Real-time X-ray scattering study during the thermal conversion of a precursor polymer to poly(p-phenylene vinylene)

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The thermal conversion of poly(xylilidene tetrahydrothiophenium chloride) (PXTC) into poly(p-phenylene vinylene) (PPV) has been followed *in situ* using real-time X-ray diffraction. At temperatures higher than 75°C, the elimination reaction is associated with a change in the wide-angle X-ray scattering pattern, indicating the thermal conversion of the precursor polymer PXTC into imperfect PPV semicrystalline domains embedded within a matrix of amorphous precursor. At temperatures higher than 120°C, the elimination process takes place simultaneously with the improvement of chain packing within the semicrystalline domains of PPV.

(Keywords: conducting polymers; precursors; poly(p-phenylene vinylene); real-time X-ray scattering)

INTRODUCTION

The use of precursor routes to obtain conducting polymers has been studied extensively[1-4]. The procedure is based on the synthesis of suitable soluble and stable polymers, which after thermal treatment undergo chemical transformation to other structurally different polymers. The resulting polyconjugated materials can be made to conduct electricity by chemical or electrochemical oxidation. In this way, the problems derived from the low processability of traditional conducting polymers can be overcome. In particular, the precursor route to poly(p-phenylene vinylene) (PPV) is one of the methods more extensively studied[2]. The thermal transformation of poly(p-xylene-α-dimethylsulphonium chloride) into PPV involves changes of the chemical, electronic and crystalline structure, which are well characterized[2]. A more recent development[5] shows that PPV can be made from poly(xylilidene tetrahydrothiophenium chloride) (PXTC) through a faster transformation as compared with that involved in previous cases. Real-time wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) using synchrotron radiation have been shown to be powerful techniques to follow order–disorder transitions in polymers involving crystal and microstructural changes[6,7].

The aim of the present study is to follow the thermal transformation from PXTC to PPV by using time-resolved X-ray scattering in order to characterize *in situ* the structural changes occurring during the transformation.
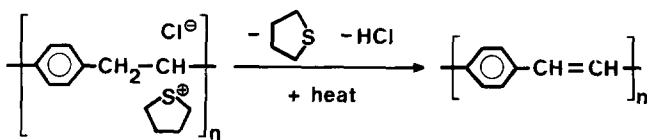
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EXPERIMENTAL

The synthesis of the PXTC polymer used in these experiments has been described elsewhere[5,8]. Approximately 0.005 cm thick PXTC solution-cast films were prepared for X-ray scattering experiments. WAXS and SAXS measurements were performed using a double-focusing mirror monochromator on the polymer beam line at HASYLAB (Hamburg, FRG). The samples were heated at different rates in a vacuum (10^{-2} torr) during the scattering experiments. Thermal contact and homogeneous heating were ensured by a thin aluminium foil covering the faces of the sample. The temperature was measured by a thermocouple embedded in the sample. The wavelength used was 0.15 nm, with a bandpass of $\Delta\lambda/\lambda = 5 \times 10^{-3}$. The scattering patterns were recorded every 20 s using a linear position-sensitive detector and corrected for fluctuations in the intensity of the primary beam and background. The temperature variation during the time required to take a measurement (20 s) gives an accuracy of $\pm 1.7°C$. An overview of the data acquisition system based on CAMAC hardware and modulator software has been published recently[9,10]. Standard samples of cornea and polypropylene were used to calibrate the peak positions in SAXS and WAXS experiments, respectively, with an error of ± 0.04 nm in WAXS. Density measurements were performed by using a density gradient column with dioxane and carbon tetrachloride.
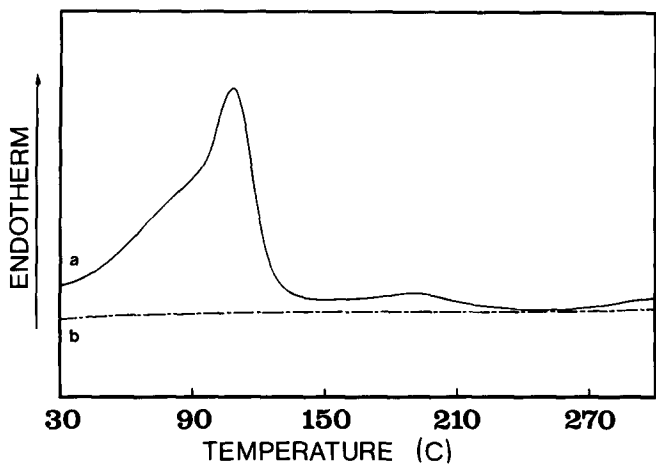
RESULTS

The precursor route from PXTC to PPV is schematically depicted in *Figure 1*. The conversion to PPV takes place under thermal treatment in a vacuum or inert-gas

Figure 1 Precursor route from poly(xylilidene tetrahydrothiophenium chloride) (PXTC) to poly(p-phenylene vinylene) (PPV)


Figure 2 D.s.c. traces during (a) heating and (b) cooling treatment

atmosphere, and involves the elimination of tetrahydro-thiophene and HCl from the initial precursor polymer. The obtained d.s.c. endotherm traces taken during the transformation process are shown in *Figure 2*. A main endothermic peak is observed around 110°C, with a shoulder at lower temperatures. A smaller, broader peak is observed at $T \approx 195°C$. The broken curve corresponds to the thermogram run during cooling. The absence here of any transition indicates that the thermal transformation is irreversible. Although these features are qualitatively the same for samples of different batches, the intensity of the main peak may change substantially and its position may shift over a range of about several degrees. The infra-red spectrum of the precursor polymer (*Figure 3a*) exhibits a strong absorption band at $3375 \, cm^{-1}$, which is characteristic of the OH stretching mode of entrapped water. The $2913 \, cm^{-1}$ band, which corresponds to the asymmetric stretching mode of the aliphatic segment in the precursor, is also present. The existence of a $3022 \, cm^{-1}$ band, characteristic of the stretching of the *trans*-vinylene CH group, indicates that some conversion, probably during the casting procedure, has already take place. *Figure 3b* shows the infra-red spectrum of a fully converted sample treated at 200°C for 5 h. The spectrum exhibits the characteristic absorption bands reported by Bradley *et al.*[2], i.e. two sharp peaks at 3022 and $965 \, cm^{-1}$ characteristic of the *trans*-vinylene CH stretch and out-of-plane bend. The i.r. region between 400 and $900 \, cm^{-1}$ is shown in *Figure 4* for a PXTC sample (a) before and (b) after conversion. The two strongest bands have been assigned[2] to the CH out-of-plane bending and to the *p*-phenylene group out-of-plane ring bending. The band appearing at $759 \, cm^{-1}$ in the prepolymer that apparently shifts to $784 \, cm^{-1}$ in the converted sample corresponds to the so-called 'crystallinity band'[11]. This band seems to relate to interactions between groups of different chains and is, consequently, sensitive to the degree of order. Most

interesting is the absence of bands in the $630-600 \, cm^{-1}$ region, which is characteristic of C–S stretching vibrations in the treated polymer. This indicates that full conversion of the prepolymer has been achieved. The densities of samples treated at different temperatures in vacuum for 45 min are collected in *Table 1* with an error of $\pm 0.0005 \, g \, cm^{-3}$. The density changes from a value of $1.2806 \, g \, cm^{-3}$ for the initial sample to $1.2235 \, g \, cm^{-3}$ for a sample treated at 200°C. The latter value is in good agreement with experimental density data reported for PPV[2,11,12].
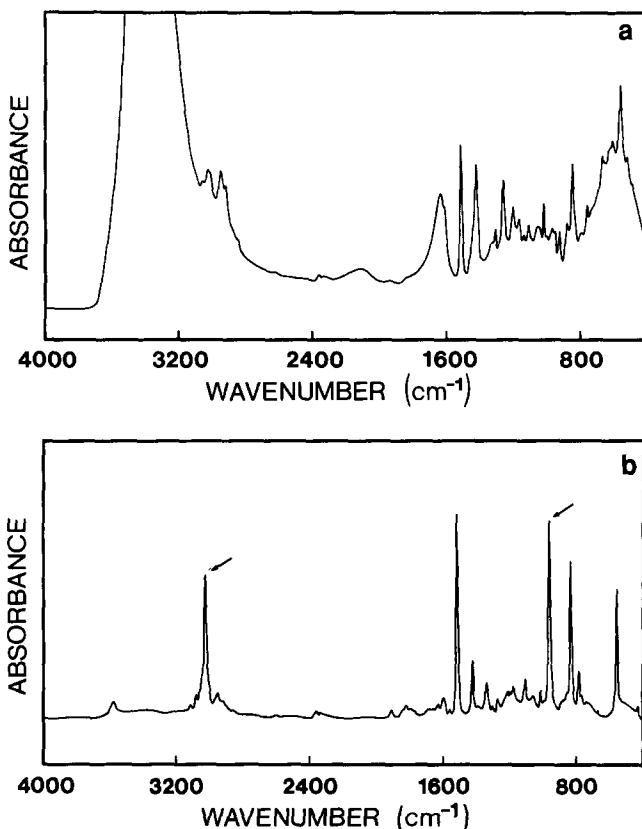

Figure 3 (a) Infra-red spectrum of PXTC prepolymer. (b) Infra-red spectrum of the fully converted sample treated at 200°C for 5 h. The arrows indicate the 3022 and $965 \, cm^{-1}$ bands characteristic of the *trans*-vinylene CH stretch and out-of-plane bend
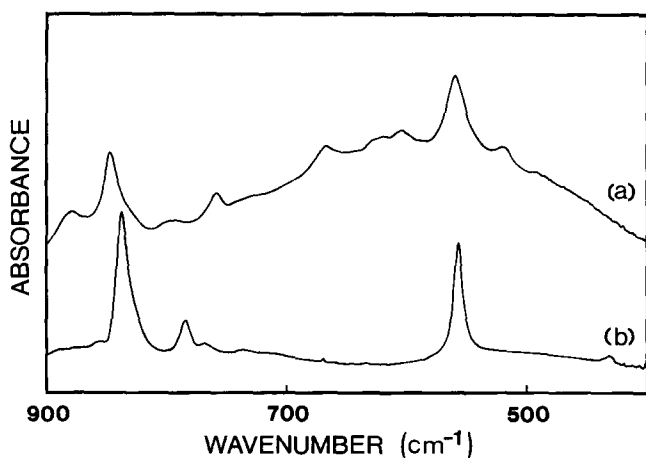
Figure 4 I.r. spectrum for (a) PXTC and (b) final polymer after conversion ($T = 200°C$, $t = 5$ h)

**Table 1** Densities of samples treated at different temperatures

| T (°C)	(g cm^{-3})
65	1.2662
100	1.2545
130	1.2491
200	1.2270
300	1.2235
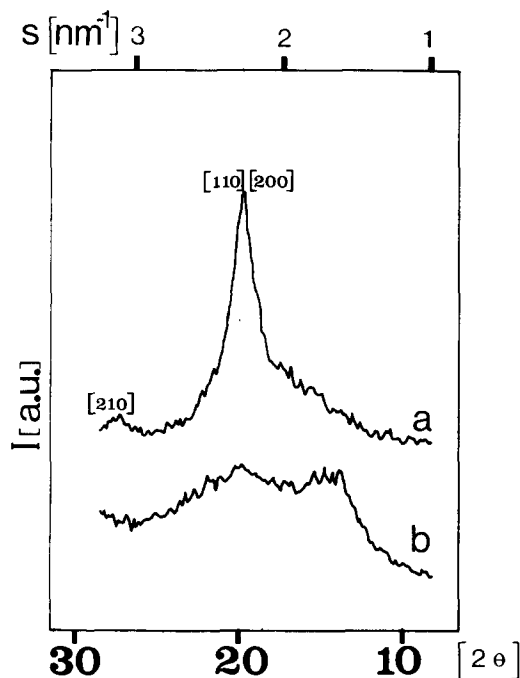
Figure 5 Wide-angle X-ray scattering (WAXS) patterns of (a) the final polymer after a treatment at $T = 335°C$ for $t = 50$ min and (b) the initial PXTC sample

The as-synthesized solution-cast precursor PXTC films are essentially amorphous, as shown in *Figure 5*. The two broad peaks observed at about 2.35 and 1.70 nm^{-1}, respectively, indicate the occurrence of a low degree of order. Upon heating to 335°C for 50 min, a better ordered structure characterized by two crystalline peaks appearing at $s = 2.28$ and 3.15 nm^{-1} is developed. It is noteworthy that the intensity of the X-ray diffraction patterns does not diminish despite the substantial material loss during heat treatment. This is probably connected with the change in the absorption coefficient of the PXTC material containing heavy S and Cl atoms as compared with the PPV final material containing mainly lighter C atoms. The spacing values are in agreement with the spacings reported for PPV in this angular range[2,11], and correspond to the d_{110} and d_{210} spacings of a rectangular P2gg two-dimensional space group projection of a monoclinic cell. According to this assignment, the (1 1 0) and (2 0 0) reflections overlap each other. During the heating process at higher temperatures, the following structural changes in the WAXS pattern were detected. In a first experiment (*Figure 6*) the sample was heated from room temperature to 130°C at a rate of 5°C min^{-1}. The appearance of a crystalline peak near 2.14 nm^{-1} ($2\theta = 18.49°$) is observed at temperatures higher than 75°C. A second run was performed by using a faster temperature rate increase (50°C min^{-1}) between 25 and 335°C (*Figure 7*). With increasing temperature the peak corresponding to the

(1 1 0) and (2 0 0) reflections gradually sharpens and shifts towards higher angles until the limiting value of 2.28 nm^{-1} ($2\theta = 19.76°$), characteristic of PPV, is reached. The treatment of the sample at 335°C does not induce further substantial changes in the WAXS pattern.

SAXS experiments were also carried out during the conversion process. The increase of the invariant quantity $Q = \int Is^2 \, ds$ between 25 and 200°C is shown in *Figure 8*. The change of Q with the storage time at 200°C is shown on the right-hand part of the figure. At low temperatures, Q remains constant until a sudden stepwise increase of
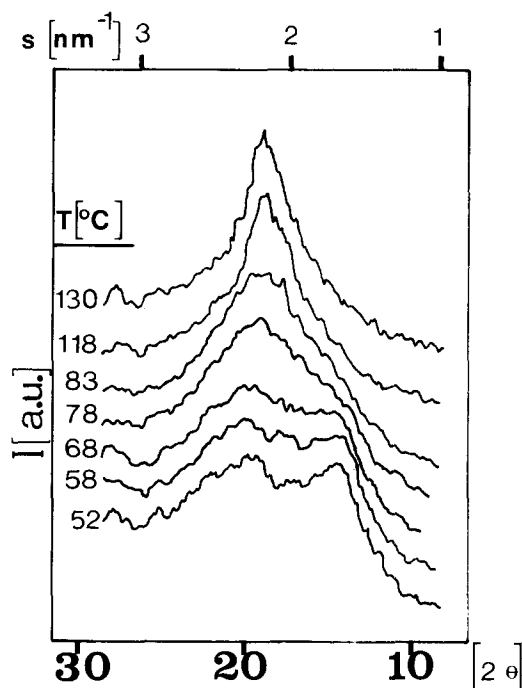
Figure 6 Real-time WAXS patterns during the heating process up to 130°C. Heating rate = 5°C min^{-1}
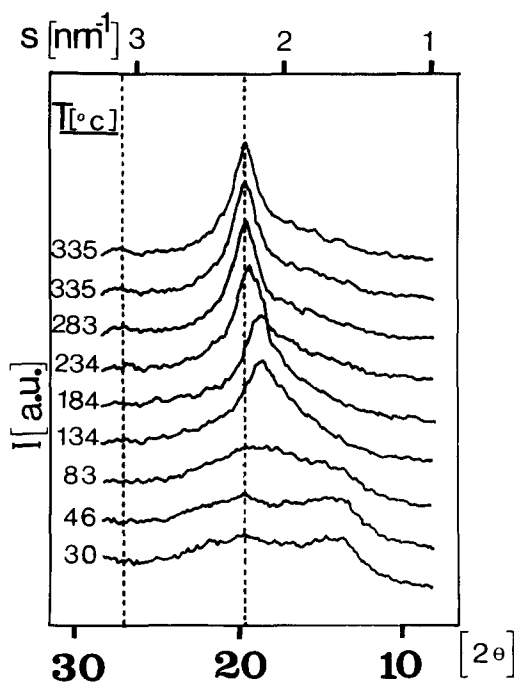
Figure 7 Real-time WAXS patterns during heating up to 335°C at a constant rate of 50°C min^{-1}
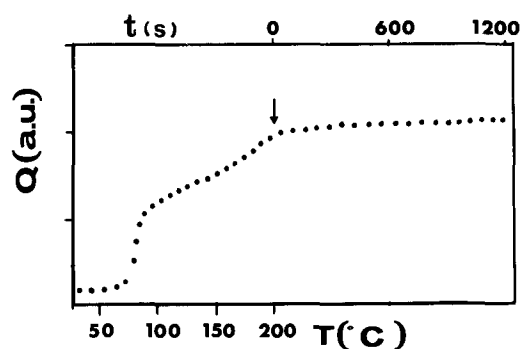
Figure 8 Change of the invariant $Q = \int I s^2 \, ds$ with temperature (up to 200°C) and with storage time at 200°C. The arrow indicates the beginning of the isothermal process

Q at $T \approx 75°C$ is observed. This increase in Q is paralleled by the appearance of a shoulder in the initially continuous SAXS pattern[13]. Finally, the treatment of the sample at 200°C produces a further, very slight, increase of Q.

DISCUSSION

PXTC is essentially amorphous, as revealed by the WAXS pattern (*Figure 5*). The films of the prepolymer contain a large amount of entrapped water as detected by i.r. During the heating treatment a loss of the water is expected, giving rise to the broad endothermic peak measured in d.s.c. experiments. *Figure 2* indicates that a water elimination process takes place continuously from room temperature. The intensity and position of the low-temperature endothermic peak depend on the amount of water present on the film and could explain the difference between samples of different batches. Although the main elimination of tetrahydrothiophene and HCl seems to occur at higher temperatures and might contribute to the second peak of the d.s.c. curve[4], the observed change in colour for samples treated at temperatures less than 100°C strongly suggests that elimination of tetrahydrothiophene and HCl takes place together with the elimination of water. This result is supported by the change of the WAXS pattern at temperatures $T > 75°C$ (*Figure 6*). The elimination process of HCl and tetrahydrothiophene continues at higher temperatures, inducing a shift of the diffraction maxima towards higher angles, i.e. smaller spacings (from $2.14 \, nm^{-1}$ at $T = 130°C$ up to $2.28 \, nm^{-1}$ at $T = 335°C$), suggesting a progressive improvement in packing of the polymer chains (*Figure 7*). The sharpening of the reflection indicates, in addition, an increase of the coherent diffraction domains on heating. By measuring the integral width of the reflection, an increase of the crystal size in the [1 1 0] direction from 2.5 nm at 134°C up to 4.5 nm at 350°C can be estimated. These values are smaller than those corresponding to oriented samples[2,12]. This is probably due to the additional crystallinity induced during the orientation process.

The invariant Q remains nearly unchanged, until $T \approx 75°C$, indicating that the system remains homogeneous in this low-temperature range. The sudden increase of Q at $T > 75°C$ might be related to the beginning of the elimination reaction. This increase of Q is correlated with the appearance of the (1 1 0) and (2 0 0) diffraction peak at higher temperatures. The

appearance of bundles of PPV segments with concentration Φ_2 embedded in a matrix of the precursor Φ_1 could contribute to the creation of an electron density difference at colloidal dimensions. This electron density fluctuation would induce a notable increase in Q according to[7]

$$Q = (\Delta \rho)^2 \Phi_1 \Phi_2,$$ $\Delta \rho$ being the difference of electron density between the two phases. As the temperature rises the total volume content of PPV segments Φ_2 would contribute further to the observed increase of Q. The PPV segments tend to crystallize already at temperatures close to 80–90°C, as deduced by the presence of incipient Bragg maxima shown in *Figure 6*, becoming well developed at temperatures higher than 118°C.

CONCLUSIONS

Poly(xylilidene tetrahydrothiophenium chloride) is an amorphous material, which, after thermal treatment, converts into semicrystalline poly(p-phenylene vinylene). For temperatures lower than 75°C, no modification on the WAXS pattern is observed, indicating the absence of any significant amount of conversion. The sudden increment of the invariant and the simultaneous appearance of a Bragg maximum observed in the range 75–90°C suggest that the elimination reaction starts in this temperature range. The density difference between PPV-rich domains and the precursor regions leads to a dramatic increase of Q. The elimination process proceeds further at higher temperatures. Near 130°C the characteristic features of an imperfect PPV crystalline structure are already present. At higher temperatures the elimination reaction parallels the improvement process of the crystalline PPV domains, as revealed by the shift of the diffraction peaks towards higher angles, thus indicating better chain packing. In addition, the size of the crystalline domains grows concurrently, as evidenced by the further sharpening of the peaks. Finally, at temperatures around 300°C the well defined crystalline maxima characteristic of PPV suggest the almost complete transformation of the precursor into the final polymer.

ACKNOWLEDGEMENTS

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