

Electronic Absorption and Raman Spectroscopic Studies of α,ω -Diphenylpolyenyl Anions with Odd Number of Polyene Carbons

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The electronic absorption and Raman spectra of α,ω -diphenylpolyenyl anions $\text{Ph}(\text{CH})_n\text{Ph}^-$ (DP_n^- , $n = 3, 5, 7, 9,$ and 13), with odd number of carbons at the polyene part, have been studied in the tetrahydrofuran (THF) solutions and in their solid film states, respectively. In the case of Raman spectra for DP_n^- , the frequencies and relative intensities of some Raman peaks regularly change with the increase of polyene chain length. The spectral patterns of anions (DP_n^-) are very similar with those of radical anion ($\text{DP}_n^{\bullet-}$). However, the C=C stretching peaks of DP_n^- anions are observed in the 25-35 cm^{-1} higher frequency region than those of $\text{DP}_n^{\bullet-}$ radical anions. In the case of long chain models such as DP_9^- and DP_{13}^- , the C=C stretching peaks are observed in even higher frequency region than those of the corresponding neutral polyenes such as $\text{DP}_8, \text{DP}_{10},$ and DP_{12} . The Raman patterns of DP_n^- anions in the THF solutions are similar with those in their solid film states. On the other hand, their electronic absorption spectra show a considerable difference each other. The $n-\pi^*$ electronic absorption bands of DP_n^- anions in the THF solutions have been observed in the 0.27-0.39 eV lower energy region than those in their solid film states due to the solvent effects on polyene anions.

Keywords : Soliton, α,ω -Diphenylpolyenyl amines, Raman spectroscopy.

Introduction

Polyene has been known as a good model compound for the study of polyacetylene $[(\text{CH}=\text{CH})_n]$, a prototype of conducting polymer, since polyene has very similar π electron properties with polyacetylene. Polyene shows a novel spectroscopic property due to its electron correlation effects. Hudson *et al.*¹ and Kohler² reported that the spectroscopic features of unsubstituted polyenes and α,ω -diphenylpolyenes are caused by the ordering of their singlet electronic excited states, 1^1B_u and 2^1A_g .

The charged species (cation, radical cation, anion, radical anion and divalent ion etc.) of conjugated polyene have also attracted considerable attention due to their interesting electronic properties.^{3,4} Comprehensive studies on these species are very important to understand the electrical properties of doped *trans*-polyacetylene (*trans*-PA).⁵ There have been many spectroscopic and theoretical studies to elucidate the structural properties for the charged species of various polyenes. For instance, Bally *et al.*⁶ and Jeevarajan *et al.*⁷ investigated the radical cations of α,ω -dibutylpolyenes, the dications of carotenoids, and the α,ω -diphenylpolyenyl anions using optical absorption spectroscopy. Kawashima *et al.*⁸ theoretically investigated the molecular structures of the radical cations and dications, for a series of linear polyenes from 1,3-butadiene to 1,3,5,7,9-decapentaene, using the *ab initio* molecular orbital calculations at the complete active

space self-consistent field (CASSCF) and the multi-reference Møller-Plesset (MP) levels. Tolbert *et al.*⁹ reported the NMR and electronic absorption spectra of α,ω -diphenylpolyenyl anions, $\text{Ph}(\text{CH})_n\text{Ph}^-$ (abbreviated as DP_n^- , $n = 3, 5, 7, 9, 13,$ and 17 ; n is the number of carbon atoms at the polyene part). These anions were considered as the model ions of a negatively charged soliton in *trans*-PA. The DP_n^- anion has a negative charge, with odd number of carbon atoms at the polyene part (n), but it does not have any spin. The Raman spectra for the radical anions of α,ω -diphenylpolyene, $\text{Ph}(\text{CH})_n\text{Ph}^{\bullet-}$ (abbreviated as $\text{DP}_n^{\bullet-}$, $n = 4, 6, 8$ and 10), were also reported. In this case, the radical anions were considered as the model radical ions of a negatively charged polaron in *trans*-PA.^{10,11} The negative polaron, $\text{DP}_n^{\bullet-}$, has even number of carbon atoms with a negative charge and a spin at the polyene part. In our previous Letter,¹² we reported the optical absorption and Raman spectra for the radical anion of all-*trans*-19,19',20,20'-tetranor- β,β -carotene (abbreviated as $\text{TNBC}^{\bullet-}$, $n = 22$), which is considered as another good polaron model in *trans*-PA.

To our knowledge, however, any structural study about α,ω -diphenylpolyenyl anions, using Raman and electronic absorption spectroscopy, has not been fully reported yet. In the present work, we have investigated the Raman and electronic absorption spectra of the α,ω -diphenylpolyenyl anions, $\text{Ph}(\text{CH})_n\text{Ph}^-$ (DP_n^- , $n = 3, 5, 7, 9,$ and 13 ; see Figure 1), in the tetrahydrofuran (THF) solutions and in their solid film states, respectively. This spectroscopic study is expected to be crucial in elucidating the chain length effects of polyene carbons as well as the solvent effects on the structural

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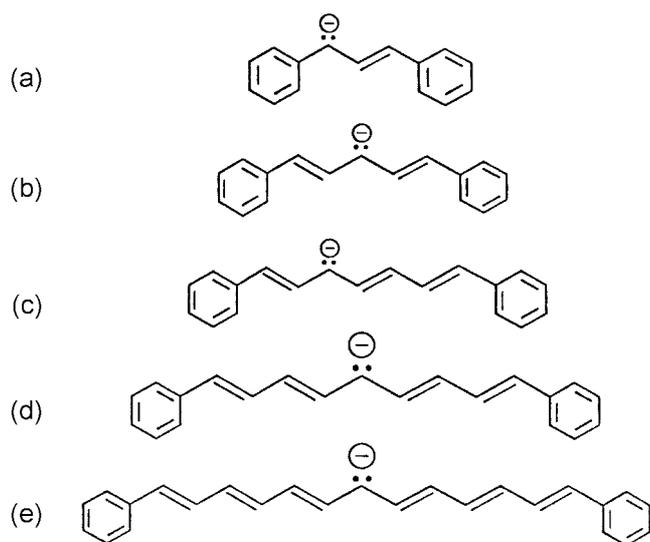


Figure 1. Molecular structures of α,ω -diphenylpolyenyl anions (DP_n^-); (a) DP_3^- , (b) DP_5^- , (c) DP_7^- , (d) DP_9^- , and (e) DP_{13}^- .

properties of DP_n^- anions. Furthermore, some Raman peaks of DP_n^- anions have been compared with the previously reported spectral data of radical anions, $DP_n^{\bullet-}$, and neutral polyenes, DP_n , in order to better understand their characteristic bond characters. The results are reported here.

Experimental Section

The α,ω -diphenylpolyenyl anions (DP_n^- , $n = 3, 5, 7, 9$, and 13) and their neutral species (DP_n) were synthesized using the previously reported methods.^{8,13,14} The anion (DP_n^-) of each neutral polyene (DP_n) was prepared by the reduction of the DP_n with 1.6 mol n -butyllithium/ n -hexane in THF. This reducing agent is well known to produce the DP_n^- anion solution which is free of ion pairing. All the anion samples were prepared in a sealed glass ampoule. This method is similar to that reported by Young *et al.*^{13,14} The concentration of sample in the THF solution was controlled to be in the 10^{-5} - 10^{-4} mol/dm³ range. These solution samples were kept in a completely sealed quartz cell. The solid film samples were prepared by evaporizing the solvents from the inter-side of cell. The reduction reactions were identified by electronic absorption spectroscopy.

Raman spectra were measured on a JEOL JIR 5500 FT-Raman spectrophotometer. A 1064-nm laser line was provided from a CVI YAG-MAX C-92 Nd:YAG laser. A liquid-nitrogen-cooled Ge detector was used for FT-Raman measurements. The spectral resolution was 4 cm⁻¹. Resonance Raman spectra, excited with the laser lines in the 457.9-632.8-nm region, were measured on a Raman spectrometer consisting of a Spex 1877 Triplemate detector. Several laser lines from a Coherent Radiation Innova 90 Ar ion laser (457.9, 488.0 and 514.5 nm) and a NEC GLG 108 He-Ne laser (632.8 nm) were used for the Raman excitation. Electronic absorption spectra were measured on a Hitachi U-3500 spectrophotometer.

Table 1. The electronic absorption maxima (λ_{max}) of α,ω -diphenylpolyenyl anions (DP_n^-)

| $Ph(CH)_nPh^-$ DP_n^- , $n =$ | in THF Sol. | in Solid Film | in DMSO Sol.* |
|------------------------------------|-------------------------|---------------|---------------|
| | λ_{max}/nm (eV) | | |
| 3 | 562 (2.21) | — | 558 |
| 5 | 598 (2.07) | 504 (2.46) | 591 |
| 7 | 648 (1.91) | 556 (2.23) | 642 |
| 9 | 706 (1.76) | 610 (2.03) | 696 |
| 13 | 816 (1.52) | 678 (1.83) | 800 |

*; reference 8

Results and Discussion

Electronic Absorption Spectra of α,ω -Diphenylpolyenyl Anions. The electronic absorption maximum (λ_{max}) of each anion, in the THF solution and in its solid state, is listed in Table 1. In both cases, the maximum of absorption band is shifted to a lower energy region with the increase of polyene chain length. The absorption maxima of DP_n^- anions in the dimethylsulfoxide (DMSO) solution, which were previously reported by Tolbert,⁸ are also listed in Table 1. The band shift pattern in the DMSO solution is very similar with our data in the THF solution and in its solid film state. The strong single absorption band of DP_n^- anion is attributed to the $n-\pi^*$ electronic transition between the nonbonding orbital and π^* LUMO orbital. According to the MO energy level diagram, the non-bonding orbital, which is occupied by two non-bonding electrons, exists in the middle of the band gap.

The electronic absorption spectra of DP_9^- anion, which were measured in the THF, 2-methyl-THF and 2,5-dimethyl-THF solutions and in its solid film state, are also demonstrated in Figure 2. The electronic absorption maximum of DP_n^- anion in the solid film state is observed in the 0.27 eV higher energy region than that in the THF solutions. The absorption maximum in the 2,5-dimethyl-THF solutions shows a similar shift pattern (λ_{max} : 2.09 eV in Figure 2(c)).

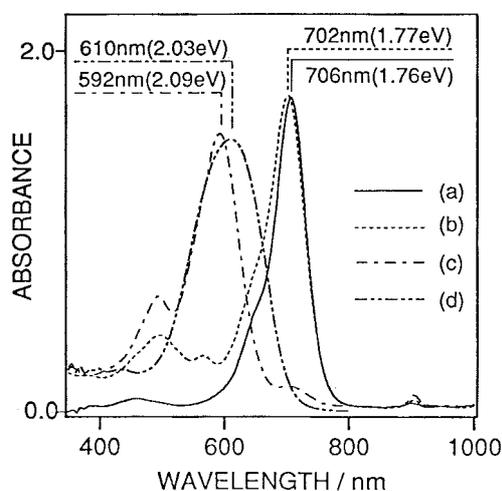


Figure 2. Electronic absorption spectra of DP_9^- in (a) THF solution, (b) 2-methyl-THF, (c) 2,5-dimethyl-THF, and (d) solid film state.

According to the report of R.N. Young *et al.*,¹⁴ this band shift may be explained by the counter ion (Li^+) effect on the charged polyene chain. According to their experimental results,¹⁴ the negatively charged polyenes (DP_5^- , DP_7^- , and DP_9^-) in 2,5-dimethyl-THF solutions are not free with Li^+ ion, and their absorption bands were shifted to 70-100 nm lower wavelength region than those in THF solution by the interaction between counter ion and charged polyenes. They explained these spectral shifts in terms of "free ion and tight ion models. Our electronic absorption spectra in different THF solutions show similar trends with their spectroscopic results. Our electronic absorption data are also consistent with the theoretical results using a continuum model. According to this model, the soliton in PA is expected to have only one electronic absorption band at the mid-gap center.

On the other hand, the radical anions of α,ω -diphenylpolyene^{10,11} and α,ω -dibutylpolyene⁶ are known to have two absorption bands caused by the $\pi\text{-}\pi^*$ transitions ($1^2\text{B}_g \rightarrow 2^2\text{A}_u$ and $1^2\text{B}_g \rightarrow 1^2\text{A}_u$). According to the theoretical calculation using a continuum model,¹⁵ the negative polaron in PA is expected to have two strong absorption bands; one is caused by the "anti-bonding level \rightarrow conduction band" transition, and the other is caused by the "bonding level \rightarrow anti-bonding level transition.

Raman Spectra of α,ω -Diphenylpolyenyl Anions. The 1064-nm laser excited FT-Raman spectra of the negatively charged soliton models (DP_n^- , n is 3, 5, 7, 9, and 13) in the

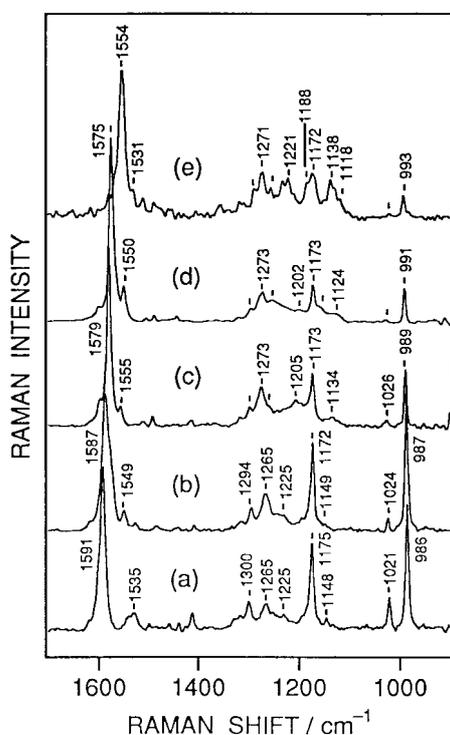


Figure 3. 1064-nm laser excited Raman spectra of α,ω -diphenylpolyenyl anions (DP_n^-) in THF solutions; (a) DP_3^- , (b) DP_5^- , (c) DP_7^- , (d) DP_9^- , and (e) DP_{13}^- . Fluorescence backgrounds are subtracted from each spectrum.

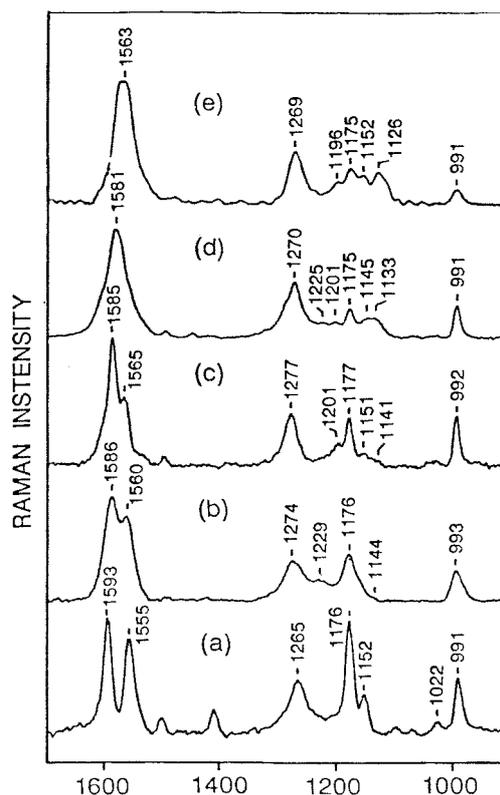


Figure 4. Resonance Raman spectra of α,ω -diphenylpolyenyl anions (DP_n^-) in the solid film state. Excitation wavelengths are 457.9, 488.0, 514.5, 514.5, and 632.8 nm for (a), (b), (c), (d), and (e), respectively. Fluorescence backgrounds are subtracted from each spectrum.

THF solutions are shown in Figure 3. The Resonance Raman spectra of DP_3^- , DP_5^- , DP_7^- , DP_9^- , and DP_{13}^- in the solid film state, observed with 457.9, 488.0, 514.5, 514.5, and 632.8-nm Raman excitations, are also demonstrated in Figure 4. The resonance Raman spectra of DP_n^- in the THF solutions could not be observed due to the strong interference of intense fluorescence backgrounds. However, the FT-Raman spectra using the 1064-nm laser line (1.17 eV) could be obtained since the energy level of laser is located at the lower energy level than the electronic absorption energy levels of DP_n^- . Some characteristic Raman peaks are observed in the FT-Raman spectra. The strong peak (ν_1) between 1593 and 1531 cm^{-1} is assigned to the C=C stretching mode, and this peak shifts downward as the polyene chain length (n) increases from 3 to 13. In Figure 5(a), the correlation between $1/n$ and observed ν_1 frequency for DP_n^- anion is plotted. For a better comparison, those of radical anions (polaron models) and neutral species are also plotted in Figure 5(b) and (c), respectively. As shown in Figure 5, the observed C=C stretching (ν_1) peaks of anions (DP_n^-) shift to 25-35 cm^{-1} higher frequency region than those of the radical anions ($\text{DP}_n^{\bullet-}$). In the case of long chain anions such as DP_9^- and DP_{13}^- , the stretching peaks shift to even higher frequency region than those of the corresponding neutral polyenes. This frequency shift indicates that the bond orders or bond alternations of the anions (soliton models) are somewhat

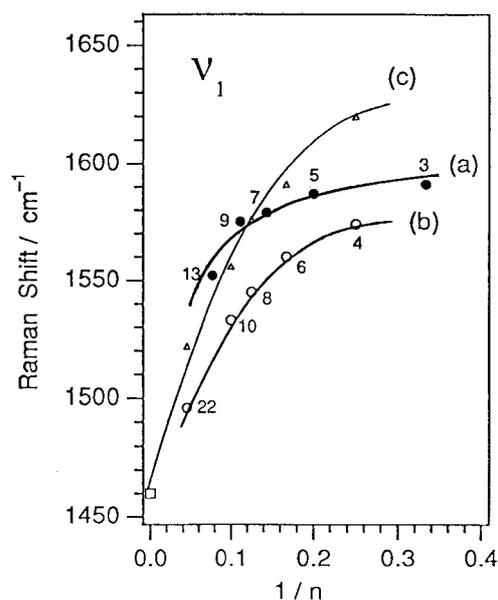


Figure 5. A plot of the C=C stretching peaks of the anions, radical anions, and its neutral polyenes against the inverse of the conjugation length ($1/n$). (a) anions (DP_n^-), (b) radical anions ($DP_n^{\bullet-}$ and $TNBC^{\bullet-}$, references 10 and 12), and (c) neutral polyenes (DP_n ; n is even number, TNBC, and *trans*-PA).

different from those of their neutral species as well as the radical anion species (polaron models). Especially, the lower frequency shift of each C=C stretching band in the radical anions reflects a decrease of C=C bond order, which means a change in regular bond alternation. According to the ab initio molecular orbital calculations of the radical cations, for a series of linear polyenes from 1,3-butadiene to 1,3,5,7,9-decapentaene reported by Kawashima *et al.*,⁹ the bond alternation appears at the center of the chain for their radical cation. The present observation suggests that a change in bond alternation also occurs in the case of the anions. However, the ν_1 peaks of the anions (DP_n^-) in the solid film state are observed at higher frequency region than that in THF solutions. In previous paper,¹⁶ we had reported that the position of the C=C stretching peaks in a lightly sodium-doped PA measured at 1446 cm^{-1} . Based on these results, we can predict that at least 33-37 carbons are needed to form the self-localized charge domains in a lightly doped PA. The number of carbons is guessed from the extension of chain lengths in our soliton models ($n = 3-13$). In this point of view, the Raman spectra of longer soliton model compounds should be extensively investigated in order to better understand the properties of self-localized charge domains in PA. According to Chung *et al.*,¹⁷ the Pauli spin susceptibility, which indicates a metallic density of states, suddenly appears at a dopant concentration of about 6 mol%/CH unit (critical value) in the case of PA. Thus, this doped PA could be regarded as a metal. When the dopant concentration is below the critical value, the charged solitons have been proposed as a spinless charge carriers.¹⁸

The second peak (ν_2) of DP_n^- is observed in the $1265-1300\text{ cm}^{-1}$ region as shown in Figure 3, and this peak is

assigned to CH in-plane bend. The relative intensity of ν_2 peak in the solid film state is remarkably stronger than that in the THF solution. The peak pattern, the peak frequency and intensity, is very similar with the corresponding peak in doped PA. On the other hand, the ν_2 peak of DP_n^- is observed in the $10-15\text{ cm}^{-1}$ lower region than that of neutral polyenes, and the polyene chain length effect is relatively small. In the case of radical anion and dianion,^{10,12} the ν_2 peak was observed at the same position with the anions. Thus, the peak position of ν_2 may be used as the marker of the negatively charged polyenes or donor doped PA.

Two or three peaks for the third group (n_3) are observed in the $1118-1225\text{ cm}^{-1}$ region. These peaks are assigned to the combination peaks for the C-C stretch and C=C stretch modes. The relative Raman intensity of ν_3 peak is strengthened with the increase of polyene chain length. The CH out-of plane mode measured in doped-PA could not be observed in the soliton compounds. A strong Raman peak corresponding to one of the phenyl ring modes is observed in the $1172-1177\text{ cm}^{-1}$ region, but the peak intensity is weakened with the increase of polyene chain length. The other phenyl ring mode is also observed in the $986-1026\text{ cm}^{-1}$ region.

As described above, the Raman spectra of the soliton models (DP_n^-) and the polaron models ($DP_n^{\bullet-}$ and $TNBC^{\bullet-}$)^{10,12} show very similar spectral patterns as a whole. However, the frequencies and relative intensities of some Raman peaks are somewhat different each other. For the more correct discussion about the anions (soliton), the MO calculations of DP_n^- at the high level are need, and more extensive studies for longer soliton model compounds are absolutely needed to clearly understand the self-localized charge domains in doped PA because the self-localized charge domains in a lightly doped PA can be predicted at least 33-37 carbons.

According to the Heeger and co-workers,^{17,19} the electrical properties of doped PA depend on dopant contents. Especially, the Pauli spin susceptibility indicative of a metallic density of states appears suddenly at a dopant concentration of about 6 mol%/CH unit (critical value),¹⁷ and doped PA can thus be regarded as a metal. Thus, when the dopant concentration is below the critical value, charged solitons that have charges but no spin have been proposed as spinless charge carriers. However, a complete understanding of the mechanism of electrical conduction has not been achieved yet, though several arguments have been proposed.

Summary

The electronic absorption and Raman spectra of the DP_n^- anions (n ; 3, 5, 7, 9, and 13) have been measured in the THF solutions and in their solid film states, respectively. The electronic absorption maximum of DP_9^- anion, caused by the $n-\pi^*$ electronic transition, in the solid state is observed in the $0.27-0.39\text{ eV}$ higher energy region than that in the THF solution. In the case of Raman spectra for DP_n^- , the C=C stretching peak shifts downwards with the increase of polyene chain. The observed C=C stretching (ν_1) peaks of anions

(DP_n^-) shift to 25-35 cm^{-1} higher frequency region than those of the radical anions ($DP_n^{\bullet-}$). This means that the C=C bond characters of anions (soliton model) are somewhat different from those of radical anion species (polaron model), even though the overall spectral patterns are very similar with each other.

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