Molecular orientation of highly drawn poly(p-2-methoxyphenylene vinylene)

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Poly(p-2-methoxyphenylene vinylene) (MeOPPV) becomes preferentially oriented when its precursor polymer films are subjected to heating and uniaxial stretching. The orientation of the molecular chains is achieved as a result of both rigid unit formation and the transient plasticization by release of small molecules during stretching. The orientation of the aggregated chains was studied by infra-red dichroism. A high degree of orientation was observed, but the efficiency of orientation by drawing was found to be lower in MeOPPV than reported for poly(p-phenylene vinylene), indicating that the substituted methoxy group gives rise to disorder in the fully converted polymer.

INTRODUCTION

Investigations of the structures and deformation mechanisms in orientable conducting polymers have resulted in an understanding of the origin of anisotropy of the inter- and intrachain electron–electron interactions[1,2] and have thus provided valuable information about the optical, electronic and mechanical properties of these materials.

Highly oriented, high molecular weight films of poly(p-phenylene vinylene) (PPV) have been produced from a water soluble precursor[3–5]. PPV films are obtained from the precursor polyelectrolyte by thermal conversion of a uniaxially drawn film cast from an aqueous solution. The advantages of using a cyclic sulphide derivative instead of a dialkyl sulphide precursor in producing coherent, more completely eliminated PPV films have been reported[6]. To expand the studies of this class of highly conducting polymers it is desirable to synthesize other PPV derivatives with controllable redox properties. In this approach, we have successfully synthesized poly(2-methoxyphenylene vinylene) (MeOPPV)[7] and poly(2,5-dimethoxyphenylene vinylene) (DMeOPPV)[8].


PPV   MeOPPV   DMeOPPV
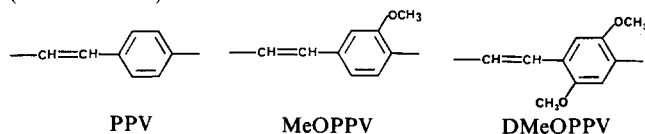
In previous studies, PPV[9,10] and DMeOPPV[11] were found to be highly crystalline. Cast films of the PPV precursor polymer could be highly stretched, resulting in a highly oriented, highly crystalline conjugated polymer upon thermal conversion, but the maximum uniaxial elongation ratio in the DMeOPPV process was low[11]. The nature of this resistance to drawing in DMeOPPV films is under further investigation. Stretch oriented films of PPV showed the expected highly anisotropic conductivity[8,12]. The structural orientation was studied by infra-red dichroism[13] and values as high as 0.97 (ref. 14) were obtained for the Hermans orientation function.

In this paper, we report the preparation of high molecular weight, highly oriented films of MeOPPV and we present the results of molecular orientation determined for the prepared films studied by infra-red spectroscopy. The general features and possible mechanisms of polymer deformation will be discussed together with the molecular orientation characteristics.

EXPERIMENTAL

The preparation of the precursor polymer, poly(p-2-methoxyxylylidene-α-tetrahydrothiophenium bromide) has been reported elsewhere[7]. An aqueous solution of the precursor polymer was dialysed against deionized, distilled water before casting films. Films were cast at room temperature under ambient conditions or under vacuum and were subsequently subjected to uniaxial stretching. Film orientation with nominal draw ratios of 2, 3, 4, 5, 6 and 7 was accomplished at 120°C according to a previously described method[15]. The final thermal conversion to the conjugated polymer, MeOPPV, was carried out by heating the samples at 280°C under vacuum for 12 h and was confirmed by elemental analysis (University of Massachusetts Microanalytical Laboratory).

Infra-red spectra were recorded using an IBM IR30-S FTIR spectrometer. For the oriented samples, infra-red dichroism measurements were made using the above instrument fitted with a Perkin-Elmer gold wire grid polarizer. Sample films between 1 and 3 μm thick were cut into strips along the machine stretch direction. The strips were placed directly facing the incident radiation beam at an angle of 45° and −45° to the vertical. To ensure accurate measurement of the absorbance, the infra-red band at 964 cm^{-1} was taken as a reference and the polarizer was adjusted before each spectrum was obtained so that a maximum absorbance was obtained for the perpendicular polarization. Over 200 scans were taken for each spectrum with a resolution of 2 cm^{-1} and were averaged to give the final spectra.

STRETCH
AXIS

CHAIN
AXIS

TRANSITION
MOMENT

θ

$E_{\parallel}$

$E_{\perp}$
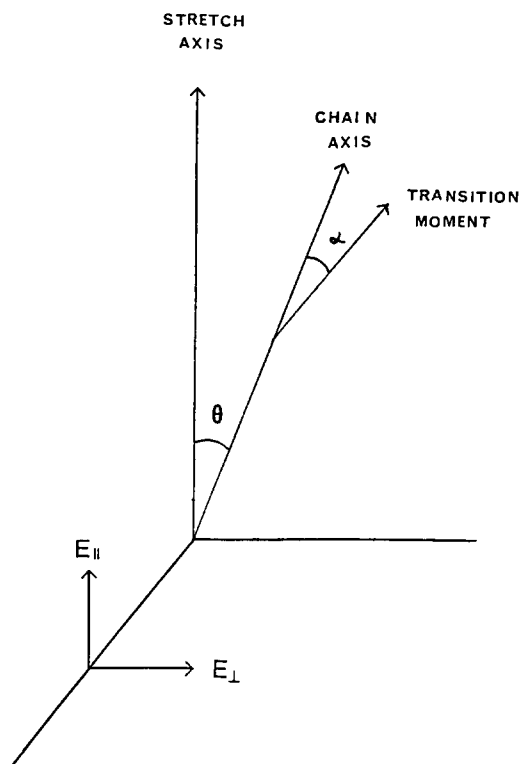
Figure 1 Schematic diagram of the polymer chain axis and the transition moment with respect to the preferential orientation axis

RESULTS AND DISCUSSION

Because the uniaxial stretching of the films was performed at 120°C, elimination of tetrahydrothiophene (THT) and hydrogen bromide is significant during the orientation process. The molecular species released during elimination, THT and HBr, act as transient plasticizers. The plasticizing effect may reduce the final polymer orientation obtained by drawing if the kinetics of molecular chain relaxation permit this. Thermal elimination at elevated temperature converts the saturated polyelectrolyte into a conjugated rigid structure and with further elimination leads to the formation of a crystalline phase. The orientational mechanism in these systems is therefore complex. Given the rigidity of the polymer backbone, it is appropriate to use a Kratky pseudo-affine deformation model[16] to describe the characteristic behaviour of chain orientation, especially for samples with higher elongation ratios.

Infra-red dichroism has been widely used to characterize molecular orientation[1,17]. The intensity of an infra-red absorption band depends upon the angle between the transition moment, M, of that specific vibration mode and the electric vector, E, of the incident radiation. The dichroic ratio, R, is defined as:

$$R = A_{\parallel}/A_{\perp} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are measured absorbances with the incident radiation polarized parallel and perpendicular to the preferential orientation axis. The dichroic ratio can be related to the orientation function by[17]:
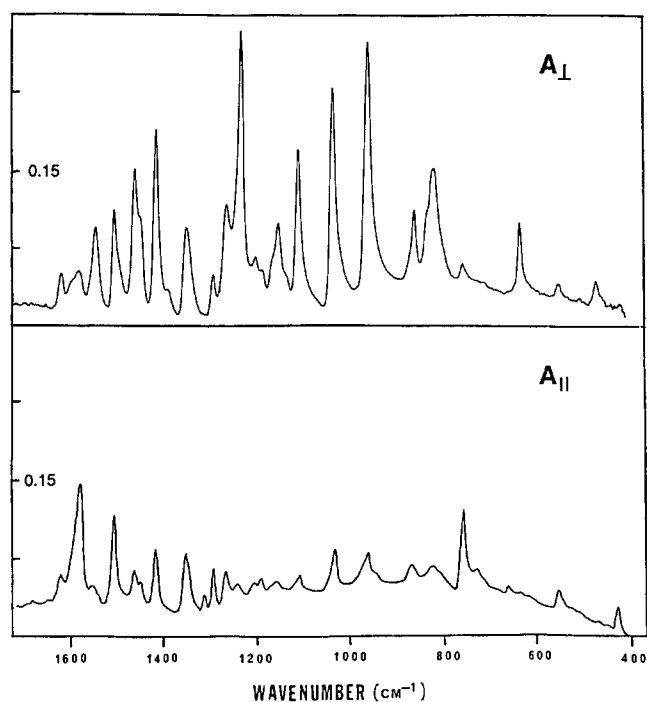
$$f = \frac{(R-1)}{(R+2)} \frac{(R_0+2)}{(R_0-1)} \tag{2}$$

$$= 1/2(3\langle\cos^2\theta\rangle - 1)$$

where θ is the angle between the molecular chain axis and the preferential orientation axis (stretching axis) and $R_0 = 2\cot^2\alpha$, α being the angle between the transition moment M of the specific absorption band and the chain axis (*Figure 1*). Consequently, if the angle α is known, the average orientation of the chain segments can be determined from the measured dichroic ratios of each specific band.

The polarized infra-red spectra for MeOPPV films with a draw ratio of 7 are shown in *Figure 2*. *Table 1* lists the measured infra-red dichroic ratios for selected bands for samples with nominal draw ratios from 2 to 7. Only those bands showing strong infra-red dichroism and relatively high absorption intensities are included.

As can be seen from *Table 1*, the dichroic ratio increases with draw ratio for the perpendicular bands ($A_{\perp}/A_{\parallel} > 1$) while changes for the parallel bands ($A_{\perp}/A_{\parallel} < 1$) are less significant. Up to a draw ratio of 7, there is still no

$A_{\perp}$

0.15

$A_{\parallel}$

0.15

1600   1400   1200   1000   800   600   400

WAVENUMBER (cm^{-1})

Figure 2 Polarized infra-red spectra for a MeOPPV film with a draw ratio, $l/l_0 = 7$, with incident radiation polarized perpendicular ($A_{\perp}$) and parallel ($A_{\parallel}$) to the stretch direction

Table 1 Measured infra-red dichroic ratios for MeOPPV films[a]

Band	Draw ratio, l/l_0					
(cm^{-1})	2	3	4	5	6	7
758	0.25	0.28	0.26	0.24	0.23	0.21
820	2.80	3.90	4.00	4.20	4.60	5.32
863	2.40	2.43	2.52	2.69	3.08	3.47
964	2.90	3.31	3.67	4.71	5.34	6.32
1038	2.24	2.65	2.62	3.15	3.63	4.31
1112	3.20	3.48	3.84	4.85	5.38	6.24
1236	3.30	4.10	4.33	5.55	6.31	8.54
1294	0.82	0.75	0.72	0.68	0.71	0.76
1418	2.27	1.89	2.36	2.70	2.37	3.17
1463	2.86	2.40	3.16	3.42	3.70	4.67
1584	0.28	0.25	0.24	0.29	0.26	0.26

[a]Dichroic ratios shown are presented as $D = A_{\perp}/A_{\parallel} = 1/R$

Table 2 Calculated angles α between the transition moment and the molecular chain axis

Band (cm^{-1})	Draw ratio, l/l_0				
	3	4	5	6	7
758	26	28	30	30	30
820	90	82	78	78	77
863	74	73	70	72	73
964	84	79	79	79	80
1038	79	73	73	74	74
1112	88	80	78	79	79
1236	90	83	82	81	83
1294	48	49	48	49	50
1418	69	71	71	68	70
1463	75	76	75	74	77
1584	23	27	33	32	33

indication of a saturation in the dichroic ratio indicating that the film orientation is still imperfect or is not the maximum obtainable orientation. In fact, a draw ratio of $l/l_0 = 11$ has been achieved for MeOPPV by orienting the film with a heating zone apparatus[18].

Although draw ratios of up to 13 have been obtained for PPV films, the orientation in the drawn PPV films approaches a maximum at a much lower draw ratio[13,14]. The methoxy side groups in MeOPPV will introduce an inherent disorder, which contributes to this difference. X-ray diffraction studies of stretched MeOPPV films have also shown that the monomethoxy substituted PPV derivative has a lower degree of crystallinity compared to both PPV and DMeOPPV[19].

To determine the degree of orientation using the polarized infra-red data, the angle α must first be determined. The Kratky model[16,20] was adopted in the present work for the analysis. The model assumes that an orientation of randomly distributed rigid chains is obtained in the drawing process. The molecular chains become preferentially oriented along the stretch direction and the transition moments of each vibrational mode are symmetrically distributed along the molecular chain axis with the angle α. The distribution function $u(\theta)$ is assumed to be rotationally symmetric along the stretch direction and is normalized, i.e.

$$\int_0^{\pi/2} u(\theta) \, d\theta = 1 \tag{3}$$

In this model, the dichroic ratio can be expressed by[20]:

$$R = A_\parallel/A_\perp = (2 \cos^2 \alpha + s)/(\sin^2 \alpha + s) \tag{4}$$

where s is an orientation parameter defined by:

$$s = F/(1 - 3/2F) \tag{5}$$

and F is the integral:

$$F = \int_0^{\pi/2} \sin^2 \theta u(\theta) \, d\theta \tag{6}$$

Zbinden[20] derived a distribution function for such a model as a function of draw ratio λ:

$$u(\theta) = \frac{\lambda^{3/4} \sin \theta}{(\lambda^{-3/2} \cos^2 \theta + \lambda^{3/2} \sin^2 \theta)^{3/2}} \tag{7}$$

where λ is the draw ratio of the sample, defined as $\lambda = l/l_0$.

From this model, equations (3)–(7) and the data in *Table 1*, the values of the unknown parameter α can be

calculated for each absorption band at various draw ratios. The results are listed in *Table 2*. It is noted that the results for samples with higher draw ratios ($l/l_0 > 4$) are consistent for each absorption band; the values of α become independent of draw ratio. However, the calculated values of the angle α for samples with $l/l_0 \leqslant 3$ deviate significantly from those calculated for samples with higher draw ratios, which suggests deviations from the Kratky model. The orientation exhibited by the MeOPPV films, however, is greater than predicted by the model. Such high degrees of orientation have also been reported for PPV films with a draw ratio of 5 and above and have been attributed to the enhanced orientation resulting from an elimination-induced increase in the unsaturation of the chain during stretching[13].

Based on the values of the transition moment angle α the orientation functions can be obtained using equation (2). The obtained infra-red orientation function (f_{ir}) values calculated from different absorption bands are listed in *Table 3*. When dealing with vibration modes that are independent of the local conformation of the main chain, infra-red dichroism will represent an average orientation of the chain segments. Thus the same value of the orientation function should be obtained even though different absorption bands corresponding to different α values are used in the calculation. This can be observed from the data in *Table 3*. Different absorption modes with differing transition angles approach the same values of chain orientation for each draw ratio. Deviations for the orientation function are noted to be more apparent for samples with low draw ratios (*Figure 3*).

It is evident that the efficiency of chain orientation by uniaxial stretching of the films is lower for MeOPPV than for PPV. For example, at a draw ratio of 5, PPV showed an orientation function value of 0.94–0.97 (refs. 13, 21), whereas the value for MeOPPV was only 0.80.

Lower values for the angle α between the transition moment and the polymer chain axis have been observed for MeOPPV than for PPV. The *trans* vinylene out-of-plane C–H bending mode at 964 cm^{-1} is expected to have a transition moment angle α of 90° if perfect orientation is obtained for the polymer having a rigid planar delocalized backbone. The angle is found to be 80° in MeOPPV ($l/l_0 = 7$) while the corresponding

Table 3 Infra-red orientation function values for MeOPPV films with various draw ratios

| Band (cm^{-1})	Draw ratio, l/l_0					
	2	3	4	5	6	7
758	0.50	0.65	0.73	0.82	0.84	0.87
820	0.65	0.66	0.71	0.78	0.81	0.88
863	0.48	0.64	0.68	0.81	0.81	0.84
964	0.56	0.63	0.72	0.81	0.83	0.87
1038	0.45	0.59	0.70	0.79	0.82	0.88
1112	0.59	0.63	0.72	0.83	0.84	0.87
1236	0.60	0.67	0.72	0.80	0.85	0.87
1294	0.43	0.58	0.72	0.79	0.82	0.89
1418	0.46	0.61	0.71	0.78	0.82	0.89
1463	0.55	0.60	0.72	0.79	0.83	0.84
1584	0.46	0.65	0.74	0.81	0.84	0.88
f_{ir} (avg)	0.53 ±0.07	0.63 ±0.03	0.72 ±0.02	0.80 ±0.02	0.83 ±0.01	0.87 ±0.02
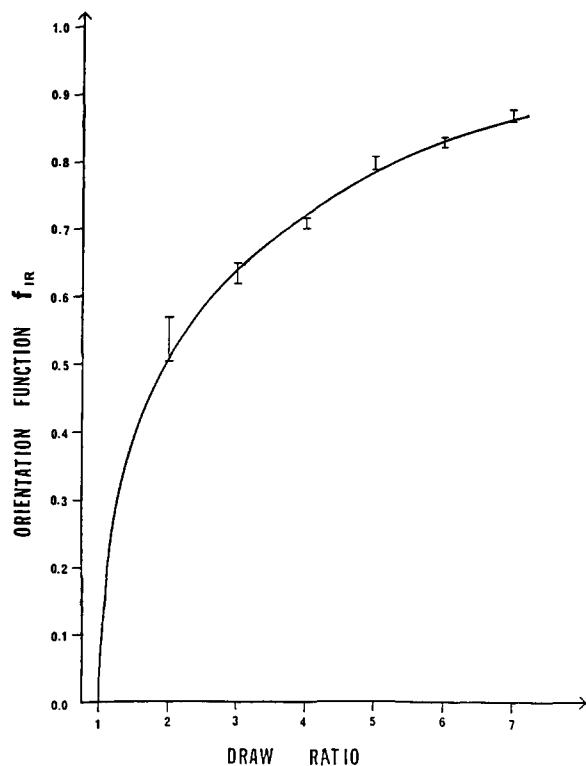
Figure 3 Infra-red orientation function *versus* draw ratio for MeOPPV films

transition moment angle in PPV has been reported as 83–84° (refs. 13, 14).

The deviations observed for the angles between the transition moments of each specific vibration mode and the chain are observed for other bands as well. In comparison with that observed in PPV, the difference is several degrees larger for MeOPPV.

CONCLUSIONS

We have shown that the molecular chains of uniaxially drawn MeOPPV films are highly preferentially oriented along the stretch direction. Samples with higher draw ratios ($l/l_0 > 3$) show Kratky type chain deformation. The efficiency of orientation by drawing is lower in MeOPPV than in PPV, which may result from disorders caused by asymmetric phenylene ring methoxy substitution on the polymer chain.

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