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Electron-energy-loss spectroscopy of polydiacetylenes

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Electron-energy-loss spectra in the range 0.2—300 eV were measured for two types of polydiacetylene thin films with different sidegroups: polymers of 2,4-hexadiyn-1-ol and Langmuir-Blodgett films of the pentacosa-10,12-diinoic acid—Cd salt. The valence excitations are dominated by a π-electron plasmon above the 2-eV fundamental absorption edge. The plasmon dispersion is linear with a slope identical to similar plasma excitations in polyacetylene [$(\mathrm{CH})_x$]. This implies that the π-electron bandwidth and interband excitation spectra are similar in these materials as suggested by recent theoretical band-structure calculations. Absorption begins at 2.0 eV for all momenta even at low temperature, consistent with the dominance of localized excitations at the fundamental edge, thus confirming the interpretation of earlier experimental work.

INTRODUCTION

Many polymers which, when pure, are good insulators and can be transformed by oxidation or reduction in the solid state into materials with metallic conductivity.[1] The electronic structure of these materials is now the focus of much experimental and theoretical research.[2] The most studied polymer in this class of materials is polyacetylene [$(\mathrm{CH})_x$] which has an extended π-electron system of alternating double and single carbon—carbon bonds.[1] These electrons dominate the low-energy electronic ground and excited states of the polymer and are responsible for the many interesting phenomena that are observed. Theoretical calculations[1–5] show that the π-electronic structure of polydiacetylenes (consisting of double, single, and triple bonds) is quite similar to that of polyacetylene so that studies of polydiacetylene ought to contain information applicable to polyacetylene. Moreover, polydiacetylene samples have several distinct advantages over the samples of polyacetylene studied to date. Polydiacetylenes can be prepared as large single crystals where the length of the chains is known to exceed 5×10^4 carbon atoms.[6] In polyacetylene the length of the conjugated π system is still controversial and the relative significance of crystalline and amorphous regions is debatable.[1] Even the orientation of the polymer chains within the larger morphological units is in dispute.[1] The nature of the electronic states in polydiacetylenes has been probed by measurements of the anisotropic optical properties[7–9] and electroreflectance,[10] as well as by x-ray-photoemission,[11] photoconductivity,[12] and mobility[13] measurements. From these measurements, which focus primarily on the fundamental absorption edge near 2 eV, a reasonably consistent description of the low-lying electronic states and their excitations has emerged. However, attempts at reacting polydiacetylenes with the molecules known to create highly conducting polyacetylene compounds have not produced high-conductivity materials despite the similarities in their electronic structure.[2,14,15]

In order to further the understanding of electronic states and their excitations in polydiacetylenes over a wide range of energies, we have carried out electron-energy-loss measurements. These results provide additional new information about the nature of the fundamental absorption edge. In addition, the dispersion of electronic excitations can be related to the overall energy band structure. Moreover, a direct comparison of electronic excitations in polydiacetylenes can be made with polyacetylene where the momentum dependence of valence excitations and the core-level excitations have already been measured.[16–18]

SAMPLE PREPARATION AND CHARACTERIZATION

In order to carry out high-energy- [(80—170)-keV] electron transmission experiments very thin samples ($<$1000-Å thick) are desirable in order to minimize multiple inelastic scattering. Unfortunately, the best single crystals containing the polydiacetylene backbone are made by polymerizing molecules such as *bis* (*p*-toluene sulfonate). In this case not only are very thick crystals obtained but also the electronic structure is dominated by the many electrons in the side groups so that excitations of the backbone are difficult to isolate except at lowest energies.[9,11] In an attempt to overcome these difficulties we have prepared reasonably well-oriented samples of polydiacetylene from the molecule 2,4-hexadiyn-1-ol given below[19]:

$$CH_3-C\equiv C-C\equiv C-CH_2OH\ .$$

The unpolymerized monomer, prepared at Queen Mary College, London, England, was loaded into a closed glass cylinder containing pure nitrogen. The original material was held at 34 °C and in a few days large thin crystals grew down from the upper surface of the glass container which was held at 27 °C. These monomer crystals were perfectly clear, had areas on the order of a 1 cm^2, and were perhaps several micrometers thick. They were partially polymerized by a brief exposure to uv light from a mercury lamp at which point they appeared bright orange. Since the uv light is absorbed near the surface, the sample could be gently heated to drive off the unpolymerized monomer leaving behind a dense mat of oriented fibers whose anisotropic optical properties could be observed easily through a polarizing filter. Unfortunately the thinnest samples with an area of a square millimeter or more which we could prepare were several thousand angstroms thick. This was thin enough to obtain energy-loss spectra up to 100 eV for momentum transfer up to 0.4 Å^{-1} with the use of 80-keV electron beams and up to momentum transfer of 0.7 Å^{-1} with the use of 170-keV electron beams. The carbon 1*s* core electron excitations could also be measured with the use of the 170-keV electron-beam energy.

These samples were not very good single crystals, however, as can be seen by the diffraction pattern shown in Fig. 1. Three broad peaks could be observed for momenta parallel and perpendicular to the polymer chains. Perpendicular to the chains peaks were observed at 0.8, 1.7, and 2.5 Å^{-1} corresponding to a periodicity of 7.6 Å. While this number is of the order of unit-cell parameters perpendicular to the chains the precise orientation of the crystals perpendicular to the chains is not known. Parallel to the chains peaks near 1.4 and 2.6 Å^{-1} correspond to a periodicity of about 4.8 Å in agreement with typical repeat distances along the chain axis.[10] In perfect polydiacetylene crystals no peak would appear near 1.4 Å^{-1} due to the relative orientation of chains within the unit cell. The presence and large width of this feature implies disorder in the registration of chains parallel to each other. The peak at 0.7 Å^{-1} along the chain axis corresponds roughly to twice a unit-cell dimension and must be associated with defects or voids in the samples. The disorder in the samples implied by the width of the diffraction peaks is probably the result of partial polymerization of the monomer and subsequent evaporation of unpolymerized monomer. This process leaves behind voids which could cause local distortions of the polymer chains and thus break the long-range order required for narrow diffraction peaks. Nevertheless, the diffraction data as well as the anisotropic optical properties show that the samples contain oriented polymer chains.

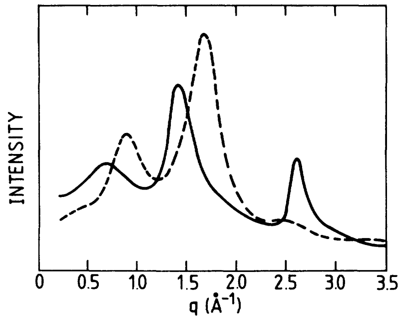

FIG. 1. Diffraction patterns in PDA-1OL thin-film samples for momenta parallel (solid curve) and perpendicular (dashed curve) to polymer chain direction.

These samples were also characterized by a computation of the dielectric function at small values of the momentum transfer by a Kramers-Kronig analysis of the energy-loss data for the different crystal directions. The results were in good qualitative agreement with optical results[8,9] although the thickness of the samples required such large corrections for multiple inelastic scattering that accurate quantitative results could not be obtained.

A second type of polydiacetylene was also studied. These samples were prepared at the Albert-Ludwigs University in Freiburg, Germany in the form of very thin (only 20 layers) Langmuir-Blodgett films of the pentacosa-10,12-diinoic acid—Cd- salt given below:

$$H_3C\text{—}(CH_2)_{12}\text{—}C{\equiv}C\text{—}C{\equiv}C\text{—}(CH_2)_8 \\ \text{—}CO_2^-Cd_{1/2}^+ \,.$$

These layers were polymerized by exposure to uv light.[20] Layers which were only partially polymerized by uv light were quickly polymerized completely when exposed to the electron beam. This was observed in the characteristic color change from blue to red as 50% polymerized films became completely polymerized.

RESULTS

Electron-energy-loss spectra with an energy resolution of 0.1 eV were obtained using two different energy-loss spectrometers, the spectrometer at the Xerox Webster Research Center, Webster, New York (U.S.A.) with 80-keV beam energy, and the newer spectrometer at the Kernforschungsanlage Jülich, West Germany with 170-keV beam energy. The beam intensity of both machines was between 1 and 4 nA and the momentum resolution was between 0.03 and 0.1 Å^{-1}.

The momentum dependence of valence excitations in polymerized 2,4-hexadiyn-1-ol (PDA-1OL) is given in Fig. 2. For momenta along the chain direction there is a threshold at 2.0 eV in good agreement with the optical measurements.[7–9] This threshold is independent of momentum for all values of momentum measured. This behavior is very similar to the absorption threshold in polyacetylene.[16] Above this threshold there is a peak in the energy-loss probability at 3.5 eV at $q = 0.1$ Å^{-1}. This peak corresponds to a minimum in the absolute value of the dielectric function, and from the shape of the dielectric response function it can be identified as a plasmon similar to that observed in polyacetylene.[9,14,16,18]

Also shown in Fig. 2 is the spectrum of excitations measured perpendicular to the nominal chain direction. These excitations are much weaker than the excitations measured parallel to the chains. The fact that we observe any absorption at all is most likely due to misalignment of the fibers in the sample so that some excitations polarized along the chain direction are observed in the nominally perpendicular direction. Optical experiments on very good single crystals show essentially no absorption perpendicular to the polymer chains.[8,10] The fact that the synchrotron-radiation measurements also show some absorption perpendicular to the chain direction is also most likely due to slight misalignment.[9]

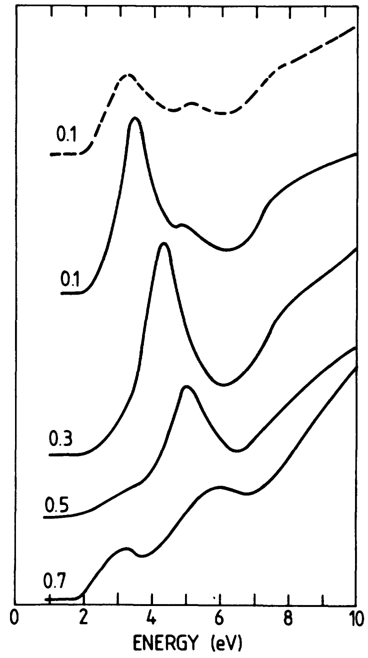

FIG. 2. Valence excitations as a function of momentum q (in Å^{-1} shown for each solid curve) parallel to the chain direction in PDA-1OL. Data at 0.1 Å^{-1} perpendicular to the nominal chain direction are given in the dashed curve.

The data in Fig. 2 also show a weak peak at 5 eV which is independent of polarization but which decreases very rapidly in intensity with increasing momentum. There is an absorption edge at about 7.5 eV which is independent of momentum. Neither of these excitations are observed in polyacetylene. Further absorption beginning between 8 and 9 eV is most likely associated with the onset of σ-electron excitations as is observed in polyethylene.[21]

Energy-loss spectra of the polydiacetylene molecules prepared from Langmuir-Blodgett films are shown in Fig. 3. These samples contain crystalline regions with polymer chains in the plane of the sample but with crystallites oriented randomly within the plane. For momentum transfer in the plane of the sample no polarization dependence is observed. Nevertheless, as shown in Fig. 3(a), above the absorption edge at 2 eV there is a plasmon peak which shows strong positive dispersion. The absorption onset is momentum independent. A shoulder at 7.2 eV is also momentum independent. Note that in these spectra the 5-eV peak in PDA-1OL is not observed. In addition, the π-electron excitations giving rise to the plasmon are relatively weaker than the σ excitations above 8 eV since the Langmuir films contain relatively more saturated bonds than PDA-1OL.

In Fig. 3(b) the effects of radiation damage on the

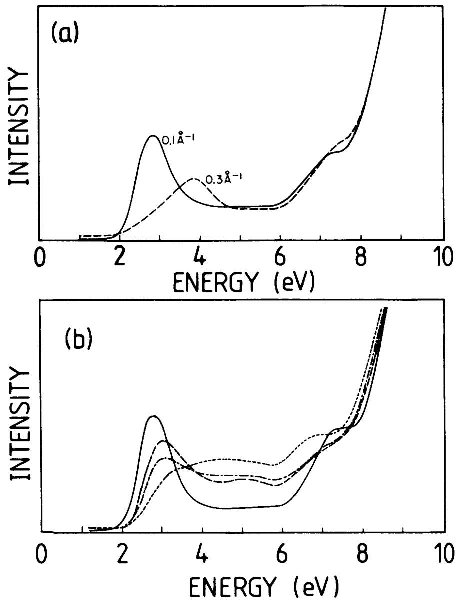

FIG. 3. Plasmon dispersion and radiation damage in Langmuir-Blodgett polydiacetylene films: (a) spectra at momentum transfer indicated, and (b) spectra at $q = 0.1$ Å^{-1} for total radiation doses of 80-keV electrons 1.25 C/m^2 (——), 10.3 C/m^2 (– – –), 14.2 C/m^2 (—·—·—·), and 29.5 C/m^2 (— — —).

Langmuir films is shown in the valence excitation spectra as a function of dosage. The π-electron plasmon decreases in intensity with increasing dosage and shifts to higher energy. This is consistent with the visual bleaching of the sample. The 7.3-eV peak is destroyed even more rapidly than the π-electron peak and new structure is observed at about 6.8 eV and in the region between 3 and 6 eV. These latter features are similar to radiation-damage effects in polyethylene[21] and are most likely associated with damage in the unsaturated side groups in the Langmuir films. In fact, these samples are about as sensitive to radiation damage as polyethylene is, whereas the samples of PDA-1OL are much more radiation resistant, presumably because they contain fewer unsaturated bonds. In all of the spectra reported here care has been taken to distinguish the intrinsic electronic excitations from effects of radiation damage.

Even though the samples were an ideal thickness for energy-loss spectra, the core-level excitations of the Langmuir films could not be measured due to the rapid radiation damage. Core-level excitations are much weaker than the valence excitations and require long radiation times. We were able to measure the carbon 1s core excitations in PDA-1OL using the 170-keV spectrometer and these data are shown in Fig. 4. The lowest-energy peak at 284.9 eV is about 1 eV wide and is easily identified as excitations from the carbon 1s states into the antibonding π bands. Similar excitations are associated with carbon 1s excitations in the benzene rings of polystyrene[22] and graphite,[23] as well as polyacetylene.[17] As the radiation time is increased, this peak does not decrease in intensity relative to the σ-band excitations, which make up the broad continuum extending to 293 eV in Fig. 4. This is in contrast to the behavior of the sharper peak at 286.0 eV which is only 0.5 eV wide and which decays quite rapidly with increasing radiation dosage. This latter peak is not present in polyacetylene,[17] and its sharpness and high oscillator strength identify it as excitations from the carbon 1s states into the narrow antibonding states associated with the triple bond in the polydiacetylene chain.[2,3] The fact that the peak associated with the triple bonds in polydiacetylene is quite radiation sensitive is undoubtedly associated with the relative instability and greater reactivity of localized triple bonds as opposed to delocalized π states.

DISCUSSION

The polydiacetylene molecules we have chosen to study have no other π electrons other than those contained in the backbone of interest. Thus, below about 9 eV and near the threshold for excitations of the carbon 1s electrons, the dominant excitations will be those of the backbone π states. The weak peak near 5 eV in PDA-1OL is most likely associated with the sidegroup CH_2OH since it is not observed in the Langmuir-Blodgett films which con-

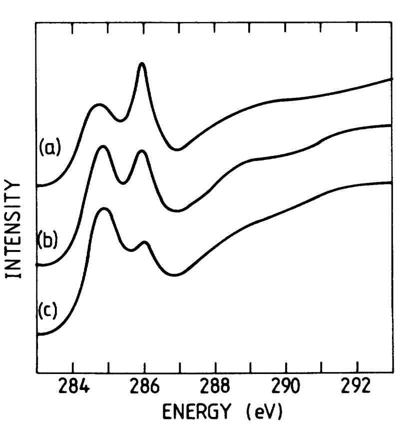

FIG. 4. Core-level excitation spectra as a function of exposure time to a 4-nA, 170-keV electron beam for (a) 10 min, (b) 54 min, and (c) 78 min.

tain different sidegroups, nor has it been observed in other polydiacetylene molecules.[9] On the other hand, the energy of this excitation cannot be simply understood since methanol in the vapor phase has only a weak absorption at 6.7 eV.[24] Thus the 5-eV peak in PDA-1OL is not fully explained. The 7.5-eV threshold, on the other hand, is close in energy to the expected excitations of triple bonds.[24] It is polarized along the chain direction and is observed in both molecules we have studied. It is quite sensitive to radiation damage as are the excitations to antibonding triple-bond states from the carbon 1*s* core levels described earlier. Optical studies report a peak in the imaginary part of the dielectric function at 7.6 eV in polydiacetylene *bis*(*p*-toluene sulfonate) after polymerization.[9] While conceding that this peak could be associated with triple-bond excitations, the earlier workers favored the identification of this feature with an $n=3$ Wannier exciton state.[9] Since a variety of experiments have established the single-particle gap to be about 2.3 eV in polydiacetylenes, the Wannier exciton description is not reasonable.[10,20]

The most important aspect of the data presented in Figs. 2 and 3 is the strong positive dispersion of the π plasmon. The plasmon-peak position as a function of momentum is plotted in Fig. 5 along with the dispersion relation of plasmons in polyacetylene.[16] The remarkable feature is that plasmons in polyacetylene and polydiacetylenes have a linear dispersion relation with essentially the same slope over the region of momentum space measured. This dispersion has been correlated to the nearly linear dispersion of the strong peak at the leading edge of the spectrum of interband transitions in polyacetylene.[18] The spectrum of interband transitions was calculated in a simple tight-binding model which neglected matrix-element effects.[18] The implications of this model are that the plasmon is driven to higher energies by the interband transitions between the valence and conduction bands each of which are about 5 eV wide and which are separated by a bandgap of about 1.5 eV. This linear dispersion relation may not be valid at very small momenta (<0.1 Å^{-1}). Moreover, at large momenta (>1 Å^{-1}) the excitation spectra should be increasingly dominated by the spectra of single-particle excitations.[18] In any case, the measured plasmon dispersion is undoubtedly related to the shape and width of the energy bands in these materials although a really satisfactory calculation of plasmon dispersion is yet to be done. Accurate calculations of plasmon dispersion contain information relating to band-structure and many-body effects as well as local-field and correlation effects and have now only been carried out in detail for the simple metals.[25] Nevertheless, the data of Fig. 5 show that the π-electron excitations in polydiacetylenes and polyacetylene are quite similar. The main difference being that the π plasmon in the polydiacetylenes occurs at lower energy (despite the larger band gap) than in polyacetylene. The reason for this is that since the density of all of these materials is nearly the same,[1,19,20] the π-electron density in the Langmuir films is less than the π-electron density of PDA-1OL which is less than that in polyacetylene. Low density reduces the oscillator strength of the π-electron excitations. If the peak in ϵ_2 occurs at the same energy in these materials reducing its strength also reduces the divergence in ϵ_1. This causes the peak in the energy-loss probability [Im$(-1/\epsilon)$] to occur nearer to the peak in ϵ_2 (which is at ~ 2 eV). Thus, apart from this density effect which influences the macroscopic dielectric functions, the microscopic excitations in polydiacetylenes and polyacetylene must be very similar. And, to the extent to which the measured plasmon dispersion is related to the electron-energy band structure, we conclude that the band structures are similar in these materials.

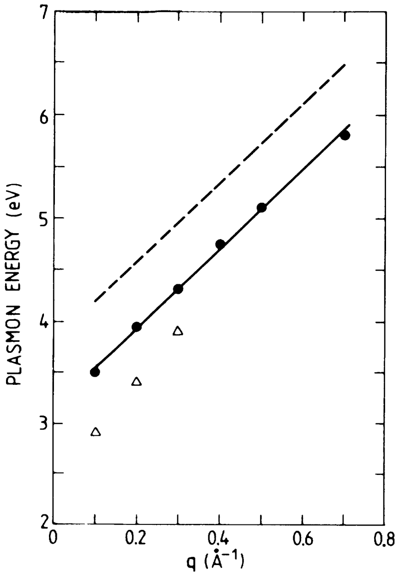

FIG. 5. Plasmon dispersion relations: polyacetylene—dashed line (Ref. 16), and PDA-1OL—solid-line fit to experimental points shown; for Langmuir-Blodgett polydiacetylene films, triangles are data points.

It is also significant that the absorption threshold at 2 eV in polydiacetylenes is independent of momentum as seen in Figs. 2 and 3 although the intensity just above the edge decreases with increasing momentum. To further investigate the threshold region at large momenta we have measured energy-loss spectra at low temperature (30 K). Lowering the temperature should test the extent to which the absorption edge is influenced by phonons. Phonon-assisted absorption can result from single scattering events in which the incident electron creates a phonon with large momentum and an electronic excitation with small momentum. Such phonon-assisted indirect transitions at finite q have not yet been observed but they would appear between 2 eV and the direct interband edge at finite q in the absence of other effects. Phonon-assisted absorption can also result from so called "thermal diffuse" scattering in which the incident electron experiences two separate scattering events.[26] This multiple-scattering process depends on thickness as well as temperature. It depends on temperature since the phonon population is temperature dependent. It can never be completely eliminated since the fast electron can always create a phonon but its intensity will decrease at low temperature. For momenta up to and including $q=0.5$ Å^{-1} lowering the temperature had no effect on the energy-loss spectra shown in Fig. 2. But, at $q=0.7$ Å^{-1} the weak peak near 3 eV was greatly reduced. Since this peak is at nearly the same energy as the π plasmon at $q=0$ we can identify it as a thermal diffuse scattering process.[26] However, in all spectra the onset of absorption at all momenta is at 2.0 eV even at low temperature. Thus, this absorption is not due to indirect transitions at finite q nor to thermal diffuse scattering.

The lack of temperature and momentum dependence at the absorption edge may be due to static disorder. The diffraction peaks shown in Fig. 1 are quite broad indicating a lack of perfect translational symmetry. This lack of symmetry means that the electronic crystal momentum is no longer a good quantum number and is not necessarily conserved in the scattering process. Thus at finite q electronic excitations at all momenta are observed, and hence, the threshold would always remain at 2 eV. On the other hand, the disorder indicated in the diffraction pattern is most likely due to a lack of registration between polymer chains each one of which contains a very long ordered sequence. If the microscopic electronic excitation is governed primarily by the single chains (which seems to be the case[5,10,20]), then the extent of disorder suggested by the diffraction pattern may not be relevant for electronic excitations.

The most likely explanation for the momentum independence of the absorption edge is that the absorption edge is due to localized excitonic states, which because they are spatially localized, have components at all momenta. In the polydiacetylenes it has been very well established that the absorption edge is in fact excitonic. Theoretical calculations,[5] optical-absorption measurements,[7,8] electroreflectance measurements,[10] and photoconductivity measurements[12,20] all indicate that this is the case. However, the momentum dependence of excitons in these systems has not been calculated theoretically so that the detailed information contained in the shape and relative intensity of the absorption edge at finite momenta cannot at this time be related to the wave function and transition matrix elements of the exciton. It is interesting to note that polyacetylene also has a momentum-independent absorption edge which has been interpreted as evidence for excitonic effects in this material.[16,18] The measurements presented here on polydiacetylenes where the excitonic nature of the absorption edge is well established tend to support the earlier conclusions on polyacetylene.[16,18]

Further comments are also in order concerning the core-level spectra in Fig. 4. There is a broad peak at 284.9 eV and a continuum to higher energy corresponding to excitations from carbon 1s states into the delocalized π bands. There is also a narrow peak at 286.0 eV corresponding to excitations into the localized states associated with the triple bonds. In polymers such as polystyrene where all the final states are localized, the spectrum of core excitations exactly corresponds to the distribution of final states since the electron-hole interaction and relaxation effects are nearly the same for each final state.[22] In the case of polydiacetylene it is tempting to ascribe the 1.1-eV difference seen in Fig. 4 to the relative position of the antibonding triple-bond states above the conduction-band edge, but this is not likely to be correct. Being delocalized the π states should have a smaller core-exciton binding energy and less relaxation than the more localized triple-bond states. Thus 1.1 eV is a lower limit to the separation of the antibonding triple-bond band from the conduction-band edge. Theoretical calculations show this separation to be between 3 and 6 eV (Refs. 2 and 3) which does not contradict the present results.

CONCLUSIONS

Although they differ in detail, the backbone electronic excitations in polyacetylene and polydiacetylenes are very similar, in agreement with recent theoretical calculations. Both materials show a π-electron plasmon above the fundamental absorption edge which has a linear dispersion relation between 0.1 and 0.7 Å^{-1}. This indicates that the π-band structure in these materials is quite similar. Both materials have a momentum-independent absorption threshold which is also temperature independent in polydiacetylene. This effect is most likely associated with excitons which are known to dominate the edge in polydiacetylene. Apart from excitations in the many possible side groups which can be attached to the polydiacetylene backbone, the principal differences in the excitation spectra of polydiacetylene and polyacetylene are in excitations at 7.5 and 286.0 eV which are associated with the triple bond in polydiacetylene.

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