PHYSICAL REVIEW B VOLUME 53, NUMBER 20 15 MAY 1996-II

Wannier excitons and Franz-Keldysh effect of polydiacetylene chains diluted in their single crystal monomer matrix

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(Received 25 September 1995)

Electric field induced changes of the absorption spectra are used to study the π electron states of isolated 4BCMU and 3BCMU polydiacetylene (PDA) chains. The strong excitonic transition, common to all PDA chains, responds to moderate electric fields according to a quadratic Stark effect. Weak transitions below this exciton respond identically. The polarizability of all these excitons is the same and equal to that in fully polymerized PDA's. About 580 meV higher in energy an additional response broadening with increasing field is observed whose amplitude increases sublinearly with field. This behavior is in perfect agreement with what is expected for the Franz-Keldysh effect of continuum states, yielding a reduced mass of only $0.05m_0$. This small mass is consistent with an exciton size of 5 repeat units, estimated from the Stark shift of the excitons. The spectral range of the well resolved Franz-Keldysh oscillations points to a coherence length of π states of 200−400 Å. [S0163-1829(96)02620-3]

I. INTRODUCTION

Polymers with π-conjugated chains show unusual optical properties like strong polarization dependence and large nonlinear optical susceptibilities, which are closely related to the quasi-one-dimensional character of the electronic states.[1–3] Polydiacetylenes with two conjugated bonds in their short repeat unit have extremely large $\chi^{(3)}$ and can be modified by attaching different side groups, which increases the flexibility for technical application. Modeling of the electronic properties of polymers is based on the symmetry of a perfect chain, which is considered as a strongly correlated one-dimensional system.[4–6] Interchain interaction is ignored, partly for lack of experimental information. Polydiacetylenes (PDA's) offer a unique opportunity since some of them can be obtained as macroscopic single crystals by solid state polymerization of monomer single crystals.[7,8] PDAs then avoid the ambiguities that arise from disorder in films; however, in bulk polymer crystals interchain interactions are present.

Polymerization of diacetylenes (DA's) of interest proceeds through monomer-polymer mixed crystals for any polymer content x. If the concentration is kept low ($x<10^{-3}$ in weight, for instance), one can achieve the situation of polymer chains diluted in their single crystal monomer matrix, which is much closer to the theoretical models.[9,10] Although the interchain interaction is suppressed in highly diluted samples, isolated chains are still in a periodic potential imposed by the surrounding monomer crystal. This potential can induce strain on the chain, influencing its optical and electronic properties.

The diacetylenes named 3BCMU and 4BCMU [formula $R-C\equiv C-C\equiv C-R$, with the sidegroup R being $(CH_2)_n-OCO-NH-CH_2-COO-C_4H_9$ with $n=3$ and 4, respectively] were chosen for the present study. Isolated chains can be obtained in both these DA's since thermal polymerization does not occur, and the polymer content can be kept very low and adjusted by controlled low-dose γ irradiation. However, the monomer crystal structures are different. It has been shown by Enkelmann *et al.* that the 3BCMU monomer is monoclinic with a lattice parameter along the chain growth direction of 4.9 Å at 110 K,[11] equal to the usual repeat unit length along the chain in all bulk PDA's.[12] Thus the 3BMCU monomer matrix induces no significant strain on the isolated polymer chains it contains. For 4BCMU, on the contrary, a recent study of the monomer crystal structure using neutron scattering has shown that the unit cell parameter along the chain direction is smaller than in the bulk polymer by 1.4% at 300 K, and this mismatch increases with decreasing temperature to 3% at 15 K.[13] Thus the polymer chains isolated in the 4BCMU monomer are under quite large and temperature-dependent compressive stress.

Low-temperature absorption spectra of both poly-3BCMU and poly-4BCMU isolated chains are dominated by the intense and narrow excitonic line with several associated vibronic replicas. The linewidths are approximately one order of magnitude smaller than those of the corresponding exciton absorption in bulk PDA's. The exciton transition energy at 5 K for the poly-3BCMU isolated chain is 1.90 eV, close to the typical values for bulk PDA's. In the case of poly-4BCMU isolated chains, the exciton transition energy is 1.81 eV at 5 K, considerably less than that observed in bulk poly-4BCMU (1.915 eV at 15 K). This energy increases rapidly with T and at room temperature it becomes equal to the polymer bulk value of 1.97 eV. This rapid shift is interpreted as a consequence of the temperature-dependent strain on the polymer chain.[13] Two electronic transitions below the exciton were observed in both materials, appearing as additional absorption lines, much weaker than the exciton line, but also polarized along the chain direction.[9,10] Their attribution is still an open question.

Delocalized π electron states in single crystals respond sensitively to moderate electric fields resulting in a quadratic Stark shift of the excitons[14–17] and in a few cases also in a Franz-Keldysh effect of the exciton continuum.[18] The excitonic electromodulation experiments probe local properties on a scale of the size of the exciton states. Electroabsorption (EA) spectra of disordered 4BCMU polymer films show additional effects that distort the line shape from that of a redshift by a quadratic Stark effect.[19] The line shape resembles more a second energy derivative of the absorption spectrum, a line shape that prevails also in spectra of other disordered polymers.

In this paper we study the electroabsorption spectra of 4BCMU and 3BCMU polymer chains highly diluted in their respective monomer single crystals to explore their polarizabilities and to resolve differences between the strong exciton, common to all PDA's, and the weak low-energy transitions. We explore further whether these isolated polymer strands show also a Franz-Keldysh effect at the gap to the exciton continuum.

II. EXPERIMENTAL DETAILS

Monomer single crystals of 3BCMU and 4BCMU were grown in the dark at 4 °C from saturated acetone solutions of purified powders. Crystals grow as transparent platelets, 50 to 200 μm thick, with the polymer chain growth direction parallel to the surface. In such crystals, the polymer content is less than 10^{-4} in weight as determined by measuring the optical density at the wavelength of maximum absorption. Higher polymer contents are obtained by controlled γ irradiation.[9] The samples were mounted onto the cold finger of a He flow cryostat. For electroabsorption measurements gap electrodes separated by 0.3 mm were evaporated to apply a field parallel to the chains. A sinusoidal field of 1 kHz frequency was applied and the resulting changes were measured with a lock-in amplifier tuned to twice that frequency. The response at the fundamental frequency was absent or very small, consistent with symmetric contacts and a uniform field. Cooling down the samples frequently caused peeling or cracking of thin evaporated contacts, possibly related to phase transitions that occur in the monomer crystals.[9] This problem was avoided by using thin metal plates gently pressed to the sample surface as contacts, but it turned out that the field was not well defined and deviated notably from the ratio of applied voltage and electrode spacing. These spring loaded contacts, therefore, were used only for measurements on intermediate temperatures but not for quantitative evaluation of the Stark effect. Light source was a tungsten halide lamp filtered by a 1-m grating monochromator to a band pass of about 1 meV. The field-induced change $\Delta\alpha$ was obtained from the thickness d of the crystal and from the field-induced change ΔI of the transmitted light intensity I:

$$\Delta\alpha = -\frac{1}{d}\frac{\Delta I}{I}. \tag{1}$$

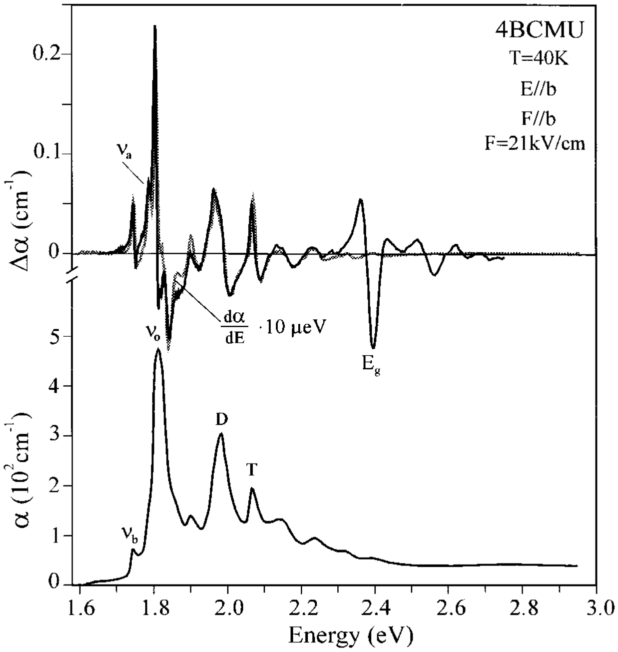

FIG. 1. Comparison of the electroabsorption spectrum (dark line) of diluted 4BCMU chains with the absorption spectrum and its energy derivative (gray line), which describes the excitonic part of the EA spectrum almost perfectly. D and T refer to vibronic satellites of the dominant exciton ν_0, E_g refers to the onset of continuum states. For the weak lines ν_a and ν_b, see text.

III. EXPERIMENTAL RESULTS

A. Spectra of 4BCMU

Figure 1 compares a low-temperature (40 K) electroabsorption spectrum for field and polarization parallel to the chain with the absorption and its derivative with respect to energy. The thickness of the sample was 120 μm and the polymer content estimated from the oscillator strength of the π-π^* transitions was below 10^{-3}. The absorption spectrum is dominated by a strong exciton ν_0 at 1.810 eV; the vibronic satellites, the strongest D at 1.985 eV and T at 2.071 eV, correspond to coupling of the main transition to the stretching modes of the double and triple bonds, respectively. Despite the low polymer content the transmittance near the main peak was in the range of scattered light that prevented an accurate evaluation of its height. We estimate its true height to be at least twice as large. This transition energy is 100 meV lower than in fully polymerized samples. A weak transition, ν_b, is observed at even lower energy near 1.75 eV in all 4BCMU samples with diluted chains.[10] Except for some thermal broadening and a small blueshift by about 2 meV the absorption spectrum agrees well with that measured at lower temperature in a He exchange gas.[9]

A moderate electric field parallel to the chain alters the absorption, giving rise to numerous sharp peaks. This electroabsorption spectrum $\Delta\alpha$ clearly shows another weak transition, ν_a, which in absorption gives rise only to a barely visible shoulder on the main peak. Unresolved vibrational structure leads also to the relatively large width of the vibronic exciton D, which is broader than the other spectral features. Indeed, resonance Raman studies show four clearly

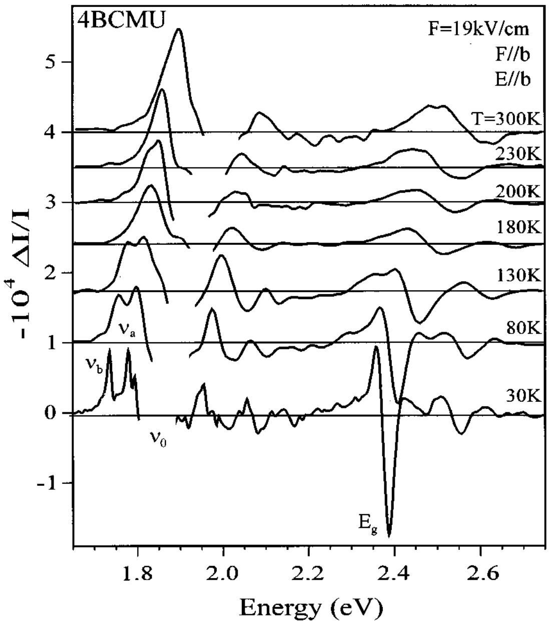

FIG. 2. Variation with temperature of the EA spectrum of 4BCMU with a slightly larger concentration of chains blocking the light in the region of the exciton ν_0.

spaced lines in this region, which are also resolved in the fluorescence spectrum. Below 2.3 eV the signal increases quadratically with field strength and its shape agrees very well with the first derivative of the absorption spectrum. As in other PDA crystals we observe a rigid redshift of the exciton and its vibronic satellites by a quadratic Stark effect.[14–17] The amplitudes match very well to a redshift by 10 μ eV for a field of 21 kV/cm. The weak low-energy transitions ν_a and ν_b show the same shift and have therefore the same polarizability as the strong exciton ν_0. A different signal increasing sublinear with higher fields is observed above 2.3 eV. None of the sharp features there is reproduced by the derivative spectrum. We attribute this signal, which has also its vibronic satellites, to the Franz-Keldysh effect of the continuum states. This effect results from mixing of continuum states and is commonly observed in high-quality semiconductors. In organic materials its distinct features have been observed unambiguously only in DCHD, a PDA with carbazole sidegroups.[18] We assign the first zero crossing at 2.378 eV to the band gap of the isolated chain in 4BCMU. Comparison with the exciton transition energy leads to an exciton binding energy of 570 meV, 85 meV larger than in DCHD.

Figure 2 shows the temperature dependence of the EA spectrum of a sample of slightly larger polymer content as measured with spring loaded contacts. The field has been calibrated to the Stark effect at low temperature of the weak exciton lines, ν_a and ν_b, which are well resolved while in the range of the main exciton, ν_0, the light is blocked by a too large absorption. The excitons show the large blueshift with increasing temperature reported earlier[9] and within spectral resolution the same shift is observed for the band gap E_g. Above 200 K the weak transitions ν_a and ν_b are no longer resolved and disappear in the positive peak resulting from the redshift of the main exciton. 4BCMU monomer crystals have a first-order phase transition at 227 K (Refs. 9 and 13) and absorption and resonant Raman spectra show that ν_a and ν_b disappear in the high-temperature phase. All features of the electroabsorption spectrum broaden rapidly at higher temperature, in particular the signal from the band gap near 2.4 eV, which decreases also rapidly in strength.

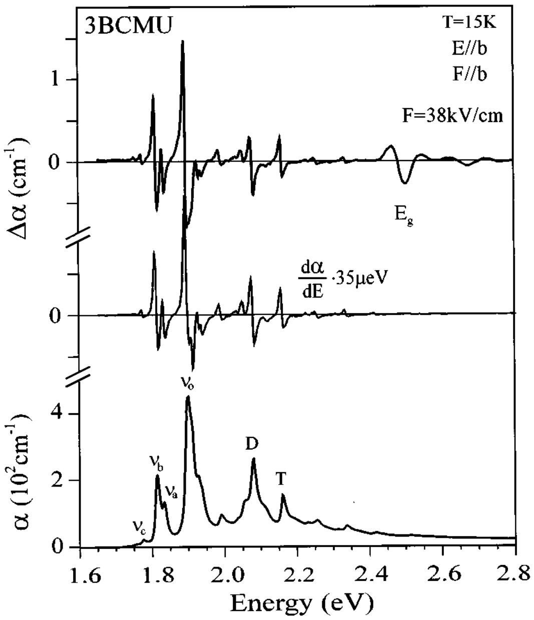

FIG. 3. Comparison of the electroabsorption spectrum of diluted 3BCMU chains with the absorption spectrum and its energy derivative, which again reproduces only the excitonic part of the EA spectrum.

B. Spectra of 3BCMU

It is interesting to compare the spectra of poly-3BCMU diluted chains. Figure 3 displays absorption and electroabsorption spectra at low temperature of a 150-μm-thick sample with a polymer content again below 10^{-3}. The main exciton ν_0 is observed at 1.896 eV where the transmittance again was too low to determine its peak height. The spectral features are even narrower than in 4BCMU and again two excitons of notable strength, ν_a and ν_b, are observed below the transition energy of the main exciton. The absorption spectrum resolves a third low-energy exciton ν_c and indicates a fourth line, ν_d, at 1.756 eV. Above the excitonic transitions vibronic fine structure is resolved with dominant peaks *D* and *T* again attributed to the stretching modes of the π bonds. The narrow linewidth of all spectral features leads also to a very large signal in the electroabsorption spectra where a field of 38 kV/cm alters the absorption by almost 1%. The peak-to-peak width of the excitonic peaks is between 8 and 9 meV as compared to $10-11$ meV in 4BCMU; this is the smallest width observed for any polymer. The excitonic EA spectrum below 2.4 eV increases quadratically with the field strength and its line shape gain agrees with the derivative of the absorption spectrum. All excitonic transitions including their vibronic satellites are redshifted by 35 μ eV in a field of 38 kV/cm. The derivative spectrum shows no resemblance to the relatively broad features above 2.4 eV, which increase sublinearly with the field and which again are attributed to the Franz-Keldysh effect of the con-

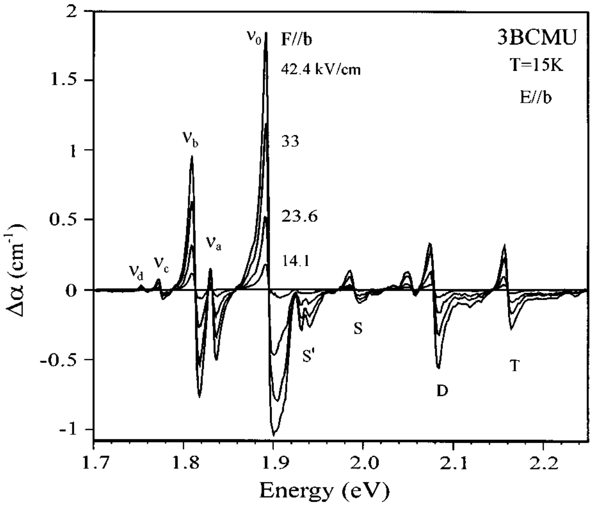

FIG. 4. Variation with field of the excitonic EA spectrum of 3BCMU revealing a line shape, which is independent of the field.

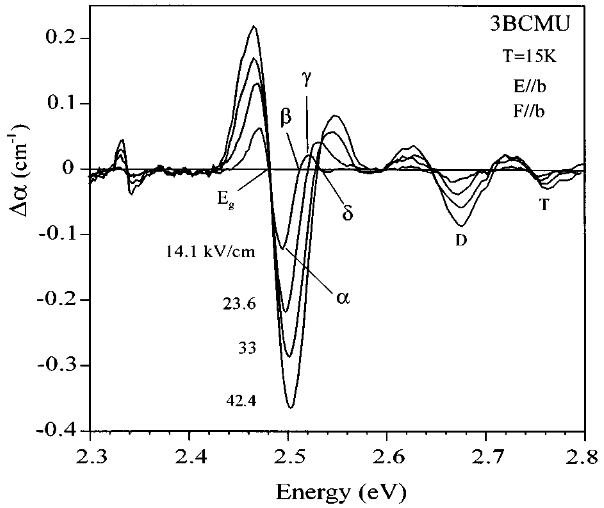

FIG. 5. Field broadening of the high-energy part of the EA spectrum of 3BCMU with extrema and zero crossings shifting away from the gap energy E_g.

tinuum states. The band gap is located at 2.482 eV, corresponding to an exciton binding energy of 586 meV, which is slightly larger than in 4BCMU. The thermal blueshift of the transitions is much smaller in 3BCMU so that at room temperature the excitonic transition energies are not very different in both samples. It is noteworthy that the ν_b exciton that disappears in 4BCMU at 200 K is in 3BCMU still clearly resolved at room temperature.

Figure 4 shows the excitonic part of the electroabsorption spectra for different fields. All transitions show the same behavior. The signal of each transition increases quadratically with field and zero crossings between positive and negative peaks agree perfectly with the positions of the respective absorption peaks. We attribute the zero crossings to the excitonic transition energies; they are listed in Table I together with those of 4BCMU. S,D, and T are vibronic satellites of the main exciton ν_0 and are similar to those observed in bulk PDA's. The doublet S' lies about 100 meV above the weak excitons ν_a and ν_b, which is close to the energy of the vibron S. Unless the vibrational coupling to the weak excitons is very strong, the signals of their vibrational satellites should be much smaller than S' and disappear under the response of vibrational states of the much stronger ν_0 exciton. S' is thus attributed to low-energy vibrations (31 and 40 meV) of the main exciton. Such low-energy vibrations have also been observed in Raman spectra.[13]

None of the excitonic transitions shows any field broadening, which indicates that the field is still a small perturbation of the excitons as expected for a quadratic Stark effect where the redshift determines the line shape of the electroabsorption spectrum. This behavior is in striking contrast to that of the signal attributed to the Franz-Keldysh effect shown in Fig. 5. This signal broadens considerably as the field increases. The first maximum shows a small redshift, while the deep minimum α, the next maximum γ, and the zero-crossing β in between show a blueshift. Only the first zero which is attributed to the gap energy E_g remains fairly stable. In addition the peak amplitudes grow slowly at higher field, a striking contrast to the quadratic increase of the amplitude of the excitonic signals. Both the slow increase of the signal and the field broadening suggest that the field is not a small perturbation of the electronic states involved. It will be shown below that this behaviour is in perfect agreement with the Franz-Keldysh effect. A redshift with field is also observed for the zero δ following the positive peak γ. Its shift, however, is stopped at high fields by the response of a further transition near 2.6 eV, likely to be related to the vibron of about 100 meV which is well resolved in the narrower excitonic spectra.

TABLE I. Electronic transition energies and exciton binding energy R.

	Transition energy (eV)						
	ν_d	ν_c	ν_b	ν_a	ν_o	E_g	R
3BCMU (15 K)	1.756	1.775	1.813	1.833	1.896	2.482	0.586
4BCMU (40 K)			1.747	1.790	1.810	2.378	0.568

IV. DISCUSSION

A. Quadratic Stark effect of the excitons

All excitonic transitions show a common redshift that increases quadratically with field without any change of the spectral line shape, indicating that the field is only a small perturbation. The shift of a state $|l\rangle$ then results from virtual excitation to all levels $|k\rangle$ with nonvanishing electric dipole moment $\overrightarrow{\mu_{lk}}=\langle l|e\vec{r}|k\rangle$ by the field F:

$$\Delta E_l=\sum_k \frac{|\overrightarrow{\mu_{lk}}\cdot\vec{F}|^2}{E_l-E_k}. \tag{2}$$

The shift of an optical transition is the sum of the shifts of ground and excited states. If we assume a negligible shift of the ground state the redshift of the excitons results from their coupling to states at higher energy, which in turn should also respond to an electric field but differently from the transition into the state $|l\rangle$. The only response at higher energy that

TABLE II. Parameters evaluated from the quadratic Stark shift of the excitons.

Material	Polarizability	Dipole moment	ΔE (μ eV)	$\frac{\Delta f}{f}$ (10^{-5})
	p (Å ^{3})	μ (e Å)	F=30 kV/cm	
3BCMU	7120	12.0	22.2	3.8
4BCMU	6480	11.3	20.4	3.6

deviates from the general redshift is the signal attributed to the band gap, about 0.6 eV above the exciton. Presuming that the inversion symmetry of the π-conjugated chains is maintained in the monomer matrix the states in BCMU are either even or odd parity states and all dipole allowed excitons to a ground state of even symmetry A_g must be of odd parity B_u. Their Stark shift therefore involves only even parity states that have a vanishing dipole moment to the ground state and contribute little to the absorption spectrum. If we assume that an even parity state near 2.4 eV is solely responsible for the Stark shift Eq. (2) simplifies to

$$\Delta E_l = \frac{|\vec{\mu}\cdot\vec{F}|^2}{E_l - E_k} = \frac{p}{2}F^2, \tag{3}$$

where μ is the dipole moment between the two excited states and p to the polarizability of the exciton $|l\rangle$. Coupling of states of different parity leads also to transfer of oscillator strength f to the forbidden transition, which is proportional to the energy shift:

$$\frac{\Delta f}{f} = \frac{|\vec{\mu}\cdot\vec{F}|^2}{(E_l - E_k)^2}. \tag{4}$$

The evaluation of the Stark shift of the excitons ν_0 leads to the large polarizability p of the excitons listed in Table II together with the dipole moments μ, which result if the shift is caused by coupling of the excitons to their continuum separated by the exciton binding energy $R = E_k - E_l$. The values depend sensitively on the knowledge of the field and on the derivative of the absorption spectrum. Inaccuracy of the absolute value of the absorption constants resulting from the uncertainty in the concentration of chains, however, has no effect because both the derivative of the absorption and the electroabsorption spectrum scale linearly with this concentration. The small differences are not significant and within experimental resolution all excitons have the same large polarizability. It is noteworthy that the polarizabilities of the excitons of poly-3BCMU and poly-4BCMU chains dispersed in their monomer matrices seem insensitive to the likely stress on the polymer chain. Although the exciton transition energy in 4BCMU is much lower than in 3BCMU, which is interpreted as a consequence of compressive strain in 4BCMU, the polarizabilities and dipole moments are the same. Very similar values have also been obtained for the excitons in fully polymerized poly[2,4-hexadiyne-1,6-diol-bis(p-toluene sulfonate)] (PTS), poly[1,6di(n-carbazolyl)2,4-hexadiyne] (DCHD), and poly[2,4-hexadiyne-1,6-diol-bis(p-fluorobenzene sulfonate)] (PFBS) from electroreflectance spectra.[17]

The transfer of oscillator strength Δf from the exciton to the continuum is in the range of 10^{-5}, more than one order of magnitude smaller than the relative change of the absorption constant and therefore without influence on the line shape of the electroabsorption spectra. If the transition at E_g responsible for the Stark shift of the exciton ν_0 were a forbidden exciton as occasionally proposed[15,16] this transfer of oscillator strength must lead to a peak in the electroabsorption spectrum at E_g growing quadratically with field. Such growth of a forbidden exciton transition has indeed been observed in CuCl.[20] If we assume that this forbidden exciton were as narrow as the other excitons the transfer of oscillator strength to the forbidden state by a field of 38 kV/cm (Fig. 3) should lead to a sharp peak at E_g in the $\Delta\alpha$ spectrum of 3BCMU with an amplitude of 0.06 cm^{-1}. The actual signal there is much larger in spite of a larger width, does not have the shape of a growing peak, and does not increase quadratically with the field. We therefore exclude a forbidden exciton as cause for the signal at E_g.

The dipole moment μ derived from the Stark shift exceeds the repeat unit of the polymer by a factor of 2.5. Such large dipole moments cannot be confined to a unit cell. The excited state must extend well beyond the limit of the repeat unit, which leads to large spatial overlap of translational equivalent states and therefore to wide energy bands. If we consider the excitons as Wannier excitons their Stark shift results from coupling to the continuum[21] and the dipole moment is equivalent to the radius of the exciton in the field direction.[22] The exciton ground state then extends over about 10 π bonds, which seems sufficient to consider it as a Wannier exciton. The radius of the isotropic Wannier exciton scales with the dielectric constant and with the inverse of the reduced mass m^*. If we assume a dielectric constant of the monomer of about 2.5 and attribute the dipole moment to a radius of 12 Å we obtain a reduced mass of $0.1m_0$ and a binding energy of 0.22 eV of an isotropic exciton. We expect, however, the binding energy to be strongly enhanced by the confinement of electron and hole to a single chain coming closer to the observed binding energy of $0.5-0.6$ eV. These values are similar as those derived by Suhai in a Green's-function approach.[23] He found an even larger exciton radius of 25 Å and a binding energy of 0.4 eV.

B. The Franz-Keldysh effect of the continuum

The transitions near 2.4 eV play a key role in the evaluation of the electroabsorption spectra. For a Wannier exciton it is the reference energy, the ionization energy to free carrier states in energy bands $E(k)$, which are classified by their momentum k. In an electric field the plane wave part of a Bloch state is replaced by Airy functions,[24] the solutions of a free particle in a constant field. The resulting changes of the absorption constant scale with the Airy function Ai(ξ), which is an oscillating function of ξ. The argument ξ of the Airy function is the ratio of the excess energy with respect to the gap and a scaling energy $\hbar\theta$, which leads to oscillatory changes $\Delta\alpha$ above the edge of the continuum:

$$\Delta\alpha = \Delta\alpha(\xi), \quad \xi = \frac{E - E_g}{\hbar\theta}. \tag{5}$$

The scaling energy contains the interaction of a free particle of mass m^* with the electric field F:

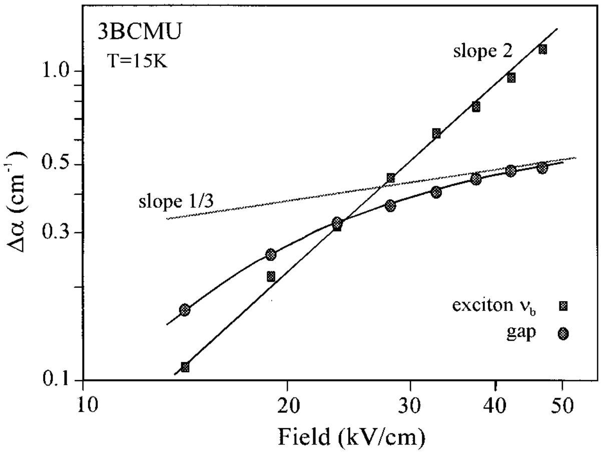

FIG. 6. Field strength dependence of the peak amplitudes of excitonic signals and of the signal at the band gap in 3BCMU. Only the excitons show a quadratic field strength dependence.

$$\hbar\theta = \left[\frac{(e\hbar F)^2}{2m^*}\right]^{1/3}. \tag{6}$$

Field broadening of the electroabsorption spectrum is observed if $\hbar\theta$ becomes comparable to lifetime broadening of the electronic states. Due to its peculiar dependence on the field strength the EA spectrum of band states then should broaden with a $F^{2/3}$ power dependence. If the field is the dominant perturbation of the continuum states the amplitude $\Delta\alpha$ should increase with $F^{1/3}$, a limit rarely approached even in semiconductors.

The different field strength dependences of the excitonic EA spectra and of the response of the continuum states are shown in Fig. 6. The excitonic transitions are represented by the exciton ν_b whose response is not distorted by a too strong absorption. The excitonic response obeys perfectly a quadratic field strength dependence quite in contrast to the peak-to-peak height of the band-gap signal, which deviates already at low fields from the quadratic behavior. At higher field the band-gap signal increases sublinearly and approaches a $F^{1/3}$ power law. Similar deviation from a quadratic field strength dependence has been observed in DCHD, the only fully polymerized polydiacetylene with a similarly large band-gap signal.[18] The different field strength dependence excludes an interpretation of the band-gap signal as a forbidden exciton coupled to the dipole allowed transitions by a quadratic Stark effect.

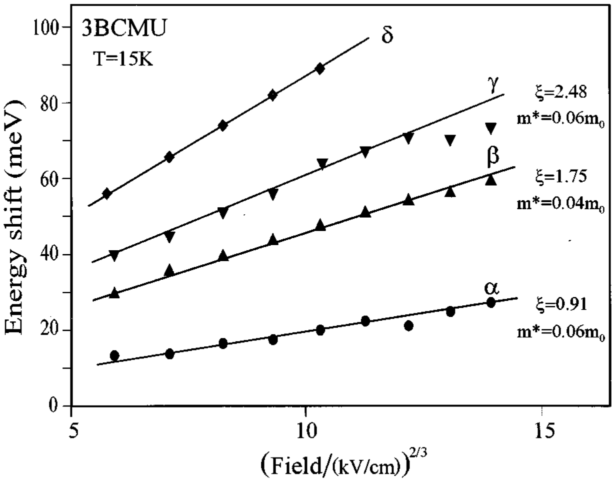

FIG. 7. Shift of distinct points of the band-gap signal in 3BCMU, marked in Fig. 5, with electric field confirming the $F^{2/3}$ power dependence of linewidth broadening of the Franz-Keldysh effect. The points correspond to distinct values of the argument of Airy functions, which allows an estimate of the effective mass.

Linewidth broadening by the field confirms the assignment to the Franz-Keldysh effect. Figure 7 shows the energy separation $E-E_g$ of the peaks and zeros marked in Fig. 5 from the energy gap. These distinct points shift with a $F^{2/3}$ power dependence unique to the Franz-Keldysh effect. Only points further away from the gap energy E_g deviate from the straight line due to interference with a weak vibronic satellites of the band-gap signal. Peaks and zeros correspond to the arguments ξ_j of the Airy function listed on the straight lines. Combining Eqs. (5) and (6) yields a relation between the effective mass, the argument ξ_j, and the slope s_j of the straight lines in Fig. 7:

$$m^* = \frac{e^2\hbar^2}{2}\left(\frac{\xi_j}{s_j}\right)^3. \tag{7}$$

Evaluation of the first three lines yields a mass between $0.04m_0$ and $0.06m_0$. This mass, which depends sensitively on the slope of the straight lines, confirms the value estimated from the Stark shift of the excitons, which provided only an upper limit because it did not account for the reduction of the size of a Wannier exciton by confinement to a single chain. The same mass was obtained from electroreflectance spectra of DCHD, the only organic material so far where such a power dependence of field broadening has been observed.[18] All other polydiacetylene crystals show also about 0.5 eV above the exciton a signal that cannot be described by the derivative of the reflectance spectrum, but this response is small and maintains a quadratic field strength dependence, typical for the case where the field cannot compete with other broadening mechanisms. The mass is surprisingly small for an organic solid but consistent with the large changes of the absorption constant at moderate fields, which is comparable to those in semiconductor single crystals of high quality and small effective mass. It implies a large bandwidth and a high electron mobility on the chain. Bandwidths of about 3.5 eV for both the conduction and valence bands including polaron effects were derived for PTS,[23] consistent with the small reduced mass derived from the Franz-Keldysh effect.

The range of oscillations of the Franz-Keldysh effect is related to the coherence length of band states.[25] Field broadening can be expected only if the potential due to the external field across the size of a coherent state exceeds inhomogeneous broadening or competing lifetime broadening. For a field of 20 kV/cm where interference with other transitions is avoided Franz-Keldysh oscillations extend about 70 meV beyond the gap, which points to a coherence length of 350 Å, about 70 repeat units. This coherence length can be viewed as the mean free path between scattering events that destroy coherence. A mean free path of 350 Å is difficult to achieve in linear chains because it requires perfect alignment over

TABLE III. Vibronic energies measured from the respective transition.

	Material			
	3BCMU		4BCMU	
	Electronic transition			
	ν_0	E_g	ν_0	E_g
D' (meV)	31		27	
	40			
S (meV)	96		99	
D (meV)	183	164	179	163
T (meV)	265	261	265	$\sim$252
2 D (meV)	359		328	
$D+T$ (meV)	442		426	
2 T (meV)	523		507	
2 D $+T$ (meV)	620		583	
2 T $+D$ (meV)	705		678	

such a distance. This is probably the reason why field broadening and a large signal of the Franz-Keldysh effect at moderate fields is rarely observed. The Stark effect of the excitons is much less sensitive because of their much smaller size. Defects of the chain on a scale larger than its size of about 5 repeat units will cause inhomogeneous broadening, which increases the linewidth and reduces the amplitudes of the excitonic electroabsorption spectrum; the Stark shift itself, which depends only on the presence of even parity states near the gap should be the same even if the band edge is strongly broadened by disorder.

C. Low-energy excitons

The weak low-energy excitons have up to now only been observed on these BCMU's. Their intensities relative to the main exciton ν_0 are about 1/20 in 3BCMU and 1/30 in 4BCMU with little variation among different samples. A possible interpretation of the weak transitions would be their assignment to forbidden excited states below the main exciton. Model calculations predict besides the dipole allowed B_u states also even parity states A_g, which play an important role in the interpretation of nonlinear optical properties. The position of these A_g states, above or below the strong B_u exciton is still controversial.[4,5,26,27] Although forbidden transitions may gain some strength by vibronic coupling or by internal fields,[28] the absorption by the ν_b exciton seems too strong for a forbidden transition. A forbidden exciton furthermore is inconsistent with the Stark effect. Field coupling of an even parity state to the higher-lying B_u exciton results according to Eq. (2) in different shifts of the two transitions. Because of its relative small separation from the B_u state transfer of oscillator strength [Eq. (4)] would contribute considerably to the signal, causing significant deviation from the line shape of a first derivative. The fact that all excitonic transitions have the same redshift excludes their mutual coupling by the field. In 3BCMU and 4BCMU all the low-energy excitons observed differ from the strong ν_0 transition by their transition energy only. The polarizability that depends on the size of the states and on the sequence of energy levels is the same, which strongly suggests that all excitons are the same B_u exciton but on different chains.

This conclusion is supported by resonance Raman experiments using an excitation wavelength corresponding to the different absorption maxima of ν_0, ν_a, and ν_b excitons. The double bond stretching vibrational frequencies show small but distinct differences for different excitation wavelength.[13] Since these frequencies relate to the ground state, these excitons correspond to different ground states and, therefore, they lie on different chains. Pump-probe photobleaching experiments have shown that also the kinetics of absorption recovery of all lines have the same time dependence,[13] which confirms further that these exciton states are not coupled. Another evidence for their spatial separation is that luminescence spectra of diluted 4BCMU chains show the same transitions in comparable strength as the absorption spectrum.[9] If the excitons were not spatially separated the excited state would thermalize down to the lowest level.

Since for all excitons the vibrational frequencies in the ground state are not very different, and in the excited states as well (Table III), and since the polarizabilities are equal within experimental accuracies, we assume that the conformations of the different chain populations are very similar. Assuming that the oscillator strengths are the same, the relative absorption intensities (1/20 and 1/30) correspond to population concentration ratios. The small differences in transition energies would then mainly be due to different environments. The fact that the excitons ν_a and ν_b disappear in the room-temperature phase of 4BCMU is a further indication of the importance of the environment. These different environments must be well defined to account for the distinct transition energies and the narrow linewidth of all transitions. A working hypothesis that agrees with all we know at present on these materials is to assume that the lower-energy excitons lie on chains that are nearest (or possibly next-nearest) neighbors to a stacking fault. Both 3BCMU and 4BCMU are lamellar crystals in which a stacking fault would be a plane of mismatch between two successive lamellae, which are parallel to the crystal (b,c) plane. These faults are produced during crystal growth, and their number remains constant in a given sample thereafter. Indeed, the intensities of the weak lines relative to the main one seem to be, in a given sample, independent of temperature as long as it can be resolved. However, slight differences from sample to sample are possible, and are, at least in 3BCMU, observed. A stacking fault is expected to have a well-defined, though small, effect on the conformation of polymer chains near to it, hence the observation of sharp absorption lines and well-defined excitons, only slightly different from the main one.

V. CONCLUSIONS

Diluted π-conjugated polymers in their single crystalline monomer matrix show properties of a quantum wire with a one-dimensional electron gas of small effective mass and Wannier type excitons extending over 10 π bonds or 5 repeat units. Very little oscillator strength is found for transitions into the exciton continuum. The optical transitions in isolated chains are much narrower than in fully polymerized material. This enables better resolution of excitons including their vibronic satellites and the observation of field broadening of the Franz-Keldysh effect at the band gap, which agrees well with the predictions of band-structure theory. The binding energy and the polarizability of the excitons is almost the same in 3BCMU and 4BCMU and very similar to fully polymerized PDA's. We conjecture that the basic properties of the polydiacetylenes, their conjugation, which determines the sequence of electronic states, and the effective mass of the exciton continuum are insensitive to the sidegroup attached and to the environment. The transition energy from the ground state on the other hand differs considerably between 3BCMU and 4BCMU and among fully polymerized material. We assign these differences to the interaction of the chain with its environment and, in particular, to the compressive strain on isolated chains in 4BCMU. Observation of the Franz-Keldysh effect requires large coherence length, which needs well aligned chains and a homogeneous environment. The necessary homogeneity exists in the monomer crystals so that field broadening of the Franz-Keldysh effect occurs in diluted chains of BCMU but with the exception of DCHD not in fully polymerized material.

Below the strong exciton B_u common to all polydiacetylenes the diluted chains of BCMU show additional weaker excitons. The origin of these states is not clear yet. They show a Stark shift identical to that of the B_u exciton, which excludes their assignment to even parity states with spatial overlap to the dominant B_u exciton and suggests that they are excitons from chains in a different environment. The narrow linewidth and the well-defined transition energies exclude fluctuations in the matrix as an explanation and can be understood only if different but well-defined environments exist that shift the energy level but have otherwise little impact on the π electrons.

ACKNOWLEDGMENT

We thank the Deutsche Forschungsgemeinschaft and the SFB 383 for financial support. We are grateful to Dr. J. Berréhar for preparation of the samples and in particular for growing the high-quality crystals.

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