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THE CHEMICAL MODIFICATION OF ARYLAMINE-SUBSTITUTED POLYDIACETYLENES AS A SIDE-CHAIN PROCESS: INSIGHTS FROM RAMAN SPECTROSCOPY

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ABSTRACT Single crystals of the polydiacetylenes with carbazole and diphenylamine side groups, DCH and THD, respectively, interact with halogens to give chemically modified materials. Using oxidation potentials of model molecular compounds, the relative reactivity of poly-DCH and poly-THD with bromine correlates with the side group oxidation potential. The modified materials have been studied by Raman spectroscopy at room temperature using several incident wavelengths for each material,including 1060 nm. Fourier transform (FT) Raman spectra obtained using 1060-nm light are particularly useful because the light, which is not absorbed, penetrates the bulk of the sample, not merely the surface region. The Raman studies confirm conclusions about the structure and properties of the modified materials reached earlier in ^{13}C CP-MAS NMR, FTIR, and electron spin resonance studies. Bromine interacts with poly-DCH to give a crystalline brominated material deduced to have a mixed polyacetylene structure, while bromine and iodine interact with poly-THD in an electron transfer process. The Raman spectra of the latter materials reveal graphitic or glassy carbon and provide no evidence for the preservation of the polydiacetylene or a related structure.

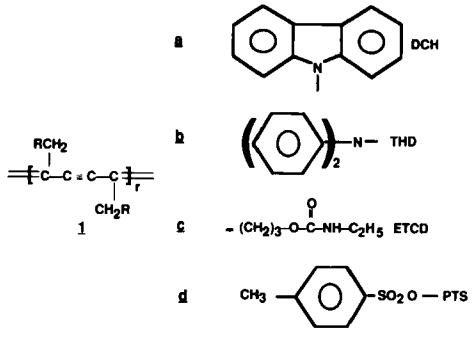
INTRODUCTION

The polydiacetylenes (PDA, 1), formed by topochemical polymerization of appropriately substituted 1,3-diynes, are the best known example of polymers available in the form of macroscopic single crystals.[1-3] Examination of PDA crystallography[3] reveals van der Waals tight-packed structures with no channels for facile diffusion of reagents. Nevertheless, as first reported at ICCOSS VII,[4,5] poly-DCH(1,6-(di-N-carbazolyl)-2,4-hexadiyne, 1a) interacts with bromine, chlorine, and other reagents to give products where reaction is complete throughout the crystal and which appear homogeneous upon examination by electron microscopy. These reactions and related ones of poly-THD (1,1,6,6-tetraphenyl-2,4-hexadiynediamine, 1b), also to be discussed herein, involve the side-chain group in their initial stages and hence may be referred to as "side-chain processes."

The considerable attention devoted to PDA in recent years derives from the intense visible transition associated with the conjugated chain. Yet the side chain groups

inevitably occupy more than 90% of the unit cell volume. This point is readily understood by using 9-methylcarbazole as a model for the side chain of poly-DCH,[6] recalling that the latter has two repeat units in the unit cell.[3] Hence, it is natural to ask what role the side chain plays in PDA spectroscopy, electronic structure, and processes.

The notion of a PDA "side-chain process" includes chemical,[4,5] thermal, radiative, and magnetic processes which affect the electronic structure, spectroscopy, and situations associated with the conjugated chain, yet their origin may be traced to the side-chain group. The thermochromism of poly-ETCD(bis–ethyl urethane of 5,7–dodecadiyne–1,12–diol, 1c), in which the electronic spectral maximum shifts from 635 nm at 25°C to 540 nm above 125°C, is an example of a thermal side-chain process. At present, poly-ETCD is the best defined example of a thermochromic polymer with a conjugated backbone. Its thermochromism is associated with an endothermic first-order phase transition involving an increase in unit cell volume.[7] The conformer population of the side-chain CH_2 groups changes on heating from 25 to 125°C, but backbone planarity and hydrogen bonding do not appear to be significantly disrupted during the transition.[7,8] Indeed, the presence of unreacted monomer in poly-ETCD single crystals affects the electronic states detected in resonance Raman spectral studies.[8]



In this paper, recent Raman spectral studies of chemically modified poly-DCH and -THD are reported. These studies provide insights into these materials not available from earlier work. The usefulness of resonance Raman (RR) spectroscopy as a sensitive probe of PDA structure and electronic states was amply demonstrated by Batchelder and Bloor.[9] In this work, we not only report RR spectra of chemically modified PDA materials, but also make the first report of Fourier transform (FT) Raman spectra, using 1060 nm as wavelength of excitation, of a PDA and of a derived material. Light of 1060 nm wavelength is largely transmitted by PDA and the derived material and hence is not merely a probe of surface regions as may be the case for RR spectra of thick PDA samples.[9]

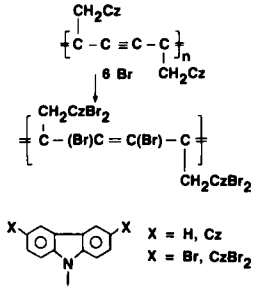
EXPERIMENTAL

Raman spectra using 457.9, 488.0, 514.5, and 632.8 nm were recorded at room temperature as previously described.[10] The samples of brominated and chlorinated poly-DCH and brominated poly-THD were prepared as previously described.[10–12] A Nicolet 800 FT-Raman system was used to record spectra at the excitation wavelength of 1060 nm. The spectra of poly-DCH and brominated poly-DCH were recorded at laser powers of 50 and 600 mW, respectively, using 2 cm^{-1} resolution and 32 scans.

POLY-DCH AND BROMINE

While poly-DCH crystals are inert to dense bromine vapors, liquid bromine reacts anisotropically to introduce 3 to 8 Br atoms per repeat unit depending on the experimental conditions and with retention of crystallographic order.[4,5,11] Solid state ^{13}C CP-MAS NMR studies of the brominated materials and model molecular compounds were used to deduce the positions of C-Br covalent bond formation.[13,14] The NMR studies reveal that the first step is the selective anisotropic bromination in the 3 and/or 6 positions of the carbazole groups. Subsequently, the backbone participates in the reaction, and for materials which have gained approximately 6 Br atoms per repeat unit, the extensive conversion of the PDA structure to that of a mixed polyacetylene was deduced, as illustrated in Scheme 1. While the modified materials appear homogeneous upon examination by electron microscopy,[5,11] the NMR spectra of the materials which have gained approximately 6 and 8 Br atoms per repeat reveal, in delayed decoupling experiments, residual concentrations of triple bonds in conjugated environments.[13,14] Hence the brominated polymers are not homogeneous at the molecular repeat level. This point will be further emphasized in discussion of the Raman spectra of the brominated polymers.[15] The magnetic properties of the modified polymers have been reported[5,11,16] and were discussed in terms of conjugation defects in the main chain.[11]

Scheme 1



The mixed polyacetylene structure deduced for poly-DCH which has gained 6 Br atoms per repeat unit requires that its Raman spectrum differ from that of poly-DCH, especially in the region of the normal mode associated with double-bond stretching. As a prelude to a discussion of the Raman spectra, we note that the maximum absorption of poly-DCH is at 656 nm,[17] and the solid state spectrum of poly-DCHBr_6 reveals shoulders near 630 and 550 nm.[4,10] Absorption at wavelengths shorter than 400 nm is dominated by carbazole excitations.[4]

The Raman spectrum of poly-DCH is a valuable point of reference for a discussion of the consequences of bromination. Shown in Figure 1 is a Fourier transform (FT) Raman spectrum of a single crystal of poly-DCH obtained with 1060 nm excitation. It is in general agreement with previous reports using 632.8 nm excitation;[10,15] the shift at 2081 cm^{-1} is associated with the normal mode primarily involving triple-bond stretching.[9] The shifts 1491, 1466, 1450, and 1420 cm^{-1} are associated with a Fermi resonance[9] involving the double-bond, methylene, and carbazole groups. The shifts at 1339, 1221, 1211, and 678 cm^{-1} are in satisfactory agreement with spectra observed with 632.8 nm excitation, while the shift at 1329 cm^{-1} has not been previously reported.

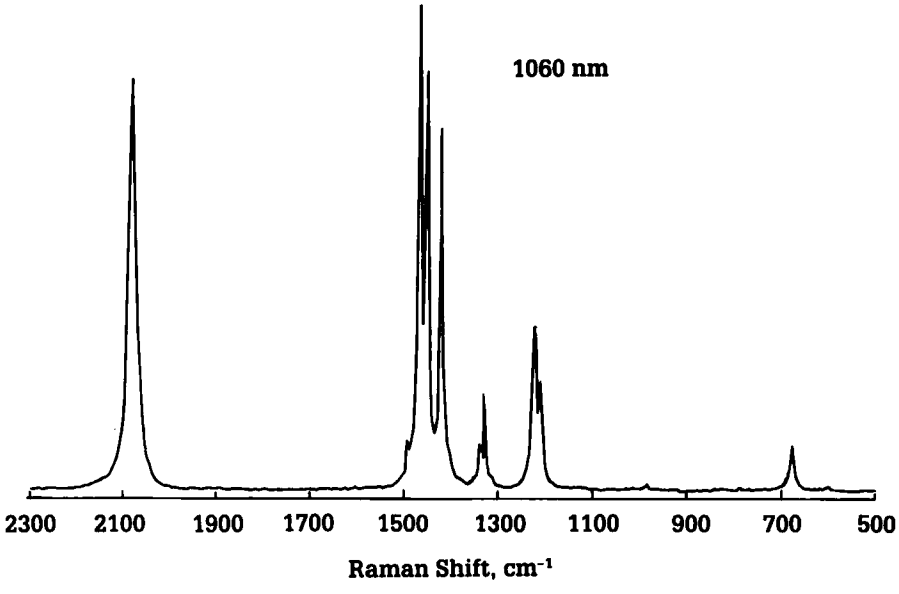


FIGURE 1 FT-Raman spectrum of a poly-DCH single crystal.

The Raman spectrum of "poly-DCHBr_6" has been studied as a function of the wavelength of excitation.[10,15] The observed spectra are not sensitive to variation in bromine content in the range of 5–7 Br atoms per repeat unit. The spectra obtained with

488.0 nm and 514.5 nm excitation are dominated by background emission; the former is displayed in Figure 2. Shifts near 1500 and 2100 cm^{-1}, associated with normal modes involving primarily double-bond and triple-bond stretching, are discernible in Figure 2; they are somewhat more pronounced in the 514.5-nm spectrum.[10]

The spectrum obtained using 632.8 nm excitation (Figure 3) has much less background emission than those observed with 488.0 nm and 514.5 nm excitation. With reference to Figure 3, a shift of 2107 cm^{-1} with a shoulder near 2130 cm^{-1} is revealed in the region of triple-bond stretching. The region of double-bond stretching reveals shifts of 1427, 1454, 1469, 1486, and 1522 cm^{-1}. While these shifts are similar to those of the pristine polymer, for this material they are likely a composite associated with situations such as brominated double bonds in the extended conjugated backbone[13] or a possible Fermi resonance involving the conjugated backbone, methylene group, and 3,6-dibromocarbazolyl groups.

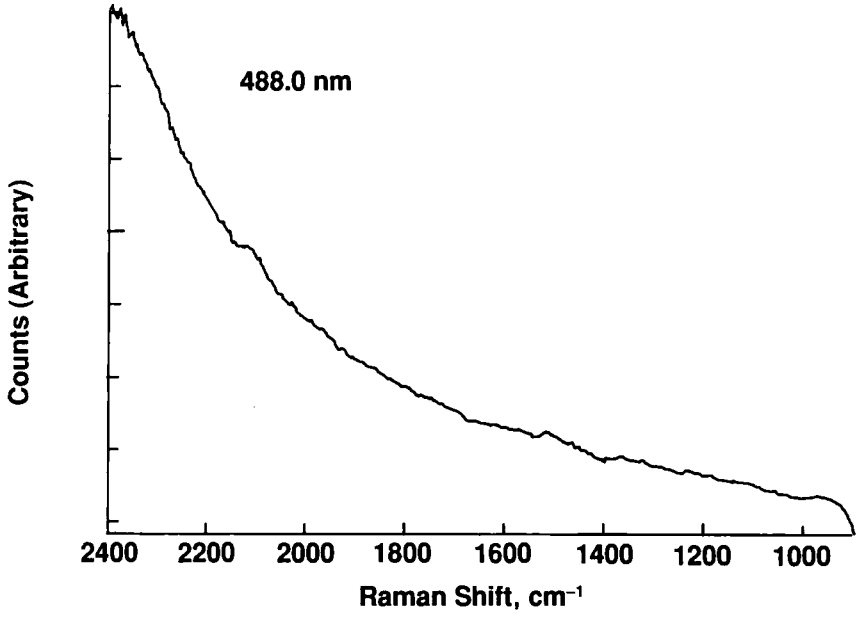


FIGURE 2 Raman (λ_o = 488.0 nm) spectrum of a poly-DCHBr$_6$ single crystal.

The information obtained at wavelengths between 488.0 and 632.8 nm, which are in the region of absorption of poly-DCHBr$_6$, may be representative of only the surface regions of these crystals.[9] This is not the case for 1060 nm light, a wavelength at which both poly-DCH and poly-DCH Br$_6$ are transparent. The FT-Raman spectrum obtained

using this wavelength is displayed in Figure 4. Comparison of the spectrum of Figure 4 with that in Figure 1 reveals that the shifted lines are much broader in the brominated polymer than in pristine poly-DCH. As revealed in Figure 4, the shift in the triple-bond stretching region is at 2117 cm^{-1}, and the shoulders in it could imply several triple-bond species, consistent with the NMR spectra.[13,14] With reference to Figure 3, the shift at 1518 cm^{-1} is now the most intense feature in the spectrum; the other shifts in the region of double-bond stretching are at 1494, 1470, and 1426 cm^{-1}. A Raman shift near 1520 cm^{-1} is a characteristic of an extended polyene chain.[18] Hence, we conclude that the FT-Raman spectrum supports the deduction of the NMR study[13,14] that poly-DCH is extensively converted to a mixed polyacetylene structure in poly-$DCHBr_6$.

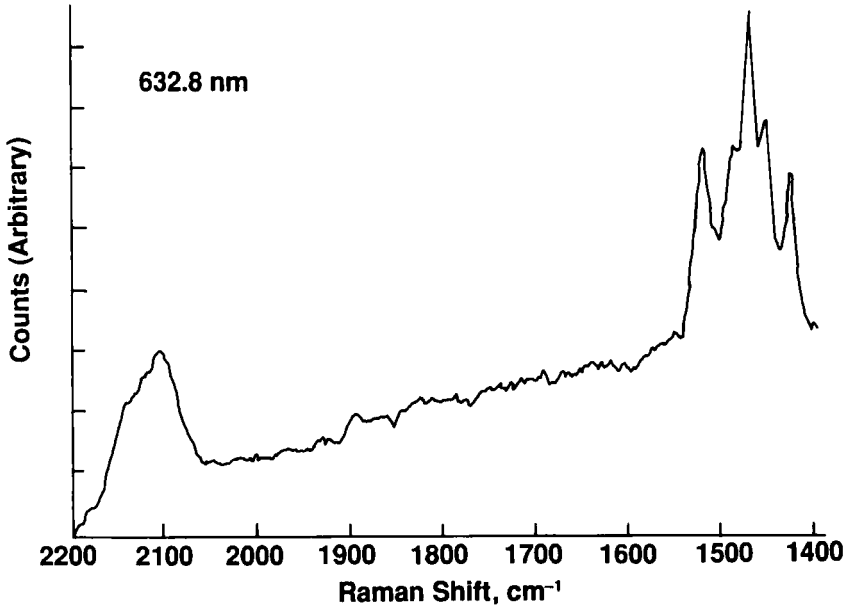


FIGURE 3 Raman (λ_o = 632.8 nm) spectrum of a poly-$DCHBr_6$ single crystal.

The marked change in Raman spectrum with excitation wavelength noted here for poly-$DCHBr_6$ is not a characteristic of poly-PTS (bis-p-toluenesulfonate of 2,4-hexadiyn-1,6-diol 1d)[9] or poly-DCH. The Raman spectrum of the partially crystalline polyacetylene, $(CH)_x$, also changes with wavelength of excitation.[19] A common characteristic of both poly-$DCHBr_6$ and $(CH)_x$, in addition to conjugated backbones, is a distribution of crystalline environments, and each environment may have a different electronic spectrum and hence give a different Raman spectrum with varying wavelengths of excitation.

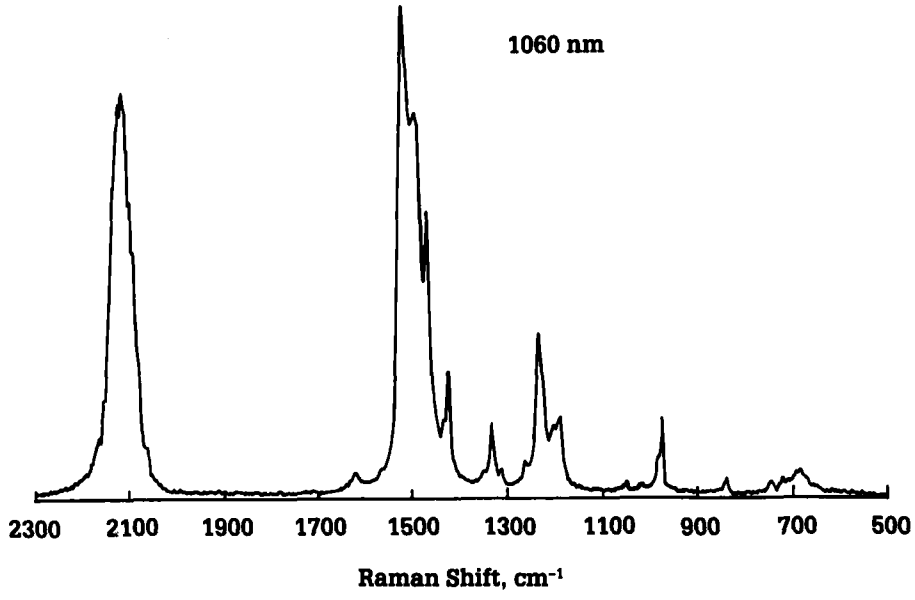


FIGURE 4 FT-Raman spectrum of a poly-DCHBr_6 single crystal.

The ^{13}CP-MAS NMR studies[13,14] revealed that brominated poly-DCH is not homogeneous at the molecular repeat level, and the Raman studies reported herein are consistent with that view.

POLY-DCH AND CHLORINE

Poly-DCH reacts with liquid and gaseous chlorine, or a solution of chlorine in dichloromethane to introduce 12–15 Cl atoms per repeat unit as found by elemental analysis.[11] These reactions are also anisotropic, and while the overall shape of the reactant crystal is retained, x-ray powder diffraction reveals the products to be largely amorphous. The reaction products are less well defined than the products of bromination. FTIR spectra clearly indicate that modification of the carbazole has occurred.[11] ^{13}C CP-MAS NMR spectra reveal that the conjugated backbone has remained intact by observation of a triple-bond resonance at 102 ppm.[14] Additionally, resonances whose chemical shifts indicate a –CHCl– pattern are observed, and they indicate that addition, rather than simple electrophilic substitution, of chlorine to carbazole has occurred.[14] The products of chlorination are orange to red-orange in color; diffuse reflectance revealed a

broad maximum at 410 nm which tailed to beyond 600 nm, suggesting a PDA chain in a structurally disordered environment.[20]

The Raman (632.8-nm excitation) spectrum of a sample of poly-DCH which gained 12 Cl atoms per repeat unit on exposure to liquid chlorine is shown in Figure 5. While the spectrum shown in Figure 5 has substantial background emission, it is better resolved than the spectrum observed with 514.5-nm excitation. The spectrum reveals shifts of 2120 and 1499 cm^{-1} associated with triple-bond and double-bond stretching, respectively. Comparison of the spectrum in Figure 5 with those in Figures 1, 3, and 4 reveals a much simpler double-bond stretching region. Assuming that the spectrum in Figure 5 is representative of the bulk sample, the simplicity of the 1500 cm^{-1} region might indicate that the addition of chlorine to the carbazole groups, as indicated by the NMR study,[14] changes the local symmetry sufficiently to alter the interactions, leading to the Fermi resonance attributed to this region in poly-DCH.[9] Hence the observed Raman spectrum for chlorinated poly-DCH is consistent with the conclusions of the FTIR[11] and NMR studies.

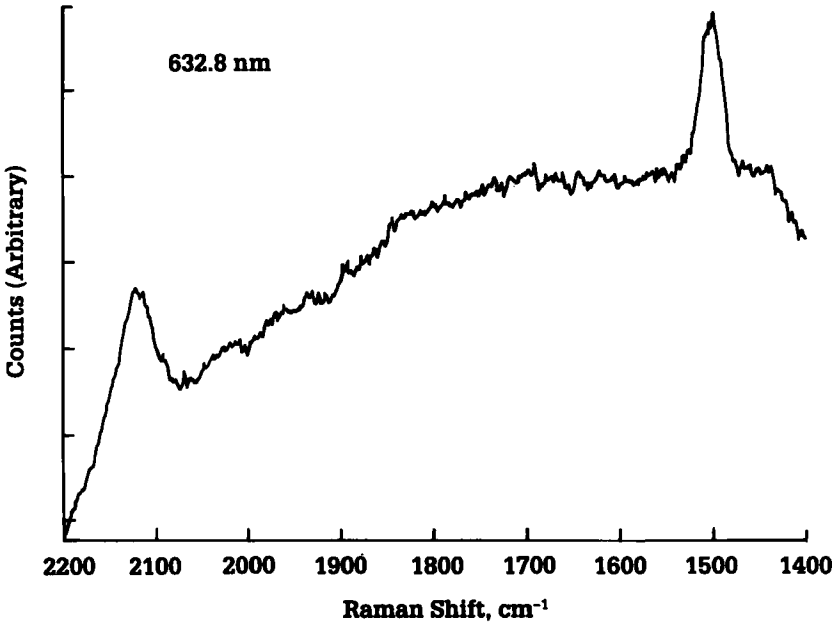


FIGURE 5 Raman (λ_0 = 632.8 nm) spectrum of chlorinated poly-DCH.

CHEMICAL REACTIVITY OF POLY-THD

Since both poly-DCH and poly-THD are completely polymerized, the similarity of the chemical structures of their side chains provides a basis for comparison of their chemical reactivity. In particular, probes of the highest occupied molecular orbital for isolated molecular model compounds are particularly instructive. This information is summarized in Table I, where gas-phase vertical ionization energies (I_G), obtained from ultraviolet photoelectron spectroscopy, and acetonitrile solution redox potentials (E_1) for N-methyldiphenylamine and N-ethylcarbazole are listed. Other issues, such as crystal morphology and defects, being equal, the question as to whether I_G or E_1 is a relevant figure of merit leads to a testable prediction. If I_G is a relevant figure of merit, the I_G values of the two model compounds are the same, within experimental error, and reactivity of poly-THD and poly-DCH should be similar. If E_1 is the figure of merit, then poly-THD should be more reactive than poly-DCH, since the diphenylamine is more easily oxidized in solution than the carbazole. Parenthetically, the lack of correlation between I_G and E_1 has been discussed.[21]

Table I Model compounds for side-chain energy levels

PDA	Model Compound	I_G (eV)	E_1 (Volts vs S.C.E.)
THD	N-Methyldiphenylamine	7.33	+0.84
DCH	N-Ethylcarbazole	7.29	+1.12

Experimentally, in contrast to poly-DCH, which is unreactive to dense bromine vapor and to solutions of bromine in CCl_4 less than 75% bromine by weight, poly-THD reacts readily at 20°C with bromine, 10% by weight, in CCl_4, or with a dense bromine vapor. The product of these reactions is a black, largely amorphous solid which has gained 8–9 Br atoms per repeat unit.[12] The FTIR spectrum of brominated poly-THD reveals that substitution of the aromatic rings has occurred, and the diffuse reflectance spectra reveals a broad tail into the near infrared region, suggesting that electron transfer occurred.[12] The DC resistivity of brominated poly-THD was not less than 10^8 Ω-cm, and electron spin resonance (ESR) spectra reveal a single line 11.5–17.3 gauss in width, with a spin count of 1–8 × 10^{18} spins/g. The g value (at crossover) of the ESR spectrum is 2.0045–2.0050.[12] This value is markedly lower than the value of 2.0198 observed in brominated poly-DCH, where the paramagnetic species interacts with bromine.[16]

While the ESR spectra indicated that the paramagnetic species is not interacting with bromine, the fate of the conjugated backbone is uncertain. This was probed by Raman

spectroscopy, and as a prelude to discussion of the spectrum of brominated poly-THD, we have recorded the spectrum of poly-THD prepared thermally using 632.8-nm and 457.9-nm excitation. The spectrum observed using 632.8-nm excitation is in good agreement with the previous report,[17] with shifts at 2119, 2102 (shoulder), and 1485 cm^{-1}. The spectrum observed using 457.9-nm excitation, displayed in Figure 6, exhibits shifts at 2105 and 1504 cm^{-1} for the triple-bond and double-bond stretch, respectively.The spectrum (457.9 nm) of brominated poly-THD, displayed in Figure 7, is dominated by background emission and features at shifts of approximately 1350 and 1600 cm^{-1}, respectively. Such shifts are reminiscent of those observed for graphitic and glassy carbon.[22] The spectrum in Figure 7 provides no indication of the preservation of the PDA backbone.

Poly-THD crystals interact with a 20-fold molar excess of iodine in refluxing glacial acetic acid over 48 hours to give a black solid material. When this black material is cut open with a razor blade, the color of pristine poly-THD is revealed. Hence, under these conditions, interaction of poly-THD with iodine leads to a heterogeneous material. Using 457.9 nm as the incident wavelength, the Raman spectrum of the solid product of poly-THD/I_2 interaction (Figure 8) reveals features near 1600 and 1350, again indicating graphitic or glassy carbon.[22] Additionally a Raman spectrum (488.0-nm excitation) of the material used to obtain the spectrum in Figure 7 revealed a shift at 133 cm^{-1}, suggestive of the presence of I_3^-.[23]

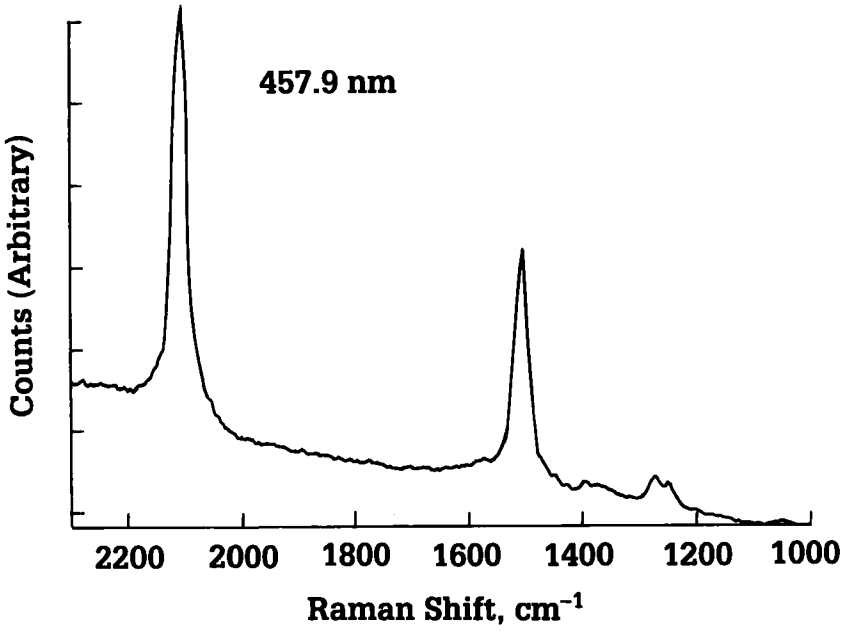


FIGURE 6. Raman (λ_o = 457.9 nm) spectrum of a poly-THD single crystal.

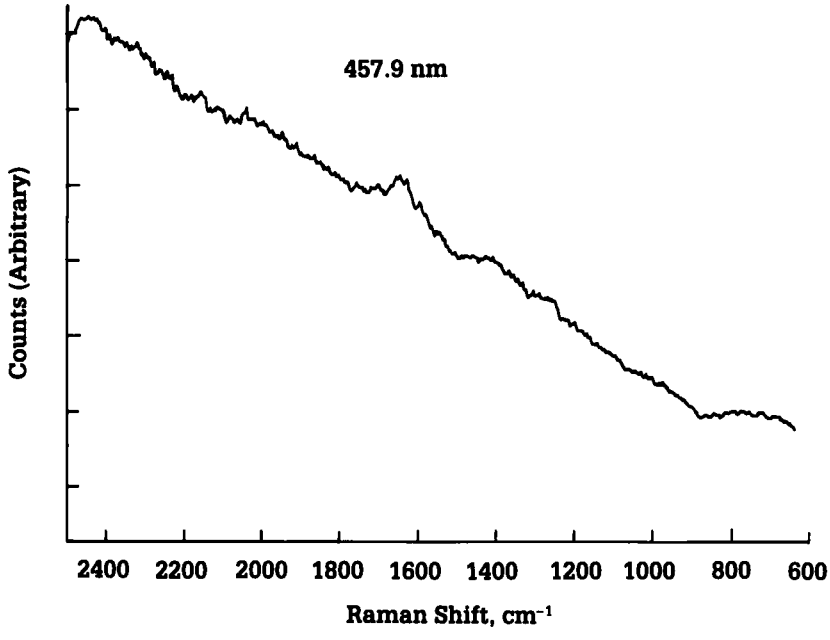


FIGURE 7. Raman (λ_o = 457.9 nm) spectrum of brominated poly-THD.

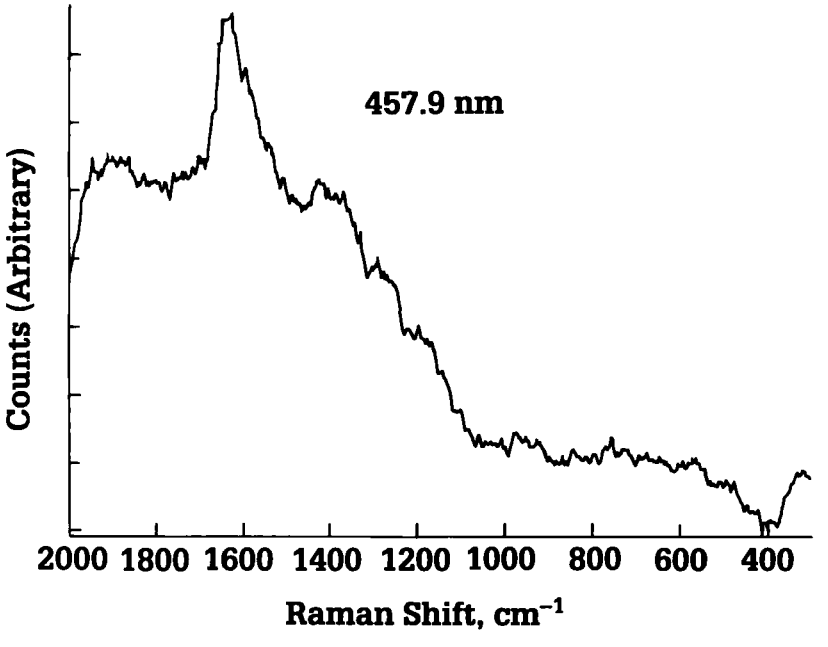


FIGURE 8. Raman (λ_o = 457.9 nm) spectrum of the material resulting from interaction of iodine and poly-THD.

CONCLUSIONS

One reason for the interest in the chemical reactivity of PDA is the possibility of obtaining a crystalline conductive polymer. While there have been a number of reports of conductivity enhancements in PDA,[24] the detailed fate of the conjugated backbone is uncertain from previous studies. In the case of silver-perchlorate-doped poly-PTS, crystalline order is retained only at low dopant levels.[25] For the present case of the reactions of poly-THD with halogens, which have not yet led to conducting materials, it appears the reaction involves electron transfer from arylamine side chains followed by reduction by the conjugated backbone, as previously proposed.[24] The Raman spectra obtained in this study, which may be only surface probes, do not reveal the spectrum of a PDA but rather that of a graphitic or glassy carbon.[22]

The reactivity of the arylamine-substituted PDAs, DCH and THD, toward bromine correlates with side-chain oxidation potential. With poly-DCH, the PDA is converted to a mixed polyacetylene structure, while with poly-THD, an electron transfer process is observed. Since both ^{13}CP-MAS NMR studies[13,14] and the Raman work herein reveal brominated poly-DCH to be inhomogeneous at the molecular repeat level, it is appropriate to inquire into the length of the mixed polyacetylene structure deduced for the poly-DCHBr$_6$ material. While a definite answer is not available at present, a lower limit may be set. This statement follows from the observation[4,10] of significant solid state absorption at wavelengths longer than 600 nm in poly-DCHBr$_6$ and the low temperature spectroscopic studies of the "stable oligomers" formed in a diacetylene monomer crystal.[26] The latter studies indicate that the spectrum of an oligomeric PDA chain with 8–10 monomer units is comparable in wavelength of maximum absorption to the complete polymer. Hence, we assume that the mixed polyacetylene structure deduced for poly-DCHBr$_6$ extends over a range of at least 32–40 carbons along the conjugated backbone.

The use of several incident wavelengths in the Raman studies of PDA in general[9] and the modified materials herein is a useful strategy. While the Raman spectra observed with wavelengths in the absorbing region may probe only the surface region of a solid sample[9] this is not the case with FT-Raman using a wavelength in the transparent region (1060 nm).

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