

# Preparation, spectroscopic and cyclic voltammetric studies of poly(1,4-naphthalene vinylene) prepared from a cycloalkylene sulphonium salt precursor polymer

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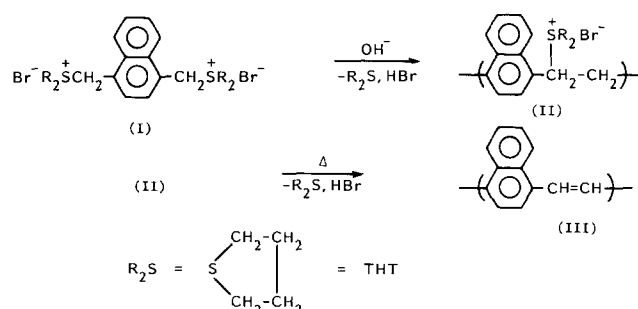
Films of poly(1,4-naphthalene vinylene) (P-1,4-NV) were obtained by the thermal elimination of a cycloalkylene sulphonium salt precursor polymer. The ultra-violet/visible (u.v./vis.), fluorescence and Raman spectra and the small-angle X-ray scattering diagrams were examined, and the oxidation and reduction potentials of P-1,4-NV were determined by cyclic voltammetry. The u.v./vis. spectra of P-1,4-NV films made from a sulphonium salt polymer based on the cyclic sulphide, tetrahydrothiophene, which was converted to P-1,4-NV at a temperature about 30°C lower than the temperature needed to obtain P-1,4-NV from the dimethylsulphide sulphonium salt polymer, showed phonon sidebands at room temperature as well as at -200°C. The phonon sidebands were apparently associated with a narrow distribution of crystallite sizes, which had an average long-period spacing of 140 Å, and was obtained when P-1,4-NV was made from the cyclic sulphonium chloride precursor polymer. The oxidation potential was found to be 0.75 V vs. SCE (saturated calomel electrode), the reduction potential was found to be -1.60 V vs. SCE and the band-gap energy was found to be around 2.05 eV. The high value for the oxidation potential of P-1,4-NV, in comparison to the oxidation potential of triiodide (0.52 V vs. SCE), from which an approximate value of  $2 \times 10^{-8}$  for the oxidation equilibrium constant was obtained, explains why very low conductivities are obtained when P-1,4-NV is doped with iodine. Films of the cycloalkylene sulphonium salt precursor polymer could be drawn to as much as 1.6 times their original length, and the drawn films showed a significant degree of orientation according to X-ray diffraction and polarized infra-red spectroscopy.

(Keywords: spectroscopy; poly(1,4-naphthalene vinylene); X-ray scattering; orientation; cyclic voltammetry)

## INTRODUCTION

Poly(1,4-naphthalene vinylene) (P-1,4-NV; **III**) can be prepared from a high-molecular-weight water-soluble precursor polymer (**II**) by adaptation<sup>1,2</sup> of the synthetic route used for the synthesis of poly(*p*-phenylene vinylene) (PPV), which was first described by Wessling and coworkers<sup>3</sup>. The solubility and high molecular weight of the precursor polymer allow P-1,4-NV and PPV to be obtained in film form. The precursor polymer can be readily prepared in aqueous solution at low temperature by the polymerization of a bis-sulphonium salt of 1,4-dimethylnaphthalene (**I**) on reaction with sodium hydroxide. The reactions involved in the synthesis of **III** are shown in *Scheme 1*.

Lenz and coworkers<sup>4</sup> have shown that the use of cyclic sulphides, such as tetrahydrothiophene (THT), in the reaction sequence for the synthesis of PPV leads to higher yields and higher molecular weights for the preparation of the precursor polymer and also to more efficient elimination reactions in the conversion of the precursor polymer to PPV. It is reasonable to assume that the side-reactions and/or residual impurities present in the PPV system will also be present in the P-1,4-NV system



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and that the use of cyclic sulphides in the synthetic route to P-1,4-NV should also show improvements similar to those reported by Lenz and coworkers<sup>4,5</sup>. In the present study, u.v./vis., Raman and fluorescence spectra and small-angle X-ray scattering patterns were examined for **III** prepared from the cycloalkylene sulphonium salt monomer and precursor polymer.

The films of the acyclic sulphonium salt precursor polymer for P-1,4-NV that were synthesized by Lenz and coworkers<sup>1,2</sup> could not be drawn, which may have been due to either a lower molecular weight or an intrinsic property of the precursor polymer. It is of interest, therefore, to attempt to draw the films of the precursor polymer (**II**) with a cyclic sulphide and to examine the degree of orientation achieved by polarized i.r. spectroscopy.

Another objective of the present study was to compare the oxidation potential for **III** with the oxidation potential of iodide and triiodide, which could provide supporting evidence to the suggestions made by Lenz and coworkers<sup>5</sup> for the cause of the very low conductivities that were obtained when the samples of P-1,4-NV and PPV were doped with iodine. PPV has an oxidation potential of 0.80 V vs. the saturated calomel electrode (SCE) and triiodide has an oxidation potential of 0.52 V vs. SCE, from which an oxidation equilibrium constant of  $2.3 \times 10^{-10}$  was estimated<sup>5</sup>. The conductivities reported<sup>5</sup> for iodine-doped PPV were much less than  $10^{-6} \text{ S cm}^{-1}$ , and those reported<sup>1,2</sup> for iodine-doped P-1,4-NV were of the order of  $10^{-5} \text{ S cm}^{-1}$ .

In this report, the u.v./vis., fluorescence and Raman spectra and the small-angle X-ray scattering patterns of **III**, which was prepared from the tetramethylene sulphonium chloride precursor polymer (**II**), were examined. The u.v./vis. spectrum was compared with the u.v./vis. spectra reported by Lenz and coworkers<sup>1</sup>. Cyclic voltammetry was used to determine the oxidation and reduction potentials of **III**, and the results were compared with the oxidation and reduction potentials of poly(*p*-phenylene vinylene) (PPV) of 0.80 V and  $-1.80 \text{ V}$  vs. SCE, respectively<sup>5</sup>. These results are discussed in terms of the explanation presented for the low iodine-doped conductivities for P-1,4-NV and PPV. The degree of orientation of stretched films of P-1,4-NV was determined by polarized i.r. and by X-ray diffraction.

## EXPERIMENTAL

### Monomer and polymer syntheses

The precursor for the synthesis of monomer, 1,4-bis(bromomethyl)naphthalene, was synthesized according to the method of Ried<sup>6</sup>, with a yield of approximately 60%. Elemental analysis: calculated, 45.90% C, 3.21% H, 50.89% Br; found, 46.04% C, 3.22% H, 50.76% Br; melting point (uncorrected) 181–183°C (literature 180°C).

The monomer, 1,4-naphthalene dimethylene bis(tetramethylenesulphonium chloride) (**I**), was prepared from 1,4-bis(bromomethyl)naphthalene by the following procedure. Into a 500 ml round-bottomed flask equipped with a magnetic stirrer were placed 10 g (0.032 mol) of 1,4-bis(bromomethyl)naphthalene, 15 g (0.17 mol) of tetrahydrothiophene and 300 ml of methanol. The mixture was stirred and heated to 40°C for 4 days. The solution was cooled slowly to room temperature, then cooled quickly to  $-50^\circ\text{C}$  and filtered. The yield was approximately 15 g (65%). The monomer was unstable on

removal of the solvent by the use of a rotary evaporator, so it was immediately used for polymerization.

To 600 ml of a 0.034 M aqueous solution of the sulphonium salt monomer (0.02 mol) was added dropwise under argon 60 ml of a 0.19 M aqueous solution of NaOH (0.11 mol), after which (approximately 5 min) the mixture turned into a gel<sup>4</sup>. According to pH measurements, all the base had reacted within this time period. The gel was redissolved by adding about 10 litres of distilled water under stirring. The polymer solution was dialysed with a dialysis membrane having a molecular weight cut-off at 10 000, and films were cast from this solution. The polymer yield was approximately 45%.

The optimum conversion temperature was determined by converting three different precursor polymer films at temperatures of 250, 270 and 300°C for 24 h *in vacuo* and by comparing the u.v./vis., fluorescence and i.r. spectra and elemental analyses for each film.

### Polymer characterization

I.r. and fluorescence spectra were performed on fully converted cast films. Samples for u.v./vis. and Raman spectroscopy were made by casting thin films of the precursor polymer onto quartz substrates and converting the sample to P-1,4-NV by the appropriate conditions, as described in the previous section. I.r. spectra were obtained on a Nicolet 60SX spectrophotometer. U.v./vis. spectra were obtained on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Fluorescence spectra were obtained on a Spex Fluorolog with a 450 W xenon lamp using wavelengths of 440, 420 and 380 nm. Raman spectroscopy was performed on a Spex spectrometer using an excitation wavelength of 758 nm. Elemental analyses were provided by Analytische Laboratorien in Gummersbach 1 Elbach, FRG.

### Cyclic voltammetry

Cyclic voltammetry was performed under highly pure conditions using the equipment described by Heinze<sup>7</sup>. Films were cast upon the positive (working) electrode by adding about 0.01 ml of the precursor polymer solution and heating under vacuum at the appropriate temperature.

The cyclic voltammograms were obtained against a Ag/AgCl reference electrode under inert conditions using dried dichloromethane or acetonitrile (dichloromethane could not be used for reductions) as the solvent with *t*-butylammonium perchlorate as the supporting electrolyte. The scan speed was varied between 1 and  $100 \text{ mV s}^{-1}$ . The electrochemical cells were calibrated by using a ferrocene standard<sup>8</sup>.

### Stretching studies

Films of the precursor polymer (**II**) were oriented either by drawing by hand or by using an Instron tensile tester equipped with an environmental chamber. Stretched precursor polymer films were then converted to P-1,4-NV using the conditions listed previously, and their degree of orientation was examined using polarized i.r. spectroscopy and X-ray diffraction.

### X-ray scattering

Small-angle X-ray scattering (SAXS) measurements of free-standing films were performed under vacuum using a Kratky Compact Camera equipped with a

position-sensitive detector (M Braun). The absolute intensity was measured with a moving-slit device. Slit-smear data were desmeared using the method of Glatter<sup>9</sup>.

## RESULTS AND DISCUSSION

According to the spectroscopic results and elemental analyses, it was found that 270°C was the best temperature of the three studied to convert the precursor polymer (II) to P-1,4-NV (III). The precursor polymer yields were therefore determined gravimetrically from the concentration in the dialysed solution after evaporation and conversion to III by heating at 270°C for 24 h *in vacuo*.

As summarized in Table 1, the use of tetrahydrothiophene resulted in significant improvements in the polymer yields. That is, the polymer yield doubled, even though the concentration used in this study was a factor of 7 lower than the concentration used for polymerization of the acyclic bis-sulphonium salt<sup>1,2</sup>. However, as in previous reports for the PPV system<sup>4</sup>, the yield of P-1,4-NV showed no further increase after the mixture gelled.

The u.v./vis. spectra of the film of III at various temperatures are shown in Figure 1. The u.v./vis. spectrum of III made by the cyclic sulphonium precursor polymer (II) is markedly different from the previously reported u.v./vis. spectrum<sup>1</sup> for P-1,4-NV, which had been prepared from an acyclic sulphonium salt. In particular, the spectrum shows phonon sidebands even at room temperature. However, the band gap of 2.05 eV ( $16\,100\text{ cm}^{-1}$ ) is in excellent agreement with the band gap of 2.04 eV ( $16\,050\text{ cm}^{-1}$ ) reported by Lenz and coworkers<sup>1</sup>. The structure of the u.v./vis. spectrum of III is even better defined at 77 K, with peaks at 461.2 and 496.8 nm ( $21\,680$  and  $20\,130 \pm 100\text{ cm}^{-1}$ ). This result suggests that, similar to the results reported by Lenz and coworkers<sup>4,5</sup>, there are apparently few or no side-reactions in either the polymerization or thermal conversion of the cyclic precursor polymer (II) to P-1,4-NV that would disrupt the polymer structure.

The fluorescence spectra for P-1,4-NV made from the cyclic sulphonium precursor polymer (II) taken at different excitation wavelengths were identical. By the use of peak resolving methods, the fluorescence spectrum for P-1,4-NV was found to have peaks at  $17\,900$  and  $16\,300 \pm 100\text{ cm}^{-1}$ , although the possibility of excimer formation could not be ruled out<sup>10</sup>. However, the differences in energy between neighbouring peaks in the fluorescence spectrum are similar to the differences in

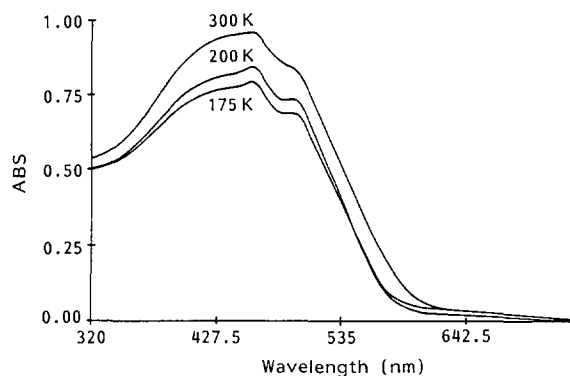


Figure 1 U.v./vis. spectra for P-1,4-NV at various temperatures

energy between neighbouring peaks in the u.v./vis. spectrum for P-1,4-NV prepared from the cyclic sulphide precursor (II) ( $1550 \pm 100\text{ cm}^{-1}$  for u.v./vis. and  $1600 \pm 100\text{ cm}^{-1}$  for fluorescence).

### Raman spectroscopy

The large amount of fluorescence found in P-1,4-NV made the measurements difficult, so that in the overview Raman spectrum only the peaks at  $1210$ ,  $1322$  and  $1562\text{ cm}^{-1}$  were easily distinguishable. Therefore, only the spectral range from  $1100$  to  $1700\text{ cm}^{-1}$  was studied in detail. Three fairly sharp peaks were observed at  $1210$ ,  $1322$  and  $1562\text{ cm}^{-1}$ , and three very weak peaks were found at  $1356$ ,  $1510$  and  $1612\text{ cm}^{-1}$ . The peak in the Raman spectrum at  $1562\text{ cm}^{-1}$  corresponds to the double-bond stretching mode. It may be noted that this mode is similar to the double-bond stretching mode in polydiacetylenes<sup>11,12</sup> and in PPV<sup>5,13</sup>. The peak at  $1562\text{ cm}^{-1}$  showed by far the highest relative intensity, which could explain why there are no other peaks observed in the u.v./vis. spectrum. These peaks could also be washed out by the absorption of another type of transition, or they could coincidentally cover their peak positions.

### Small-angle X-ray scattering (SAXS)

The reason for the appearance of phonon sidebands in the u.v./vis. spectrum of P-1,4-NV made from the cyclic sulphide precursor polymer (II) is presumably that there were fewer defects in the polymer so formed. As shown in Figure 2, the SAXS pattern of P-1,4-NV prepared from the precursor polymer (II) shows a long-period spacing of about  $140\text{ \AA}$ . This higher degree of crystallinity suggests that there are fewer defects in P-1,4-NV when it is obtained from the cyclic sulphide precursor polymer (II). Similar to PPV, the long-period spacing was also dependent upon annealing conditions<sup>5</sup>.

### Cyclic voltammetry

As shown in Figure 3, the oxidation potential of P-1,4-NV measured at a scan speed of  $1\text{ mVs}^{-1}$  in dichloromethane showed an anodic peak at  $0.87\text{ V}$  vs. Ag/AgCl ( $0.77\text{ V}$  vs. SCE) and a cathodic peak at  $0.83\text{ V}$  vs. Ag/AgCl ( $0.73\text{ V}$  vs. SCE);  $E_{1/2} = 0.75\text{ V}$  vs. SCE. The reduction potential of P-1,4-NV was measured at  $1\text{ mVs}^{-1}$  in acetonitrile and found to be  $-1.55\text{ V}$  vs. Ag/AgCl ( $-1.60\text{ V}$  vs. SCE) with peaks at  $-1.50\text{ V}$  vs. Ag/AgCl and  $-1.60\text{ V}$  vs. Ag/AgCl ( $-1.55$  and  $-1.65\text{ V}$  vs. SCE, respectively). The difference between the oxidation and

Table 1 Conditions and productions for the synthesis of P-1,4-NV

Monomer type	Monomer yield (%)	Polymer yield (%)	Concentration (M)	Conversion temp. <sup>a</sup> (°C)
Acyclic <sup>b</sup> I	61	20 <sup>c</sup>	0.2	300
	65	40 <sup>d</sup>	0.033	270

<sup>a</sup> Temperature at which less than 0.1% by weight of sulphur was detected

<sup>b</sup> From ref. 2, dimethylsulphonium chloride salt of 1,4-dimethylnaphthalene

<sup>c</sup> Reaction time 1 h

<sup>d</sup> Reaction mixture became a gel after dropwise addition of 50% of the equivalent amount of base (5 min)

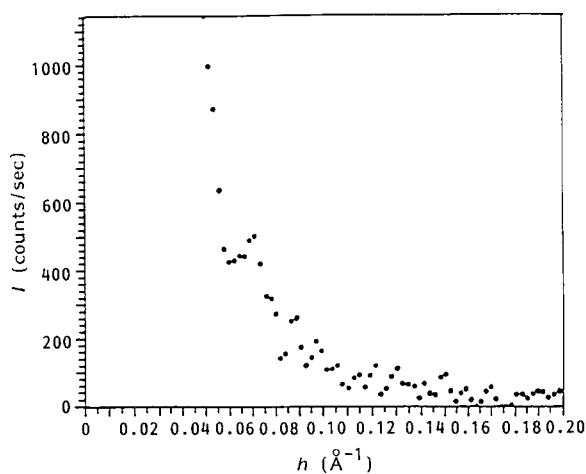


Figure 2 Small-angle X-ray scattering pattern for P-1,4-NV prepared from precursor polymer II

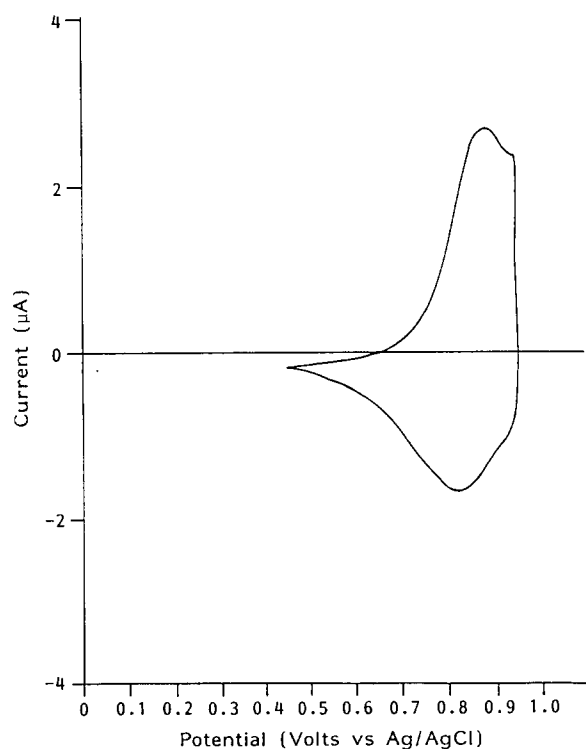
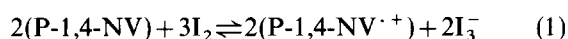


Figure 3 Oxidation potential of P-1,4-NV measured at a sweep speed of  $1 \text{ mV s}^{-1}$

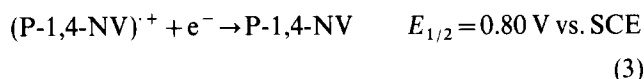
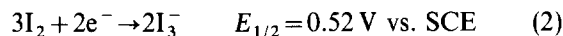
reduction potentials is also in good agreement with the band-gap energy, which is consistent with the results for other arylene vinylene polymers are discussed by Hörhold and coworkers<sup>14</sup>.

#### Oxidation equilibrium constant

Lenz and coworkers<sup>5</sup> have previously estimated the oxidation equilibrium constant for PPV doped with iodine. By using the reported value of 0.52 V vs. SCE for the oxidation potential for triiodide<sup>5</sup> and the value of the oxidation potential for P-1,4-NV obtained in this study, it is possible to calculate the oxidation equilibrium constant using the following equation:



which can be written as the difference of the following half-cell reduction potentials<sup>5,15</sup>:



By multiplying equation (3) by a factor of 2 ( $n=2$  for the number of electrons) and by subtracting equation (3) from equation (2), the following estimates are obtained for the Gibbs free energy of reaction and the equilibrium constant  $K$ :

$$\Delta G = -nFE = -2 \times 96.485 \times (-0.23) = +44 \text{ kJ mol}^{-1} \quad (4)$$

from which:

$$\ln K = nFE/RT = -44/RT = -17.7 \quad (5)$$

$$K = 2.0 \times 10^{-8} \quad (6)$$

where  $F$  = Faraday's constant =  $96.485 \text{ kC mol}^{-1}$ ;  $R$  = gas constant =  $0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ;  $T = 300 \text{ K}$ .

The extremely low value of the equilibrium constant, indicative of a high positive Gibbs free energy of reaction, explains the low conductivities obtained with iodine-doped P-1,4-NV. The conductivities of iodine-doped P-1,4-NV made from the precursor polymer (II) were found to be of the order of  $10^{-4} \text{ S cm}^{-1}$ , which is slightly higher than the value previously reported<sup>1,2</sup> and higher than the values reported for iodine-doped PPV<sup>5</sup>. These results are consistent with the estimates of the oxidation equilibrium constants for each system, although the nature of these conductivities is unclear.

#### Stretching of precursor polymer films

Table 2 lists the i.r. dichroism of stretched films at various frequencies. Samples could be drawn to as much as 1.6 times their original length under conditions similar to those used for drawing precursor polymer films of PPV. Figure 4 shows a typical X-ray diffraction pattern for a drawn, fully converted film of P-1,4-NV. There was no discernible dependence of the orientation of the films upon the method of drawing.

Compared to the precursor films for PPV, the precursor polymer films of II were very difficult to draw, suggesting that the inability to obtain high draw ratios may be an intrinsic property of the precursor polymer (II) rather than a function of molecular weight. Indeed, the drawing of prepolymer films of both P-1,4-NV and PPV is a very complicated process and is discussed in detail elsewhere<sup>16</sup>. The films do show a significant i.r. dichroism considering the draw ratio, although the exact angles of the transition dipole moments are not exactly known.

Table 2 Infra-red dichroism at various frequencies for oriented P-1,4-NV film ( $l/l_0 = 1.6$ )

Sample No.	$A_{\perp}/A_{\parallel}$ ( $1395 \text{ cm}^{-1}$ )	$A_{\perp}/A_{\parallel}$ ( $970 \text{ cm}^{-1}$ )
1 <sup>a</sup>	0.26	4.0
2 <sup>a</sup>	0.33	3.2
3 <sup>b</sup>	0.29	4.0

<sup>a</sup> Stretched using the Instron

<sup>b</sup> Stretched by hand

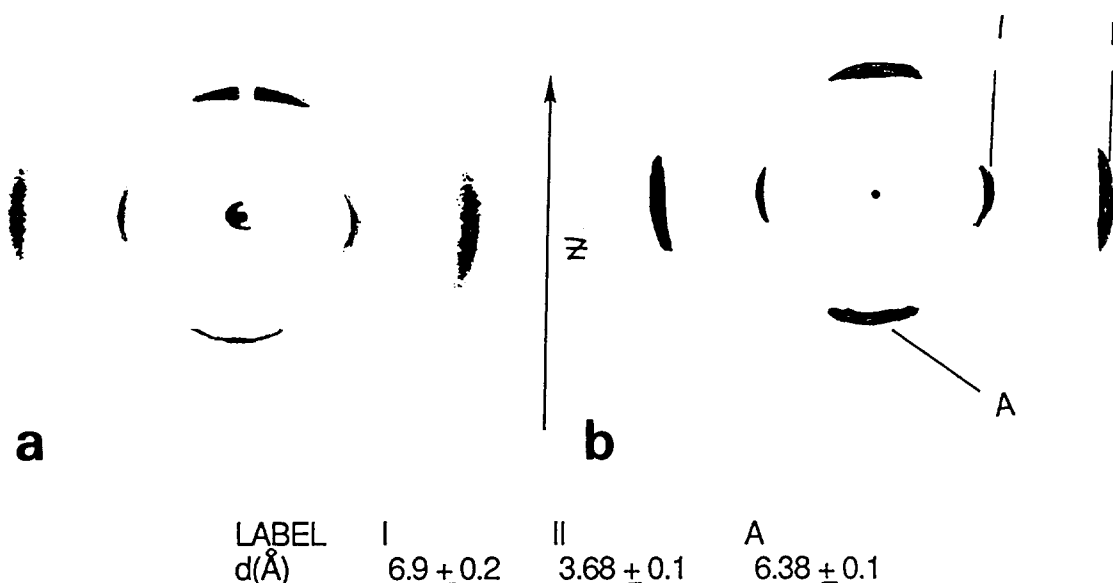


Figure 4 X-ray diffraction pattern of stretched film of P-1,4-NV: (a) original; (b) artist's impression

### SUMMARY AND CONCLUSIONS

The visible part of the u.v./vis. spectrum of P-1,4-NV (III) prepared from the cycloalkylene sulphide sulphonium salt precursor polymer (II) shows phonon sidebands at room temperature presumably because of the absence of harmful side-reactions in the conversion of the precursor polymer to P-1,4-NV. That is, side-reactions that would also disrupt polymer crystallite formation are apparently absent. The phonon sidebands are well defined at liquid-nitrogen temperatures. The u.v./vis. spectrum of P-1,4-NV obtained from the precursor polymer (II) is the most structured u.v./vis. spectrum ever reported for P-1,4-NV. The low conductivities obtained when P-1,4-NV was treated with iodine most probably result from the high oxidation potential of P-1,4-NV. In contrast to previous reports, the films of the precursor polymer (II) could be stretched to as much as 1.6 times their original length during the elimination reaction and showed significant degrees of orientation despite their still relatively low draw ratios.

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