Infra-red characterization of oriented poly(phenylene vinylene)

D. D. C. Bradley and R. H. Friend
Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

and H. Lindenberger and S. Roth
Max Planck Institut für Festkorperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, West Germany
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We present i.r. spectra of oriented films of poly(phenylene vinylene), PPV. Stretch-alignment of the amorphous precursor polymer, poly(p-xylene-α-(dimethyl sulphonium chloride)) *during* its thermal conversion to PPV enables highly oriented films of PPV to be produced that exhibit considerable crystallinity. From an analysis of the dichroic ratios of the main infra-red-active modes for a film of stretch ratio 5, we obtain an orientation parameter, $s = 0.04$, corresponding to a value of 0.94 for the Hermans orientation function ($\langle p_2(\cos\gamma)\rangle = 0.94$). This is an unexpectedly high degree of orientation for these initially amorphous films. Using the orientation parameter we derive values for the orientation of the transition moments of the main infra-red modes with respect to the molecular chain axis. We find in particular that the vinylene C–H stretch mode at 3024 cm^{-1} lies at 30° to the chain axis and that this is very different from the value of 74° expected from the molecular geometry. This deviation may be accounted for if the vibration induces a large charge flux along the chain. Such behaviour is consistent with a well delocalized π electron system.

(Keywords: infra-red spectroscopy; poly(phenylene vinylene); orientation)

INTRODUCTION

Recent interest in conducting polymers has extended to materials which, unlike *trans*-polyacetylene, have a preferred sense of bond alternation. Theoretical models for these polymers show that polaron or bipolaron states are produced upon doping[1-3] and the contrast with the soliton-like states produced in polyacetylene[4] has provided an interesting area of study.

Recent synthetic routes to these polymers have given much improved control and processibility of the final polymer. The Durham precursor route to polyacetylene[5] gives fully dense films[6,7]. Furthermore, it is possible to stretch-align films of the precursor during thermal conversion to polyacetylene and to produce films showing a very high degree of orientation[8]. These non-fibrous stretched films make possible the investigation of the intrinsic anisotropy of intra- and inter-chain electron motion[9-12].

Progress towards achieving processibility in polaron-supporting polymers includes the synthesis of the soluble conjugated polymer poly(diphenylenediphenylvinylene)[13,14]. This provides a good example of a phenylene-based polymer, but it is not at present possible to obtain oriented samples. High molecular weight films of poly(phenylene vinylene), PPV, have been produced by using a soluble precursor[15,16]. The water-soluble sulphonium polyelectrolyte precursors can be cast as films and subsequently converted to PPV by thermal elimination of dialkyl sulphide and hydrogen halide, as shown in *Figure 1*. A significant advantage of this synthesis is that, in analagous fashion to Durham-route polyacetylene, the precursor can be stretch-aligned during its thermal conversion to PPV[16-18]. PPV prepared by this route is the only current example of a non-degenerate gound state polymer which can be prepared in a highly oriented form.

Oriented films of PPV show very high conductivities when doped with AsF_5 and considerable anisotropy[17-20]. Murase *et al.*[18] have reported a value of $\sigma_{\parallel} = 2780$ S cm^{-1} at high doping levels for a film of stretch ratio 9, and anisotropies of up to 100 in the conductivities of SO_3-doped films. This enhancement in conductivity with the degree of orientation is also reported for Durham polyacetylene[11] and has been associated with an increase in the lengths of straight chain sequences.

In this paper we report an infra-red study of well-oriented films of PPV. The dichroic ratios of the main infra-red-active modes are used to assess the degree of orientation produced by stretching. They are then used to determine the angles between the molecular chain axis and the transition moments of these modes. The observed spectra are discussed and evidence for π electron delocalization is considered.

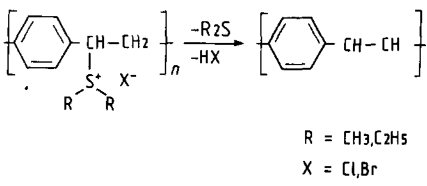

Figure 1 Conversion of the precursor sulphonium polyelectrolyte to PPV by elimination of dialkyl sulphide and hydrogen halide

EXPERIMENTAL

The precursor polymer, poly(*p*-xylene-α-dimethylsulphonium chloride) was prepared by the method of Wessling and Zimmerman[15] as detailed by Karasz *et al.*[20]. An aqueous solution of the product was pipetted onto a dichlorodimethylsilane-treated glass petri dish in a dessicator under N_2, which was then evacuated to pump off the water. The colourless cast films were carefully washed several times with N_2-saturated water to remove any remaining monomer and the NaCl formed during the polymerization of the precursor. The final films produced were transparent, and a fluorescent green/yellow colour. This colour change indicates that some elimination occurs even during the casting and washing procedure. Precursor films used in this study were approximately 2–4 μm in thickness. Stretching of these films was performed in a temperature-controlled glass jacket under a dynamic vacuum (pressure $<10^{-5}$ mbar). With tensile stresses in the range 150–300 kg cm^{-2} and corresponding temperatures in the range 60°C–150°C, stretch ratios of 5 were consistently obtained. Thermal analysis of the conversion process by t.g.a. and d.s.c.[17–20] shows three major endotherms associated with weight loss, at 102°C, 124°C and 184°C, which are taken to be the loss of water and two stages of the elimination reaction. Estimates of the degree of unsaturation as judged by residual sulphur content[17–20] indicate that full conversion is only achieved at temperatures above 300°C. To achieve this, our stretched films were sealed under N_2 in glass tubes and held at 350°C for several days. Higher stretch ratios have been reported for films stretched at temperatures up to 300°C[17,18], but as discussed later, the degree of orientation in our samples is already very high.

RESULTS

Figure 2 shows the infra-red spectra of a film of stretch ratio 5 with a thickness determined from the weight of a piece of the film and the reported density[17] at 2.8 μm. The thickness was also checked from an edge-on view of the film in an electron microscope. With this value we can estimate from the interference fringes apparent in *Figure 2* the two refractive indices for the PPV film; we find average values of 2.1 ± 0.2 and 1.5 ± 0.2 for light polarized parallel and perpendicular respectively to the stretch direction. These well-defined interference fringes are a clear indication of the macroscopic uniformity of these stretched films.

ANALYSIS OF THE DEGREE OF ORIENTATION

In order to determine the degree of orientation from the infra-red spectra shown in *Figure 2*, we have followed the analysis of Zbinden[21] for the case of partial axial orientation. This is the simplest form of alignment consistent with the stretching procedure in which the films are clamped at both ends and subjected to a tensile stress directed along a single axis. The model assumes that the molecular chains become preferentially aligned along the stretch direction, but are randomly distributed with respect to a rotation about their axis. The fraction of chains pointing in a specified direction is given by the rotationally symmetric distribution function, $f(\gamma)$, where γ is the angle between the chain axis, c, and the stretch direction, z. The dichroic ratio, R, expected for such a model is given by

$$R = A_{\perp}/A_{\parallel} = (\sin^2\theta + s)/(2\cos^2\theta + s) \qquad (1)$$

where $A_{\perp}$ and $A_{\parallel}$ refer to the measured integrated absorbances for infra-red radiation polarized perpendicular and parallel to z, θ is the angle between the transition moment for a given mode and c, and s is an orientation parameter defined by

$$s = F/(1 - 1.5\,F) \qquad (2)$$

where

$$F = \int_0^{\pi/2} \sin^2\gamma\, f(\gamma)\,\mathrm{d}\gamma \qquad (3)$$

and $f(\gamma)$ is normalized so that

$$\int_0^{\pi/2} f(\gamma)\,\mathrm{d}\gamma = 1 \qquad (4)$$

s is thus determined by the shape of the distribution function $f(\gamma)$ and varies from 0 to ∞ for the extreme cases of perfect axial orientation and a random chain distribution.

In general, as in the present case, the form of $f(\gamma)$ is not known. In order to obtain an estimate for s it is therefore necessary to assume that we know the value of θ for at least one of the infra-red active modes; s may then be derived from the measured dichroic ratio through equation (1) and can then be used to find the values of θ for the other bands. The greatest anisotropy is observed for the modes at 784 and 555 cm^{-1}, which are polarized

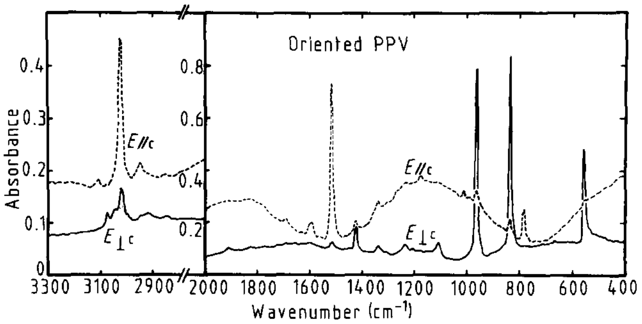

Figure 2 Infra-red spectra of an oriented film of PPV for light polarized with the electric vector parallel and perpendicular to the stretch direction. The spectra were recorded at 2 cm^{-1} resolution using a Nicolet 5SXB instrument

parallel and perpendicular to the stretch direction respectively. The measured dichroic ratios are $A_\perp/A_\parallel = 0.021 \pm 0.002$ and $A_\perp/A_\parallel = 26 \pm 4$ respectively. The form of s (see Zbinden[21], ch. 5, Fig. 19) is such that for $A_\perp/A_\parallel = 26$, $\theta > 83°$ and for $A_\perp/A_\parallel = 0.021$, $\theta < 10°$. The mode at 555 cm^{-1} is readily identified as an out-of-plane ring-bending mode for the phenylene ring, which for a planar ring should have a transition moment at 90°. Using this value for θ, equation (1) gives $s = 0.040 \pm 0.006$. If θ were less than 90° the value then derived for s would be smaller. Thus this value represents the *maximum* value for s (i.e. minimum degree of orientation) that is consistent with the observed anisotropy. We have not identified the mode at 784 cm^{-1}, but if a value of $\theta = 0$ is taken, a similar value for s, of 0.043 ± 0.004, is obtained.

We have insufficient information to determine the form of $f(\gamma)$, but it is useful to consider some simple models in order to visualize the degree of orientation corresponding to $s = 0.04$. If the sample is assumed to consist of a randomly oriented fraction, r, and a fully oriented fraction, $1-r$, then $f(\gamma)$ takes the form $f(\gamma) = r\sin\gamma + (1-r)\delta(\gamma)$ and $s = (2/3)r/(1-r)$ (Fraser[22]). With our value of $s = 0.04$ we find $r = 0.06 \pm 0.01$. The fully oriented fraction $(1-r)$ corresponds to the Hermans orientation function[23] that can be derived from X-ray diffraction data and which is often quoted as a measure of the degree of orientation. If the distribution function $f(\gamma)$ is expanded in terms of spherical harmonics, $(1-r)$ can be shown to be equal to the average of the second order term in the expansion, the orientation function $\langle p_2(\cos\gamma)\rangle$[24]. Another simple form for $f(\gamma)$ is that in which all chains are at the same angle, γ_0 to z. In this case, $f(\gamma) = \delta(\gamma - \gamma_0)$ and $s = 2\sin^2\gamma_0/(2-3\sin^2\gamma_0)$ so that for $s = 0.04$ we get $\gamma_0 = 11.2°$.

Clearly the degree of orientation of this film is very high despite the relatively low stretch ratio. In general, amorphous polymer films do not draw well and hence the orientation seen here is unexpected. We now consider a more realistic distribution function derived from the Kratky[25] or pseudo-affine deformation model[26]. This model, first proposed by Kratky to describe orientation of crystallites, is known to work quite well for many glassy or semicrystalline polymers and provides a useful reference point for discussion. In the model, molecular orientation of chain segments or crystallites is assumed to correspond to the macroscopic deformation of the sample with the rigid units rotating during stretching in the same manner as lines joining pairs of points in the bulk. Assuming a constant volume it is then possible[21] to derive a distribution function for the model in terms of the stretch ratio, λ, and to determine $s(\lambda)$ through equations (2) and (3). The distribution function is given by Zbinden as

$$f(\gamma) = \frac{\lambda^{3/4}\sin\gamma}{(\lambda^{-3/2}\cos^2\gamma + \lambda^{3/2}\sin^2\gamma)^{3/2}} \tag{5}$$

For $\lambda = 5$ we expect $s = 0.14$, which is clearly much larger than found experimentally. To obtain $s = 0.04$ in the Kratky model we need a value of λ equal to 11. Thus the actual orientation process in PPV appears more efficient than that described by the Kratky model. This result is unexpected. Normally the Kratky model gives an upper limit for the orientation of a semicrystalline polymer and factors such as viscous flow that are not explicitly considered will tend to reduce the orientation actually achieved. Furthermore, in the case of an amorphous polymer, where chain segments cannot be considered as rigid units, the orientation would normally be expected to be considerably less, especially at low stretch ratios[26]. The solution-cast precursor films used here are amorphous as are films of PPV produced by thermal conversion in the absence of stress[17], yet stretching these films during the conversion reaction gives PPV films that show better alignment than could be expected from this model for an initially semi-crystalline material.

The enhanced orientation seen in PPV results from stretching during an elimination reaction in which conjugated units are formed on the chain. The increase in unsaturation is expected to be an added driving force for the orientation and may be accompanied by a stress-induced crystallization.

INTERPRETATION OF THE VIBRATIONAL SPECTRA

The frequencies of the infra-red modes shown in *Figure 2* are listed in *Table 1* along with their relative strengths and preliminary assignments. The substantial completion of the thermal conversion is clear from the absence of bands at 632, 1047, 1318, 1433 and 2998 cm^{-1} which are present in the precursor polymer. These bands are associated with the dimethyl-sulphide moiety and correspond[27] respectively to the C–S stretch, S–CH_3 rock, CH_3 symmetric deformation, CH_3 asymmetric deformation and CH_3 asymmetric stretch modes. Another band that is lost from the precursor spectrum following thermal conversion is that at 2913 cm^{-1} which is thought to arise from the asymmetric stretch of the R–CH_2–R unit[27] of the precursor. Conversly, the bands seen at 965 and 3024 cm^{-1} in *Figure 2* are all but absent in the precursor spectrum and are thus readily assigned as vibrations of the unsaturated vinylene groups that are produced by the elimination reaction (*Figure 1*). The relatively weak bands at these frequencies in the precursor spectrum arise from the unsaturated linkages that are formed even during casting and washing and which give the films their yellow/green appearance. As previously noted by Gagnon *et al.*[17] and Murase *et al.*[18] the band at 965 cm^{-1} may be assigned to an out-of-plane CH bending mode which is characteristic of the *trans* configuration for the vinylene group. The corresponding mode for the *cis* configuration would be expected in the range 730–650 cm^{-1}, and no bands are seen in this range. (The bands at 768 and 784 cm^{-1} have the wrong polarization and are too high in frequency.) The band at 3024 cm^{-1} is assigned to a CH stretch mode.

The vibrations of the paraphenylene unit do not appear to change greatly during the conversion reaction though in some cases this is difficult to assess due to overlapping bands. The changes that are observed are a shift of the strongest ring stretching vibration from 1513 to 1519 cm^{-1} and a moderate increase in the relative strength of the CH out-of-plane bending mode at 837 cm^{-1}. The former is indicative[28] of an increase in the electron donating character of the substituents of the phenylene ring as the degree of unsaturation increases. The latter most probably arises through a reduction of steric hindrance by elimination of the bulky dimethyl-sulphide group.

Table 1 Frequencies of the infra-red active modes seen in *Figure 2*

	Relative strength[a]		
$\bar{\nu}$ (cm^{-1})	$E_\parallel$	$E_\perp$	Assignment
3105	vw	–	aromatic C–H stretch
3076	–	w	
3047	–	w	
3024	s	m	*trans*-vinylene C–H stretch
2950	w	–	C–H stretch from remnant saturated aliphatic groups
2920	–	w	
2852	vw	vw	
1691	vw	vvw	C=O stretch[b]
1629	vw	–	C=C stretch[c]
1594	m	vw	C–C ring stretch
1561	vw	–	
1519	vs	w	
1423	w	m	
1336	w	w	
1267	w	vw	C–H in-plane bend
1210	–	vw	
1176	w	vw	
1108	vvw	w	
1013	w	vvw	
993	vw	vvw	ring breathe
965	w	vs	*trans* vinylene C–H out of plane bend
837	w	vs	phenylene ring C–H out of plane bend
784	m	vw	–[d]
768	vw	–	
555	vw	s	phenylene out of plane ring bend

[a] The relative strengths of the parallel and perpendicular components of the vibrational modes are listed under column headings $E_\parallel$ and $E_\perp$ respectively

[b] Samples usually show some evidence of the C=O band. The precursor films are prone to oxidation, especially during the thermal conversion reaction

[c] This band is very close to the Raman active C=C stretching mode of *trans* stilbene[33]

[d] These bands are not readily identified. Their polarization and frequency precludes an assignment to *cis* vinylene out of plane bending. Furthermore, as they are also seen in samples of PPV prepared from the diethyl sulphonium bromide presursor they cannot involve the Cl atoms

Using the previously determined orientation parameter $s = 0.04$ and the observed dichroic ratios we can obtain values for the angle, θ between the dipole transition moments and the molecular chain axis, c. *Table 2* lists both the observed dichroic ratios and the values of θ derived through equation (1). Comparison can be made between the values in *Table 2* and those that might be expected for the molecular geometry that is shown in *Figure 3*[29,30]. The bands at 837 and 965 cm^{-1} which are both assigned to out-of-plane CH vibrations would be expected to have moments at 90° for a planar molecule and the observed deviation may indicate that the molecule is not perfectly planar. Alternatively, the deviation from 90° may be simply due to the steric interaction between the *ortho* hydrogens of the phenylene ring and the vinylene hydrogens. Indeed, the opening out of the vinylene zig-zag angle to $\phi = 130°$ is attributed to the effect of this steric interaction[30]. The band at 1519 cm^{-1} shows the value expected for θ if the transition moment for this ring-stretching vibration is parallel to the line joining the *para* carbon atoms in the ring. This is compatible with assignment to the higher frequency component of 'semicircle-stretching'[27] vibrations expected for the phenylene ring. The band at 1423 cm^{-1} is then assigned to the lower frequency component of this pair.

The value of θ for the vinylene CH stretch band at 3024 cm^{-1} is found to be 30°; this is very different from the value of 74° expected from the molecular geometry. Steric effects would be expected to increase this angle[30] and cannot thus account for this deviation. It must be assumed that the deviation arises because the moment for this vibration is no longer directed along the CH bond. It is possible that mixing of the phenylene and vinylene stretch modes might occur (they belong to the same

Table 2 Observed dichroic ratios and derived θ values (using equation (1))

$\bar{\nu}$ (cm^{-1})	$R = A_\perp / A_\parallel$	θ
784	0.021	3°
837	14	83°
965	16	84°
1423	1.95	64°
1519	0.033	9°
1594	0.24	34°
3024	0.19	30°

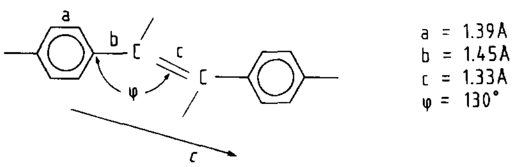

Figure 3 Molecular geometry of PPV as proposed by Dugay and Fabre[29]

symmetry species for a planar molecule) and thus in principle allow the CH stretch dipole moments to point in any direction within the plane of the molecule. However, such mixing would in the present case need to be strong and this is inconsistent with the large difference in intensity between the band at 3024 cm^{-1} and the others. The different behaviour for these modes during the thermal transformation reaction is further evidence against such mixing.

Similar effects have been reported for the CH stretch mode in *trans*-polyacetylene[31] for which the value of 48° found experimentally contrasts with the value of 90° expected from the geometry. In this material there are no other infra-red active modes with which this might mix. Castiglioni *et al.*[31] account for the deviation by proposing that the CH stretch mode induces a large charge flux along the chain. This requires that the CH stretch mode involves motion of the carbon atoms on the chain that modulates the amplitude of the Peierls dimerization. Similar fluxes are found in other unsaturated hydrocarbons and recent studies[32] indicate a close link with electron delocalization in the backbone. The magnitude of the effect seen in polyacetylene suggests considerable charge mobility, which is expected from the well delocalized π-electron system. We interpret the observation in PPV of a similarly strong orientation of the dipole moment away from the CH bond and towards the chain direction in the same way, i.e. we consider that the vinylene CH stretch mode couples to the delocalized π-electron system. This indicates that in comparison with polyacetylene PPV still has a significant π-electron delocalization along the chain despite having a considerably larger band-gap (2.5–3.0 eV)[29].

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