

Electronic Structure of Mono- and Dimeric Cation Radicals in End-Capped Oligothiophenes

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Received February 24, 1993[®]

Abstract: A temperature-dependent spectroelectrochemical investigation was carried out on a series of end-capped oligothiophenes (ECnT, 1, $n = 3-5$) and an alkyl-substituted derivative (EC5T5Br, 2). Due to the stability of the oligomers in the various oxidation states, the corresponding optical transition energies could be determined by applying controlled electrolysis in a thin-layer cell. Dimeric cation radical formation was observed for all oligomers at low temperature (200–235 K). An inverse correlation was found between the chain length and the transition energies of each species. We propose a simple energy-level diagram which can account for the spectroscopic data.

Introduction

Because of their interesting molecular properties as well as their promise for providing new materials for modern technology, conducting polymers have attracted considerable attention in the last decade.¹ In recent years, most synthetic efforts were focused on developing materials with both improved physical characteristics and chemical stability. Among these, polythiophenes (PT) exhibit, at the same time, good conductivity and environmental stability.² Their mechanical processibility has been improved, e.g., by the attachment of solubilizing alkyl chains.³ In order to understand the electrical and optical properties of conducting polymers in general and of polythiophenes in particular, detailed information on the molecular properties of the constituents is prerequisite. In particular, the electronic structure of the redox states of those molecular subunits which are responsible for the conductivity along the conjugated chains needs to be characterized.

Oligothiophenes with a defined number of thiophene rings and conjugation length have been investigated recently by optical and electrochemical methods.⁴ Upon oxidation of the oligothiophenes to the corresponding cation radicals and dication,⁵ a drastic reorganization of the optical levels and the transition strength is observed. Such investigations suffer, though, from the inherent reactivity of oligothiophene radicals ($n \leq 5$) in solution on one hand and from the poor solubility with increasing chain length ($n \geq 6$) on the other hand. Nevertheless, steady-state absorption spectra of the quinque- and sextithiophene cation radical were observed under high-dilution conditions.⁵ The reactivity of the cationic species is reduced to some extent when the thiophene oligomers are introduced into zeolite channels.⁶ These intrinsic problems, e.g., follow-up reactions and/or low solubility, may be

overcome either by blocking the reactive positions in smaller members of the series^{7,8} or by introducing solubilizing alkyl side chains into the longer oligomers.⁹ Only then does a precise characterization of the oligomers in solution appear feasible.

All report vis/near-IR spectra of the oligothiophene cation radicals exhibit two closely spaced pairs of peaks in the visible and in the near-infrared, respectively, with one minor exception.⁶ The first pair lies between 600 and 1100 nm and the second between 800 and 1500 nm, depending on the chain length and the substitution pattern of the oligothiophene. Different interpretations of the spectra have appeared in the literature so far. Fichou and co-workers attributed the transitions found for unsubstituted quinque- and sextithiophene cation radicals to the four allowed transitions predicted by the polaron-bipolaron model based on band theory.⁵ Since these monodisperse oligomers do not form real electronic band structures, this type of theory is questionable for the description of oligomers composed of only up to six monomers. In contrast, Bässler and co-workers concluded from their investigations on cations and anions of oligophenylenevinyls that the spectra of charged oligomers and even of their related conjugated polymers should be analyzed within MO theory rather than within the polaron model.¹⁰ Diaz, Tour, and co-workers assigned the four absorption peaks in a series of α,α -bis(trimethylsilyl)-substituted oligothiophenes to two strong absorptions and attributed the shoulders on the high-energy side to vibronic couplings.⁸ Caspar et al. stabilized shorter oligothiophene cation radicals in the cages of zeolites and observed spectra which exhibited only poorly resolved vibronic structures.⁶ Since in this case only a small percentage ($\sim 0.1\%$) of the oligomers was oxidized, the spectral evaluation is difficult. In more recent temperature-dependent experiments, Miller et al. found for α,α -bis(methylthio)-substituted bi- and terthiophene and for α,α -dimethylterthiophene (DM3T) that the two peaks of each pair

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[®] Abstract published in *Advance ACS Abstracts*, September 15, 1993.

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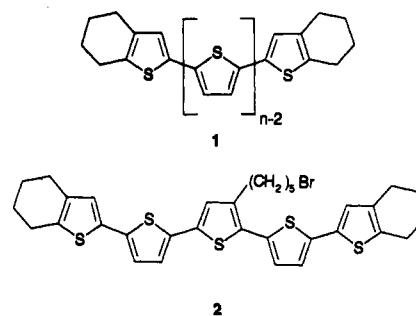
correspond to two different species, namely the monomer and dimer of the cation radicals.¹¹ Independently, we could demonstrate that this dimerization process occurs also for cation radicals of didodecylsexithiophene (DD6T).^{9b} In this case, the room-temperature absorption spectrum is nearly identical to that of the corresponding sexithiophene cation radical investigated by Fichou et al.⁵ We could show, by variable-temperature measurements in combination with ESR results, unequivocally that the main peaks belong to the cation radical and the corresponding peaks on the high-energy side belong to a dimeric cation radical which is reversibly formed upon cooling, in agreement with the results of Miller et al.¹¹ It is therefore surprising that in the series of α,α -bis(trimethylsilyl)-substituted oligothiophenes, π -dimer formation should not play a role.⁸ However, no temperature-dependent investigations were undertaken, but the authors exclude π -dimerization due to the steric hindrance by the substituents.⁸ Nevertheless, the dimerization process found for several oligothiophenes, as reported here, seems to be rather universal. This is in accord with the observation of Caspar et al.,⁶ who find only weak high-energy shoulders at the main absorption peaks for an oligothiophene caged in a zeolite, where π -dimerization is prohibited by the restricted space.

The interpretation of the oligothiophene cation radical absorption spectra in the light of a reversible π -dimerization process is further supported by the fact that other organic ion radicals tend to form π -dimers in solution, e.g., those of tetrathiafulvalene,¹² Wursters blue (tetramethyl-1,4-diaminobenzene),¹³ viologens,¹⁴ and other large aromatic cations of porphyrins,¹⁵ phthalocyanines,¹⁶ and perylene.¹⁷ The same phenomenon was observed for anion radicals, e.g., those of TCNQ.¹⁸ In the case of a water-soluble naphthalenetetracarboxylic diimide in the strong polar solvent water, even the assembly of anion radicals in π -stacks has been reported.¹⁹ The analogy between the π -dimerization of ion radicals and the formation of conducting charge-transfer salts is very likely.^{19,20} Therefore, we propose that the temperature-dependent formation of diamagnetic dimeric cation radicals provides a route for the doping behavior of polythiophenes and of conducting polymers in general.^{9b,11}

Stable oligothiophene dications, often considered as models for bipolarons, also show two closely spaced peaks in the visible. The dication spectra can better be explained by the vibrational splitting of a single π - π^* -band^{11b} rather than by the two electronic transitions predicted by polaron-bipolaron theory.⁵

The present contribution is focused on the controlled chemical and electrochemical preparation of singly- and doubly-oxidized states of four different end-capped oligothiophenes. A dependence of certain physical properties on the chain length may be observed within the series of oligomers **1** (ECnT, $n = 3-5$).⁷ The influence of an alkyl side chain on the electronic properties can be evaluated, e.g., from the bromoalkyl-substituted end-capped pentamer **2** (EC5T5Br).²¹ As has been found for other β -substituted

Chart I



oligothiophenes,²² the conjugation length of the oligomers is reduced by a distortion of the π -system. The "end-caps" shield the radical cation from secondary σ -bond formation. Thus, *in situ* UV/vis/near-IR spectroscopy may be employed to characterize the electronic structure of the cationic species over a much wider temperature range (200–293 K). The data obtained can be correlated with the (inverse) chain length. From this correlation, it is possible to extrapolate the transition energies of the respective "ideal" polymer with a hypothetical "infinite" chain length and to compare it with the "real" polythiophene. Additionally, an energy-level diagram for the mono- and dimeric cation radicals may be set up.

Experimental Section

The synthesis of the end-capped oligothiophenes **1** follows the published procedure.⁷ The synthesis of the alkyl-substituted end-capped pentamer **2** was analogous to that of EC5T, employing 3-(5-bromopentyl)-2,5-dibromothiophene as the central building block instead of 2,5-dibromothiophene.²¹

The electrochemical and spectroelectrochemical experiments were performed in methylene chloride as the solvent, which was purified and dried by distillation from CaH₂ prior to use. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte; it was recrystallized twice from methanol/ethanol and dried *in vacuo* at 100 °C for several days. Concentration of the oligothiophene solutions was in the range of 10⁻⁴–10⁻³ mol L⁻¹ for EC3T and EC4T but less than 10⁻⁴ mol L⁻¹ for EC5T because of its lower solubility.

Cyclic voltammetry was performed with a computer-controlled EG & G PAR 273 potentiostat. Platinum disks (o.d. = 1 mm) were used as the working electrodes, a platinum wire as the counter electrode, and an Ag/AgCl wire as the reference electrode; this was internally calibrated vs the chemical redox couple ferrocene/ferrocenium (Fc/Fc⁺).

All optical measurements were carried out in a thin-layer spectroelectrochemical cell (solution film thickness 0.2 mm) incorporating ITO glasses as the optical transparent electrodes, a platinum sheet as the counter electrode, and an Ag/AgCl wire as the reference electrode.²³ For the temperature-dependent measurements, the whole cell was thermostated by a double-walled cooling chamber. The cell was placed in the probe beam of a Varian CARY 2400 spectrophotometer and the applied potential controlled by a JAISSE IMP83 potentiostat.

Results

It is well known that oligothiophenes are oxidized either chemically (e.g., by FeCl₃ as oxidant) or electrochemically.^{5-9,11} The resulting cationic (radical) species are highly reactive, though, and undergo facile chemical follow-up reactions. It is extremely difficult, therefore, to obtain reliable spectral information on these cationic (radical) states. Chemical follow-up reactions of electrochemically generated species are readily detected as

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Table I. Redox Potentials of End-Capped Oligothiophenes 1 (ECnT) and 2 (EC5T5Br)

	E°_1 (V)	E°_2 (V)
EC1T	(1.01) ^b	
EC2T	(0.53) ^b	(1.20) ^b
EC3T	0.38	(0.79) ^b
EC4T	0.32	0.66
EC5T	0.26	0.55
EC6T	0.22	0.41
EC5T5Br	0.32	0.52

^a Potentials in CH₂Cl₂/TBAHFP (0.1 M) vs internally calibrated Fc/Fc⁺ at a platinum disk electrode, oligomer concentration $c = 5 \times 10^{-4}$ M except for the less soluble EC6T. ^b Irreversible wave; E° was taken at $i_0 = 0.855i_p$.²⁵

nonsymmetric, irreversible redox peaks in a cyclic voltammogram. This is indeed found for "regular" oligothiophenes. End-capped oligothiophenes (ECnT), where both the reactive α - and β -positions of the terminal thiophene units are blocked by a cyclohexane "cap", display reversible redox peaks, thus indicating the generation of species which are stable within the time scale of the voltammetric experiment. In this series, starting with the trimer EC3T, the oligomers can be oxidized reversibly to the monocation radical. From the tetramer EC4T, surprisingly, even stable dications can be created. The redox potentials of the various end-capped oligothiophenes investigated are summarized in Table I. It is evident that the corresponding redox potentials correlate linearly with the (inverse) number of thiophene rings in the oligomers.⁷ Relative to EC5T ($E^{\circ}_1 = 0.26$ V and $E^{\circ}_2 = 0.55$ V vs Fc/Fc⁺), the first reversible oxidation of the substituted derivative 2 (EC5T5Br) is shifted to a higher potential ($E^{\circ}_1 = 0.32$ V), the second one being shifted to a somewhat more negative potential ($E^{\circ}_2 = 0.52$ V) (Figure 1).

Both observations reflect the interplay of two effects due to the alkyl substituent. First, steric interaction of the alkyl chain with the respective thiophene rings causes a distortion of the conjugated π -system; this effect dominates over the electron-donating properties of the substituents. The ensuing reduction in overlap of the corresponding orbitals results in a lesser electron density in 2 and, hence, in an increased first oxidation potential. Upon oxidation, the twisted neutral π -system is planarized to a cationic quinoidal structure, analogous to the well-known polarons in the corresponding polymers.²⁴ Consequently, the inductive effect of the alkyl chain lowers the corresponding redox potential in the second oxidation step.

The optical spectra of the various oligothiophenes, in the different oxidation states, were measured in a special spectroelectrochemical thin-layer cell, described in the Experimental Section. Controlled potential electrolysis is applied to the small volume of the oligomer solution between the optically transparent working electrodes. After the required oxidation state is reached, an absorption spectrum is recorded each time. In Table II, all spectral transitions of the prominent optical absorption lines are listed for the different oxidation states of the oligomers investigated. Electrochemical oxidation of the oligothiophenes appears to be favorable with respect to chemical oxidation with FeCl₃ since, first of all, the possible influence of the electroactive dopant FeCl₄⁻ and the simultaneously present FeCl₂ can be excluded. Second, the degree of oxidation is easier to control by the amount of charge passed. Figure 2 shows a typical set of optical spectra, at room temperature, for the successive oxidation of EC3T to EC3T⁺. Upon increasing the electrode potential in 50-mV steps, we observed the appearance of two new absorption bands at lower energies [$\lambda_{\max} = 620$ nm ($E = 2.0$ eV) and 939 nm ($E = 1.32$ eV)], which gain intensity at the expense of the strong absorption band of the π - π^* -transition of the neutral form [$\lambda_{\max} = 375$ nm

Table II. Prominent Optical Transition Energies of the Various Redox States of the End-Capped Oligothiophenes 1 (ECnT) and 2 (EC5T5Br)^a

	E_1 (eV)	E_2 (eV)	E_3 (eV)	dimer formation enthalpy ΔH (kJ mol ⁻¹) (method)
DM3T	3.44			
DM3T ⁺	2.17	1.41		
(DM3T) ₂ ²⁺	2.66	1.75	1.43	-42 (UV)
EC3T	3.31			
EC3T ⁺	2.00	1.32		
(EC3T) ₂ ²⁺	2.57	1.63	1.25	
EC4T	3.02			
EC4T ⁺	1.79	1.05		-58 (± 5) (ESR)
(EC4T) ₂ ²⁺	2.25	1.37	1.09	-64 (± 10) (UV)
EC4T ²⁺	1.77	1.60		
EC5T	2.87			
EC5T ⁺	1.71	0.99		-65 (± 3) (ESR)
(EC5T) ₂ ²⁺	2.10	1.19	0.93 (sh) ^b	
EC5T ²⁺	1.50	1.34		
EC5T5Br	2.92			
EC5T5Br ⁺	1.64	0.89		-55 (± 10) (ESR)
(EC5T5Br) ₂ ²⁺	2.03	1.13	0.88 (sh)	
EC5T5Br ²⁺	1.47	1.30		
ECnT	2.2 ^c			
ECnT ⁺	1.25 ^c	0.45 ^c		
(ECnT) ₂ ²⁺	1.38 ^c	0.54 ^c		
PT	2.0-2.8			
PT ⁺	1.3-1.4	0.3-0.5		
PT ²⁺	1.4-1.6	0.5-0.6		

^a The extrapolated data set for an ideal polythiophene (ECnT), with a hypothetical infinite chain length, is compared to polythiophene (PT). The data of DM3T are taken from ref 11b and those of PT from ref 5c. ^b sh = shoulder. ^c Values from extrapolation of regression lines to $1/n = 0$.

($E = 3.31$ eV)]. The clean interconversion between the two species is reflected by a well-defined isosbestic point. In comparison to the respective forms of EC3T, the transitions of DM3T, which was recently investigated by the same technique, show distinct blue shifts.¹¹ DM3T has only two electron-donating alkyl substituents as compared to the four alkyl-substituted positions of the end-capped EC3T.

The typical absorptions of both redox states are gradually shifted to lower energies when the oligomer π -system is extended. This trend becomes clearly apparent in going from EC3T to EC4T and EC5T (Figure 3). As expected from the electrochemical results, the π - π^* -transition of the neutral pentamer 2 (EC5T5Br) [$\lambda_{\max} = 425$ nm ($E = 2.92$ eV)] displays a blue shift relative to that of the homologous EC5T [$\lambda_{\max} = 432$ nm ($E = 2.87$ eV)]; this effect is due to the distortion of the π -system. In contrast, the oxidized (planar) form of 2 shows a bathochromic shift of the respective absorption bands; in this structure, it is only the electron-donating effect of the alkyl substituent which is operative.

The situation changes dramatically when the thin-layer cell is cooled to 200-235 K. The corresponding absorption spectra of the three oligomers 1 are shown in Figure 4. Upon oxidation, absorption spectra are obtained for each oligomer, which differ from the room temperature spectra. We attribute this effect to a reversible dimerization equilibrium between the cation radicals (ECnT⁺), predominantly formed at room temperature, and the dimeric cation radicals [(ECnT)₂²⁺], formed at lower temperatures. Three new bands are attributed to the newly-formed dimeric cationic species. Two of these have distinctly higher energy than the corresponding transitions of the room temperature species (Table II). In the case of EC3T⁺, the dimer is formed only partially at 200 K. Consequently, the additional third band in the near-IR regime interferes with the longest wavelength absorption of the monocation still present. In the case of the pentamer EC5T, this transition appears only as a low-energy shoulder of the main absorption band. Band positions for these transitions have been determined from difference spectra.

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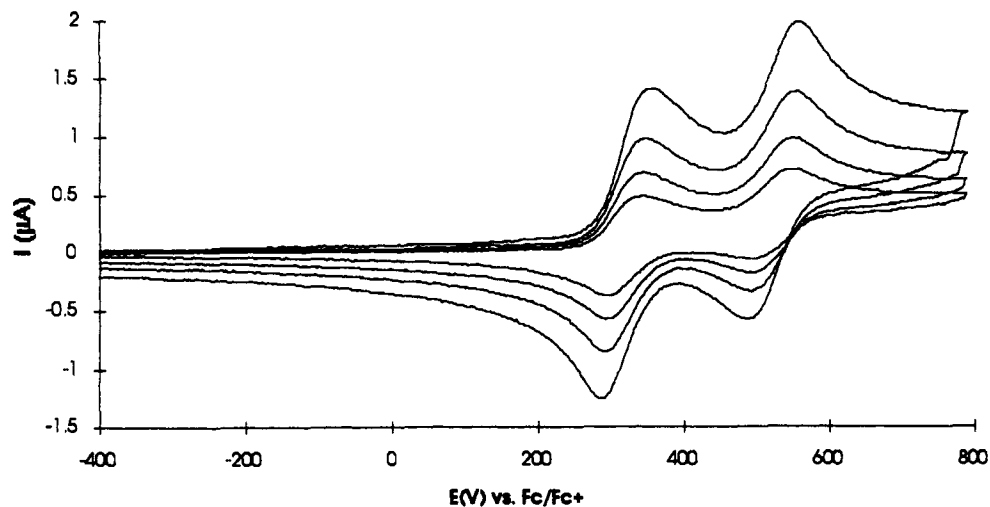


Figure 1. Cyclic voltammogram of pentamer **2** (EC5T5Br) in CH₂Cl₂/TBAHFP (0.1 M) at a platinum disk electrode (o.d. = 1 mm); reference electrode Ag/AgCl, internally calibrated vs Fc/Fc⁺; sweep rates 50, 100, 200, and 400 mV s⁻¹.

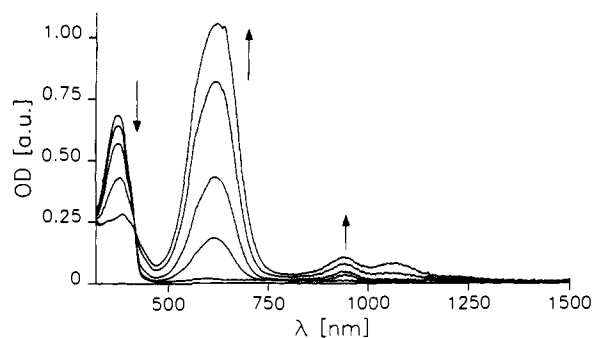


Figure 2. Set of optical spectra during the successive oxidation of EC3T to EC3T²⁺ (potential steps 50 mV). The arrows mark specific spectral features and indicate the growth or decay of characteristic bands with increasing oxidation.

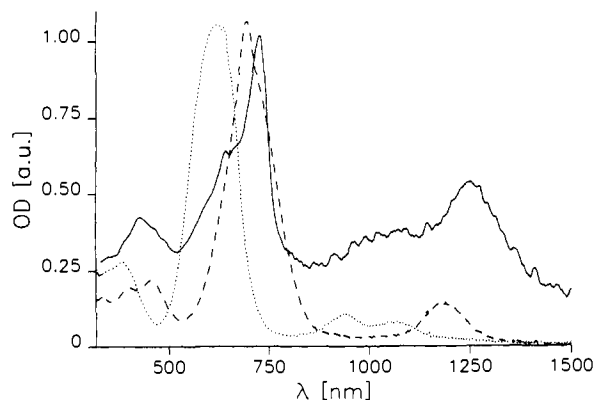


Figure 3. Optical spectra of the first oxidation state of different oligothiophenes (EC3T, EC4T, and EC5T) at room temperature (··· EC3T, --- EC4T, —EC5T).

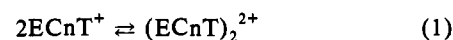
This temperature-dependent behavior was studied more extensively for EC4T. The solution was oxidized only partially to (EC4T)₂²⁺ at 235 K, and absorption spectra were recorded successively upon warming to 271 K (Figure 5). The two absorption bands [$\lambda_{\text{max}} = 551 \text{ nm}$ ($E = 2.25 \text{ eV}$) and 905 nm ($E = 1.37 \text{ eV}$)] of the dimeric cation disappear, and a strong new band evolving at $\lambda_{\text{max}} = 693 \text{ nm}$ ($E = 1.79 \text{ eV}$) appears, which is due to the monomeric cation radical. The possibility that the new spectral features belong to a doubly-oxidized state of the oligomer (arising from a disproportionation process) had to be excluded, however. We therefore have additionally determined the absorption spectra of the dicationic species. Since EC3T cannot be oxidized reversibly to the dication, only spectra of

EC4T²⁺ and EC5T²⁺ are presented in Figure 6. In the respective absorption spectra, two new, independent bands evolve instead of those of the monocationic states. Thus, the formation of dications by a disproportionation equilibrium of the monocations can be ruled out definitively (Table II).

From the temperature-dependent spectra of EC4T, we have extracted the concentration ratios by comparing the areas of the most prominent lines for both species which were normalized by the relative extinction coefficients. Employing the equilibrium expression $K = [\text{dimer}]/[\text{monomer}]^2$, we determined K for different temperatures. From standard thermodynamic arguments, K is expected to follow the expression $K = A \exp(\Delta H/RT)$. Figure 7 displays the result of a van't Hoff plot derived from this expression. The slope of the straight line drawn gives an enthalpy of formation of $\Delta H = -64 (\pm 10) \text{ kJ mol}^{-1}$. This value for the enthalpy is neatly confirmed by independent ESR measurements giving $\Delta H = -58 (\pm 5) \text{ kJ mol}^{-1}$ in the case of (EC4T)₂²⁺.²⁶ ESR experiments performed at different temperatures showed an activated increase in signal intensity with increasing temperature which allowed the independent determination of ΔH .^{9b,26}

Discussion

Optical Spectroscopy of the End-Capped Oligothiophenes. The most striking feature of our experiments, described above for end-capped oligothiophenes, is the reversible, strongly temperature-dependent spectral change in the first oxidized state of oligothiophenes **1** and **2** when the oxidation experiments are run at low temperatures (200–235 K) and at room temperature, respectively. The changes are illustrated in Figures 2–5. Chemical follow-up reactions at room temperature are suppressed almost completely in comparison to those of regular oligothiophenes. Sufficient solubility at lower temperature is guaranteed by the cyclohexane caps. These observations can be rationalized in terms of a reversible π -dimerization of the cation radicals to the dimeric species, with paired spins, at low temperature (eq 1).



This mechanism is further supported by ESR^{9b,26} measurements which show decreasing spin density upon cooling. At 200 K, very little ESR activity is observed, and the dimer consequently must

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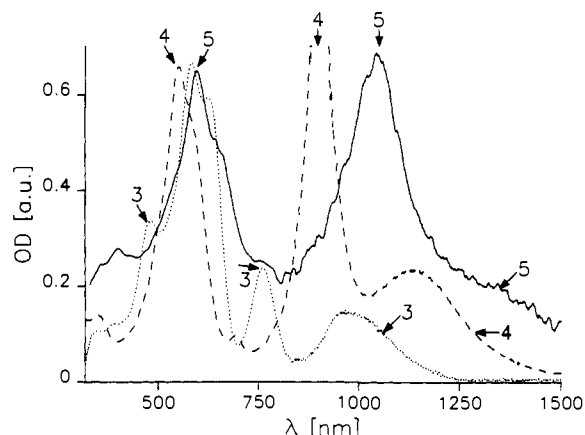


Figure 4. Optical spectra of the first oxidation state of different oligothiophenes (EC3T, EC4T, and EC5T) at 200–235 K (··· EC3T, --- EC4T, — EC5T).

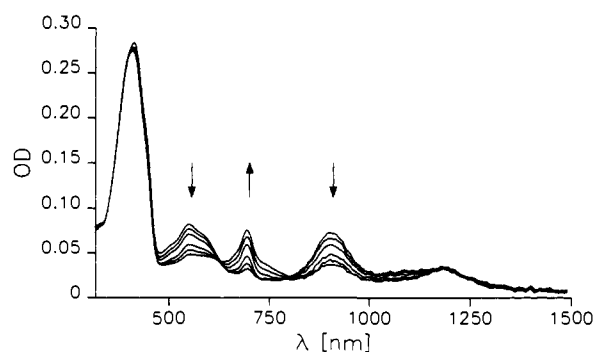


Figure 5. Set of optical spectra of the first oxidation state of EC4T at different temperatures. Partial oxidation was performed at 235 K; the subsequent spectra were obtained upon warming up to 271 K.

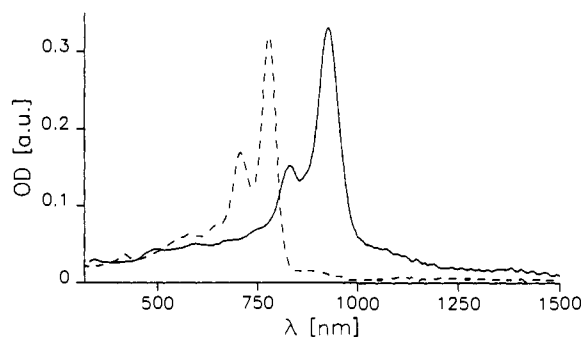


Figure 6. Optical spectra of the second oxidation state of EC4T (---) and EC5T (—).

be considered to be diamagnetic. NMR investigations on oxidized EC4T confirm this conclusion.²⁷

We observed two optical absorptions (labeled M_1 and M_2) for the monomeric cation radicals of the end-capped oligothiophenes EC n T, in agreement with previous data.¹¹ In every case, the formation of the π -dimer is accompanied by a distinct blue shift of these intramolecular transitions (D_1 and D_2) and the simultaneous emergence of a new low-frequency absorption peak (D_3) in the dimer spectrum (Table II). By analogy with other solution dimer systems, this new absorption is assigned to a charge-transfer band due to an intermolecular excitation of the two cation radicals. A blue shift has been discussed in the context of exciton–exciton interaction and was termed Davydov blue shift.²⁸ It results from the interaction of the dipole moments on adjacent molecular

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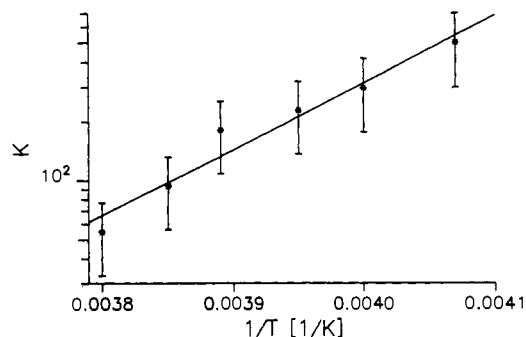


Figure 7. van't Hoff-type plot of the dimer-to-monomer equilibrium constant K (see text) vs inverse temperature for EC4T. The solid line corresponds to an enthalpy of $\Delta H = -64 (\pm 10)$ kJ mol⁻¹.

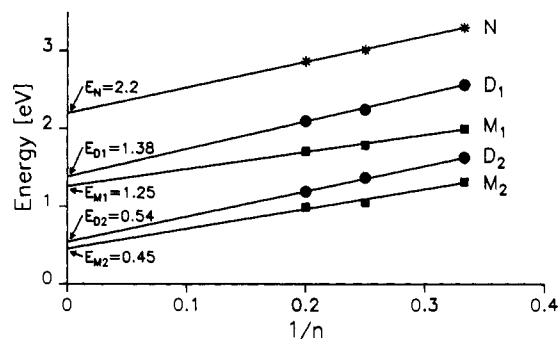


Figure 8. Excitation energy of the prominent optical absorption lines of the neutral (N), the monomeric cation radical (M), and the dimeric cation radical (D) state vs inverse chain length $1/n$ (n = number of thiophene rings).

excitation and suggests a “side by side” (stack) orientation of the molecules. In contrast, a possible “tail to tail” orientation would lead to a red shift of the absorption bands. The parallelism to the π -dimer is interesting. The Davydov shifts $\Delta E_{M/D} = D - M$ for the end-capped oligothiophenes EC n T ($\Delta E_{M1/D1} = 0.57$ – 0.39 eV and $\Delta E_{M2/D2} = 0.31$ – 0.20 eV) may be extracted from the data in Table II and are comparable to those found for other ion radical dimers [(TTF)₂²⁺ $\Delta E_{M/D} \approx 0.3$ eV¹²]. The energy splitting gradually decreases with increasing chain length (see Table II). This chain-length dependence of the Davydov shift supports the assumed stacklike orientation of the cation radicals in the dimer.

The optical spectra of the EC n T dications reported here are also in good agreement with other reports of oligothiophene dications.^{5,6,8,11} Two closely spaced peaks in the visible laying in between the main bands of the monocation radicals may be assigned to the vibrational structure of one π - π^* -band, with vibrational splittings of $\Delta E = 0.16$ – 0.17 eV. In contrast to the polaron–bipolaron theory which predicts two transitions for a bipolaron, MO (PPP) calculations on a terthiophene dication give only one band for the oligomeric dication.^{11c} Although we investigated only two members of the series (EC4T and EC5T), we saw a clear dependence of the band positions on the chain length. As the π -system increases, the bands shift to lower energies, as expected.

Chain-Length Dependence of the Optical Spectra. For a comparison of the electronic levels of the various oxidation states of EC n T, we have correlated the transition energies of the prominent absorption bands of neutral (N), monomeric cationic (M_1 and M_2), and dimeric cationic species (D_1 and D_2) with the inverse length of the oligothiophenes (i.e., inverse number of thiophene rings, Figure 8). All transition energies increase linearly with increasing inverse chain length. Since the energies of the third dimer bands D_3 are very close to those of M_2 , D_3 has been omitted in Figure 8 but shows the same linear dependence on inverse chain length. If the regression line for each data set is extrapolated to $1/n = 0$, a value for an ideal PT with a hypothetical

infinite chain length is obtained. In the case of the neutral form, a value of $\lambda_{\max} = 564$ nm ($E_N = 2.2$ eV) is derived for the π - π^* -transition which expectedly lies lower than those determined experimentally for solid PT films [$\lambda_{\max} = 513$ nm ($E_{PT} = 2.42$ eV)].²⁹ The difference could be attributed to defects and interruptions of the conjugated chain in the bulk material. The energy gap between the two regression lines for the mono- and dimeric cation radical is diminished gradually as the chain length increases. Extrapolation of both sets to a hypothetical infinite chain length reveals that at this extreme point, the regression lines for both transitions almost intersect. This result clearly implies that the charge becomes more and more delocalized in very long chains and that coulomb repulsion decreases with increasing chain length. The electronic structure of the dimeric cation radical thus approaches that of the monomeric cation. There is a considerable variance in the experimental data for polarons in PT ($E_{PT1} \approx 1.3$ – 1.4 eV and $E_{PT2} \approx 0.3$ – 0.5 eV).^{5c} Therefore, determination of the energy for the lowest band is problematic, and there is unavoidable uncertainty in the estimation of the conjugation length in doped real PT from this diagram. The hypothetical energies, determined for an infinite chain length ($E_{M1} = E_{D1} = 1.25$ – 1.38 eV and $E_{M2} = E_{D2} = 0.45$ – 0.54 eV), do basically correspond to the experimental values. The $E_{M1/D1}$ energy value is slightly lower than the one expected from experimental values, whereas the lower energy value is of the same order of magnitude as the one experimentally determined for solid polythiophene films.

The systematic variation of the peak positions in the absorption spectra of the various oligothiophene species with inverse chain length has also been reported for other oligothiophene series and seems to be a general phenomenon.^{6–8} The inverse dependence of absorption maxima of conjugated systems on chain length is predicted theoretically³⁰ and applies likewise to absorption, emission, and redox potentials for the whole series of end-capped oligothiophenes⁷ and other oligothiophene series,^{6,8} as well as to the absorption data of different conjugated π -systems.³¹ This observation reflects directly the electron delocalization, as is evident even from simple molecular orbital models.

Proposed Energy-Level Diagram of Mono- and Dimeric Cation Radicals. Since the oligomers investigated must be treated as discrete molecules without the cooperative effects present in a solid, the results of their spectroscopy should definitely be interpreted in the framework of MO theory. We have thus used the observed two intense optical transitions M_1 and M_2 of the oligomeric monocation radicals to set up a simple MO diagram. For $EC4T^+$, three different energy levels Φ_1 – Φ_3 are derived from the experimental transition energies. Φ_1 represents the highest fully occupied MO, Φ_2 is the singly-occupied MO (SOMO), and Φ_3 in a nonoccupied antibonding orbital. M_2 (1.05 eV) corresponds to the transition from Φ_1 to Φ_2 and M_1 (1.79 eV) to the transition from Φ_2 to Φ_3 . Figure 9 depicts the energy-level diagram for $EC4T^+$ and the corresponding dimer ($EC4T_2^{2+}$). The energy levels for the dimer species are constructed by formal linear combination of the monomer MOs; each monomer MO is split into an energetically lower (Φ^+) and higher lying MO (Φ^-) upon dimer formation. In this process, only fully occupied (Φ_1^+ , Φ_1^- , and Φ_2^+) and unoccupied (Φ_2^- and higher) states result. This setup is in agreement with the experimental observation that the ESR signal of the monomer disappears upon dimer formation. The splittings in the energy level diagram for $(EC4T_2)^{2+}$ were chosen so as to represent the experimentally observed intramolecular transitions D_1 and D_2 . In addition, we assumed that combined states of distinct parity are formed. The selection rules

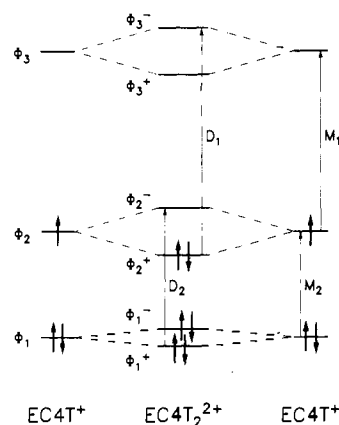


Figure 9. Proposed energy-level diagram for $EC4T^+$ and the corresponding dimer complex $(EC4T_2)^{2+}$, based on the transition energies of the monomer ($M_1 = 1.79$ eV and $M_2 = 1.05$ eV) and the dimer ($D_1 = 2.25$ eV and $D_2 = 1.37$ eV).

for dipolar-allowed transitions between states of different parity were taken into account.²⁸ Considering these assumptions, transition D_2 (1.37 eV) would correspond to the transition from Φ_1^+ to Φ_2^- and D_1 (2.25 eV) to the one from Φ_2^+ to Φ_3^- . The distinct blue shift of the dimer transitions therefore results from the interaction of the monomers which leads to the orbital splitting. The corresponding binding energy can be visualized as the lowering of the energy by placing the two unpaired electrons in the monomer into the Φ_2^+ state. This electronic rearrangement is accompanied by an estimated energy gain of $\Delta E \approx 2 \times 0.15$ eV as obtained from the energy-level diagram. This value includes the coulomb repulsion of the positively charged radicals but does not account for the entropy changes within the solvent shells. Despite the simplicity of this approach, this simple scheme may nevertheless prove to be useful in explaining the dimerization phenomenon.

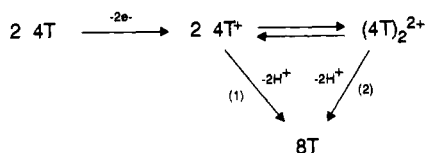
π -Dimer Formation. Although it is rather difficult to obtain reliable information about the concentration of the different species from their spectra due to the overlap of the relevant bands, we have tried to extract the concentration ratio and hence the equilibrium constant K for the dimerization process. For the first time, these experiments clearly reveal that the dimerization of the oligomeric thienyl cation radicals depends on the chain length. With increasing extension of the conjugated π -system, ΔH gradually increases. This trend is obvious when proceeding from DM3T which gives a value of $\Delta H = -42$ kJ mol⁻¹ (UV/vis),¹¹ via $EC4T$ with $\Delta H = -58$ (± 5) kJ mol⁻¹ (ESR)²⁶ to -64 (± 10) kJ mol⁻¹ (UV/vis), to $EC5T$ with $\Delta H = -65$ (± 3) kJ mol⁻¹ (ESR).²⁶ Sexithiophene DD6T with a dimerization enthalpy of $\Delta H = -87$ (± 16) kJ mol⁻¹ (ESR)²⁶ is in line with the trend found and also fits well in this series. For the alkyl-substituted $EC5T5Br$ (**2**), however, a smaller value of $\Delta H = -55$ (± 10) kJ mol⁻¹ (ESR) is determined as compared with that of $EC5T$.²⁶ This may be explained by the flexibility of the alkyl side chain which somewhat hinders the association of the cations. Especially in the case of longer oligomers, a substantial amount of dimeric species is already present at room temperature. These findings have consequences for the reinterpretation of older data.⁵ With increasing chain length of the oligomers, the formation of dimeric cation radicals is more and more favored. In this respect, one can readily explain the observation reported very recently that no ESR activity is observed in monooxidation of a duodecithiophene.^{3d} Cooperative interaction between oligomers found in solution should likewise be operative in the solid state where the proximity of the molecules is much more pronounced. This dimerization process may very well provide a clear, new alternative to the description of the polymer growth on one hand and the doping behavior of polythiophenes and conducting polymers on the other hand. Two possible mechanisms for the chain growth of polyheterocycles have been controversially discussed so far. The solid-state polym-

(29) Polythiophene was measured under the same conditions deposited as solid film on ITO obtained by polymerization of thiophene (0.1 M) in $CH_3CN/TBAHFP$ (0.1 M).

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Scheme I



erization of oligo-*p*-phenylenes, for instance, clearly indicates the growing chain to be formed by radical coupling of (larger) oligomeric cation radicals [(1) in Scheme I].³⁶ For the alternative stepwise addition of monomeric cation radicals to the growing chain, so far no clear-cut evidence has been found. π -Dimerization of the cation radicals generated in the course of the oxidation process now has to be considered as an additional pathway [(2) in Scheme I]. This alternative becomes more likely the longer the oligomeric cation radicals are. Scheme I depicts the situation for the dimerization of a thiophene tetramer to the respective octamer.

Participation of π -dimerization processes in the solid state would explain the puzzling fact that ESR activity of polarons is unexpectedly observed only at very low doping levels of the polymer and that the ESR signal disappears upon further doping.³⁷ So far, this phenomenon has been rationalized in terms of the formation of the energetically favored spinless bipolarons.³⁸ Our results now suggest the formation of the dimeric cation species to be the triggering step in doping at low doping levels. At the moment, it appears as an interesting question if the π -dimers are also an alternative explanation for bipolaronic bands in higher doped conjugated polymers. The spatial proximity of neighboring chains makes this dimerization process even more likely in solids than in solution. As already stated by Miller et al.,¹¹ we also believe that these findings deserve much more attention in the interpretation and description of the doping behavior and charge-transport properties in conducting polymers.

In this context, the analogy between the π -dimerization of oligothiophene cation radicals and highly conducting charge-

transfer salts is astonishing. Two other aspects also point in this direction. Zotti and co-workers very recently proposed a mixed-valence conduction to be operative upon oxidation as a result of combined *in situ* conductivity and ESR measurements on α,α -dimethyloligothiophenes in the solid state.³⁹ This concept originally was introduced for polypyrrole.⁴⁰ On the other hand, surprisingly large conductivities are found for doped oligothiophenes. A value of 20 S cm⁻¹ is reported for a (microcrystalline) sample of an alkylated undecithiophene,^{9c} 5 S cm⁻¹ for an alkylated duodecithiophene,^{9g} and 10⁻² S cm⁻¹ for iodine-doped crystals of the trimer EC3T.⁷ Since increased crystallinity and orientation in polyacetylene have led to an increase in conductivity,⁴¹ one might conclude that in analogy to the crystalline conducting charge-transfer salts, conductivity in conducting polymers and even more in well-defined oligomers is due to charged (micro)crystalline stacks of conjugated segments.

Conclusions

We have presented optical spectra of a series of end-capped oligothiophenes in various redox states. A temperature-dependent spectroelectrochemical investigation allowed us to draw specific conclusions about the spectral properties of the different species. Excellent inverse correlation is obtained between the transition energies and the chain length; this reflects increasing electronic delocalization with increasing number of thiophene rings for all species investigated. By extrapolation of these data to infinite chain length, the real polymer can be compared with a hypothetical, ideal material. The most prominent observation concerns that of the π -dimer formation upon cooling. The same chain-length dependence of the optical transition energies holds for the dimers and the monomers. Moreover, it was found that the dimer binding energy increases with chain length, a fact which may be relevant for the doping process in polymers. From the optical transitions, a simple energy-level diagram could be derived for the mono- and dimeric cation radicals of EC4T.

Acknowledgment. We gratefully acknowledge helpful discussions with Dr. N. S. Sariciftci (2.Physikalisches Institut) and Dr. P. Fischer (Institut für Organische Chemie). This work was supported by the Deutsche Forschungsgemeinschaft (SFB 329), the Fonds der Chemischen Industrie, and the Bundesminister für Forschung and Technologie (TK 0325-1). We would like to thank both referees for giving valuable comments with respect to the discussion of the energy scheme.

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