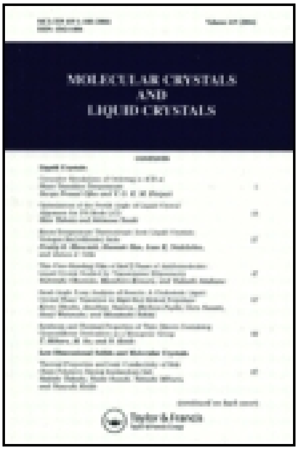

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Ground State and Excited State πElectron Structures of Linear-Chain Conjugated Model-Systems

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GROUND STATE AND EXCITED STATE π-ELECTRON STRUCTURES OF LINEAR-CHAIN CONJUGATED MODEL-SYSTEMS

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Abstract Recent optical spectroscopic investigations of linear-chain polydiacetylene (PDA) molecules are interpreted with respect to the electronic ground state and excited state structures. It will be demonstrated that PDA oligomer molecules represent a unique model system for the study of the non-degenerate butatriene and acetylene (ynene) ground state configurations and radical electron structures of diradicals, carbenes and dicarbenes. The optical absorption spectra and emission spectra of short chain PDA molecules are analyzed. Optical spectra of long matrix isolated chains show all essential features of electron-hole excitation and polaron recombination processes. The p_z-radical electron distribution deduced from the ESR-spectra is used in the discussion of neutral and charged elementary excitations of the PDA chain.

INTRODUCTION

Up to date the solid state polymerization reaction of diacetylenes represents the only method of preparing nearly perfect macroscopic single crystals[1-3]

In this reaction a monomer single crystal is completely transformed into a fully polymerized polymer crystal. The reaction mechanisms of this exceptional chemical reaction have been investigated in detail by solid state spectroscopy.[4-6] The most essential advantage of this system is the fact that all reaction intermediates are non-reactive at temperatures below 80 K.

The most important features of the reaction mechanisms are summarized as follows:

(a) In the photoinitiation reaction dimer ($n = 2$) diradical molecules are produced.
(b) Subsequent low temperature reaction steps are characterized by thermal chain addition polymerization and by optical chain termination reactions of the reaction intermediates.
(c) In the chain addition polymerization reaction at temperatures above 100 K monomer molecules are added to the reactive chain ends of the intermediates.
(d) Chain termination reactions at low temperatures are observed only by photoexcitation of the reaction intermediates. In this reaction the radical electron structure is removed.
(e) All reaction intermediates have a radical electron structure at least at one chain end. The intermediates observed in the polymerization reaction are diradicals, dicarbenes and carbenes, which can be prepared with different chain lengths ($2 \leq n \leq 14$).

The important relevance of the polydiacetylenes (PDA's) with respect to the unusual electrical and optical properties exhibited by the whole class of polyconjugated molecules is based on several advantages, which render them ideal model systems for spectroscopy. Detailed information on basic elementary excitations such as kinks, antikinks, polarons and excitons is expected due to the following properties of the PDA systems.

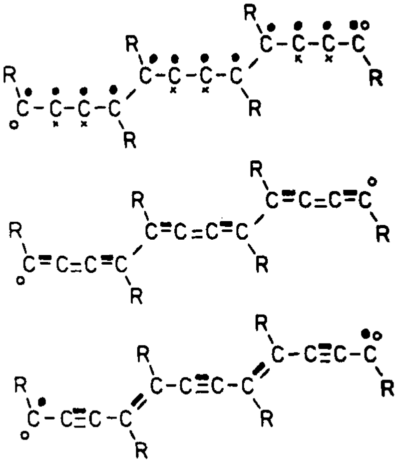
(a) The planar polymer backbone is fully conjugated with single, double and triple bonds.[3,7]
(b) The conjugation length of the polymer chains is of the order of 1000 unit cells.[8]
(c) All polymer molecules are perfectly oriented and form macroscopic single crystals.[1-3]
(d) The physical properties are highly anisotropic due to the interchain distances of about 0 7 nm. Therefore the PDA's represent ideal one-dimensional model systems.
(e) The two possible electronic ground state structures (butatriene and acetylene) are non-degenerate.[9,10]

ELECTRONIC CHAIN CONFIGURATIONS

π-Bonds

The basic electronic structures of the carbon backbone are shown in Fig. 1 for trimer molecules as example, which are formed by the addition of three monomer diacetylene molecules. Figure 1a shows the different types of electrons. The sp_x

and sp^2 electrons are bound to σ-bonds and form the carbon zig-zag backbone structure. Due to the finite length of the molecule the hybridized radical electrons (open circles) at the ends of the molecule are unbound. The p_z- and p_y-electrons are represented by full points and crosses. Pairing of the p_z-electrons and p_y-electrons to π-bonds results either in the butatriene structure (b) or in the acetylene structure (c).



(a) p_y(x), p_z(•) and σ-electrons (o)

(b) butatriene structure, diradicals DR

(c) acetylene structure, dicarbenes DC

FIGURE 1 Electron configuration of a diacetylene trimer molecule.
The two possibilities in the pairing process of the p_z-electrons to π-bonds (thick bonds) lead to two different structures (b) and (c).
All diacetylene molecules discussed in this contribution are obtained as reaction intermediates in the solid state polymerization reaction. Therefore they all carry unsaturated radical electrons and are observed in the spectra either as diradicals or dicarbenes.

The change from the butatriene to the acetylene structure implies (1) flipping of the π-bonds by one position and (2) disruption of a π-bond. Consequently the radical structure changes from a diradical to a dicarbene.

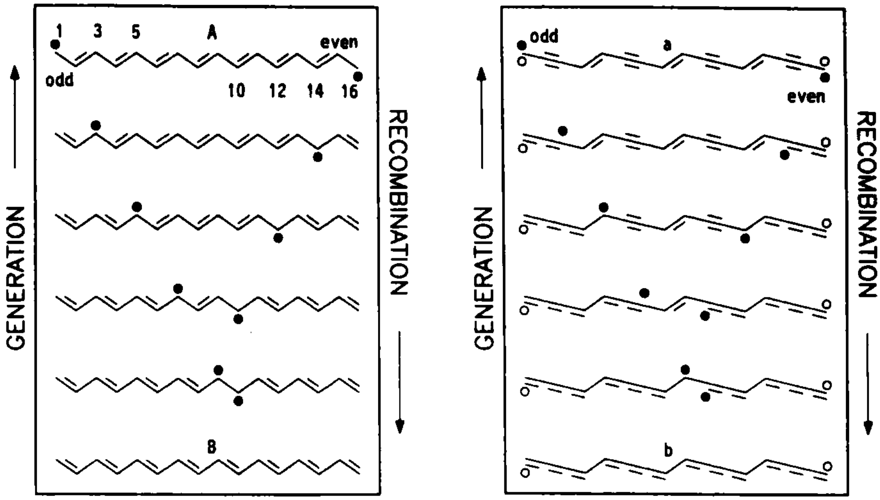


FIGURE 2 Soliton and antisoliton (kink and antikink) motion, generation and recombination in trans-$(CH)_{16}$ and a diacetylene tetramer molecule. The σ-electrons of the PDA system are fixed at the chain ends.

The flipping of the π-bonds involves the motion of radical electrons as shown in Fig. 2 by comparison of short chain polydiacetylenes with the simplest conjugated polymer, which is given by the trans-polyacetylene. The butatriene-to-acetylene and the reverse transition is involved with the recombination or generation of p_z-radical electrons. In both cases we have to distinguish between kinks and antikinks (odd and even radical electrons). The kinks move only on odd carbon atom positions. The motion implies a flipping of the π-bonds. Due to symmetry the trans-polyacetylene structures A and B are degenerate. From our ESR and optical experiments, which are explained in terms of a simple Hückel-type theory, we know that the diacetylene structures a and b of Fig. 2 are different by an amount of $\Delta\varepsilon = 0.4$ eV per unit cell.[9] Therefore, going from a to b in Fig. 2, an energy of about $n \cdot \Delta\varepsilon \cong 1.6$ eV is required. However, the formation of a π-bond (upon recombination of the radical electrons) yields an energy of $\varepsilon_\pi \cong 2.8$ eV. Therefore owing to energy arguments, the system will prefer to stay in the butatriene structure at short chain lengths and in the acetylene structure at long chain lengths.

For $n > 6$ the product $n \cdot \Delta\varepsilon$ becomes larger than ε_π. In the heptamer situation, shown in Fig. 3, the butatriene structure is expected to be unstable against a phase transition to the acetylene structure. Upon disruption of a π-bond a kink-antikink pair is generated. The motion of the two radical electrons to the outer ends of the oligomer chain is determined by an energy gain of $n \cdot \Delta\varepsilon$ involved in the butatriene-to-acetylene transition. Therefore only the acetylene structure of the PDA's is stable in long chains. This fact is well established by X-ray diffraction investigations[7] on the TS-PDA system. By means of optical and ESR absorption spectroscopy of the dimer, trimer, tetramer etc. reaction intermediates at low temperatures we have been able to demonstrate the change of the electronic configurations at n ≧ 6.[10]

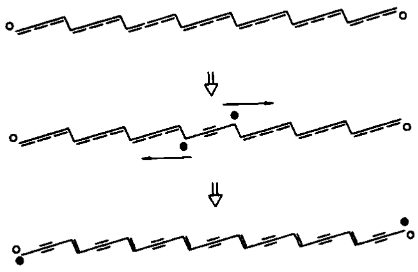


FIGURE 3 Butatriene-to-acetylene transition in long-chain polydiacetylenes. The radical electron structure changes from diradicals to dicarbenes. DR → DC.

Carbenes

As shown in Figure 1 the radical electron structure of the chain ends is dependent on the π-bond arrangement within the chains. Carbene states are obtained with the acetylene configuration of the chains (Figure 1c). As shown by the circle and the full points the two radical electrons of every carbene are different. Depending on the bond angles two limiting situations arise as shown in Figure 4 (a) and (b).

Figure 4(a) schematically shows the electron configuration of the carbon atom at the chain end with an angle of 120° corresponding to the expected configuration for a perfect "infinitely' long polymer chain. The orbitals shown in Figure 4 (a) are given by a p_z and a hybridized sp_y^2 state,

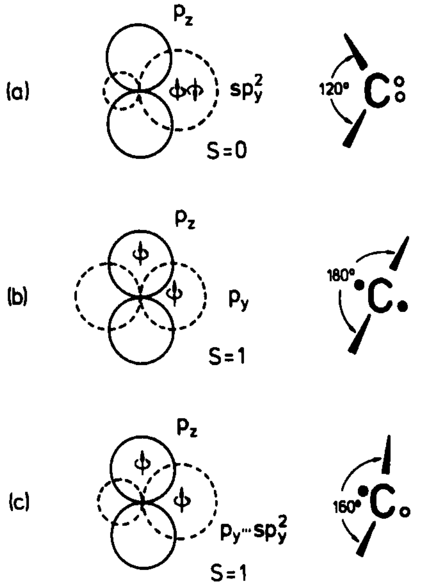


FIGURE 4

(a) Singlet state configuration of the non-degenerate p_z and sp_y^2-electron orbitals in a bent carbene.

(b) Triplet state configuration of the degenerate p_z and p_y electron orbitals in a linear carbene.

(c) Approximate electron structure of the triplet carbenes in PDA oligomer systems.

which are obtained from the double bond when cutting the chain. Owing to the fact, that the σ-electron states are lower in energy than π-states the two radical electrons at the chain end will occupy the sp^2-state with antiparallel spins forming a singlet ground state with $S = 0$.

Figure 4(b) schematically shows the electron configuration of the carbene atom with an angle of 180°, which is the state of highest symmetry with degenerate p_y- and p_z-states. According to Hund's rule the ground state situation then is given by the state of highest spin multiplicity, which is the triplet state with $S = 1$. This state is given by single occupation of the p_z and p_y electron orbitals.

As shown by early experiments on the diacetylenes[11] the carbene ground state is a triplet with a bond angle of approximately 160° as shown in Figure 4(c). Adding a conjugated chain to the carbene, we have to account for the delocalization of the p_z-radical electron along the chain. Therefore the triplet S = 1 ground state of the diacetylene carbenes with one p_z-radical electron and one sp^2-radical electron is the favoured configuration even at an angle of approximately 160° as shown in Figure 4(c).

Motion, Localization and Distribution of the p_z-Radical Electrons

The best known system containing stable p_z-radical electrons even at room temperature is the trans-polyacetylene (PA). The p_z-radical electrons of the PA and PDA system are shown schematically in Figure 5 (a) and (b). They represent a phase boundary between two different structures, or a bond alternation defect.[13] A change in the bond alternation is correlated with a change in the carbon bond lengths. Due to symmetry the structures

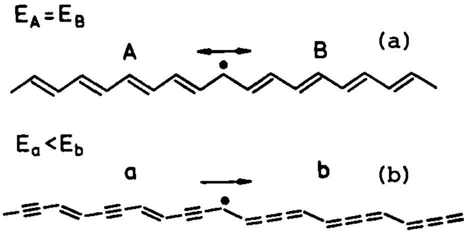


FIGURE 5

Radical electrons in trans-PA (a) and PDA (b) are combined with a bond alternation defect structure.

A and B are degenerate and the electron can move along the chain in all directions. This leads to motional narrowing of the ESR line of the trans-PA radical electrons. However, the structures a and b of the PDA system are non-degenerate with an energy difference of 0.4 eV per unit cell.[10] Due to energy arguments the radical electron is therefore forced to move at the outer end of the right side of the chain. The resulting localization of the electron at the chain end then leads to a characteristic hyperfine structure.

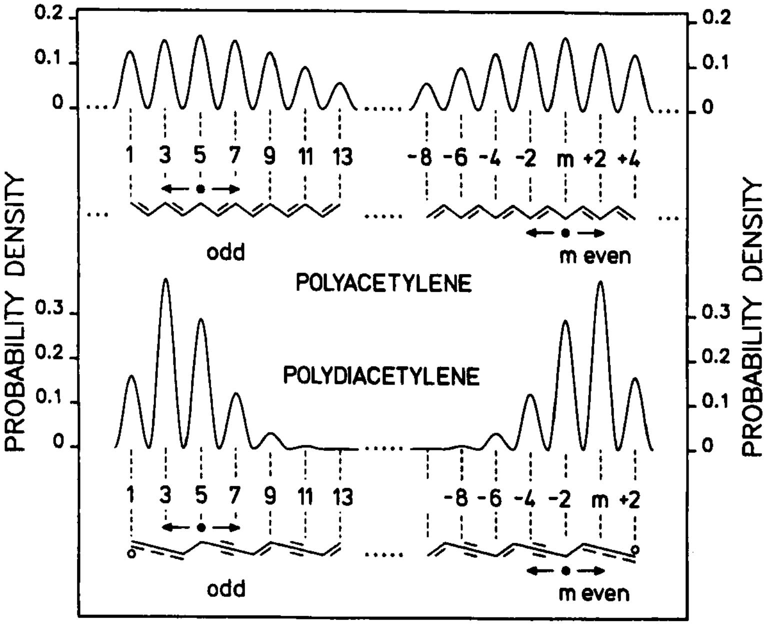


FIGURE 6 Distribution of the odd and even p_z-radical electrons along the trans-PA and the PDA chains. In PDA chains the particle and the corresponding antiparticle are localized at the chain ends.

The p_z-radical electron distribution has been calculated.[10,14] The result of the SSH-theory[14] for PA are solitons and antisolitons shown in comparison to the respective states in the PDA system[10] in Figure 6. The probability density of the odd radical electrons is shown on the left and that of the even radical electrons is shown on the right.

OPTICAL ABSORPTION SPECTROSCOPY

Diradical Series

The optical absorption spectra obtained after UV-irradiation at 10 K and thermal reaction are shown in Figure 7. The thermal reaction times at 100 K are given in minutes. The first spectrum shows the optical absorption after photoinitiation by three excimer laser pulses. Only the dimer ($n= 2$) and some trimer ($n = 3$) molecules are produced photochemically. In thermal addition reaction steps longer reaction intermediates ($n = 3,4,5,6$) are generated. The number of diradical (DR_n) states is limited to $2 \leqq n \leqq 6$. The individual dicarbene (DC_n) absorptions with $n \geqq 7$ all appear at the same spectral position. In the hexamer molecule the butatriene and acetylene structure are roughly degenerate.

Chain Termination Reactions

In the chain termination reaction the radical electrons are removed. This reaction shows a pronounced isotope effect. The thermal termination reaction

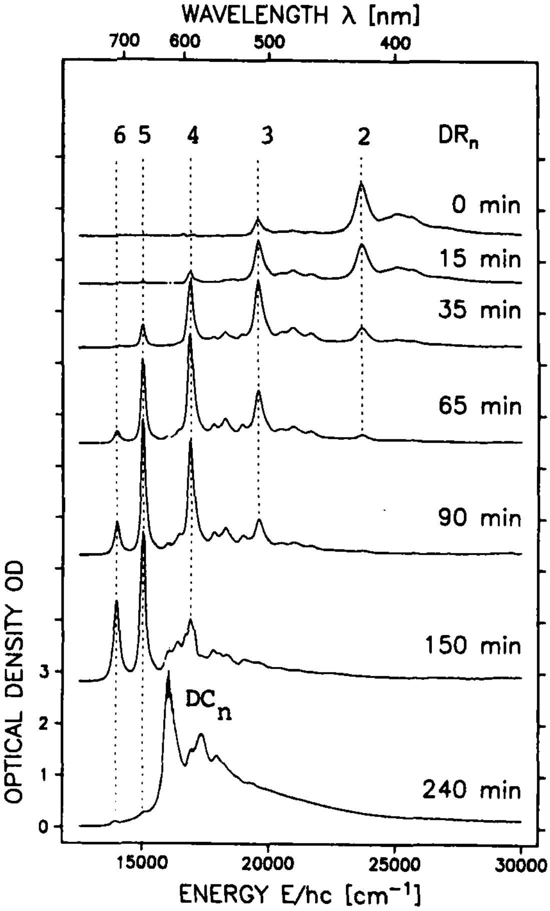
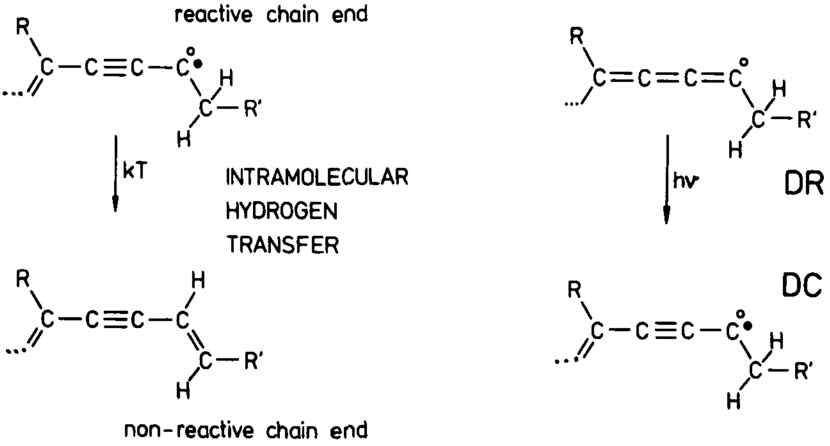


FIGURE 7 Optical absorption spectra of a diacetylene crystal after photoinitiation and thermal reaction.

2,3,4,5 and 6 are the dimer, trimer, tetramer, pentamer and hexamer absorption of diradical intermediates.

All absorptions of the dicarbene intermediates DC_n with $n > 6$ are located at about the same spectral position.

rate constant is reduced by a factor of about ten[15] upon deuteration of the CH_2-group, linking the substituents R to the carbon backbone of the chain where R = $-(CH_2SO_3C_6H_4-CH_3) = -(CH_2R')$. Therefore this reaction is interpreted as being an intramolecular hydrogen transfer reaction following the reaction scheme on the left, below.



In this reaction the sp^3-hybridization of the CH_2-group is changed to a sp^2-hybridization and the radical electrons are completely removed.

In case of the diradicals the butatriene structure obtains acetylenic character following photoexcitation according to the reaction scheme on the right, above. Subsequently the reaction follows the same route as before. In case of the carbenes, the acetylene structure acquires butatriene character following photoexcitation. This is less favorable for a termination of the chains. It implies a low quantum yield of the diradical as compared to a high yield for the carbene photochemical termination reaction. This is in accordance with the ratio of about 100 : 1 observed experimentally by Gross.[16]

The intramolecular termination reactions therefore follow the route

$$DR_n \xrightarrow{h\nu} AC_n \xrightarrow{h\nu'} SO_n$$

The chain termination is a two step reaction. In a first step the diradicals (DR_n) are changed to the asymmetric carbene (AC_n). Upon termination of the second chain end the AC-molecules are changed to stable oligomer molecules (SO_n). The SO-molecules finally are thermally and optically stable.

Optical Absorption Series

The optical absorption series of short trans-polyacetylene and short polydiacetylene molecules are shown for comparison in Figure 8. The excitation energies of the PA-molecules (oligomers) are taken from textbook.[17] The data for PDA-molecules are taken from our spectra[6], see e.g. Figure 7. Due to the different lengths of the unit cells the n-values of the PA and PDA systems differ by a factor of two.

The existence of a single PA-series is due to the degenerate ground state of the π-electron structures in trans-PA. Due to the non-degeneracy of the acetylene and butatriene structure only two series are expected for the PDA system. The AC-series is lower in energy but almost parallel to the SO-series. This is due to the identical backbone structure. However, in the AC-molecules one chain end carries a carbene with a delocalized p_z-

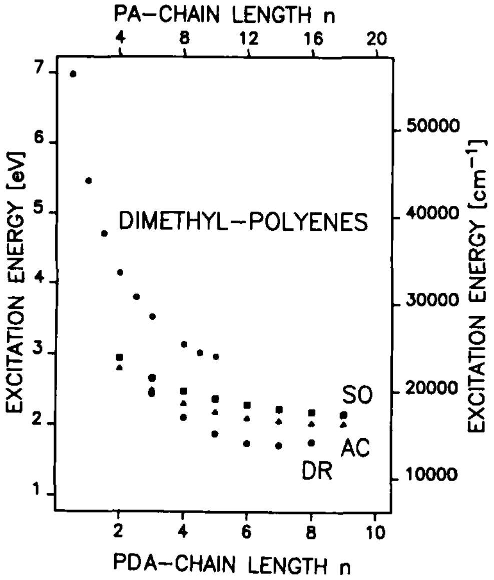


FIGURE 8 Experimental data on the absorption energies of short oligomers of trans-PA[17] and PDA[6,16] n = 2,3,4... corresponds to the dimer, trimer, tetramer,... units of $\{HC{=}CH\}_n$ and $\{RC{-}C{\equiv}C{-}CR\}_n$ or $\{RC{=}C{=}C{=}CR\}_n$.

radical electron and a short butatriene-like chain section. The optical absorptions of the diradical DR-molecules with butatriene structure are distinctly lower in energy as compared to those with acetylenic structure.

By a simple Hückel calculation[18] of infinitely long chains, we are able to understand (a) the different convergence energies of the butatriene and acetylene structures as well as (b) the higher stability of the acetylene chain structure in the ground state configuration. Figure 9 shows a band structure calculation on the basis of the Hückel theory taking into account the different bond lengths in the different structures. As seen from

Figure 9 the band gap of the butatriene structure is almost zero, whereas the band gap of the acetylene structure is very large. This corresponds to low convergence energy of the optical absorption in chains containing butatriene as compared to high convergence energy for the acetylenic structure. In addition, it is obvious from Figure 9 that the electrons of the filled valence band are higher in energy in the case of the butatriene chain structure. Therefore the PDA chains gain energy in a butatriene-to-acetylene phase transition (Pierls transition) due to the higher degree of bond alternation obtained in the acetylene chain structure.

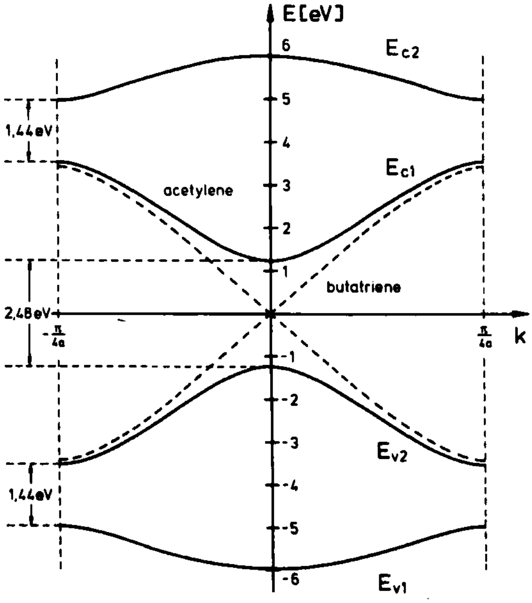
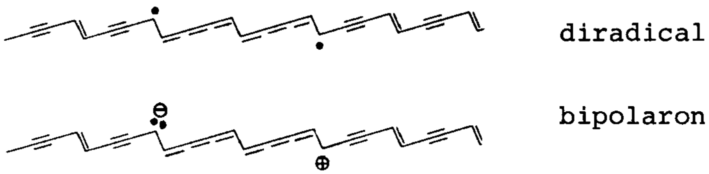


FIGURE 9 Energy dispersion of the p_z-electron system in PDA chains.
E_{v1} and E_{v2} are the two occupied valence bands. E_{c1} and E_{c2} are the two empty conduction bands of the p_z-electron system.

Comparing the different series of the PDA-molecules with the PA series in Figure 8 reveals that the SO-molecules, which have no free radical electron, are closest to the polyene absorptions of the PA-molecules. All series are too low in energy. This may be explained by the chain end structure, which, due to the hydrogen transfer reaction, increases the conjugation length of the SO-molecules and therefore lowers the corresponding excitation energies.

Excitations of Long Chains

The electronic configuration of the excited state of long SO-molecules can be approximated by two alternative simplified schemes

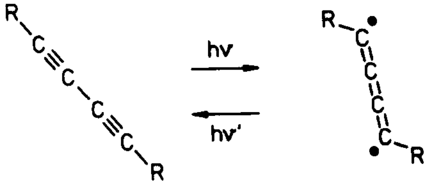


with a non-polar or a polar (neutral bipolaron) dipole-active configuration. The rapid convergence of the SO-systems (which have the acetylene structure of the polymer) suggests a localized excited state structure of the optical excitation in PDA polymer chains. This is consistent with the radical electron distribution shown in Figure 6 with an average extension of the radical electron wavefunction of about one PDA unit.

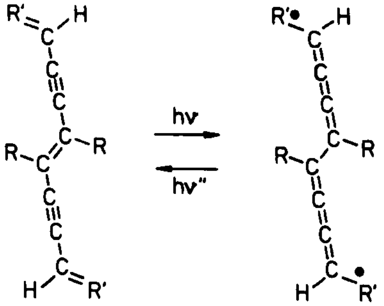
OPTICAL EMISSION SPECTROSCOPY

Short Chain Emission

Apart from the emission of diacetylene monomer molecules, emission from short PDA molecules has been observed only in the case of the SO-molecules. Characteristic for the monomer emission spectra is a large bathochromic shift.[15] This shift ($\nu >> \nu'$) is due to large conformational changes of the molecules as shown schematically below.



The spectral shift is much smaller ($\nu \gtrsim \nu''$) in the spectra of the dimer, trimer,... etc. SO-molecules. This is due to minor changes of the ground state and excited state equilibrium positions of the carbon atoms as shown schematically below.



The major differences between the $n \geq 2$ oligomers and the monomer diacetylenes arise from the fact that the p_y-electron system is excited in the monomer diacetylene molecules. Therefore the hybridization is changed resulting in large changes of the carbon-carbon-R angles. This is in contrast to the dimer, trimer,... etc. SO-molecules, where the p_z-electron system is excited. Therefore, in this case only carbon-carbon distances are changed.

Figure 10 shows the absorption and emission spectra of the SO dimer molecules in the monomer diacetylene matrix as well as the decay of the fluorescence emission. The spectra of the SO_n-molecules are similar to that of the SO dimer spectrum but they are much less intense. Therefore radiationless processes become dominant at longer chain length, which is consistent with a non-linear increase of the fluorescence decay constants with increasing chain length n.[19]

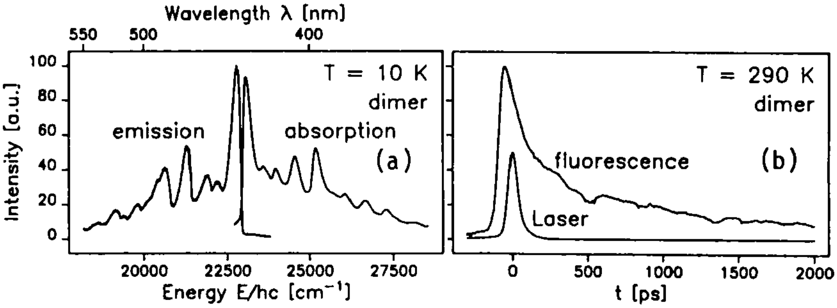
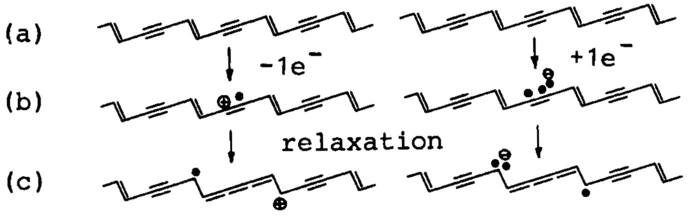


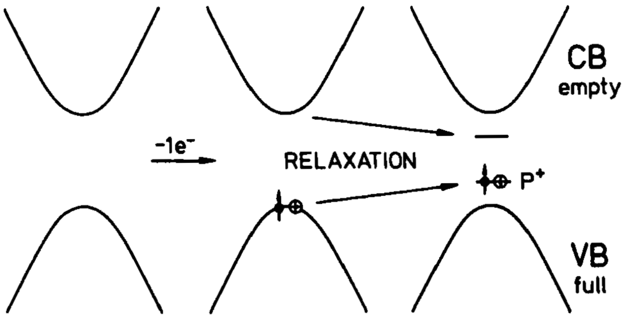
FIGURE 10 Absorption and fluorescence spectra (a) and fluorescence decay (b) of dimer PDA molecules. Excitation wavelength for the emission was 366 nm, the decay time is 1 ns.

Electrons, Holes and Polarons

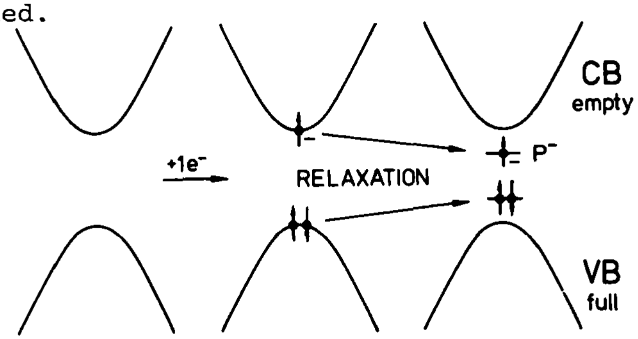
Positive or negative charging of conjugated polymer systems (a) implies disruption of a π-bond (b) followed by lattice relaxation (c) as shown in the following simplified scheme



In the hole formation process a p_z-electron is removed from the valence band of the PDA chain and therefore an unpaired radical electron is left. According to the probability density of Figure 6 it is delocalized to an average distance of about one unit cell. This implies a local change of one unit cell to the butatriene structure with altered bond distances and an approximate energy gain of $\gtrsim 0.4$ eV due to the relaxation of the hole to higher energies. According to the band structure of Figure 9 the local butatriene structure at the hole site implies two split off states within the acetylene band gap. The local lattice deformation due to charging of the chain is typical for polarons (P^+).



In the electron formation process a p_z-electron is added into the conduction band of the PDA chain. At the site, where the electron enters a p_z-orbital the corresponding carbon atom becomes saturated and therefore is unable to maintain a π-bond with the adjacent carbon atom. Consequently this atom is left with a p_z-radical electron. The lattice again relaxes locally at the electron site and splits off two electron states from the CB and VB-band. Due to the local formation of the butatriene structure of approximately one unit cell an energy of $\gtrsim 0{,}4$ eV is gained.



Evidence for Electron-Hole and Polaron States in PDA Systems

Action spectra of the electron-hole generation process have been given by different authors.[20] The band-gap of the π-electron system of almost infinitely long chains is given by about 2.5 eV.[21]

The delayed emission and excitation spectra of short chain PDA molecules are shown in Figure 11. They are interpreted[19] as electron-hole generation and P^+,P^--polaron recombination luminescence. This interpretation is based on (a) the striking difference of the exciton absorption and emission, (b) the luminescence lifetime, (c) the large bathochromic shift, (d) the spectral position of the absorption and emission, which is consistent with the electron-hole excitation and photoinduced polaron absorption spectra, and (e) the excellent agreement with the theoretical expection.

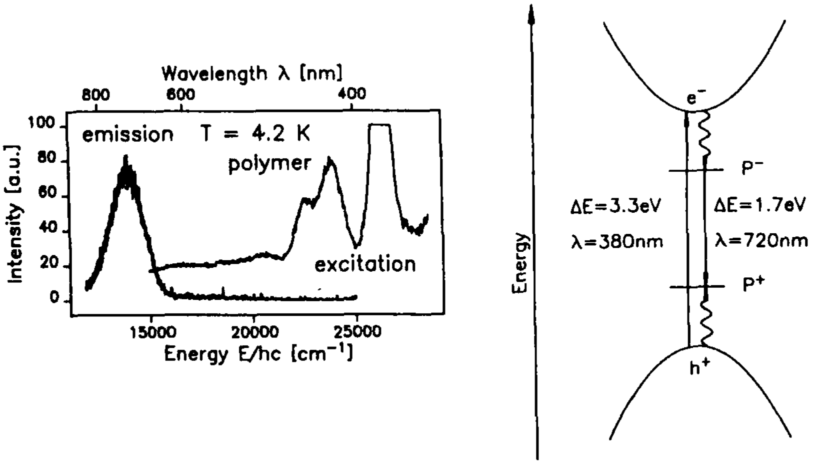


FIGURE 11 Electron-hole excitation and polaron P^+, P^--recombination spectra in PDA molecules.[19] Absorption and emission are correlated to a schematic band structure on the right.

Absorption, relaxation and emission are shown schematically in an energy level diagram. According to the energy level diagrams of the polarons it should be possible to observe a short-lived absorption between the two split off gap states during their lifetimes. This photoinduced transient absorption has been successfully observed in all conjugated systems under consideration.[22]

CONCLUSIONS

It has been shown in this contribution that linear-chain, fully-planar PDA molecules are ideal model systems for the spectroscopy of elementary excitations and of the different ground state and radical electron structures of conjugated systems.

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REFERENCES

1. G. Wegner, Molecular Metals (W.E. Hatfield, Plenum Press, N.Y. 1979) 209 and Chemistry and Physics of One-Dimensional Metals (H.J. Keller, Plenum Press, N.Y. 1977) 297.
2. R.H. Baughman and R.R. Chance, Synthesis and Properties of Low-Dimensional Materials (J.S. Miller and A. Epstein, Ac. of Science, N.Y. 1978) 705.
3. V. Enkelmann, Adv. in Polym. Sci. 63 (1984) 91.
4. H. Sixl and H. Gross, Mol. Cryst. Liq. Cryst. 93 (1983) 261.
5. H. Sixl and W. Neumann, Mol. Cryst. Liq. Cryst. 105 (1984) 41.
6. H. Sixl, Adv. in Polym. Sci. 63 (1984) 49, H. Sixl, Polydiacetylenes (D. Bloor and R.R. Chance, to be published 1985) and Electronic Properties of Polymers and Related Compounds (H. Kuzmany, M. Mehring and S. Roth, Springer-Verlag, N.Y. 1985) 240.
7. D. Kobelt and E.F. Paulus, Acta Cryst. B30 (1984) 232.

8. R. Mondong and H. Bässler, Chem. Phys. Lett. 78 (1981) 371, D. Bloor, D. Koski, L. Stevens, G.C. Preston, F.H. Ando, J. Mat. Sci. 10 (1975) 1678.
9. A. Karpfen, J. Phys. C13 (1980) 5673, J.L. Bredos, R.R. Chance, R. Silbey, G. Nicholas and Ph. Durand, J. Chem. Phys. 75 (1981) 255.
10. H. Sixl, W. Neumann, R. Huber, V. Denner and E. Sigmund, Phys. Rev. B 31 (1985) 142.
11. W. Hartl and M. Schwoerer, Chem. Phys. 69 (1982) 443.
12. M. Jones, Jr. Sci. Am. Febr. (1976) 101.
13. J.A. Pople and S.A. Walmsley, Mol. Phys. 5 (1962) 15.
14. W.P. Su, J.R. Schrieffer and A.J. Heeger, Phys. Rev. Lett. 42 (1979) 1698, Phys. Rev. B22 (1980) 2099.
15. H. Niederwald, thesis Universität Bayreuth (1983) and H. Niederwald, K.-H. Richter, W. Güttler and M. Schwoerer, Photochemistry and Photobiology (A.H. Zewail, Verlag Harwood Academic Publishers (1983) 1155).
16. H. Gross, thesis Universität Stuttgart (1983).
17. A. Streitwieser, Molecular Orbital Theory for Organic Chemists, John Wiley, New York (1961) and F. Bohlmann and H.J. Mannhardt, Chem. Ber. 89 (1956) 1307.
18. C. Kollmar and H. Sixl, to be published.
19. H. Sixl and R. Warta, Chem. Phys. Lett. 116 (1985) 307 and unpublished results.
20. K. Lochner, H. Bässler, B. Tieke and G. Wegner, Phys. Stat. Sol. 88b (1978) 653.
    H. Donovan and G.E. Wilson, Phil. Mag. B44 (1981) 31.
21. L. Sebastian and G. Weiser, Chem. Phys. Lett. 64 (1979) 396.
22. S. Etemad, G.L. Baker, J. Orenstein and K.M. Lee, Mol. Cryst. Liq. Cryst. 118 (1985) 389.
    J. Orenstein, S. Etemad and G.L. Baker, J. Phys. C: Solid State Phys. 17 (1984) L 297.
    T. Hattori, W. Hayes and D. Bloor, J. Phys. C: Solid State Phys. 17 (1984) L 881.