oriented fibril films but also to very long and wide fibrils.

Transmission electron observations were performed with a Jeol 200 CX microscope working at 120 kV. *Figure 1e* shows the grid with as grown oriented $(CH)_x$ fibrils. A detailed region of this sample is observed in *Figure 1f*, where fibrils appear to be constituted by the gathering of aligned microfibrils.

X-ray and electron diffraction

X-ray diffraction experiments have been performed with Mo Kα radiation. The average fibril axis (*L*) is oriented perpendicular to the direction of the incident X-ray beam (K_i); an angle of more than 60° between K_i and a direction perpendicular to the film has been used in order to increase the scattering volume. The X-ray diffraction pattern (*Figure 2a*) shows that the maximum of the diffracted intensity is localized in lobes situated on different circles with a reflection symmetry.

This pattern characterizes both the intra- and interfibrillar misorientations. A $\pm 20°$ value of the whole misorientation with respect to *L* has been deduced.

In electron diffraction experiments a small sample area containing one or a few well aligned fibrils can be selected. A typical electron diffraction pattern of a *cis–trans* $(CH)_x$ is shown in *Figure 2b*, where the misorientation has been evaluated to $\pm 10°$. By comparing the two techniques we

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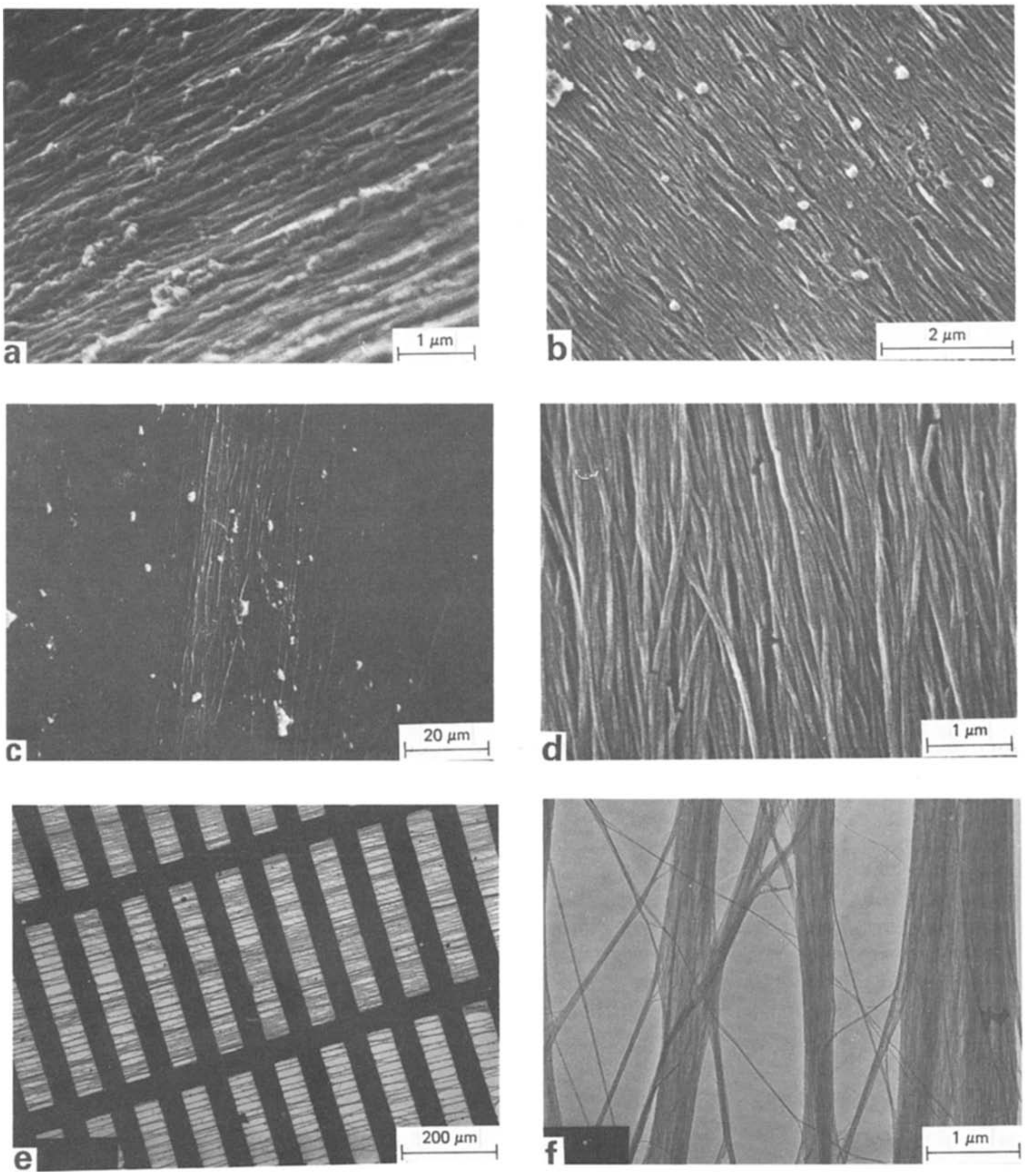

Figure 1 SEM and TEM micrographs of oriented $(CH)_x$. (a) SEM, gas side; (b) SEM, glass side; (c) SEM, low magnification; (d) SEM, fibrils detail; (e) TEM, overview of the fibrils; (f) TEM, internal morphology of fibrils

can deduce that misorientation shown in the X-ray diffraction pattern must be attributed to interfibrillar effects.

Raman spectroscopy

Polarized resonant Raman scattering by oriented *cis–trans*, *trans* and *cis–trans* iodine doped $(CH)_x$ have been performed on a Coderg T800 triple monochromator spectrometer. The Raman spectra were excited by an argon ion laser operating at 514.5 or at 487.9 nm. In order to avoid a degradation of films the stabilized output power has been limited to 10 mW and the laser beam was defocused. A back scattering geometry has been used in order to minimize the experimental errors; in this way the alignment of the laser beam can be better realized.

In this paper we discuss only the values of the depolarization ratio $R = I_{zy}/I_{zz}$.

I_{ab} is the Raman intensity, after correction for the spectrometer efficiency, for an a incident polarization and ab scattered polarization: $a(b) = z$ indicates a polarization along the fibrils, $a(b) = y$ indicates a polarization perpendicular to the fibrils. Keeping the same incident polarization (z) ensures that the effective incident power on the sample and the area under study are exactly the same in the two spectra. No corrections of the experimental spectra for absorption and reflection of the beams and for the multiple scattering effect have been realized. The procedure used in these experiments is the same as the one employed by other groups working on oriented $(CH)_x$[7,8]; so our results can be directly compared to theirs. These ratios have been measured for different positions of the incident beam on the film.

Figure 3a shows the $1250\,\mathrm{cm}^{-1}$ Raman line in the *cis–trans* $(CH)_x$ at $T = 80\,\mathrm{K}$. The band shapes are similar for the two polarizations. The depolarization ratio is about $R = 22(4)\%$.

The Raman spectra at room temperature of the same film after thermal isomerization are reported in *Figure 3b*

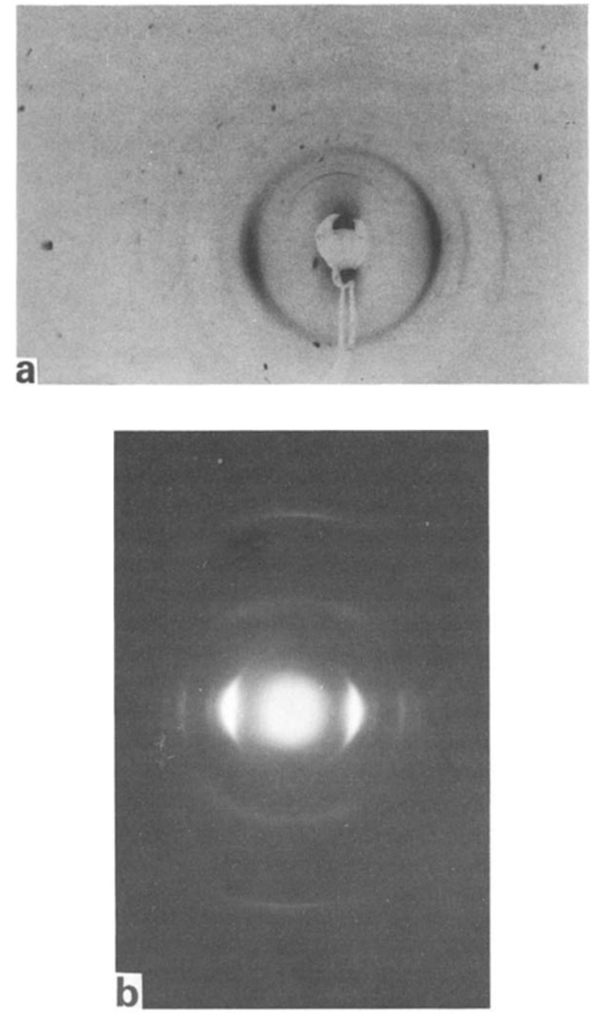

Figure 2 (a) X-ray diffraction patterns of $(CH)_x$ films, (b) electron diffraction of $(CH)_x$ deposited onto grid

(only the frequency range 1025–1200 cm^{-1} is shown). The usual double peak structure attributed to the inhomogeneous distribution of chain lengths[5] or electron–phonon dispersion coupling[6] is observed. This structure was deconvoluted into symmetric lines, the first peaked at the main frequency $\nu_p = 1088\,\mathrm{cm}^{-1}$ and a satellite line pointed at $\nu_s = 1122.5\,\mathrm{cm}^{-1}$. The experimental ratio $R = 12(3)\%$ is the same for the main and the satellite lines. We remark that this R value is lower than the one obtained for the *cis* lines in the original *cis–trans* sample. The profiles of the Raman scattering in the two polarizations are close to those obtained by Masset *et al.*[7]; however the peaks of the zy spectrum do not show a shift with respect to peaks of the zz spectrum, in disagreement with the Raman data of Lefrant *et al.*[8].

In *Figure 3c* we show a part of the Raman spectra of an iodine doped *cis–trans* $(CH)_x$:$(CHI_y)_x$ with $y = 0.07$. These spectra have been recorded at room temperature and with films directly in air. All the features of the *cis* Raman spectrum are always predominant, at least for $y < 7\%$, as previously observed[9]. In addition, an increase of the intensity of the *trans* bands with a small shift under doping is observed. As these spectra have been recorded with films at room temperature, heating by the laser beam can lead to a *cis–trans* isomerization. Then the effects observed about the *trans* bands can be due to doping or (and) to thermal isomerization. The *cis* Raman lines (1 in *Figure 3c*) and the stretching I_3 mode (2 in *Figure 3c*) have the same depolarization ratio $R = 17(4)\%$. R is slightly stronger for the *trans* part of the spectra (3 in *Figure 3c*): $R = 29(4)\%$. In agreement with previous results[9], this suggests when the *cis–trans* sample is doped, the iodine penetrates the *cis* parts and takes the orientation of the *cis* fibrils.

Infra-red spectroscopy

Transmission infra-red spectra with polarized light have been recorded on a Fourier transform Bruker Spectrometer type IFS 113V. During measurement, samples were kept under vacuum to avoid oxidization. *Figure 4a* reports the absorbance in the range 400–4000 cm^{-1} with the electric field parallel (*Figure 4a*$_\parallel$) and perpendicular (*Figure 4a*$_\perp$) to the fibril orientation. Two significant features are observed: the absorbance is modulated by interference effects on the film. The analysis of this modulation gives a measurement of the optical index. We found $n_\parallel = 3.5$ and $n_\perp = 2$.

Cis and *trans* vibration modes are enhanced in one of the two curves and reduced in the other, according to the orientation of their dipole moments.

The quality of orientation of the chains can be checked by the ratio of the absorbance of *cis* lines which can be separated into parallel (450, 1321 cm^{-1}) and perpendicular to the chain (745 cm^{-1}), or by the ratio of the absorbance of the out-of-plane *trans* mode (1015 cm^{-1}).

From these absorption line intensities we deduced the

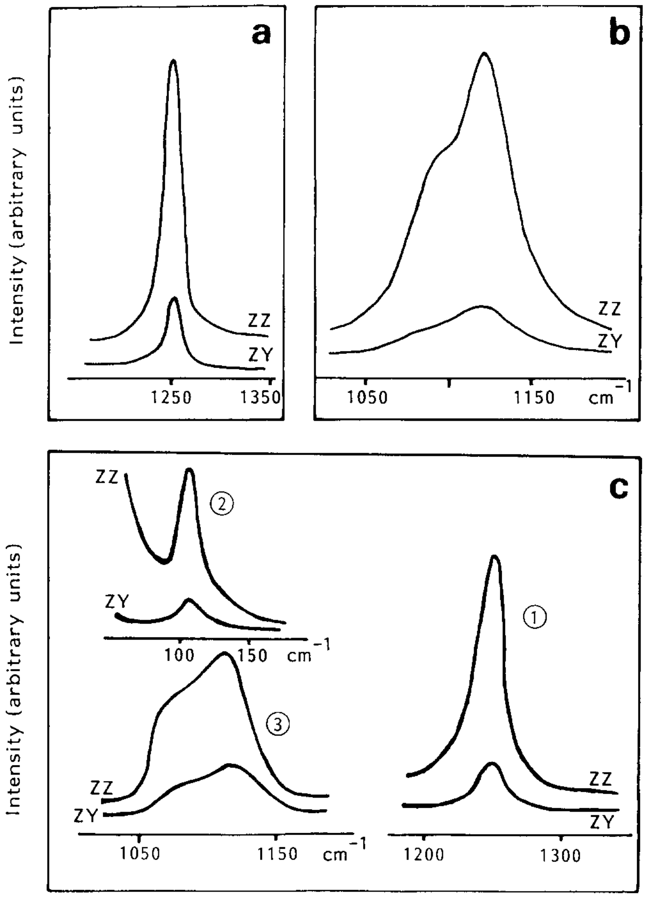

Figure 3 Traces of Raman spectra. (a) Pristine $(CH)_x$, (b) *trans* $(CH)_x$, (c) iodine-doped $(CH\,I_{0.07})_x$

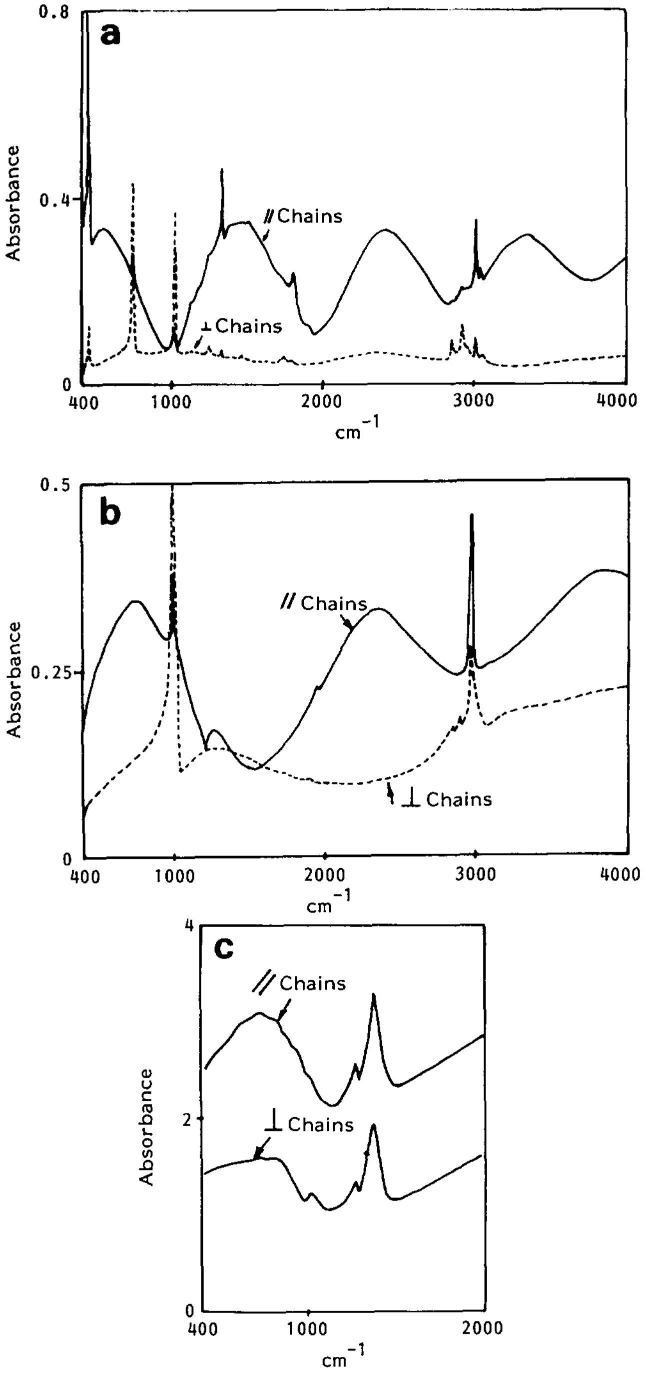

Figure 4 (a) Polarized light absorbance of pristine $(CH)_x$, (b) absorbance of *trans* $(CH)_x$, (c) absorbance of iodine-doped $(CH)_x$

mean value $\overline{\cos^2\phi}$ (ref. 10), where ϕ is the angle between the direction of one chain and the mean direction of the chains. We found $\overline{\cos^2\phi} = 0.76$.

In *Figure 4b* the same spectra are reported for thermally isomerized samples (20 min at 150°C). Similar results are observed for the $3010\,\mathrm{cm}^{-1}$ and $1015\,\mathrm{cm}^{-1}$ modes, and also for the index anisotropy. Such results clearly indicate that thermal isomerization does not destroy or strongly affect the orientation.

Figure 4c shows the parallel and perpendicular absorbance in the range 400–$2000\,\mathrm{cm}^{-1}$ obtained on iodine-doped *cis–trans* $(CH)_x$ film with $y = 0.03$: $(CHI_{0.03})_x$.

In this case, a difference in background absorbances higher than one order of magnitude is observed. The same result holds in the near infra-red.

D.c. conductivity

$(CH)_x$ films were doped in iodine vapour, the dopant level being fixed by the doping temperature. After doping, the excess iodine is removed by dynamical pumping for 1 h and the dopant amount measured by weight uptake. Measurements were performed by the usual four probes technique.

The main result is a very high room temperature parallel conductivity, $\sigma_{\parallel} \simeq 20\,000\,\Omega^{-1}\,\mathrm{cm}^{-1}$ for $(CH\,I_{0.15})_x$ samples. This value is similar to values reported elsewhere[11] for samples highly oriented by another method.

On the other hand an anisotropy factor of $\sigma_{\parallel}/\sigma_{\perp} \geqslant 20$ has been measured. However as this value is strongly sample dependent, it is probably related to geometrical effects (cracks) rather than to transverse properties of the fibrils.

CONCLUSION

In this study, following Akagi's method slightly improved by the combination of a strong vertical magnetic field and gravitational flow, we obtained highly oriented $(CH)_x$ films.

These films are shown to be constituted of very long fibrils, and the fibrils are themselves built of microfibrils. In one fibril the orientation of microcrystalline domains, with respect to the fibril axis is very well defined while the orientation of the different fibrils in the sample spreads over 20°.

The room temperature longitudinal conductivity after iodine doping is 100 times greater than the conductivity of Shirakawa's polyacetylene. This poses the question of the reason for this significant improvement. We have pointed out that the fibril lengths are much greater than in Shirakawa's samples (100 times). This could be the explanation for the conductivity improvement.

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