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TITLE: RESONANCE RAMAN EXCITATION PROFILES OF POLYACETYLENE / POLYISOPRENE BLOCK CO-POLYMERS IN TOLUENE

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Resonance Raman Excitation Profiles of Polyacetylene/Polyisoprene Block Co-Polymers in Toluene

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Abstract

We have measured the resonance Raman spectra and excitation profiles of a soluble polyacetylene/polyisoprene block-copolymer in toluene solution. These are the first reported excitation profiles that have been referenced to an internal solvent standard, the toluene Raman bands. We find that this copolymer exhibits the same two bands in the C=C stretch region, i.e., 1463 and 1519 cm^{-1}, that have been attributed to a bimodal distribution in conjugation length for polyacetylene thin films. The 1519 cm^{-1} peak has been associated with short chain segments of polyacetylene and we assign it to an average chain length of N=11 C=C's based on the frequency of the peak of its excitation profile. The excitation profile of the 1463 cm^{-1} mode peaks at 2.15 eV corresponding to a chain length of 31 C=C's. Based on the relative integrated intensities of these two excitation profiles, our block copolymer contains a 35% mole fraction of long chain segments to short chain segments. In contrast to previous results, we find that the 1294 cm^{-1} band, which is a mode with a mixture of C-C stretch and C-H deformation, is resonance enhanced, with an excitation profile that peaks at 2.6 eV, the same energy as the 1519 cm^{-1} mode's profile

Excitation profiles often provide extremely useful information about the electronic origin of any resonance enhanced Raman features. Critical for the accurate determination of an excitation profile is an internal standard with Raman features that are not resonance enhanced and with which one may therefore compensate for sample absorption. Although there have been two reports[1,2] of the resonance Raman excitation profiles of polyacetylene films, neither measurement was referenced to an internal standard, since the film's insolubility precluded solution studies. One measurement used the $1294\ \mathrm{cm}^{-1}$ band as a reference, with the assumption that it was not appreciably resonance enhanced, while a second study endeavored to perform an absolute measurement on the thin films, making absolute corrections for both absorption and reflection of the film.

Two research groups have presented papers[3,4] in the literature dealing with the interpretation of the dispersion or splitting as a function of excitation frequency that is observed for both the C=C and the C-C bands for polyacetylene thin films. However, the models for the conjugation length distribution have had to calculate the relative absorptions (and therefore excitation profiles) due to the different conjugation lengths, since they could not measure these absorptions directly. The synthesis of a soluble form of polyacetylene as a block copolymer allows the measurement of solution properties of polyacetylene and we report for the first time resonance Raman excitation profiles referenced to the spontaneous Raman bands of the toluene solvent.

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[1] (a) L. Lichtmann, Ph.D. Thesis, Cornell Univ., 1981. (b) D. B. Fitchen, Mol. Cryst. Liq. Cryst. **83**, 95-108 (1982)

[2] L. Lauchlan, S. P. Chen, S. Etemad, M. Kletter, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B **27**, 2301-7 (1983)

[3] H. Kuzmany, Phys. Stat. Sol. B **97**, 521-31 (1980)

[4] G. P. Brivio and E. Mulazzi, Phys. Rev. B **30**, 876-82 (1984)

Experimental

Block copolymers of polyacetylene and polyisoprene were prepared according to published techniques[5] and dissolved in nitrogen degassed toluene. The spectra were recorded in a solution cell with a concentration of the copolymer adjusted to give absorbance of 1-2 in one centimeter of solution at the absorption maximum of 2.0 eV. Resonance Raman spectra were measured with various lines available from argon and krypton ion lasers. Appreciable decomposition upon prolonged laser excitation (several hours) of the block copolymer occured, with concommitant formation of a black precipitate. The spectral features measured in the solution were unaffected by this decomposition, however significant bleaching of the solution did occur. Therefore, while complete spectra were accumulated over the period of about 20-30 minutes, they were calibrated with very short single scans over just the toluene 1004 cm^{-1}/polyacetytleneC-C band region (1163 cm^{-1}), taking pains to minimize exposure of the solution to the laser.

Results

Our resonance Raman spectra, two examples of which are plotted in Figs. 1a and 1b, are very similar to spectra that have been reported[1,2,3] for polyacetylene. The profiles shown in Fig. 2 are for the frequencies noted with intensities normalized by means of the 1004 cm^{-1} toluene band shown in Fig. 1. The slow laser induced degradation of the solution did not have any effect on the spectra we observed other than changing the relative intensities of the Raman bands between the copolymer and the toluene.

[5] M. Aldissi J. Chem. Soc., Chem. Commun., 1984, 1347-8

Discussion

Previous resonance Raman spectra of polyacetylene were all performed in solid films, whereas we have been able to measure our spectra of the copolymers in solution. The relative intensities of the two main features at 1519 and 1463 cm^{-1}, have been attributed[3,4] to a bimodal chain-length distribution with polyacetylene lengths around n=20 and n=80 C=C units. Based on a comparison of our spectra with those reported in the literature, we presume that the local morphology of the copolymer is quite similar to that of the solid film. That is, despite the fact that the copolymer is soluble, there are apparently fibrils of ordered polyacetylene, although the amounts of well ordered chain to disordered chain are different. There have been two previous reports[1,2] on the resonance Raman profiles of polyacetylene films. It has been stated[6] that the 1290 cm^{-1} band in thin film polyacetylene that corresponds to our 1294 cm^{-1} feature is not resonance enhanced, although no citation or other reason was given for so stating. The excitation spectra presented in references 1a and b were calibrated with this band as a standard, and it was stated quite clearly by Lichtmann[1a] that this was an unproven assumption. This assumption was necessary because of the lack of any other internal calibartion for these insoluable films.

We have found, on the other hand, that the 1294 cm^{-1} band is resonance enhanced as shown in Fig. 2, although its enhancement is not as strong as either the 1463 cm^{-1} or the 1519 cm^{-1} features. Thus the resonance Raman profiles reported by these workers were very broad and did not show highly peaked behavior. In particular, we find that the 1519 and 1294 cm^{-1} excitation profiles are clearly associated with the same electronic excited state and that state is distinct from that associated with the 1463 cm^{-1} mode. We note that our

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[6] F. B. Schugerl and H. Kuzmany, J. Chem. Phys. **74**, 953 8 (1981)

results for both the 1519 and 1294 cm^{-1} excitation profiles contrast very sharply with corresponding profiles reported[2] for very thin films of polyacetylene where no internal standard was used to calibrate the intensities. We believe that the lack of an internal correction for any resonance Raman excitation profile makes the measurement difficult with weakly absorbing samples, and problematic with intensely absorbing and reflecting materials.

The peak of our excitation profile for the 1463 cm^{-1} feature agrees with the measured absorption spectrum for the block copolymer[7], giving us confidence that we are actually probing a measurable quantity of these long chains. Our profile for the short chain Raman peak at 1519 cm^{-1} shows a maximum at a wavelength that the absorption spectrum for chains with 11 C=C units should also maximize (using the Hudson-Kohler short chain polyene extrapolation). The long-chain excitation profile peaks at 2.15 eV, which indicates a conjugation length of 31 C=C bonds based on the extrapolation of Hudson and Kohler,[8] which is $N=7.716/(n-1.90)$, with n in eV. Our short chain profile peaks at 2.60 eV, implying N=11 C=C's. Since both profiles are referenced to the same internal standard, we are also able to estimate the relative amounts of the two chain lengths based on the ratio of the integrated areas between the two profiles. Assuming that each C=C unit will contribute equally to the total absorption cross-section and therefore also the excitation profile cross-section, the ratio of the areas between the two profiles implies a ~2:3 ratio in the C=C's between short and long chain lengths. Thus, we estimate a 33±5% mole fraction of long conjugation length chains (N=31) in our analysis.

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[7] M. Aldissi, Synthetic Metals 13, 87-100 (1986)

[8] B. S. Hudson and B. Kohler, Chem. Phys. Lett. 14, 299 (1972)

We have not been able to confirm this trend with a block copolymer incorporating deutero-polyacetylene due to severe sample fluorescence in the 400-500 nm region. We suspect, however, that the reported resonance enhancement for the 1200 cm^{-1} band for deutero-polyacetylene is simply a manifestation of the increased participation of this mode's coordinate for the deutero polymer's short chain's excitation, and therefore its enhancement is consistent with the enhancement of the 1294 cm^{-1} feature of the polyacetylene.

There are two possible explanations for the fact of the enhancement of the 1294 cm^{-1} band in polyacetylene. The first supposes that there is a bimodal chain length distribution as noted above, one around N=11 and the other at N=31 C=C units. With this explanation, the polyacetylene resonance Raman spectra are viewed as a superposition of two spectra; the 11 C=C chain's bands at 1125, 1294, and 1504 cm^{-1} and the 31 C=C chain's bands at 1168 and 1463 cm^{-1}. The presence of this bimodal distribution would then be due to some as yet unidentified synthetic anomaly that consistently favors these two chain lengths regardless of the particular method of preparation. The absence of the 1294 cm^{-1} band for the long chains implies that very long chains either do not have this mode (i.e., that it is a C-H deformation associated with the chain ends) or that very little excited state distortion occurs along this coordinate for very long chains (i.e., the nature of the excited state changes for long chains).

A second explanation supposes that the relative change in the amounts of the two segments, 11 C=C and 31 C=C, reflects the relative amounts of chain end versus chain middle for a *single* long chain. In other words, there are actually two different electronic states in long chain polyacetylene, one for the chain middles and another for the chain ends. This explanation is consistent with the fact that we observe ~2:3 ratio (0.67) in the integrated excitation profiles, compared with the 22/31 = 0.71 ratio obtained from assuming that although the average chain length is 31 C=C's, each chain also has an electronic state associated with the ~11 C=C's at each of the chain ends. For the short chains (<22 C=C's), we have the origins for both sets of spectral features. As the chain length increases, we produce more and more disparity between the middle-chain modes and those associated with the ends of the chain. The electronic states for this system are, then, fairly complex. We have the band-like, delocalized states from the middle of the chains as well as more localized chain-end states, and these are the two states that are reflected in our excitation profiles. Comparison of our Raman data on coplymers with that of "good" thin-film polyacetylene,[1] we estimate that that the thin-film samples possess chain lengths that contain 4.8 times as many C=C moieties as our copolymer, or 148 units (the ratio of the intensities of the "1463" and "1518" cm^{-1} features under 457.9 nm excitation). The degree of crystallinity would then be (33-22)/33 = 0.29 for our soluble sample and (148-22)/148 = 0.85 for the best thin films. These numbers agree quite well with previous molecular weight determinations as well as x-ray powder pattern diffraction. This would also explain why the bimodality of the resonance Raman excitation profile seems to be an inherent property of all polyacetylene formulations, including the block copolymer studied in our work. Once chain lengths become greater than 22 C=C units, the electronic state associated with the chain middle shows different resonance Raman spectra (i.e., different excited state distortions) than that associated with the chain end.

These results have serious implications for the normal mode analyses[9,10] that have been reported for polyacetylene, since it has been assumed in these previous works that the 1294 cm^{-1} band is associated with a

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[9] F. Inagaki, M. Tasumi, and T. Miyazawa J. Raman Spectros 3, 335 43 (1975)

[10] F. B. Schügerl and H. Kuzmany J. Chem. Phys. 74, 953 8 (1981)

mode of the infinite chain. Our results indicate that this band is due instead to a short chain or a chain end. Indeed, previous workers report[11] that this band disappears upon excitation at 752.5 nm, which is consistent with the fact that this excitation is very far from resonance for the short chain (1.65 as compared to 2.65 eV for 11 C=C's). Reported[12,13,14] resonance Raman spectra of short chain polyenes are used to calibrate the chain lengths measured from the polyacetylene spectra. Our data provides two key calibration points for any expression used in the determination of the chain length, these points of which are obtained directly from polyacetylene samples. Various expressions have been proposed to express the dependence of Raman frequency on chain length, $\nu_2 = 1459 + 720/(N-1)$ by Schügerl and Kuzmany[10], $\nu_2 = 1450 + 500/N$ by Mulazzi , et al.[11], and $\nu_2 = 1461 + 151.24\ e^{-0.07808N}$ by Baruya, et al.[15] None of these expressions satisfactorily fits our data and we wonder about the utility of these expressions in general without very accurate calibrations of known chain lengths.

Conclusion

We are lead to the conclusion that the key to understanding the dispersion in the resonance Raman of polyacetylene is the realization that different electronic states are probed as a function of laser excitation over the range 1.5-2.5 eV. Quite possibly, these different states are due to the same polyacetylene chains and merely reflect the fact that one state is linked to the middle chain region while the other is "pinned" at the chain ends.

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[11] E. Mulazzi, G. P. Brivio, E. Falques, and S. Lefrant Sol. State Commun. **46**, 851-5 (1983).
[12] F. Inagaki, M. Tasumi, and T. Miyazawa J. Molecular Spectros. **50**, 286-303 (1974).
[13] V. R. Salares, N. M. Young, P. R. Carey, and H. J. Bernstein J. Raman Spectros. **6**, 282-8 (1977)
[14] I. M. Ivanova, L. A. Yanovskaya, and P. P. Shorygin Opt. Spectrosc. **18**, 115-8 (1965)
[15] A. Baruya, D. L. Gerrard, and W. F. Maddams Macromolecules **16**, 578-80 (1983)

We conclude also that the 1294 cm^{-1} peak is resonance enhanced, albeit to a lesser extent than the other bands in the spectrum. Based on the similarity of this peak's profile with the profile of the 1519 cm^{-1} peak, the 1294 cm^{-1} band is associated primarily with short chain segments, probably located at the ends of the long chain segments. We realize that this interpretation conflicts with previous force constant calcuations on polyacetylene, where it was assumed that the 1290 cm^{-1} mode was due to infinite chains and assigned to either a C-H deformation[9] or the C-C stretch[10] of the infinite chain.

Acknowledgments

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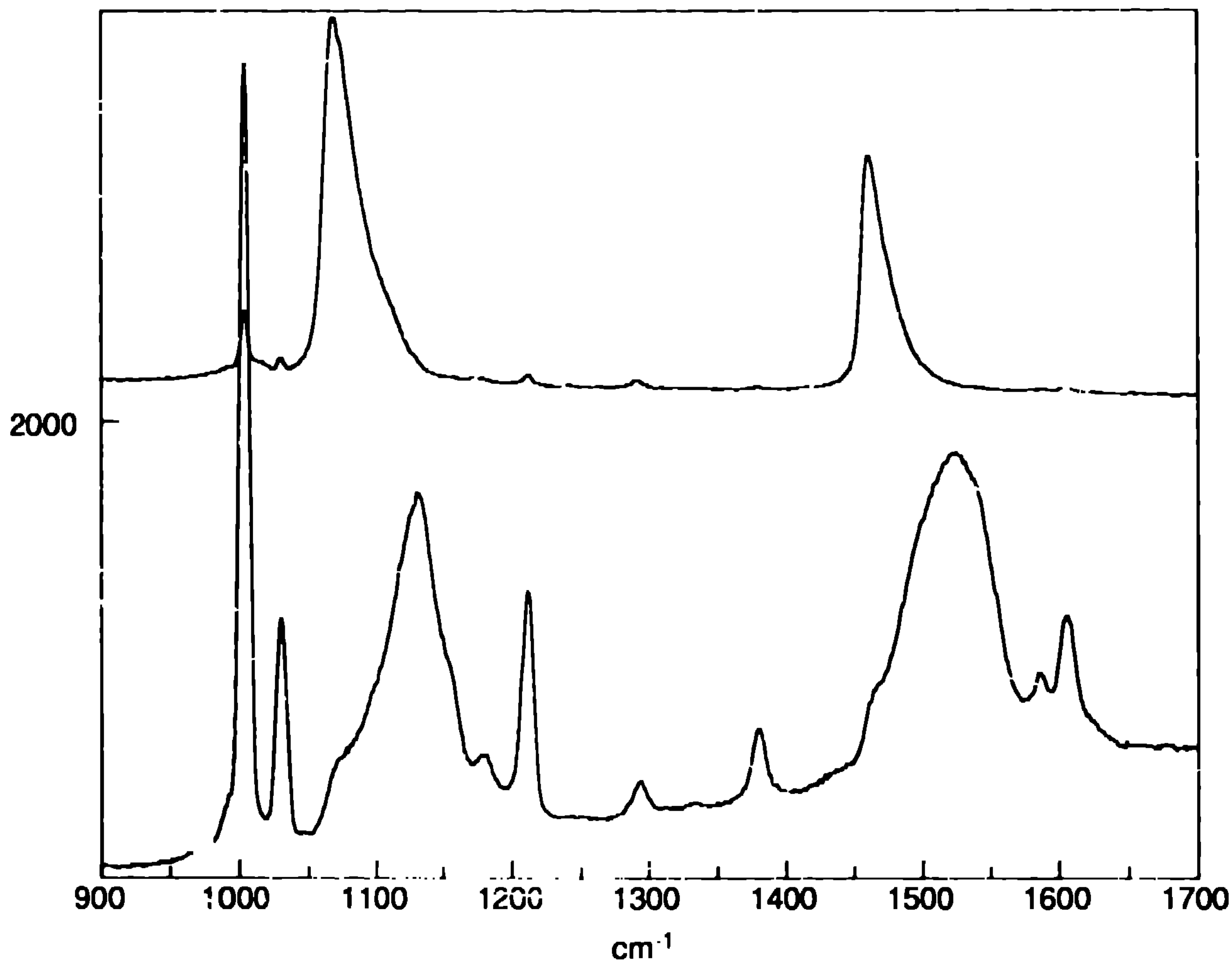
Captions

Figure 1. Polyacetylene/polyisoprene block copolymer in toluene solution, 454.5 nm excitation (lower) and 676.4 nm excitation (upper).

Figure 2. Excitation profiles for 1292, 1063 and 1518 cm^{-1} bands.



Polyacetylene/polyisoprene in toluene, 454.5 nm (lower) 676.4 (upper)

Excitation profile of polyacetylene/polyisoprene block-copolymer in toluene