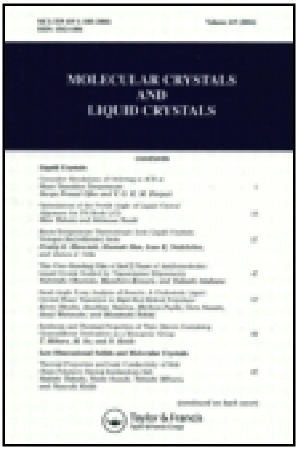

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RESONANCE RAMAN STUDIES OF THE ELIMINATION AND TRANSFORMATION REACTION OF DURHAM POLYACETYLENE

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Abstract The elimination and transformation reaction of Durham polyacetylene has been monitored by resonance Raman spectroscopy. The resonance Raman and photoluminescence spectrum from short *cis* segments, present in the pre-cursor polymer, has been recorded. A distribution of *cis* polyacetylene sequence lengths has been observed from Raman measurements made at different time intervals as the reaction proceeds, using λ_e 647.1nm. The ν_2 values recorded gradually decrease as the reaction proceeds the limiting value of 1472 cm^{-1} is significantly less than the 1450-1460 cm^{-1} values reported for the Shirakawa polymer.

INTRODUCTION

Most of the published Raman spectroscopic data on polyacetylene relate to the Shirakawa type of material. Our investigations have been, in the main, into the Durham material. The Durham route to polyacetylene is unique in that the polyacetylene is a final product from an elimination and transformation reaction(1)(Figure 1).

This study details the time - resolved resonance Raman data recorded as the elimination and transformation reaction proceeds. The reaction, performed at three temperatures, ambient, 65 and 85°C has been monitored by observing the spectral changes that occur with time. The structural implications from these observations are

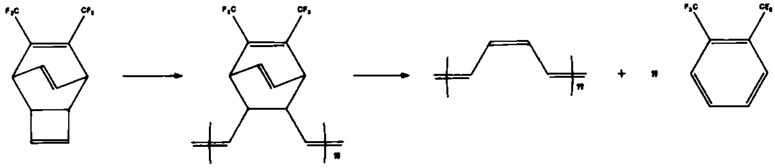

FIG 1 EDWARDS AND FEAST PREPARATION OF POLYACETYLENE

discussed.

RESULTS AND DISCUSSION

1. Pre-cursor Polymer

Figure 2 shows the resonance Raman spectrum recorded at 77K, from the Durham pre-cursor, using blue (λ_e 457.9nm) laser excitation. It is apparent from the figure that the trans polyacetylene content of the sample is low. The position of the three prominent bands is 914, 1261 and 1565 cm^{-1}, respectively. It appears that the Raman spectrum recorded from the pre-cursor polymer can reasonably be assigned to some cis polyacetylene that is present. This assignment is further supported by the presence of a long overtone/combination progression and a photoluminescence band centred at 2.3eV. A comparison of Raman data recorded from Shirakawa cis polyacetylene and from the Durham pre-cursor polymer is given in Table 1. It can be seen from Table 1 that significant differences exist between the two sets of data. The wavenumber shifts are thought to reflect a difference in cis polyacetylene chain length. The Raman spectrum obtained from the pre-cursor polymer, using λ_e 647.1nm was much weaker, since resonance conditions were far from optimum, however, the wavenumber values recorded were identical.

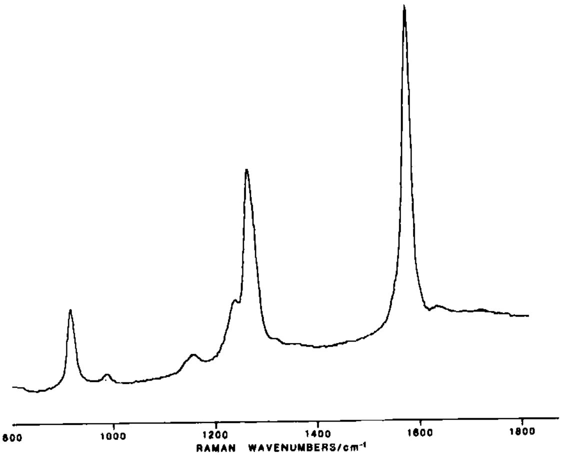

FIG 2 RESONANCE RAMAN SPECTRA RECORDED FROM DURHAM PRE-CURSOR POLYMER BETWEEN 800 AND 1800cm^{-1} λ_e 457.9 nm

The difference in the wavenumber, and photoluminescence band, values given in Table 1 coupled with the lack of dispersion of the Raman bands when changing from blue to red excitation, is attributed to the presence of short cis polyacetylene segments in the pre-cursor polymer. These segments are thought to be significantly shorter than those previously observed from Shirakawa type polymer. However, the existence of short cis polyacetylene segments, in the pre-cursor, is not unreasonable if some elimination and transformation has occurred prior to analysis.

TABLE 1 Raman wavenumbers (cm^{-1}) recorded from Durham pre-cursor polymer at 77K and Shirakawa cis polyacetylene at 77K between 800 and 1800 cm^{-1}

Durham Pre-cursor Polymer[1] Wavenumbers/cm^{-1}	Shirakawa cis Polyacetylene[2] Wavenumbers/cm^{-1}
805	825
914	910
984	980
1133*	1112*
1148*	-
1230	-
1261	1250
1316	-
-	1497*
1565	1541
1617	-

1. Photoluminescence centred at ∿2.3eV
2. Photoluminescence centred at ∿1.9eV

* Indicates trans polyacetylene bands

2. Elimination and Transformation Reaction

Figures 3 and 4 show the Raman spectra recorded at various time intervals, using λ_e 457.9 and 647.1nm, respectively, as the reaction proceeds at ambient temperature. Further details of the wavenumber shifts observed with time are given in Table 2. It is apparent from Figure 3 that the bands initially observed from the pre-cursor polymer disappear after ∿T=5 hours. However, after T=9 hours a weak feature is detected at 1255 cm^{-1}. The constant wavenumber shift recorded for the ν_2 trans polyacetylene band, using λ_e 457.9nm (see Table 2) is consistent with an isomerisation of short cis to short trans segments in the early part of the reaction. Indeed, it is only after several hours that a downward shift in the ν_2 band is observed, indicative of a significant change in the polyene chain length distribution.

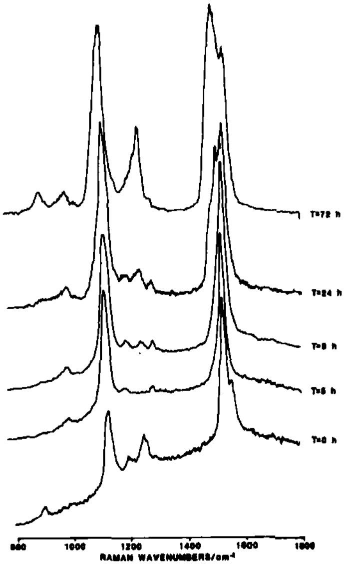

FIG 3 RAMAN SPECTRA RECORDED USING λ_e 457.9 nm FROM 800-1800 cm^{-1} MONITORING DURHAM POLYACETYLENE FORMATION AT ROOM TEMPERATURE

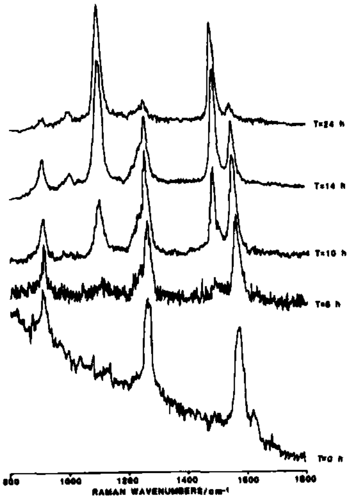

FIG 4 RAMAN SPECTRA MONITORING THE CHANGES IN DURHAM POLYACETYLENE : THE SPECTRA WERE RECORDED BETWEEN 800 AND 1800 cm^{-1}. λ_e 647.1 nm

The data obtained using red excitation (see Figure 4/Table 2) demonstrate the gradual movement of the 1261 and 1565 cm^{-1} bands assigned to short cis segments to 1250 and 1541 cm^{-1}, respectively, which previously have been assigned as the limits for an "infinitely" long cis segment.

TABLE 2 Raman ν_2 wavenumber (cm^{-1}) values of cis and trans polyacetylene isomers recorded at different stages of the reaction as it proceeded at room temperature

	λ_e 457.9nm			λ_e 647.1nm	
T/hrs	ν_2/cm^{-1} trans	ν_2/cm^{-1} cis	T/hrs	ν_2/cm^{-1} trans	ν_2/cm^{-1} cis
0	1538	1565(1260)	0	-	1565(1262)
1	1538	1565(1261)	1	-	1565(1260)
2	1538	-	2	-	1565(1261)
3	1538	-	3	-	1565(1262)
4	1537	-	4	-	1565(1260)
5	1537	-	5	1506	1564(1260)
9	1535	- (1255)	8	1495	1560(1257)
12	1535	- (1253)	10	1483	1552(1255)
24	1514(sh),1536	- (1252)	12	1483	1547(1254)
48	1507,1534(sh)	- (1251)	24	1479	1541(1251)
72	1503	1541(1251)	48	1479	1540(1251)
96	1501	1542(1251)	72	1478	-
			96	1478	-

Values in parenthesis are for ν_1 cis isomer bands, ν_2 bands are lost under the intense ν_2 of the trans isomer when using λ_e 457.9nm excitation. (sh) indicates shoulder.

It appears from these data, therefore, that the short cis segments observed initially gradually lengthen, as the elimination and transformation reaction proceeds, until they reach the limiting Raman values for an "infinitely" long chain.

Figure 4 also illustrates well the gradual build up of long trans polyacetylene chains. As can be seen, a very weak ν_2 band, at 1495 cm^{-1}, is detected after $\sim$8 hours. The gradual downward shift of both the ν_1 and ν_2 bands and the increase in band intensity is fully consistent with a change in the trans polyene sequence length distribution i.e. the concentration of long trans segments increases, as the reaction proceeds.

When monitoring the elimination and transformation reaction at 65 and 85°C, respectively, most of the subtle spectral changes, apparent when monitoring the reaction at room temperature, were missed. The gross changes were recorded and merit attention since information regarding the maximisation and elimination of the cis isomer can readily be obtained.

The most significant results obtained from the elevated temperature experiments relate to the final ν_2 values, i.e. 1496 cm^{-1} (λ_e 457.9nm) and 1472 cm^{-1} (λ_e 647.1nm), which were found to be invariant regardless of reaction temperature (up to 120°C).

In contrast to these values, the final ν_2 recorded by us from Shirakawa polymer has been 1498 cm^{-1} (λ_e 457.9nm) and 1460 cm^{-1} (λ_e 647.1nm). The similarity in ν_2 values recorded using blue excitation is not unexpected since both materials contain a certain amount of short chain length polymer. However, the difference in limiting ν_2 values using red excitation is thought to be very significant since, if the ν_2 values of 1460 cm^{-1} corresponds to an "infinitely" long trans polyene chain, then it is thought that a value of 1472 cm^{-1} corresponds to a shorter sequence length of > 30 carbon-carbon double bonds. This observation would be, in turn, consistent with the presence of some chemical or structural influence that limits the polyene chain length. Work is currently in progress to determine the exact nature of these defects.

(1) J.H. Edwards and W.J. Feast, Polymer Comm. 21, 595 (1980)

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