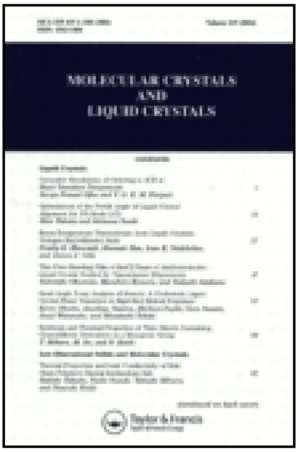

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LINESHAPE OF FIELD MODULATED SPECTRA OF ORDERED AND DISORDERED POLYMERS

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Abstract Electric field modulated spectra of polymer films are compared with those of single crystals to study the influence of disorder on size and shape of the effects. The quadratic Stark effect is similar as in crystals but reveals even in isotropic films pronounced anisotropy. Disordered films show an additional response quadratic with the field but of second derivative line shape which is interpreted as linear Stark effect due to dipole moments induced by asymmetric boundaries of chain segments.

INTRODUCTION

Electric fields of order 10kV/cm present for small size molecular states in most cases a perturbation which is too small to cause measurable changes in the optical spectra. As states become more extended or delocalized by inter-molecular coupling they respond more sensitively because the potential variation across such a state is no longer negligible in comparison to the separation of energy levels. Electric fields thus probe selectively extended states in conjugated polymers. Studies on polydiacetylene single crystals[1,2] show that the response of linear systems is very anisotropic with respect to orientation of field and polarization of light. The prevailing mechanism in crystals is a quadratic Stark effect of excitons of high oscillator strength and large size which are coupled by the field to states at higher energy[3], exciton and continuum states, the latter responding independently by the Franz-Keldysh effect[4] known from semiconductors. Spectra of disordered films are less well understood[5-8]. By comparison of spectra of disordered (4–BCMU)[9] and single crystalline (DCHD) polydiacetylene we investigate how disorder affects the response of conjugated π states to electric fields. Analysis of both lineshape and size of the field induced changes is necessary to extract the information hidden in the spectra. These studies are performed with the field parallel to the film providing access to the polarization dependence of the field modulated spectra which is observed even in optically isotropic films. Details of the apparatus and the evaluation are described elsewhere[3,8].

QUADRATIC STARK EFFECT IN POLYDIACETYLENES

Spectra of DCHD Single Crystals: poly(1,6–di(n–carbazolyl)–2–4–hexadiyne)

Electroreflectance spectra of polydiacetylene single crystals serve as reference. For quantitative analysis Kramers-Kronig transformation is recommended to obtain spectra of the absorption α or of the imaginary part ϵ_2 of the dielectric constant. Fig.1 shows spectra of DCHD for polarization of light parallel to the polymer backbone. Fields along this direction cause large changes which, as shown by the good agreement to a first derivative spectrum of the linear spectra, result from a rigid redshift of the exciton and its vibronic satellites. This shift by ΔE_x results from coupling by a dipole moment $|\vec{\mu}| = e \cdot r$ of an exciton of radius r to weakly absorbing states at higher energy E_C:

$$\Delta E_x = \frac{|e\vec{\mu}\cdot\vec{F}|^2}{E_x - E_C} = \frac{p}{2} F^2 \qquad (1)$$

Concomittantly, oscillator strength Δf is transferred to the weak transitions at E_C:

$$\Delta f = f \frac{\Delta E_x}{E_x - E_C} \qquad (2)$$

The lineshape of modulated spectra thus depends on the separation of the states involved. Transfer of oscillator strength dominates if they are close, a case observed in Ac:PMDA[10, 11] and in semiconductors quantum wells while in polydiacetylene the redshift dominates due to the large separation, E_x–E_C, related to a binding energy of 0.5 eV, and the spectra follow closely a first derivative.

The shift increases quadratically with the field and corresponds to a polarizability of 7000 – 8000 Å^3. The weakly coupling state at higher energy is revealed

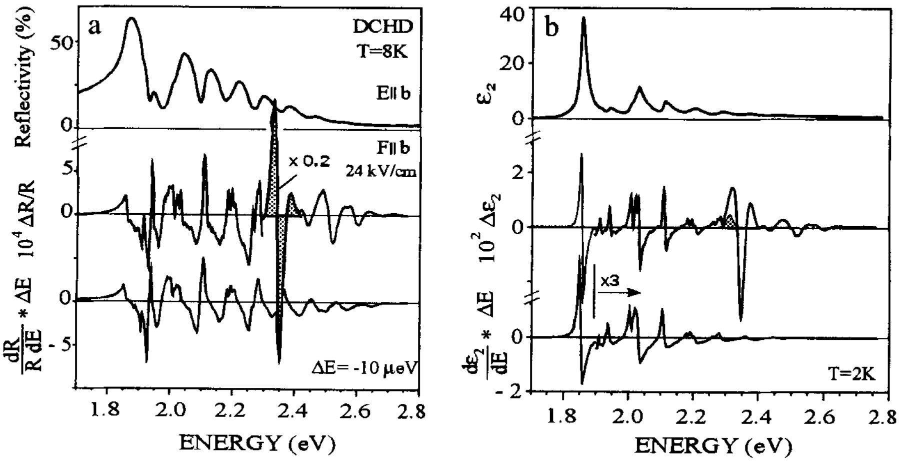

FIGURE 1 DCHD: Comparison of field modulated spectra $\Delta R/R$ and $\Delta\epsilon_2$ with the linear spectra and their first derivatives with respect to energy.

by the very large ER signal 0.5 eV above the exciton (shaded area) which has no counterpart in the derivative spectrum. Because the response increases for small fields quadratically it has been attributed to a forbidden exciton[2]. The increasing strength of such exciton, however, would create only the tiny shaded $\Delta\epsilon_2$ peak which is completely buried under the large signal at 2.35 eV. Shape, size and field strength dependence of this response are consistent with the Franz-Keldysh effect[4]. This effect requiring free motion of electrons through continuum states is sensitive to scattering and is therefore well developed only in exceptionally good crystals.

Spectra of 4–BCMU films: 4–butoxy–carbonyl–methyl–urethane

Fig.2a compares absorption and electroabsorption (EA) spectra of a 0.3μm thick spin coated film[9]. The absorption shows broad peaks at 2.39 and 2.55 eV which are attributed to an exciton and its vibronic states. The EA spectrum increases quadratically with field and shows a negative peak at 2.39 eV and a doublet at 2.58 and 2.63 eV which is assigned to stretch modes of double and triple bonds.

Despite isotropic absorption the EA response shows pronounced anisotropy. The observed polarization ratio of 3:1 in favour of parallel alignment of field and polarization of light results if the transition dipole $\vec{m}$ to the ground state and the dipole $\vec{\mu}$ coupling the exciton $|1B_u\rangle$ to high energy are both parallel to the polymer backbone[8]. Random orientation of polymer segments reduces the absorption α and its alteration by the Stark effect from the values α_0 and S in a perfectly ordered system with field and polarization parallel to the polymer backbone:

$$\Delta\alpha(E\|F) = \frac{1}{5}\,\alpha_0 S = \frac{3}{5}\,\alpha\cdot S = 3\cdot\Delta\alpha(E\perp F) \tag{3}$$

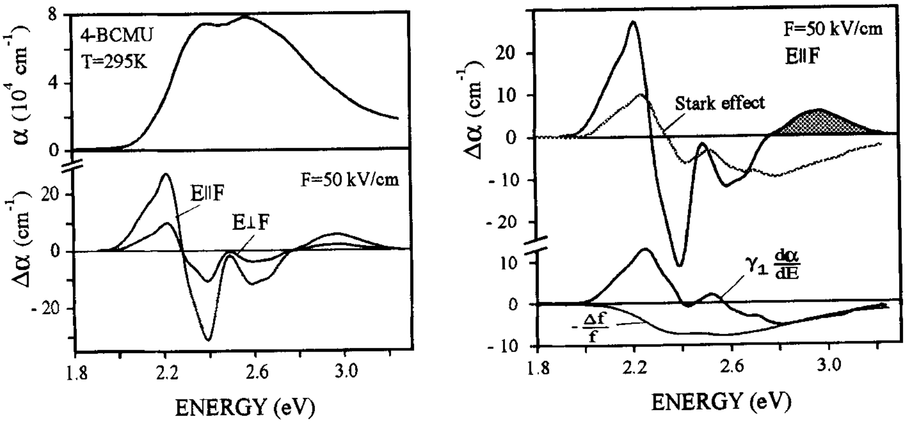

FIGURE 2 a) Absorption α and electroabsorption spectra $\Delta\alpha$ of 4–BCMU. b) Comparison of $\Delta\alpha$ and the lineshape of a quadratic Stark effect.

Using the average polarizability of single crystals (p=7000 Å^3) we calculate from eq.3 shift and reduction of strength $\Delta f/f$ of the excitonic absorption. This seems justified because redshift and exciton binding energy vary little among polydiacetylenes crystals. The loss of oscillator strength is simulated by decreasing the whole absorption band thus ignoring transfer of this strength to higher energy which is responsible for the broad shaded peak of $\Delta\alpha$ near 2.9 eV (fig.2b). The comparison of the predicted Stark effect and the experimental spectrum $\Delta\alpha$ thus is restricted to the region of strong absorption below 2.8 eV.

The quadratic Stark effect yields an incorrect lineshape. Negative peaks of EA spectra occur at absorption maxima where the Stark effect, still dominated by the redshift, predicts a vanishing signal. Furthermore, the calculated signal though of correct order of magnitude is smaller than the observed response which points to an additional effect in disordered films which has a lineshape proportional to a second energy derivative as observed also in other materials[6]. This second energy derivative of the absorption spectrum alone describes the experimental spectrum quite well (fig.3a) and this agreements improves if the quadratic Stark effect is included (fig.3b). With a somewhat reduced coefficient from $\gamma=1.2\cdot10^{-5}$ (eV)^2 to $0.8\cdot10^{-5}$ (eV)^2 the second derivative part prevails and determines the lineshape.

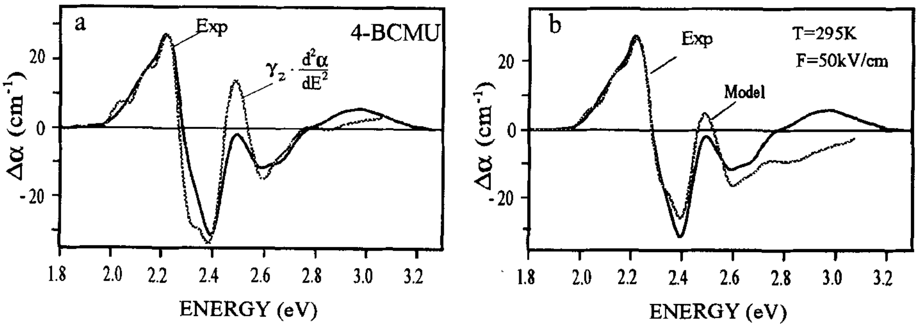

FIGURE 3 Fit of the EA spectrum by a second derivative absorption without (a) and combined with the quadratic Stark effect (b).

SPECTRA OF ISOTROPIC POLYACETYLENE FILMS

Fig.4 shows EA spectra of polyacetylene films containing cis– and trans-PA. In both regions a second derivative contribution is needed to obtain the correct positions of spectral features. It is interesting, to note that the anisotropy of the EA spectra is smaller. We found in these optically isotropic films a polarization ratio of 2.6 less than in 4–BCMU and PPPV[8] and somewhat larger than the value

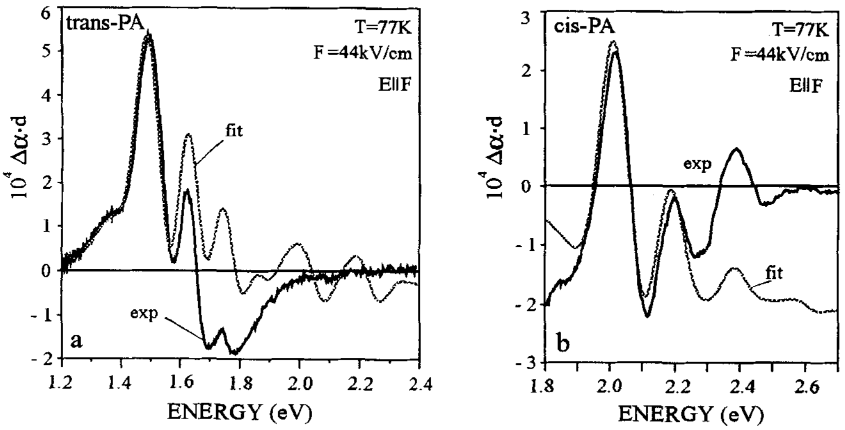

FIGURE 4 Electroabsorption spectra of polyacetylene

2.3 reported previously[5]. The smaller anisotropy may indicate that polyacetylene has less 1d–character than polymers containing large side groups which efficiently reduce inter-chain coupling of π states.

LINEAR STARK EFFECT IN DISORDERED POLYMERS

Second derivative lineshape which is common in disordered films is similar to the spectral shape expected for lifetime broadening. This explanation, however, has to be dismissed because broadening must also be observed in crystals, particularly at low temperature, where the linewidth is narrow. Second derivative contributions, however, are insignificant in spectra of PDA single crystals and even the weakly bound excitons states in semiconductors like CdS (E_b=20 meV) respond to similar electric fields primarily by a quadratic Stark shift[12].

Electroabsorption Spectra of CT Transitions in PVK:TNF

Second derivative type EA spectra have been found in the photoconductor polyvinylcarbazole (PVK) mixed with trinitrofluorenone. Fig.4a shows the absorption due to charge transfer from carbazole to the acceptor TNF mixed in a ratio 1:1. Two absorption bands are resolved which both show a quadratic response to an electric field. The EA spectrum is well described by superposition of first and second derivatives of the absorption, the latter again dominating[13]. The strong negative peak predicted for the EA spectrum at 2.8 eV is obscured by the redshifting absorption edge of TNF. It appears if the concentration of TNF is decreased (fig.4b) which reduces the CT absorption less than that of TNF *molecules*[14].

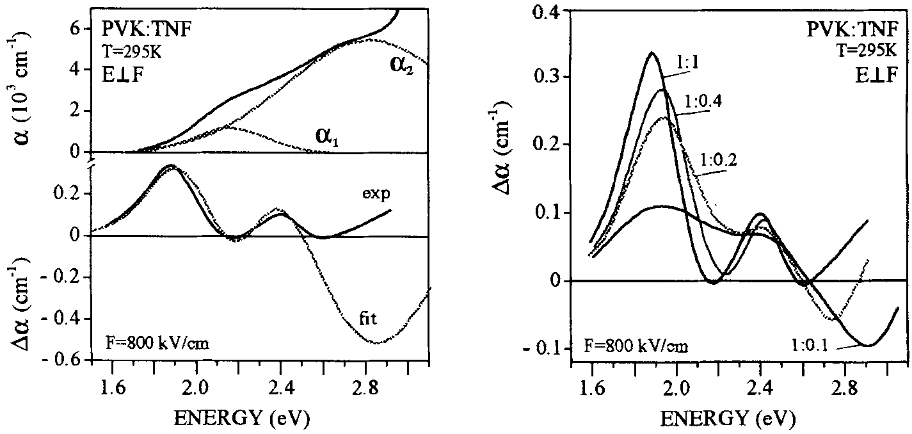

FIGURE 5 a) CT absorption bands of PVK:TNF and their EA spectrum which depends also on the ratio of donor and acceptor molecules (b)

Charge transfer dipoles couple linearly to the field shifting the transition energy by ΔE which leads to first and second order changes of the absorption:

$$\Delta\alpha = < \frac{d\alpha}{dE}\Delta E > + \frac{1}{2} < \frac{d^2\alpha}{dE^2}(\Delta E)^2 > \qquad \Delta E = -\vec{\mu}_p \cdot \vec{F} \tag{4}$$

The linear effect vanishes by summing up an isotropic distribution of dipole moments but the quadratic effect of second derivative lineshape remains. If optical dipole moment and CT dipole μ_p are parallel the spectra show the same polarization as the quadratic Stark effect. Evaluation leads to CT dipoles of 5.2 and 7.3 D for low and high energy transitions, respectively.

Inversion Symmetry in Disordered Films

The linear Stark effect yields the correct lineshape and field strength dependence of EA spectra but requires permanent dipole moments or degenerate states. Both seems incompatible with polymers where inversion symmetry is a key in describing their optical properties. Defects, however, interrupt the perfect conjugation and lead to localization, replacing the continuum states of a long chain by discrete states. Consequently, the Franz-Keldysh effect disappears and the Stark effect of the remaining states is likely to be small because of weak oscillator strength.

The boundaries affect any coherent state. By shifting the energy levels they contribute to inhomogeneous broadening, but most important they break the inversion symmetry if the terminating barriers are different on both ends. Eigenstates of mixed parity emerge which are no longer centred to the polymer segment. Like in semiconductor nanostructures the boundary conditions impose envelope

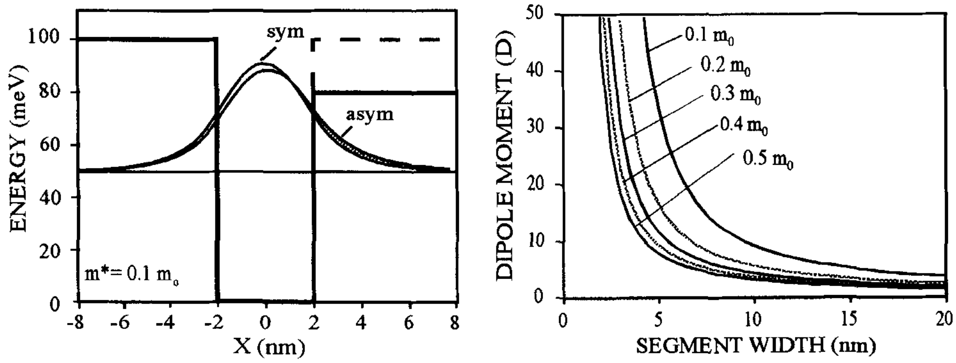

FIGURE 6 Envelope function in a polymer segment showing displacement of charge by an asymmetric potential (a). The resulting dipole moment depends on length of the chain and effective mass (b).

functions on extended states which are still built up by the interacting π orbitals.

Fig.5a shows the envelope function of a 40 Å long segment with 0.1 eV high barriers for an electron of mass $0.1m_0$, a value suggested from the size of the exciton and the Franz-Keldysh effect in DCHD crystals[3]. While symmetric barriers cause only an energy shift a small asymmetry by 20 meV displaces the charge distribution towards one barrier, equivalent to a dipole moment of 55 D. This dipole moment which is related to tunneling into the barriers decreases with increasing mass and barrier height and varies with the length of the segment (fig.5b). Large dipoles are found primarily in short segments but even longer segments contribute to electroabsorption second derivative type spectra. Excitons and continuum states are expected to behave similarly as long as the exciton radius is smaller than the size of the segment.

SUMMARY

Table 1 summarizes the coefficients γ_1 and γ_2 describing first and second derivative contributions in the electroabsorption spectra presented and the deduced polarizability p and average permanent dipoles μ_p. The exciton radius depends on its separation from continuum states which was taken as 0.5 eV, the value found for polydiacetylene single crystals. Both polarizability and the disorder induced dipole moments of conjugated polymers exceed by far the polarizability of the aromatic molecules in PVK:TNF and the CT dipoles. We assume these large values to be typical for π–conjugated linear systems with extended electron states.

The quadratic Stark effect of extended excitons dominates the EA spectra of crystalline polymers which in rare cases show also the Franz-Keldysh effect. Although the quadratic Stark effect seems not much affected by disorder spectra of films are dominated by the larger additional effect with lineshape proportional to the second derivative of linear spectra. This effect is interpreted as a residual linear Stark effect induced by disorder which destroys the inversion symmetry of extended states by asymmetric boundary conditions. The relationship of electroabsorption and $\chi^{(3)}$ suggests further that disorder may lead in centro–symmetric polymers to residual $\chi^{(2)}$ effects which cancel in isotropic samples but contribute to $\chi^{(3)}$, compensating some of the reduction due to inhomogeneous broadening.

TABLE 1 Coefficients γ_1 and γ_2, describing contributions of first and second derivative to electroabsorption spectra. The polarizability p and exciton radius r are derived from γ_1, the dipole moments μ_p from γ_2.

	γ_1 (10^{-5}eV)	γ_2 (meV)^2	p (Å^3)	r (Å)	μ_p (D)
DCHD	1.7	0	8 200	11.7	0
4–BCMU	3.6	8.0	7 000	11.0	49
cis– PA	3.7	1.25	9 200	12.5	24
trans– PA	3.0	6.0	7 200	11.2	48
PVK:TNF α_1	1.35	7.5	30		5.2
PVK:TNF α_2	0.57	15.0	13		7.3

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