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Influence of disorder on the field-modulated spectra of polydiacetylene films

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Electroabsorption and electroreflectance spectra of disordered, optically isotropic polydiacetylene films (4-BCMU) have been measured with field perpendicular to the incident light. The modulated spectra are polarized reflecting the local anisotropy of π-conjugated polymers. Based on results on single crystals, the data are interpreted as quadratic Stark effect of excitonic transitions with the same values for polarizability and dipole moments as in single crystals, accounting only for inhomogeneous broadening and random orientation of polymer segments. Line-shape analysis reveals a large additional contribution proportional to the second derivative of the absorption spectrum. This part, absent in single crystals, is interpreted as a linear Stark effect due to permanent dipole moments arising from disorder-induced asymmetry of polymer segments. Isotropic distribution of the disorder-related dipoles leads to a quadratic dependence of the signal on field strength, different from the quadratic Stark effect only by the spectral line shape.

I. INTRODUCTION

Polymers with π-conjugated chains have found considerable interest as they show aspects of low-dimensional semiconductors[1,2] due to the weak interaction between polymer strands. Strong spatial overlap of the π states along the polymer backbone results in states extending over several repeat units of the polymer[3] suggesting wide one-dimensional electron bands.[4,5] Confinement of the states to a single chain enhances Coulomb interaction of electrons and holes which leads to excitonic states of large oscillator strength,[7,8] while conjugation along the chain results in a large polarizability which makes these states sensitive to external electric fields.[9] This combination of large polarizability and large oscillator strength contributes to the large nonlinear optical susceptibility of conjugated polymers[10] promising possible application in optical switching devices.[11]

Field-modulated optical spectra, which contributed much to understanding the electronic states in semiconductor crystals, have also been measured on numerous conjugated polymers.[12–19] Detailed understanding of the spectra of polymers has been achieved only in case of polydiacetylene single crystals (PDA) where the excitons at the absorption edge respond to fields along the polymer chain with a quadratic Stark effect due to their coupling to a continuum of states lying about 0.5 eV at higher energy.[9] The response of the continuum states which have small oscillator strength is extremely sensitive to disorder and is observed only in high-quality crystals, most notably in DCHD,[12] where π interaction of the carbazole side groups may increase the rigidity of the polymer backbone.

Studies of other conjugated polymers have been limited to disordered films.[16–19] By inhomogeneous broadening almost all fine structure which was essential for the quantitative description of the field effects in crystals is lost. Spectra of different disordered materials look similar but bear little resemblance to the spectra of single crystals. Although the much broader and weaker response still depends quadratically on field strength, the line shapes of the spectra are inconsistent with a field-induced redshift of the excitonic transitions which in PDA single crystals leads to an almost perfect agreement of field-modulated spectrum and first derivative with respect to energy of the linear spectra.[9,14,15] The line shape of electroabsorption spectra of disordered films agrees quite well with the second derivative of the absorption spectra,[19] a component which adds little to the spectra of single crystals. Such a line shape and field dependence is expected from the linear Stark effect of isotropically oriented permanent dipole moments of non-centro-symmetric molecules or for optical charge transfer between different molecules in a disordered solid[20] but seems excluded for polymers with centrosymmetric repeat units.

We report a detailed study of electroabsorption and electroreflectance spectra of disordered polydiacetylene films and compare line shape, polarization dependence, and size of the response with those of PDA single crystals. Although also the crystal transition energies and the spectral line shape depend on the homogeneity of the PDA crystals and on the sidegroup attached to the polymer backbone, quantitative analysis of the spectral line shape always leads to a very similar quadratic Stark effect, that is determined by the size of the excitons along the chain and varies little for different PDA crystals. The

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comparison thus should reveal how much of the one-dimensional character of the electronic states and their spatial extension is preserved in disordered films.

II. EXPERIMENTAL DETAILS

Glassy films of 4-BCMU poly[5,7-dodecadiyne-1,12-diol-bis (n-butoxy-carbonyl-methyl-urethane)] were prepared by spin coating (thin films) or by slow evaporation onto quartz substrates which contained an array of 100-μm-wide Au strips. Details on preparation and characterization are given in.[21,22] Sinusoidal electric fields of about 1-kHz frequency were applied perpendicular to the incident light which allowed us to study the dependence of the field-modulated spectra on the polarization of light.

The contacts were separated by 100 μm, sufficiently large to have a homogeneous field in the film plane. The thickness of the soft films was checked with a Mireau interferometer attached to a microscope. Limited contrast resulted in some uncertainty of the actual thickness. Fortunately, inaccurate values of the thickness of the film have no effect on the evaluation of changes of the optical absorption due to the electric field.

Light from a tungsten halide lamp was dispersed in a 1-m-grating monochromator with spectral resolution of about 1 meV and measured with a photomultiplier. Linear spectra measured on contact-free regions were optically isotropic confirming random orientation of the polymer segments. Reflectance spectra, necessary for Kramers-Kronig transformation of electroreflectance spectra, were measured separately in a vacuum monochromator, which by avoiding windows, yields more accurate absolute values of the reflectivity. Measurements at low temperatures showed little difference to those at room temperature indicating that inhomogeneous broadening prevailed. Field-induced changes of the transmitted or reflected light intensity were measured with a lock-in amplifier tuned to twice the frequency of the field as expected for quadratic dependence on homogeneous fields. Signals at the fundamental frequency were absent proving that space charge effects and field inhomogeneities were negligible.

III. EXPERIMENTAL RESULTS

A. Absorption and electroabsorption spectra

A comparison of absorption α and electroabsorption spectra $\Delta\alpha$ of a 0.3-μm-thick spin-coated film is shown in Fig. 1. The spectra are derived from the transmitted intensity I and its field-induced change ΔI, by using the relationship between the thickness d of the film, the reflectivity R and the incident light intensity I_0:

$$I/I_0=\frac{(1-R)^2\exp(-\alpha d)}{1-R^2\exp(-2\alpha d)}\ , \tag{1}$$

$$d\cdot\Delta\alpha=-\Delta I/I\ . \tag{2}$$

Equation (1) accounts for multiple reflectance within the film after averaging through the fringe pattern in the transparent region. Equation (2) neglects changes of the reflectivity which even in thin films are much smaller than changes of the transmittance.

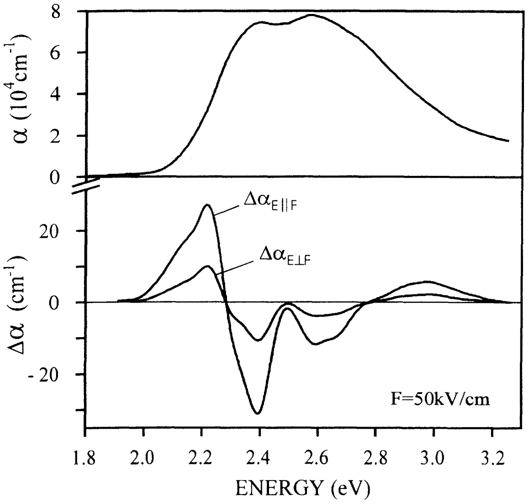

FIG. 1. Absorption spectrum of a thin spin-cast film and its field-induced change $\Delta\alpha$ for polarization E parallel and perpendicular to the field F.

The absorption spectrum of this film shows two broad peaks near 2.39 and 2.55 eV which are attributed to an exciton and a vibronic satellite strongly coupled to the π-double-bond stretch mode. The peak absorption is about one order of magnitude smaller than in single crystals due to the random orientation of polymer segments and large inhomogeneous broadening which is typical for as-spun films.[23]

The electroabsorption spectra $\Delta\alpha$ show a strong negative peak at 2.39 eV related to the exciton, and a doublet at 2.58 and 2.63 eV, assigned to stretch modes of the double and triple bonds, the latter giving rise to a barely visible shoulder in the absorption spectrum. The absorption increases with the field at low and high energy and decreases in the region of strong absorption. This broadening of the π-π^* absorption band points to redistribution of the oscillator strength and changes in the density of states.

Changes of the absorption increase quadratically with the field but are much smaller than in single crystals. In contrast to the optically isotropic absorption spectrum the electroabsorption spectrum depends on the polarization of light. The line shape is independent of polarization but for light polarized parallel to the electric field F, the response is three times larger than for orthogonal polarization.

B. Reflectance and electroreflectance spectra

Figure 2 compares the reflectance, R, of a slowly evaporated film and the change, $\Delta R/R$, induced by a field of 85 kV/cm for light polarized parallel to the field; the response again is larger by a factor of 3 compared to orthogonal polarization. For better comparison the spectrum was adjusted to correspond to a field of 50 kV/cm

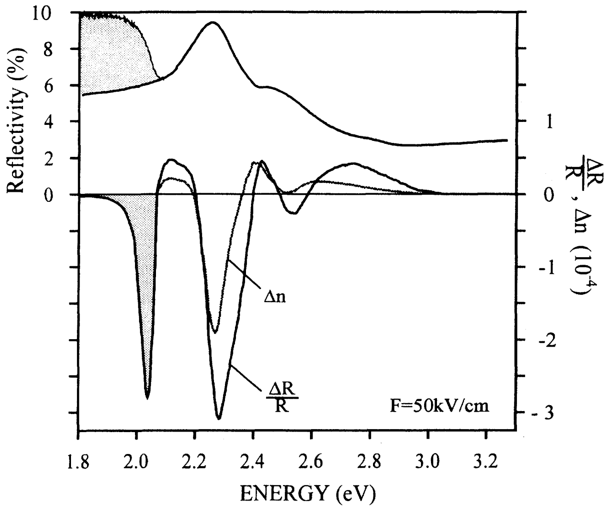

FIG. 2. Reflectance and electroreflectance spectra of a 3-μm-thick film. The $\Delta R/R$ spectrum follows closely the change of the refractive index (weaker line) derived by Kramers-Kronig transformation. Shaded areas in the transparent region show the enhanced reflectance of the film due to light reflected from the back of the film and the corresponding electroabsorption response which overlaps the near-edge electroreflectance signal.

according to the verified quadratic field strength dependence. It has furthermore been scaled up by 2 to account for the fact that half the light is reflected from the field-free region above the opaque contact stripes.

For a film thickness of 3 μm, measurements of the absorption and electroabsorption spectra were feasible only in the low-energy part of the spectrum. In the transparent region light reflected from the back surface adds to the reflected light intensity and leads to an increase below the absorption edge shown as the shaded area. The back reflected light adds also to the field-induced change of the light intensity and is responsible for the shaded low-energy peak near 2 eV, an electroabsorption response. The sign of the peak is consistent with field-induced absorption at low energy; its shape results from increasing $\Delta\alpha$ towards higher energy until the back reflected light is cut off as the sample becomes opaque. This film was sufficiently thick to avoid distortion of the electroreflectance response for most of the spectrum. Electroreflectance spectra should be measured only on opaque samples.

The electroreflectance spectrum follows closely changes of the refractive index, Δn. Field-induced changes of the real and imaginary parts of optical constants are of similar size, however, in BCMU as in most materials near the absorption edge, the real part n of the refractive index is much larger than the imaginary part ($\alpha\lambda/4\pi$) and thus determines reflectance and electroreflectance spectra. This is the reason why the electroreflectance response is smaller than changes of the transmittance.

Absorption and electroabsorption spectra are derived by Kramers-Kronig analysis of the reflectance spectra. We measured to 5.5 eV, which proved sufficient for polydiacetylene single crystals because the spectra are dominated by the strong π-π^* transitions. Towards low energy, the spectrum has been extrapolated as shown in Fig. 2. This extrapolation affects the accuracy of the absorption spectrum and was adjusted to achieve the correct position of the absorption edge.

The absorption spectrum in Fig. 3, derived from Kramers-Kronig transformation of the relatively small and broad reflectance spectra, is expected to be less accurate than that derived from the sharp and high reflectance peaks in single crystals because the influence of high-energy transitions on the spectra in the range of interest is stronger. The accuracy cannot be improved by measuring reflectivity further into the UV because scattering from surface inhomogeneities leads to increasing errors at shorter wavelength. Transformation of the electroreflectance spectra is quite accurate, distorted only in the region of the first small positive peak by the electroabsorption response of the light reflected from the back. However, calculation of Δn and $\Delta\alpha$ from $\Delta R/R$ and its transform $\Delta\theta$ requires knowledge of the real and imaginary parts of the optical constants.[24] In view of these difficulties the spectra of the evaporated film in Fig. 3 agree quite well in size and line shape with the directly measured spectra of the thin film (Fig. 1). The strong negative peak of the electroabsorption peak that coincides with the main excitonic peak occurs at 2.33 eV, 60 meV lower than in the thin spin-coated film. This difference cannot be explained by some ambiguity introduced by Kramers-Kronig transformation. Modeling the reflectance spectrum by oscillators for the exciton and its main vibronic satellites confirms these different transition energies. We expect the slowly evaporated film to be of better crystallinity and assume that this causes the small redshift of the π-π^* transitions. Closer inspection of electroabsorption spectra of the spin-coated film (Fig. 1) reveals at about the same energy a shoulder below the dominant negative excitonic peak which may also be related to regions of better crystallinity.

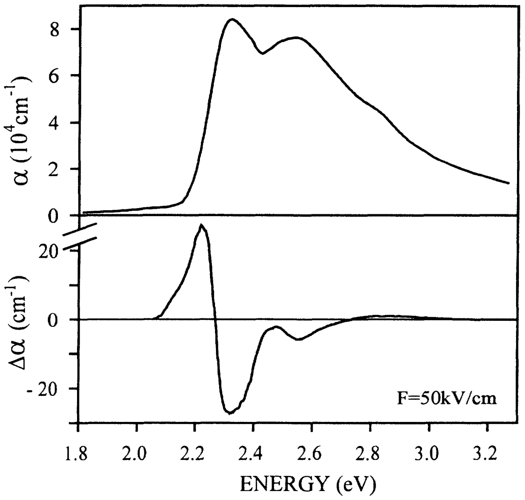

FIG. 3. Absorption and electroabsorption spectra derived by Kramers-Kronig transformation of the spectra in Fig. 2.

IV. DISCUSSION

A. Polarization dependence of the modulated spectra

Despite unpolarized absorption and reflectance spectra which confirm random orientation of polymer segments in these disordered films, the modulated spectra are polarized with respect to the electric field. It is common that the signal is much larger for polarization of light parallel to the field. The same ratio 3:1 has been observed in PPPV, poly(phenyl-p-phenylenevinylene),[17] while for polydiacetylene films a smaller ratio, 2.3, was reported.[16] In PDA single crystals the optical transition dipole **m** is parallel to the polymer backbone and the transitions are sensitive only to a field along that direction, indicating an extremely anisotropic polarizability, described by a dipole $\boldsymbol{\mu}$ parallel to the chain which couples the exciton to states at higher energy.[9,14]

Based on these results, we assume alignment of both dipoles parallel to chain segments in disordered films. In a configuration (Fig. 4) with the incident light perpendicular to a film of randomly oriented polymer segments **b**, a field in the film plane leads to anisotropic changes $\Delta\alpha$ due to the quadratic Stark effect:

$$\Delta\alpha(E\|F)=\alpha_0\xi F^2\frac{1}{4\pi}\int_0^{\pi}d\theta\,\sin^5\theta\int_0^{2\pi}d\varphi\,\sin^4\varphi\ ,$$

$$\Delta\alpha(E\perp F)=\alpha_0\xi F^2\frac{1}{4\pi}\int_0^{\pi}d\theta\,\sin^5\theta\int_0^{2\pi}d\varphi\,\sin^2\varphi\cos^2\varphi\ . \tag{3}$$

The absorption constant α_0 and the field effect ξF^2 refer to the case where the field and light polarization are parallel to the dipole moments involved. Equation (3) assumes only an isotropic orientation of polymer segments and yields the observed anisotropy of the field-modulated spectra as a consequence of parallel alignment of the dipoles **m** and $\boldsymbol{\mu}$. If S denotes the size of the field-induced signal for parallel alignment of the coupling dipole μ and external field F we obtain further

$$\Delta\alpha(E\|F)=\frac{3}{15}\alpha_0 S=3\cdot\Delta\alpha(E\perp F)\ . \tag{4}$$

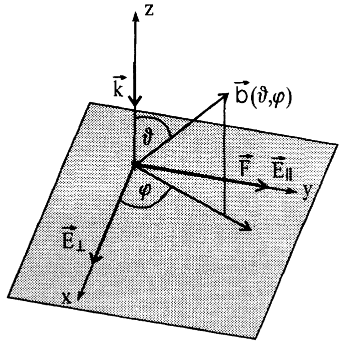

FIG. 4. Experimental configuration with the field F in the layer plane, incident light k, and randomly oriented polymer segments b.

The same averaging over isotropically distributed transition dipoles yields an isotropic absorption spectrum whose intensity is reduced by a factor of 3. Field-induced absorption changes are considerably reduced in disordered films compared to single crystals with properly oriented field and polarization of light. Additional reduction of the response results from the larger linewidth, which leads to a reduction of the peak absorption α_0, and of the energy derivatives of the absorption spectrum. If we account for linewidth broadening by comparing $\Delta\alpha$ with the actual absorption spectrum of the disordered film, we notice that $\Delta\alpha/\alpha$ for $E\|F$ reaches 60% of the value anticipated for perfectly aligned polymer segments because $\alpha=\alpha_0/3$. For $E\perp F$, corresponding also to a sandwich configuration with field perpendicular to the layer plane, $\Delta\alpha/\alpha$ is reduced by a factor of 5.

The polarization ratio of the field-modulated spectra thus seems to reflect the one-dimensional character of the π electrons in conjugated polymers where large side groups reduce interchain interaction. The smaller anisotropy (2.3) reported for polyacetylene[16] may indicate stronger interchain coupling of π electrons. We repeated measurements on cis- and trans- polyacetylene and found very good agreement with the published spectra except for a slightly larger polarization ratio of 2.6 both in electroabsorption and in electroreflectance spectra.

Although the anisotropic electroabsorption response of optically isotropic polymer films seems a natural consequence of the local anisotropy of conjugated polymers, it should be noted that similar large anisotropies have also been observed in amorphous semiconductors,[25] in particular in amorphous tetrahedrally coordinated Si where local anisotropy is not suspected,[26] and in preliminary measurements on films of the highly isotropic fullerenes.

B. Line shape of the quadratic Stark effect

Field-modulated spectra of polydiacetylene single crystals are almost in perfect accord with the first derivative with respect to energy of the corresponding linear spectrum due to a rigid redshift of the exciton and its vibronic satellites by the quadratic Stark effect. The Stark effect of the exciton results from coupling to energy states 0.5 eV higher in energy, which are assumed to be either a forbidden exciton state[14,15] or, consistent with field strength dependence and linewidth broadening of a strong response at that energy, the threshold of the weakly absorbing continuum states of a one-dimensional Wannier exciton.[9] The first interpretation leads to an unreasonably large coupling dipole μ, while in the latter view the shift is determined by the radius of the exciton ground state which extends over about five repeat units. Concomitant with the redshift of the exciton, oscillator strength is transferred to the weakly absorbing state. In a three-level system of a ground state and two excited states at E_x and E_c, the Stark shift ΔE_x of the exciton and the polarizability p are given as

$$\Delta E_{\mathrm{ex}}=\frac{|e\boldsymbol{\mu}\cdot\mathbf{F}|^2}{E_x-E_c}=\frac{p}{2}F^2\ , \tag{5}$$

while the simultaneous transfer Δf of oscillator strength is

$$\Delta f = f\frac{\Delta E_{\rm ex}}{E_x - E_c} \ . \tag{6}$$

If the gap between excited states of different parity is small, the transfer of oscillator strength determines the line shape as is observed for charge-transfer excitons in PMDA:Ac.[27,28] The striking similarity of field-modulated spectra and the first energy derivative in polydiacetylenes is due to the large separation (0.5 eV) of the two states by 0.5 eV which relegates the contribution from exchange of oscillator strength to a minor correction of the changes which results from the redshift.

The Stark shift in PDA single crystals depends little on linewidth and sidegroups. We therefore conjecture a similar Stark effect for the excitons in the disordered BCMU films. Because of lack of data for 4-BCMU crystals, we use a polarizability $p = 7000$ Å^3 which presents an average of the value found in three modifications of PDA crystals. We assume further that the shift results from coupling to weakly absorbing states about 0.5 eV at higher energy. The quadratic Stark effect of the exciton and its vibronic satellites, averaged for an isotropic orientation of polymer segments, leads to a redshift of the absorption spectrum by 3.6×10^{-5} eV for a field of 50 kV/cm and a transfer of oscillator strength $\Delta f/f = 7.3\times10^{-5}$ from the excitonic region to higher energy. This transfer is probably responsible for the broad positive peak around 2.9 eV (shaded area in Fig. 5).

Figure 5 compares the experimental spectrum (Fig. 1, $E\|F$) with a calculated spectrum based solely on the quadratic Stark effect using the same parameters which describe the spectra of single crystals. The transfer of oscillator strength is approximated by a corresponding uniform reduction of the absorption spectrum including the range above 2.9 eV where the absorption is expected to increase. It would be better to compare spectra of the imaginary part of the dielectric susceptibility, but this requires accurate knowledge of the refractive index over the whole region. For the same reason and due to the unknown width of the continuum and distribution of the gained oscillator strength, no attempt is made to simulate the increasing absorption of the weakly absorbing states. The calculated spectrum thus accounts for changes in the excitonic region only up to 2.8 eV to which the discussion will be restricted.

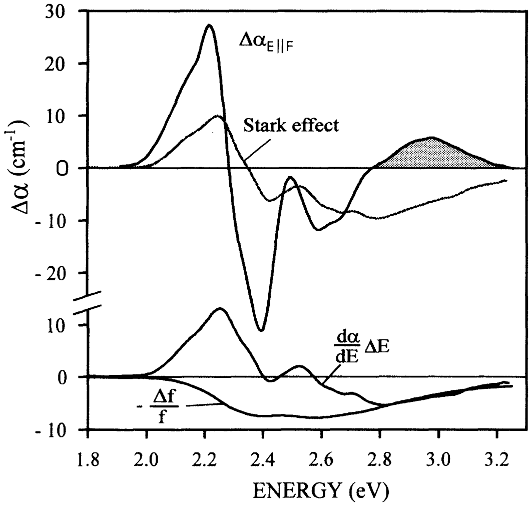

FIG. 5. Comparison of the experimental electroabsorption spectrum (Fig. 1) with a spectrum predicted for a quadratic Stark effect with the same parameters as in single crystals. The lower part shows the contributions due to shift of the excitons and due to loss of oscillator strength. The transfer of strength to high energy (shaded area) is not included in the model.

A comparison of the relative contributions of transfer of oscillator strength and redshift to the excitonic spectrum reveals that at low energy, the shape of the electroabsorption spectrum still resembles the first derivative of the absorption spectrum, but loss of oscillator strength adds significantly at higher energy, much more than in single crystals. This is not surprising because linewidth broadening reduces the magnitude of the derivative of the absorption spectrum more than the spectrum itself. This simple approach, regarding the sample as an ensemble of randomly oriented polymer segments with inhomogeneously broadened electron states of the same polarizability as in a crystal, yields already the correct order of magnitude of the spectra. While this supports the quadratic Stark effect as an important contribution, the deviation from the correct line shape is obvious.

Such deviation of the electroabsorption spectra from a first energy derivative line shape is commonly observed; the good agreement found in polydiacetylene crystals is a rare exception. It should also be noted that the experimental response is larger than calculated which suggests a second mechanism contributing to the electroabsorption spectrum.

C. Second derivative spectra

It has been noted before that electroabsorption spectra of disordered films are much better described by the second energy derivative.[19] This is true also for 4-BCMU, shown in Fig. 6(a) by the striking similarity of the electroabsorption spectrum and the second energy derivative of the absorption spectrum. An even better description of the strongly absorbing region is obtained if the second derivative part is added to the contribution from the quadratic Stark effect as discussed in the previous section. The quadratic Stark effect thus is supplemented by an additional effect which has a quadratic field strength dependence but the line shape of a second derivative. Line shapes similar to a second derivative can result from lifetime broadening. Such an effect, however, should be buried completely in the large inhomogeneous width of spectral features in disordered films. Lifetime broadening is more likely to be observed for narrow linewidths as in spectra of single crystals. Because spectra of PDA single crystals show no such contribution even at low temperature we omit lifetime broadening as explanation of a second derivative line shape.

Electroabsorption spectra having almost purely second

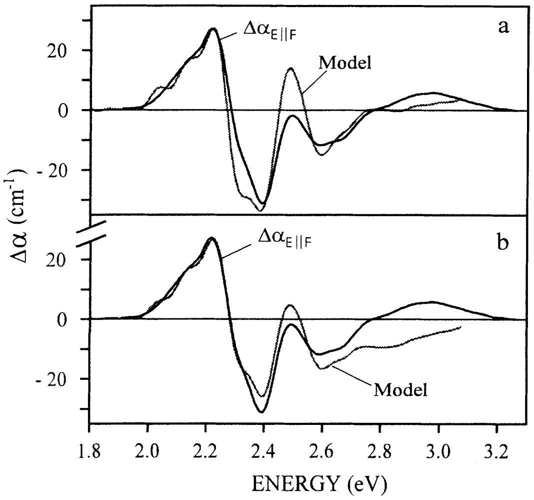

FIG. 6. (a) Fit of a second derivative spectrum (weaker line) to the electroabsorption spectrum. (b) Comparison with the quadratic Stark effect (as in Fig. 5) supplemented by a contribution proportional to the second derivative.

derivative line shapes have been reported for charge-transfer transitions in disordered films of polyvinylcarbazole and trinitrofluorenone (TNF).[20] Charge transfer from the donor carbazole to the acceptor TNF leads to a permanent dipole μ_{ct}, and to a linear shift of the transition energy in an external field depending on the orientation θ with respect to the field. Expanding the change of the absorption spectrum $\Delta\alpha$ in powers of the linear energy shift $\Delta E = -\mu_{\mathrm{ct}}\cdot\mathbf{F}$ leads to

$$\Delta\alpha = \frac{1}{2}\int_0^{\pi} d\theta \sin\theta \left[\frac{d\alpha}{dE}\mu_{\mathrm{ct}}F\cos\theta + \frac{1}{2}\frac{d^2\alpha}{dE^2}(\mu_{\mathrm{ct}}F\cos\theta)^2 \right] . \tag{7}$$

The term linear with field disappears for randomly oriented dipoles leaving only the quadratic term which is proportional to the second derivative of the absorption spectrum.

A linear Stark effect modified by disorder provides both a quadratic field strength dependence and the second derivative line shape consistent with a large part of the electroabsorption spectrum. A linear Stark effect requires either degenerate states or permanent dipole moments, both of which are inconsistent with the centrosymmetric polydiacetylene chains unless it is assumed that permanent dipoles are induced by disorder.

Table I summarizes the transfer of oscillator strength and the prefactor γ_1 for a first energy derivative resulting for a field of 50 kV/cm from the quadratic Stark effect. In order to avoid too many parameters the quadratic Stark effect has not been fitted but was based on an average polarizability $p = 7000$ Å^3 of single crystals. The energy shift, ΔE_2, of the quadratic Stark effect and the exciton radius r thus are the same as in a crystal. ΔE_1 refers to the energy shift due to the linear Stark effect derived from the scaling factor γ_2 of the second derivative spectrum and the resulting permanent dipole moment μ_p which, consistent with a polarization ratio of 3, is assumed to be parallel to the polymer backbone:

TABLE I. Energy shift ΔE_2 and transfer of oscillator strength $\Delta f/f$ due to the quadratic Stark effect in a field of 50 kV/cm and the scaling factors γ_1 and γ_2 for contributions of first and second derivative of the absorption spectrum to the electroabsorption spectrum for light polarized parallel to the field. ΔE_1 is the linear Stark shift due to the proposed dipole moments μ_p induced by disorder.

γ_1 (eV)	$\Delta f/f$	ΔE_2 (eV)	γ_2 (eV)^2	ΔE_1 (eV)	μ_p (D)
3.6×10^{-5}	7.3×10^{-5}	6×10^{-5}	1.2×10^{-5}	5×10^{-3}	48

$$\Delta\alpha = \frac{1}{2}\left\langle \frac{d^2\alpha}{dE^2}(\mu_p F)^2 \right\rangle . \tag{8}$$

The average $\langle(\mu_p F)^2\rangle$ accounts both for random orientation of polymer segments and for distribution of permanent dipole moments around a large mean value of about 50 D.

Evaluation of the electroreflectance spectra of the evaporated film (Fig. 2) is more complicated. A direct comparison of the experimental spectrum with first and second derivatives of the reflectivity suggests much larger energy shifts. However, in contrast to spectra of PDA single crystals, where the reflectivity is almost exclusively determined by the strong and narrow resonances of π-π^* transitions, the influence of transitions at higher energy onto the broad and weak reflectivity of disordered films is not negligible. Because these high-energy transitions are not sensitive to the field the direct comparison of electroreflectance and derivatives of the reflectance overestimates the field effects. Comparison of absorption and electroabsorption spectra obtained by Kramers-Kronig transformation yields much better results in spite of some inaccuracy introduced by performing the transformation of reflectance and electroreflectance spectra. Shape and size of the spectra agree quite well with the data of the spin-cast film, indicating a somewhat smaller contribution of a second derivative line shape.

D. Inversion symmetry in distorted polymer chains

Permanent dipole moments require symmetry breaking in centrosymmetric polymers where states have either even or odd parity. The strong exciton is the transition from the ground state $|1A_g\rangle$ into a state $|1B_u\rangle$. The Stark shift results from coupling of this state to even parity states at higher energy. Calculations indicate many closely spaced levels at higher energy which form a wide band of continuum states in an infinite chain.[6–8] They are also coupled by the field which gives rise to an electroreflectance signal at the edge of these states. If the signal is large like in DCHD,[12] it increases quadratically only for small field strength, followed by a sublinear increase at higher field with spectral broadening, consistent with the Franz-Keldysh effect observed in wide band semiconductors.[29] The Franz-Keldysh effect corresponds to acceleration of an electron by the field over many unit cells and depends sensitively on the crystal quality. Consequently this response is weak in most samples even if the excitons are still narrow.

Defects interrupt the perfect conjugation limiting the size of coherent states. An immediate consequence of the finite size of the system is the replacement of the continuum states by a set of discrete states, with energy gaps increasing with decreasing length of the segments. Coherent motion of the electron through these states is no longer possible and the Franz-Keldysh effect disappears and is replaced by a Stark effect as the field mixes the closely spaced states and couples them to the $|1B_u\rangle$ state. The situation resembles semiconductor quantum wells where confinement of electrons to a thin layer replaces continuum states by a set of discrete levels.

The boundary conditions affect any coherent state which extends over a whole segment. The energy levels will shift, contributing to inhomogeneous broadening but most importantly the symmetry of the states will be changed. Inversion symmetry is lost if the defects on both sides of a segment are different and the new eigenstates contain contributions of either parity. As a result electronic states are no longer centered in a chain segment creating permanent dipole moments.

In order to estimate the size of such defect-induced permanent dipoles, we simulate the boundary conditions by a small potential well with asymmetric barrier height. The boundary condition leads to an envelope function which modulates the amplitude of former eigenstates. Excitons and continuum states behave similarly as long as the Coulomb interaction remains the same which should be valid if the segments are larger than the size of an exciton. Figure 7 shows the envelope function in a 4-nm-long segment, about twice the size of the exciton, terminated by 100-meV-high barriers. An electron mass of 0.1 m_0 of the free-electron mass has been assumed as suggested by the size of the exciton and by field broadening of the Franz-Keldysh effect in DCHD. For symmetric barriers the charge density is centered in the segment, however, the small asymmetry caused by reducing one of the barriers to 80 meV displaces this state towards the lower barrier, equivalent to a dipole moment of 55 D, well within the range needed to explain the second-derivative-type electroabsorption spectra. The dipole moment results from tunneling into the lower barrier and its value thus will decrease with increasing mass, increasing barrier height and decreasing asymmetry. It will also vary strongly with the length of the polymer segment. As shown in Fig. 8 large dipole moments are anticipated in short segments but even in long segments permanent dipole moments appear. Even larger dipoles result if the barrier is thin and electrons tunnel into a neighboring segment leading to states extending over two segments. The model strongly suggests that asymmetric boundary conditions displace the charge density of coherent states on a chain segment resulting for short segments in large dipole moments which seem sufficient to explain the second-derivative-type electroabsorption spectra commonly observed in disordered films. Such dipoles are small in long segments, consistent with the observation that second-derivative-type electroabsorption spectra are absent or weak in single crystals of well ordered chains.

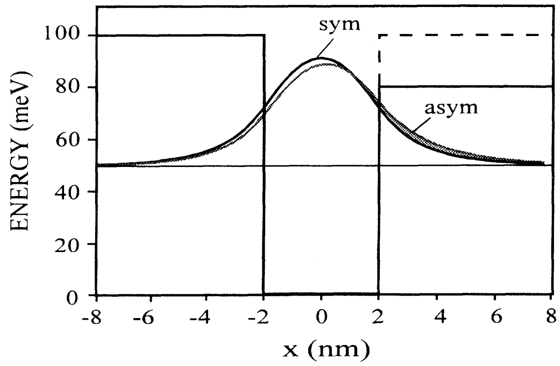

FIG. 7. Electron density related to the envelope function of a state confined by a weak potential to a short polymer segment. Asymmetric barriers lead to displacement of electron density breaking the centrosymmetric distribution of charge.

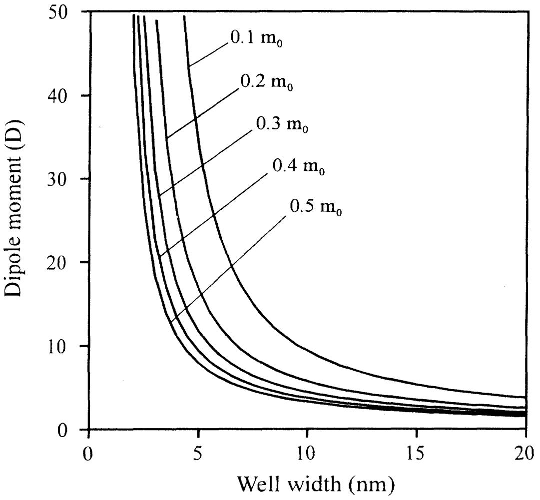

FIG. 8. Variation with length of a segment of dipole moments induced by asymmetric barriers for different electron masses. Barriers 100 and 80 meV high.

It should be noted that the dipole moment μ_p models asymmetric charge distribution in the presence of asymmetric boundaries. Depending on its orientation an external field will enhance or reduce the tunneling into the lower barrier altering again the wave function which leads to a red, respectively, blueshift as in case of a linear Stark effect. For sake of simplicity we model the shift by a linear Stark effect and an average dipole μ_p because detailed calculations require detailed information on the barriers which is not available. It should be pointed out that in the case of symmetric barriers, tunneling results always in a redshift.

V. CONCLUSION

Comparison of the modulated spectra of disordered films of polydiacetylene with those of single crystals provides insight into the influence of disorder on the π electrons in conjugated polymers where disorder restricts the extension of coherent states. The one-dimensional character of the π states is maintained as indicated by the polarization dependence of electroabsorption spectra.

The data in disordered films are compatible with a quadratic Stark effect of the same magnitude as in single crystals. Due to inhomogeneous broadening, changes of the spectra arising from the redshift of transitions are considerably reduced and contributions from concomitant exchange of oscillator strength may contribute to the spectral line shape of modulated spectra.

In the case of electroreflectance spectra a direct comparison with reflectance spectra will suggest a too large energy shift caused by the field unless the reflectivity in the range of interest is dominated by the field sensitive transitions. Although Kramers-Kronig transformed spectra may have some inaccuracy in the spectral line shape, they provide more reliable numbers for the size of the effect. The large response from continuum states at higher energy will disappear in disordered polymers because of the small extension of coherent states.

The quadratic Stark effect is not sufficient to describe the field-modulated spectra of disordered films. A supplementary contribution is observed with spectral line shape corresponding to the second derivative of the absorption spectrum and increasing quadratically with field strength. We propose that this signal arises from a linear Stark effect by disorder-induced dipoles with the linear effect vanishing due to random orientation.

We propose that these dipole moments result from asymmetric boundaries which limit the size of a coherent state on a chain segment. The asymmetry will mix states of different parity displacing the charge density of a state. The dipole moment depends on the size of the segment and is for short segments well in the range needed to explain the second derivative part of electroabsorption spectra.

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