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Notes

Chemical Modification of Polydiacetylenes: 6328-Å Resonance Raman Spectra of Brominated Poly[1,6-di(*N*-carbazolyl)-2,4-hexadiyne] (Poly-DCH)

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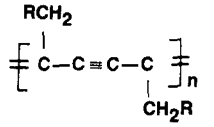
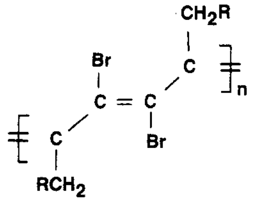
Introduction

Resonance Raman spectroscopy is a sensitive probe of the structure and electronic states of polydiacetylenes (PDA) and other conjugated systems.[1] In this study, we report our observations of resonance Raman spectra of poly-DCH (1) and its brominated analogues using 6328 Å as the wavelength of excitation, and we discuss the spectra in terms of the chemical reactions and structural changes that occur upon bromination.



$\left[\overset{RCH_2}{\overset{|}{C}} - C \equiv C - \underset{CH_2R}{\underset{|}{C}} \right]_n$

1



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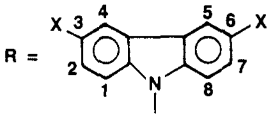

1, X=H
2, X=Br

Recent studies from our laboratory[2-6] have described anisotropic reactions of electrophiles with macroscopic single crystals of poly-DCH. In the case of bromine, this chemistry, which gives products homogeneous by electron microscopy, allows the systematic introduction of three to eight Br atoms per polymer repeat unit with retention of crystallographic order. The positions of C–Br covalent bond formation in the modified polymers were deduced by solid-state ^{13}C CP-MAS NMR studies of the brominated polymers and model molecular compounds. In particular, the NMR studies,[2,7] which probe the bulk of the samples, indicate that initial reaction involves selective bromination of the carbazole groups at the 3- and/or 6-positions. Subsequently, the conjugated backbone becomes involved in the reaction, and for materials which have gained six Br atoms per repeat, the extensive conversion of the PDA structure to a mixed polyacetylene (2) was deduced. Additional support for the deduction of the mixed polyacetylene 2 comes from X-ray diffraction studies of poly-DCHBr$_6$,[8] which reveal the requisite shortening of the lattice constant in the chain direction. Extensive disruption of the conjugated backbone was indicated for poly-DCHBr$_8$ from both NMR and electronic spectra[6] in the solid state. Not surprisingly for a chemistry based on diffusion of reagents through a crystal, the modified polymers are not homogeneous at the molecular repeat level.[2] Indeed while the NMR spectra[2,7,8] for poly-DCHBr$_6$ and -Br$_8$ reveal extensive reaction at the triple bond, low residual concentrations of triple bonds are detected in delayed decoupling spectra at chemical shifts indicating some decrease in the average conjugation length.[2] This point about molecular repeat inhomogeneity will also be apparent from the Raman spectra described herein.

Experimental Section

The samples used in this study were prepared as previously described.[6] Raman spectra using 6328-Å excitation were recorded as previously described[9] by using the 180° backscattering geometry.[1a] The incident laser power used was 1 mW.

Results and Discussion

As a prelude to the discussion of the Raman spectra, it is useful to summarize the available electronic spectral data for the materials under investigation. Poly-DCH has an intense absorption maximum at 656 nm.[10,11] Poly-DCHBr$_6$, which is copper–bronze in color, has a solid-state spectrum[3] which exhibits shoulders near 630 and 550 nm. Poly-DCHBr$_8$, straw in color indicating disruption of conjugation, displays a shoulder at 450 nm as the lowest energy feature in its solid-state spectrum.[6] Hence, 6328-Å light is strongly absorbed for poly-DCH and poly-DCHBr$_6$ and not strongly absorbed for poly-DCHBr$_8$.

As a point of reference for a discussion of the consequences of bromination, the resonance Raman spectrum of poly-DCH is given in Figure 1a; it is in good agreement with previous reports.[1a,11,12] Of particular interest is the normal mode associated with the triple-bond stretch at 2089 cm^{-1} and shifts at 1425, 1455, 1473, and 1500 cm^{-1}, assigned to the double-bond stretch in Fermi resonance with the carbazolyl groups,[1a] although other interpretations are conceivable. Our discussion of the spectra of the brominated polymers will focus on changes in the regions associated with the double- and triple-bond stretching vibrations.

For thick PDA crystals, such as the ones used in this study, resonance Raman spectroscopy is primarily a probe of the surface regions of the sample, perhaps as little as five surface planes in poly-DCH or -PTS at 6328 Å,[1a] where the absorption of these materials is intense and near the maximum.

The spectrum of poly-DCHBr$_6$ is given in Figure 1b. The intensity of the spectrum is somewhat greater than that of poly-DCH. Additionally, considerable background scattering is evident, and the peaks are slightly broader than those of poly-DCH. The triple-bond stretch is observed at 2108 cm^{-1}, a shift comparable to those of PDA with absorption maxima at 540–570 nm such as poly-ETCD at 130 °C[1a] and poly-THD.[11] Since solid-state NMR studies,[2,7,8] which revealed poly-DCHBr$_6$ to be largely a mixed polyacetylene material, show the presence of residual triple bonds, whose chemical shifts suggest relatively disordered and/or shorter conjugation lengths, it is likely that the residual triple bonds reside near the surface of the crystal. This deduction would be consistent with the observed anisotropy of the bromination reaction[3] in that reaction starts on the end of the crystal and the reagents diffuse along the direction of the backbone, leaving the surface elongated along the crystallographic *b*-axis as the least reactive part of the crystal.

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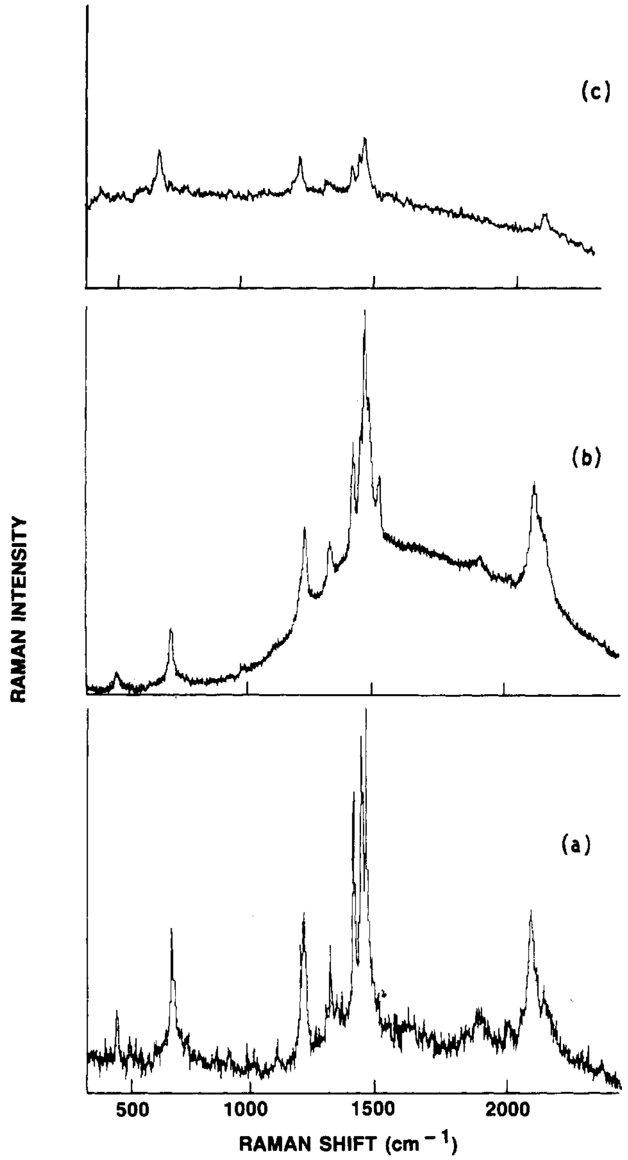

Figure 1. 6328-Å Raman spectrum of (a) poly-DCH, (b) poly-DCHBr$_6$, and (c) poly-DCHBr$_8$.

The double-bond stretching region of Figure 1b reveals observable shifts at 1429, 1458, 1472, 1487, and 1523 cm^{-1}. While most of these shifts are similar to those of poly-DCH itself, their assignments in the modified polymer would likely differ. This suggestion follows from observations of the FTIR spectra of these materials. While the FTIR spectrum of poly-DCH reveals absorption at 1430, 1456, 1486, and 1507 cm^{-1}, the spectrum of poly-DCHBr$_6$ reveals absorption at 1438 and 1472 cm^{-1}. Hence the shifts observed in the modified polymer might arise from a Fermi resonance involving the double-bond stretch and brominated carbazole groups as well as stretching vibrations associated with a new brominated double bond conjugated to an extended π-electron system.

The spectrum of poly-DCHBr$_8$, given in Figure 1c, has an intensity somewhat less than that of the spectrum in Figure 1b. Since the solid-state spectrum of poly-DCHBr$_8$ reveals a shoulder at 450 nm[6], reminiscent of a disordered PDA,[13] as its lowest energy feature, a weaker Raman spectrum using 6328-Å excitation is not surprising. The apperance of the spectrum in Figure 1c and the observed shifts are generally similar to those of poly-DCH in Figure 1a, yet the peaks are somewhat broader than those of poly-DCH. The NMR spectra of such materials reveal the presence of some residual triple bonds,[2,6] and the triple-bond stretch in Figure 1c is observed at 2100 cm^{-1}, a shift intermediate between those noted for poly-DCH and poly-DCHBr$_6$. Poly-DCHBr$_8$ materials are clearly heterogeneous at the molecular repeat level,[2] and the spectrum of Figure 1c may imply that some low concentration of poly-DCH segments remains after exposure to refluxing bromine. Such segments would dominate the interaction of this solid with 6328-Å light, in contrast to other moieties detected in poly-DCHBr$_8$.[2]

Summary

In summary, Raman spectra of samples of poly-DCH which have gained six and eight Br atoms per polymer repeat have been recorded and are compared to the spectrum of poly-DCH. The spectra of the modified polymers manifest the disordering[3,4,8] of the crystal, which occurs during the diffusion of bromine into the crystal, and are consistent with previous deductions about the anistropy of the bromination reaction[2-4,8] and the inhomogeneity of the reaction products at the molecular repeat level.[2]

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