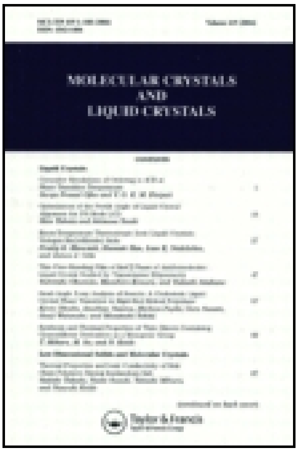

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Raman Spectra of Heavily Sodium-Doped Trans-Polyacetylene and the Radical Anions of Diphenylpolyenes and Dithienylpolyenes

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RAMAN SPECTRA OF HEAVILY SODIUM-DOPED *TRANS*-POLYACETYLENE AND THE RADICAL ANIONS OF DIPHENYLPOLYENES AND DITHIENYLPOLYENES

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Abstract The Raman spectra of *trans*-polyacetylene doped with sodium (Na) at the maximal level have been measured with excitation laser lines between 488.0 and 1064 nm. These spectra have been compared with those of model compounds, *i.e.*, the radical anions of α, ω-diphenylpolyenes (Ph-(CH=CH)$_n$-Ph, n = 3, 4) and α, ω-di-2-thienylpolyenes (Th-(CH=CH)$_n$-Th, n = 3 and 4). The similarity between the Raman spectra of Na-doped polyacetylene and those of the radical anions indicates that the observed bands of Na-doped polyacetylene arise from charged domains generated by Na-doping. The observed large wavenumber dispersion of the C=C stretching vibration of the charged domains suggests a broad distribution of localization lengths in the charged domains.

INTRODUCTION

The mechanistic relationship between chemical doping and charge transport in polyacetylene [(CH=CH)$_n$] has been studied by various physical methods.[1] Electrical conductivity of polyacetylene increases dramatically when the dopant content is less than 1 mol%/CH unit.[2, 3] On the other hand, the Pauli spin susceptibility indicative of a metallic density of states appears at about 6 mol% (critical value).[2, 3] When the dopant content is below the critical value, charged solitons,[4] which have charges but no spin, have been proposed as spinless charge carriers.[1] However, the origin of the metallic state is not fully understood. Raman and infrared spectroscopy can provide structural information useful for understanding the origin of the metallic state. Although the Raman spectra of polyacetylene doped with alkali metals at various doping levels have been reported,[5–10] definite information on the structure of the doped polymer has not been obtained from the observed spectra. Charged species of polyenes have been studied as models of doped polyacetylene.[11–16] Two of the present authors (YF and MT) have recently demonstrated that polarons and bipolarons can be identified on the basis of the Raman spectra of the radical ions and divalent ions of oligomers (oligomer approach).[17, 18] The radical ions and divalent ions of oligomers are viewed as polarons and bipolarons. In this paper, we have studied the Raman spectra of heavily Na-doped *trans*-polyacetylene and the radical anions of α, ω-diphenylpolyenes and α, ω-di-2-thienylpolyenes.

EXPERIMENTAL

All-*trans*-1,6-diphenyl-1,3,5-hexatriene (abbreviated as DP3) and all-*trans*-1,8-diphenyl-1,3,5,7-octatetraene (DP4) were purchased from the Tokyo Chemical Industry Co., Ltd. and Aldrich Chemical Company, Inc., respectively, and used without further purification. All-*trans*-1,6-bis(2'-thienyl)-1,3,5-hexatriene (DT3) and all-*trans*-1,8-bis(2'-thienyl)-1,3,5,7-octatetraene (DT4) were synthesized according to the previous method.[11] The radical anion of each oligoene was prepared by reduction of the neutral oligoene with a sodium mirror in tetrahydrofuran (THF) solution in a sealed glass ampoule. This method was similar to that reported by Hoijtink and Meij.[19] The reduction reactions were followed by absorption spectroscopy. Raman spectra were measured for such solutions in sealed cells. A *trans*-polyacetylene film prepared according to Shirakawa's method[20] was doped heavily with sodium by treating the film with a THF solution of sodium naphthalide (0.1 mol dm^{-3}) for about 60 min in a sealed glass cell. After washing the doped film with fresh THF, the ampoule was sealed again. Raman measurements were made for such a film in a sealed ampoule.

RESULTS AND DISCUSSION

Electronic absorption spectra of the radical anions of oligoenes

The maxima of the electronic absorption spectra of the radical anions of oligoenes are listed in Table I. The observed spectra of the radical anions of DP3 and DP4 (abbreviated as $DP3^{\bullet -}$ and $DP4^{\bullet -}$, respectively) are essentially the same as those reported by Hoijtink and Meij.[19] A strong band at 629 nm and a weak band at 892 nm of $DP3^{\bullet -}$ have been attributed to the two allowed transitions on the basis of the results of semiempirical self-consistent-field calculations combined with a limited configuration interaction.[21] It is reasonable to consider that a strong band at 694 nm and a weak band at 980 nm of $DP4^{\bullet -}$ are also due to the two allowed transitions. The lower energy band is called band I and the higher one band II in this paper. In the absorption spectrum of $DT3^{\bullet -}$, a strong band at 660 nm and two weak bands at 904 and 1012 nm are observed. For $DT4^{\bullet -}$ a strong band at 712 nm and two weak bands at 899 and 1000 nm are observed. The strong bands are assigned to band II and two weak bands to vibronic transitions of band I.

TABLE I The electronic absorption maxima (λ_{max}) of the radical anions of oligoenes and the excitation wavelengths (λ_{ex}) of Raman measurements.

Compounds	λ_{max} / nm (cm^{-1}) band I	band II	λ_{ex} / nm
DP3$^{\bullet-}$	892 (11.2x10^3)	629 (15.9x10^3)	632.8
DP4$^{\bullet-}$	980 (10.2x10^3)	694 (14.4x10^3)	632.8
DT3$^{\bullet-}$	904 (11.1x10^3) 1012 (9.88x10^3)	660 (15.2x10^3)	632.8
DT4$^{\bullet-}$	899 (11.1x10^3) 1000 (10.0x10^3)	712 (14.0x10^3)	710

According to a theoretical calculation[22] using a continuum model, a negative polaron in *trans*-polyacetylene is expected to give rise to two strong bands (ω_1, conduction band ← antibonding level; ω_2, antibonding level ← bonding level) and a very weak band (ω_3, conduction band ← bonding level). The observed bands (I and II) of the radical anions correspond to the ω_1 and ω_2 bands, respectively, though the intensity of band I is weak. For the radical anions, the ω_3 transition is symmetry forbidden.

Raman spectra of the radical anions of oligoenes

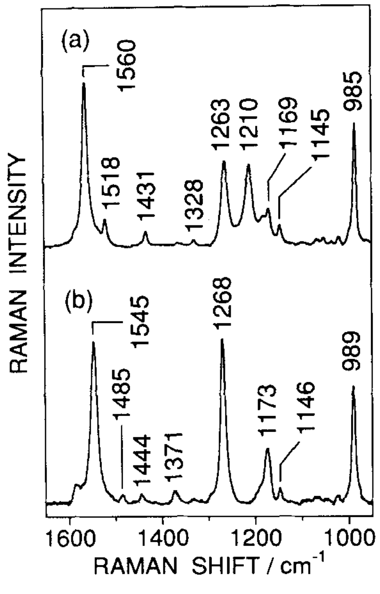
The resonance Raman spectra of DP3$^{\bullet-}$ and DP4$^{\bullet-}$ are shown in Fig. 1 and those of DT3$^{\bullet-}$ and DT4$^{\bullet-}$ in Fig. 2. The wavelengths of the excitation laser lines are within band II (see Table I). The observed Raman spectra show the following three groups of bands characteristic of the radical anions. (1) ν_1 band. A strong band is observed between 1567 and 1538 cm^{-1}, which is assignable to the in-phase C=C stretching vibration. This band shifts downward as the *n* number increases from 3 to 4: 1560 (DP3$^{\bullet-}$), 1545 cm^{-1} (DP4$^{\bullet-}$); 1567 (DT3$^{\bullet-}$), 1538 cm^{-1} (DT4$^{\bullet-}$). (2) ν_2 band. A strong band is observed between 1268 and 1254 cm^{-1}. (3) ν_3 band. One or two strong bands are observed between 1210 and 1173 cm^{-1}: 1210 (DP3$^{\bullet-}$); 1173 (DP4$^{\bullet-}$); 1205 (DT3$^{\bullet-}$); 1194 and 1178 cm^{-1} (DT4$^{\bullet-}$). Several weak bands in the range between 1169 and 1110 cm^{-1} are possibly attributed to the vibrations of the oligoene parts.

In the wavenumber region above 1000 cm^{-1} in the Raman spectra of the radical anions of α, ω-diphenylpolyenes, the phenyl-group modes are not strongly observed. Thus, these radical anions are suitable as models of negative polarons in polyacetylene.

Raman spectra of heavily Na-doped *trans*-polyacetylene

The Raman spectra of the heavily Na-doped *trans*-polyacetylene film measured with excitation wavelengths between 488.0 and 1064 nm are shown in Fig. 3. A broad absorption ranging from visible to infrared (centered at about 1700 nm) appears upon heavy Na-doping.[8, 23] The excitation laser lines are within this absorption. The 632.8-nm excited Raman spectrum is similar to that of $CHNa_{0.17}$ reported by Eckhardt *et al.*[7] and those of $CHNa_{0.13}$ and $CHNa_{0.15}$ reported by Tanaka *et al.*[8] These similarities indicate that the Na content of our sample is not less than 13 mol%. The 13 mol% content means that one electron is removed from every 3.8 CH=CH bonds on average.

The wavenumber region above 1000 cm^{-1} is dominated by four bands. (1) ν_1 band. A strong band is observed between 1580 and 1509 cm^{-1}. The band in this group shifts downward with increasing excitation wavelength: 1580, 1554, 1537, and 1509 cm^{-1} for the 488.0-, 632.8-, 753-, and 1064-nm laser lines, respectively. (2) ν_2 band. A band is observed between 1264 and 1254 cm^{-1}. The wavenumber of this band is insensitive to excitation wavelength, whereas the relative intensity decreases with increasing excitation wavelength. (3) ν_3 band. A broad band is observed in the range between 1195 and 1164 cm^{-1}, except for the 488.0-nm excited spectrum. The band in



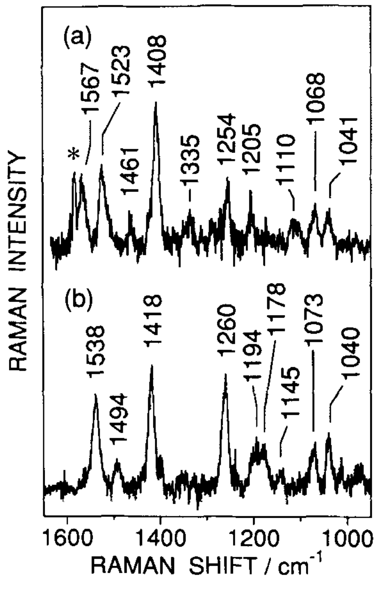


FIGURE 1 (left) Resonance Raman spectra of the radical anions of (a) 1,6-diphenyl-1,3,5-hexatriene ($DP3^{\bullet -}$) and (b) 1,8-diphenyl-1,3,5,7-octatetraene ($DP4^{\bullet -}$) in THF solutions. Excitation wavelength is 632.8 nm for both (a) and (b). Backgrounds are subtracted.

FIGURE 2 (right) Resonance Raman spectra of the radical anions of (a) 1,6-bis(2'-thienyl)-1,3,5-hexatriene ($DT3^{\bullet -}$) and (b) 1,8-bis(2'-thienyl)-1,3,5,7-octatetraene ($DT4^{\bullet -}$) in THF solutions. Excitation wavelengths are 632.8 and 710 nm for (a) and (b), respectively. Backgrounds are subtracted. The band with asterisk is due to a spontaneous emission line.

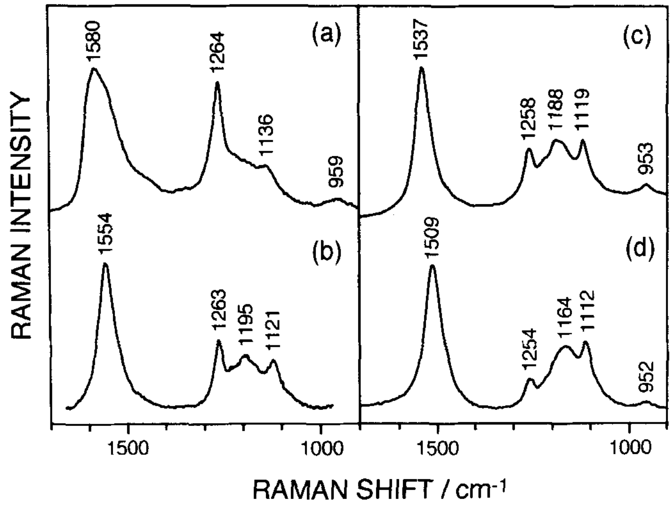


FIGURE 3 Raman spectra of heavily Na-doped *trans*-polyacetylene. Excitation wavelengths are 488.0, 632.8, 753, and 1064 nm for (a), (b), (c), and (d), respectively.

this group also shifts downward, as excitation wavelength becomes longer. (4) ν_4 band. A peak is observed between 1136 and 1112 cm^{-1}. The band in this group also shifts downward. In the Raman spectra of the radical anions of the oligoenes, no corresponding bands are observed.

The above features of the Raman spectra of heavily Na-doped polyacetylene are now compared with those of the radical anions of the oligoenes. The overall similarity between the Raman spectra of the radical anions and those of Na-doped polyacetylene shows that the latter bands arise from charged domains generated by Na-doping in the polymer chain. The large wavenumber range observed for the ν_1 bands can be explained by the existence of charged domains with various localization lengths. These domains have different electronic absorptions, and the Raman bands arising from a domain are resonantly enhanced when the wavelength of excitation laser line is located within the electronic absorption of the same domain. Studies of the Raman spectra of the radical anions of longer α, ω-diphenylpolyenes and model compounds of charged solitons are requisite for further elucidation of the charged domains.

CONCLUSION

In the wavenumber region above 1000 cm^{-1} of the Raman spectrum of heavily Na-doped polyacetylene, four groups of bands have been observed. These bands are attributed to charged domains generated by Na-doping. The wavenumber of the Raman band in the C=C stretching region varies with the wavelength of excitation laser line. This dispersion is indicative of the presence of charged domains having various lengths of electron localization.

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