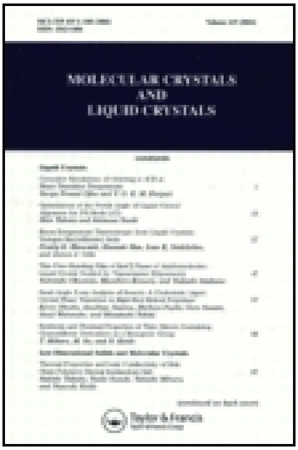

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RESONANCE RAMAN SPECTRA OF ALKALI-METAL DOPED POLYACETYLENE

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Abstract

Resonance Raman spectra of alkali-metal complexes of polyacetylene are presented. The spectra of samples with a 6% dopant level are dominated by scattering from short, undoped trans segments. At higher dopant levels, new features associated with doped chains are observed. The results are interpreted on the basis of new structural phases identified by x-ray diffraction and electrochemical measurements.

INTRODUCTION

Resonance Raman Spectroscopy (RRS) has proved to be a very useful tool for the study of vibrational and structural properties of polyacetylene. Much of the emphasis has been on undoped trans polyacetylene. It is now well established that disorder plays a major role in trans-$(CH)_x$, although the origin and the nature of this disorder is still under discussion.[1,2] This disorder has important consequences for the kinetics and energetics of the doping process, particularly if the disorder is due to a distribution of conjugation lengths.

A few Raman spectra of doped polyacetylene have been published in the literature.[3] They differ dramatically from the spectra of undoped $(CH)_x$. The strong, resonance-enhanced Raman lines of cis and trans polyacetylene are absent at high doping levels. New weak lines appear which depend on the particular dopant. The interpretation of these data has been severely hindered by several factors. The most important is an almost complete absence of structural information for the polymer/dopant system. Since the electronic structure of polyacetylene changes with doping level, it is important to control the latter. Inhomogeneities in the spatial distribution of the dopant until high dopant levels and the instability of the doped polymer, particularly with acceptor dopants, have made it difficult to achieve this goal.

We present here a preliminary Raman study of alkali-metal doped polyacetylene for three dopant levels, with emphasis on potassium doping. New ordered phases of alkali-metal complexes which evolve during the doping process have been reported at this conference.[4,5] This makes it possible to discuss the Raman results in relationship to the proposed structures. The alkali metals occupy channels in the host polymer lattice. This channel structure may be in part responsible for the relatively high crystallinity observed for these complexes[6] and the high thermal stability.[7]

It is known that the electronic structure of trans-$(CH)_x$ changes radically with doping. Upon doping to metallic levels bond alternation might disappear, which should change the RRS spectrum. The important questions in conjunction with the RRS spectra of doped samples are: a) which features are related to ionized $(CH)_x$ and which can be assigned to unionized chain segments; b) how do dopant-induced changes in crystal packing and the charge-transfer influence the Raman spectra; and c) can RRS yield information on the size and the form of the structural defects and the presence of undimerized segments in metallic samples.

EXPERIMENTAL

The polyacetylene films were doped electrochemically with potassium. After reaching molar percent dopant levels per CH unit of 6%, 12% and 16.4%, respectively, the samples were removed from the electrolyte and pumped under high vacuum. This procedure assured that solvent molecules were not present in the doped samples. The electrochemistry and x-ray diffraction data of these complexes are discussed in detail in the contributions by Shacklette et al. and Baughman et al. in these proceedings. Other samples were chemically doped with potassium naphthalide in THF for long times. This process yielded a homogeneous dopant level of about 17%.[6] At this highest dopant level, no differences were observed in the Raman spectra of chemically and electrochemically doped samples.

Fig. 1 shows the Raman spectra of $(CH)_x$ with a 6% dopant level for three different laser frequencies. The spectrum with 4579 Å excitation is reminiscent of the spectrum of undoped trans $(CH)_x$. However, the two strong Raman bands due to C-C and C=C stretching are narrower and shifted to higher energy. This becomes clear in Fig. 2 where the spectrum for the doped polymer is compared with the spectrum of trans-$(CH)_x$ taken from the literature.[8] The double peak structure typical for blue excitation of undoped trans-$(CH)_x$ is absent. For both the C-C and C=C stretching bands, the maximum in the spectrum for the doped sample is slightly shifted to the blue from the sideband in the undoped spectrum. In addition, there is a new band appearing at about 1270 cm^{-1}. When the laser line is tuned to longer wavelengths, the two strong Raman lines (see Fig. 1) shift to

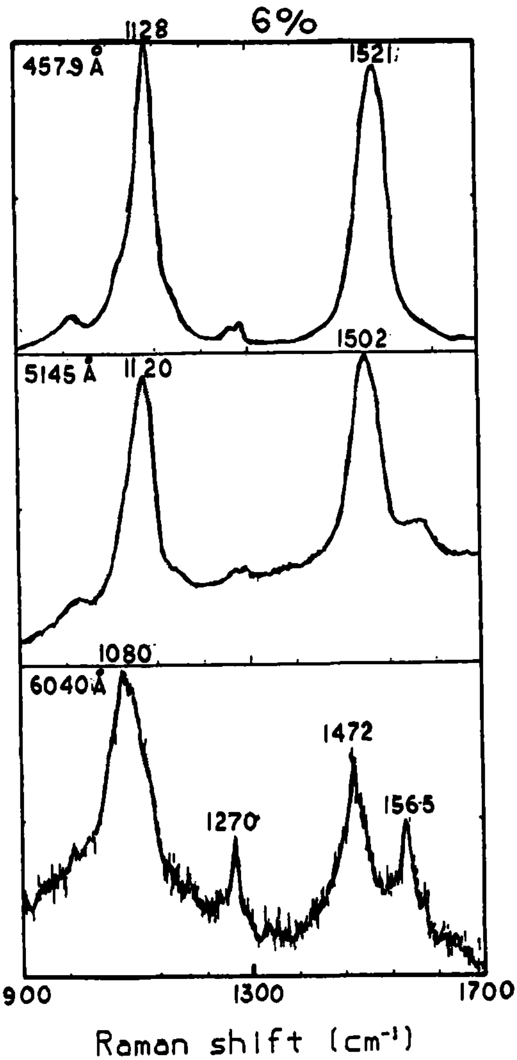

FIGURE 1 Raman spectra of potassium doped polyacetylene with 6% dopant level for three laser frequencies.

lower energy and the new sharp line at 1270 cm^{-1} together with a second line around 1560 cm^{-1} become more prominent. These two new lines can clearly be associated with the doping process. In

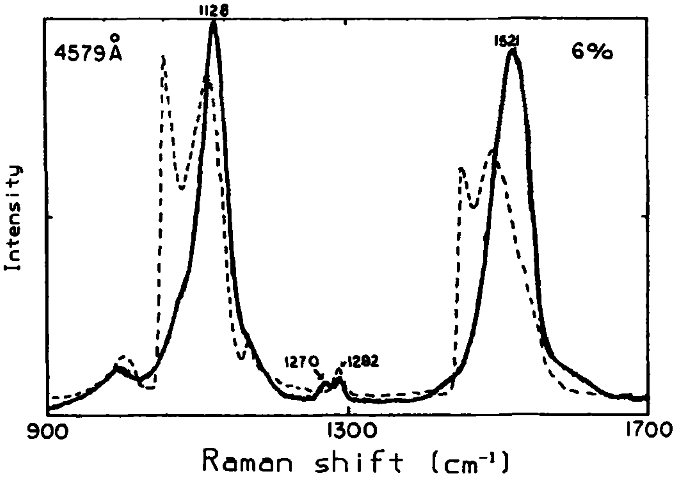

FIGURE 2 Raman spectra of undoped trans (dashed, from ref. 8) and 6% doped (solid) polyacetylene with 4579 Å excitation.

the 12% and 16.4% (Fig. 3 and 4) spectra the two bands assigned to undoped segments are removed from resonance and the 1270 cm^{-1} line has shifted to lower energy by 5 to 10 wavenumbers. There is a second strong and broad peak present between 1550 and 1600 cm^{-1}. In the case of 12% dopant concentration this band has a shoulder on the low frequency side which disappears with red excitation. Instead, a new double peak structure with maxima at roughly 1140 cm^{-1} and 1190 cm^{-1} is seen. The relative intensity of these peaks increases with increasing dopant content and increasing excitation wavelength. This is illustrated in Fig. 5, where Raman spectra obtained with 6328 Å excitation are shown. These samples were doped chemically with two different alkali metals to the highest possible doping level (17%). No differences in the Raman data between K-, Na-, Rb- and Cs-doped samples was found for these high dopant levels.

STRUCTURE OF POLYACETYLENE

The three dopant levels discussed above can be associated with different ordered phases of alkali-metal complexes of polyacetylene. We have previously shown that polyacetylene doped with alkali-metals up to a 17% dopant level forms a channel structure. The inserted ions are arranged in columns, which are each surrounded by four polyacetylene chains.[6] The separation of alkali metal ions in the column direction corresponds to the length of three CH units in the trans polymer chain. Possibly excluding Li, the structures can be described by the number of polymer chains per alkali metal column (m) and the number of CH units in a chain segment having the same length as the metal-metal separation within the metal column. Thus, fully doped stage 1 is denoted by $(C_nH_n)_mK$ with m=2 and n=3. The proposed "first stage" and "second stage" structures are shown in Fig. 6. During the doping process, the structure of polyacetylene goes through various dilute phases where the arrangement of ions in columns is preserved. We will only discuss here the structures obtained during ion insertion. (For a detailed discussion see refs. 4 and 5) At about 6% dopant level the x-ray data support the initial formation of a "second stage" structure (Fig. 6). Also, the electrochemical data indicate the existence of phases more dilute in alkali metal. These dilute phases are

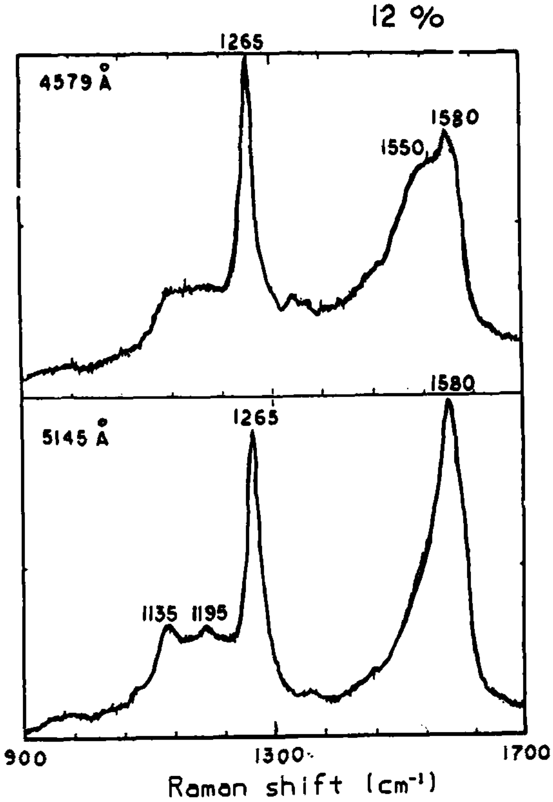

FIGURE 3 Raman spectra of potassium-doped polyacetylene with a 12% dopant level.

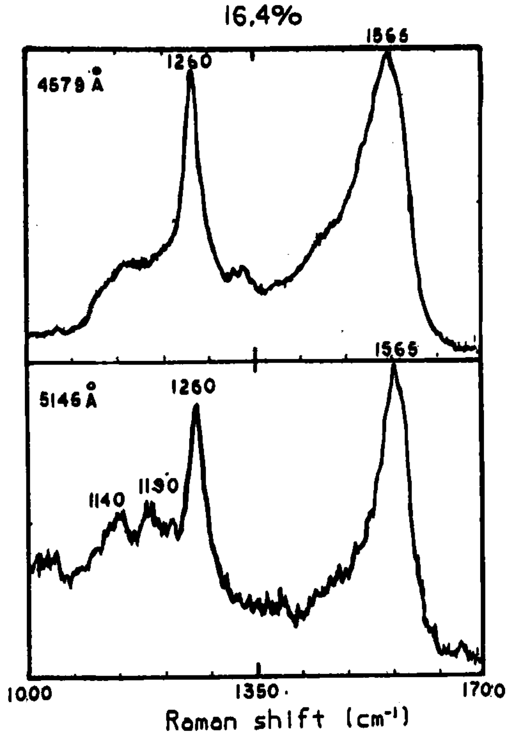

FIGURE 4 Raman spectra of potassium-doped polyacetylene with a 16.4% dopant level.

obtained from the tetragonal $(C_nH_n)_2M$ phase by either decreasing the number of alkali metal columns per polymer chain (increasing m) or decreasing the concentration of alkali metal ions in the columns (increasing n). For m>3, some of these additional chains are not adjacent to any alkali metal column. Therefore the charge-transfer to these chains is most likely much smaller than to chains which are adjacent to an alkali metal column. Also, as shown in Fig. 6, for m=3, 2/3 of the polymer chains are nearest-neighbor to only one dopant column and the remainder are nearest-neighbor to two dopant columns. Hence, the latter chains are expected to be more completely ionized. At 12.5% dopant concentration the formation of stage 1 is completed for a structure, $(C_4H_4)_2M$, with a metal-metal intracolumn spacing of 4 CH units. All chains are equivalent and adjacent to two metal columns in this structure. Further doping to the highest observed value of 17% is achieved by packing the metal columns more densely up to a final composition of $(C_3H_3)_2M$.

DISCUSSION

The Raman spectra at 6% dopant level are dominated by scattering from undoped trans chain segments, at least for short wavelength excitation (Fig. 1 and 2). It is also evident from Fig. 2 that the light is scattered predominately from short conjugation lengths compared with those indicated in the spectrum of undoped trans-(CH)$_x$. This implies that the long conjugation lengths are doped first. This is consistent with theoretical calculations and electrochemical data of polyene oligomers which predict that charge-transfer to long conjugation lengths is

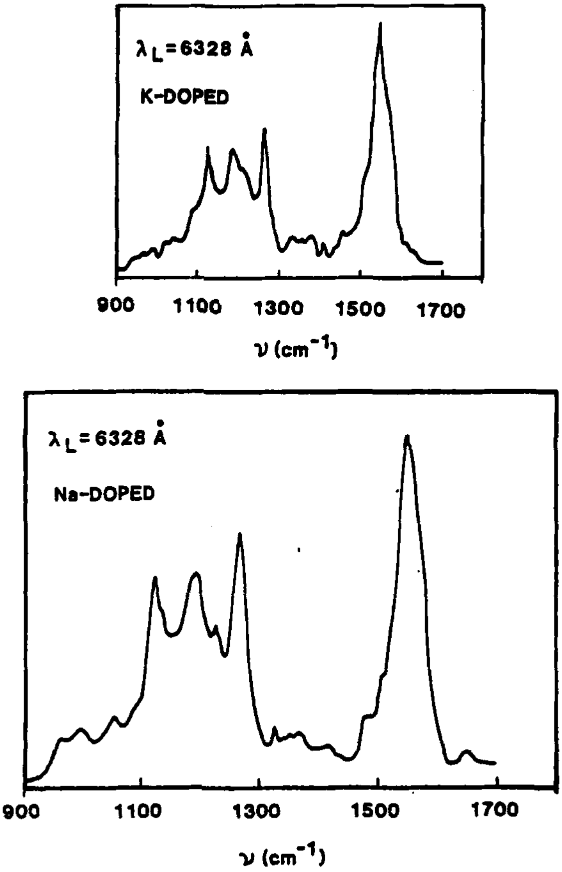

FIGURE 5 Raman spectra of polyacetylene doped chemically with K and Na to a 17% dopant level.

energetically favored.[9] By going out of resonance with these shorter conjugation lengths (shift of the laser wavelength to the red), the features which can be associated with the ionized chain segments appear. Although there are polymer chains in the more dilute phases which are not situated next to ion columns, the absence of Raman scattering from long conjugation lengths suggests that at least partial charge-transfer has occured to these chains. According to theory, until an overall dopant concentration of 8.3% is reached, there exists in the doped sample one or more phases, which contain polymer chains which are not adjacent to dopant columns.[4,5]

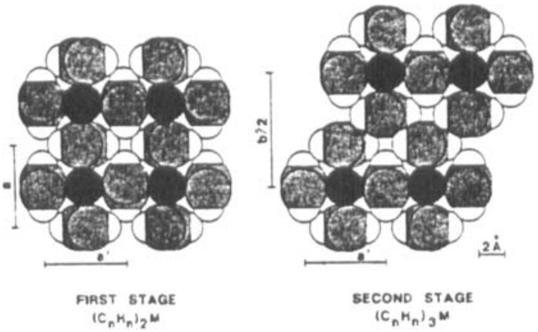

FIGURE 6 Chain-axis projection for the "First Stage" and "Second Stage" complexes. The alkali-metal ions are black, the carbons are shaded, and the hydrogens are white.

The shoulder at 1550 cm^{-1} seen with 4579 Å excitation for the 12% spectrum can be assigned to scattering from very short, unionized trans segments (about 7 double bonds) which are photoselected with blue light. From the crystallographic point of view, outlined above, no undoped segments would be expected for a dopant concentration above 12.5%, since all chains have an equivalent environment (two neighboring columns). However, it is important to realize that the proposed structural models apply only to the highly crystalline regions of the sample. Amorphous regions, which are present in the samples, may be doped to a lesser degree and contain short, undoped conjugation lengths. If this interpretation is correct, the absence of Raman lines due to unionized chains in the 16.4% spectra indicate that these regions are mostly ionized when we go to very high overall dopant levels.

What remains is the assignment of the new peaks associated with the ionized chains. An important question, frequently asked, is whether or not bond alternation disappears upon doping and if there is any clue to the existence of undimerized segments from

RRS spectroscopy. Zannoni and Zerbi[10] predict one strong A_g band at 1268 cm^{-1} for the undimerized, infinite trans chain. One is therefore inclined to take the observed strong Raman line at 1265 cm^{-1} in the 12% spectrum and at 1260 cm^{-1} in the 16.4% spectrum as a signature that bond alternation has been removed in heavily doped polyacetylene. However, the assignment is not straightforward. The group theoretical calculation of ref.10 predict only one strong Ag mode. Observed are two strong bands. They both depend in the same way on the dopant concentration and both are independent of the excitation line. Therefore they are most likely associated with the same structural defect. Furthermore, even for the tetragonal structure obtained at the highest dopant level, all bonds in the $(CH)_x$ chain cannot be equivalent with respect to the proximity of alkali metal ions.[4] There must exist at least a finite difference in the lengths of such carbon-carbon bonds having different alkali metal environments.

The picture is further complicated by the presence of the two weaker modes at 1140 cm^{-1} and 1190 cm^{-1}. The dependence of these lines upon excitation frequency is different from the dependence of the other modes, indicating association with a different type of structural defect. What is needed at this point to allow an unambiguous assignment of the observed Raman lines is: 1) on the experimental side, more spectra with different dopant levels and excitation with longer wavelengths to probe the resonance behavior and 2) on the theoretical side, refined calculations which take into account the effect of the dopant distribution on the symmetry of the chain.

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