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Polarized-electroabsorption spectroscopy of a soluble derivative of poly(*p*-phenylenevinylene) oriented by gel processing in polyethylene: Polarization anisotropy, the off-axis dipole moment, and excited-state delocalization

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We present the polarized electric field modulation spectra of dilute blends of the conjugated polymer poly[2-methoxy,5-(2′-ethyl-hexoxy)-*p*-phenylenevinylene] (MEH-PPV) oriented in ultrahigh-molecular-weight polyethylene (PE). The photoluminescence and electric-field-modulation spectra of tensile drawn MEH-PPV/PE blends are highly anisotropic, with preferred polarization parallel to the draw axis; the field-induced absorption and photoluminescence demonstrate polarization anisotropies in excess of 150:1 and 60:1, respectively. Because of the orientation, the enhanced order, and the dilution of the MEH-PPV conjugated polymer in the polyethylene matrix, the MEH-PPV/PE blend is an ideal system in which to investigate the intrinsic linear and nonlinear optical properties of oriented conjugated polymer chains. The absorption is directly proportional to the imaginary part of $\chi^{(1)}(\omega)$, and the electroabsorption is directly proportional to the imaginary part of $\chi^{(3)}(\omega,0,0)$ of the ordered MEH-PPV π-electron system. The optical data obtained from the oriented blends are therefore directly relevant to existing theoretical models which do not account for disorder. Using a model for the off-axis transition dipole moment of the conjugated polymer, which is based on the measured off-axis transition dipole moment of *trans*-stilbene and the geometric structure of MEH-PPV, we demonstrate that the observed anisotropy of 150:1 in the field-induced absorption requires that the instantaneous excited-state wave functions are delocalized over a minimum of 50 unit cells (400 Å).

I. INTRODUCTION

Although the linear and nonlinear optical properties of conjugated polymers have been investigated for over a decade, there is still controversy over the description of the elementary excitations in these systems. The central issue is the relative strengths of the electron-electron and the electron-phonon interactions. In nondegenerate-ground-state polymers these two interactions result in both lattice and Coulomb contributions to the binding energy of the excited-state wave function, which is generally referred to as a polaron-exciton. In poly(*p*-phenylenevinylene), PPV, and its derivatives, steady-state, site-selective, and time-resolved photoluminescence measurements have demonstrated that the lattice relaxation energy is rather small, less than 100 meV.[1-3] As a result, the discussion has been focused on the magnitude of the exciton binding energy and the spatial extent of the excited-state wave function.

In order to investigate the *intrinsic* properties of the quasi-one-dimensional electronic system, one needs conjugated polymer samples of sufficient order such that the optical properties of the material are not dominated by defects, impurities, or disorder. In a previous study, Hagler *et al.*[1] demonstrated that the structural order of MEH-PPV could be significantly enhanced by fabricating oriented, dilute blends of the conjugated polymer in an ultrahigh-molecular-weight polyethylene matrix. When compared to cast films of the pure polymer MEH-PPV, the oriented blends displayed a sharpening of the vibronic structure and a redistribution of spectral weight into the zero-phonon line in both absorption and emission for light polarized parallel to the draw axis. In these samples, the induced order was sufficient to determine that the intrinsic line shape of the absorption was highly asymmetric, and could be modeled accurately in terms of a Gaussian-broadened square-root singularity in the joint density of states, the characteristic signature of a one-dimensional band structure.

In contrast, Bassler and co-workers,[2-6] citing the results of site-selective fluorescence measurements on a variety of morphologically distinct samples, have concluded that the elementary excitations in PPV and its derivatives are highly localized Frenkel/Wannier excitons residing on conjugated segments delineated by disorder. This picture provides an alternative explanation of the absorption spectrum of the oriented blend, in which the observed absorption line shape is derived from a superposition of finite conjugated segments. Since the energy eigenstates are assumed to be tightly bound excitons, the absorption line shapes of the individual conjugated segments are inherently symmetric; the measured asymme-

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try simply reflects the segment distribution function and the conjugation length dependence of the $\pi - \pi^*$ energy gap.

These competing interpretations predict vastly different physical pictures for the excited-state wave functions of PPV and its derivatives, from Bloch states delocalized over a structurally ordered lattice[1] to highly localized Frenkel/Wannier excitons residing on conjugated segments delineated by disorder.[2–4,6] The principal differences between these two models are the spatial extent (coherence length) of the energy eigenstates and the intrinsic line shape of the absorption. Hence, a critical examination of either model requires knowledge of both the spectral content of the joint density of states and the spatial extent of the excited-state wave functions. A line-shape analysis in conjunction with an independent measurement of the spatial extent of the energy eigenstates would therefore provide considerable insight into the relative importance of disorder and excitonic effects in conjugated polymers.

Electric-field-modulation spectroscopy (EFMS) has recently become a valuable tool in the investigation into the electronic structure of conjugated polymers. One of the most important aspects of EFMS is that it preferentially samples only the longest conjugated segments in a given sample. Since the electro-optic response is proportional to $\chi^{(3)}(\omega, 0, 0)$ and $\chi^{(3)}$ has been demonstrated both theoretically[7–9] and experimentally[10] to depend strongly on the localization length of the energy eigenstates, EFMS probes only the longest and most ordered conjugated segments in a given sample. Hence, the information obtained from EFMS is more directly related to the intrinsic electronic properties of the pristine material, and is, therefore, more relevant to theoretical models which do not account for disorder.

We present an independent measurement of the spatial extent of the excited-state wave function based on the analysis of the polarized electric-field-modulation spectra of dilute blends of MEH-PPV oriented in polyethylene, MEH-PPV/PE. The oriented blends demonstrate electroabsorption and photoluminescence polarization anisotropies in excess of 150:1 and 60:1, respectively. Because of the orientation, the enhanced order, and the dilution of the MEH-PPV conjugated polymer in the polyethylene matrix, the MEH-PPV/PE blend is an ideal system in which to investigate the intrinsic linear and nonlinear optical properties of oriented conjugated polymer chains; the absorption is directly proportional to the imaginary part of $\chi^{(1)}(\omega)$ and the electroabsorption is directly proportional to the imaginary part of $\chi^{(3)}(\omega, 0, 0)$ of the ordered MEH-PPV π-electron system. The optical data obtained from the oriented blends are therefore directly relevant to theoretical models which do not account for disorder. Using the published results for the off-axis transition dipole moment in *trans*-stilbene,[11] we demonstrate that the intrinsic energy eigenstates of MEH-PPV are highly delocalized; the observed polarization anisotropy of the field-induced absorption requires that the instantaneous excited-state wave functions extend over a minimum of 50 unit cells, corresponding to roughly 400 Å.

II. EXPERIMENTAL DETAILS

The preparation of the oriented MEH-PPV/PE blends has been described previously.[1] The oriented sample used to obtain the polarized electroabsorption spectrum is the same sample that was used for the polarized absorption and photoluminescence studies presented in Ref. 1. The sample is 1% MEH-PPV incorporated into an ultrahigh-molecular-weight polyethylene host, and tensile drawn to approximately 50 times the original length.

The apparatus used to investigate the electroabsorption spectra consists of a 0.3 m single grating monochromator outfitted with a 500 nm blaze grating ruled 1200 lines/mm and a mechanically chopped tungsten-halogen light source. The optical resolution at the exit slits was chosen to be between 1 and 5 nm, depending on the application. To facilitate the study of polarization dependent effects, an uv/vis dichroic sheet polarizer (MG 003FPG 005) is inserted just before the sample on a rotational stage.

The electric field was applied to the oriented blends by biasing two 127-μm platinum wires which were separated by 1 mm and press-fit into the free-standing films by sandwiching the film and the wires between a Delrin faceplate and a zero-orientation sapphire substrate. This assembly fit into a copper sample holder which was mounted on the cold finger of a vacuum cryostat. Typical pressures in the evacuated cryostat were on the order of 10^{-5} torr. The oriented samples were carefully mounted to ensure that the applied electric field was parallel to the draw axis; based on the analysis of the polarization dependence, the free standing films were routinely oriented within 1° of the draw axis.

The high voltage was provided by a Trek 10/10 high-voltage power amplifier driven by a Hewlett Packard audio oscillator. Using the load configuration described above, the power amplifier was capable of providing 10 kV at 5 kHz. Hence, electric field strengths of 10^5 V/cm were available for measuring the electro-optic response of the oriented blend.

The transmitted light was detected by a silicon photodiode and the output was sent simultaneously to an analog-digital (A-D) converter, and to a lock-in amplifier (Stanford Research SR-530), which was referenced to twice the applied field modulation frequency, 2Ω. Since the lock-in amplifier only measures the modulated component of the transmitted light, the ratio $-\Delta T/T$ is obtained by simply dividing the voltage measured by the lock-in amplifier by the voltage measured by the A-D converter. Although considerable effort was made to enhance the signal-to-noise ratio by shielding the detection system and eliminating ground loops, the extremely large voltages required for the experimental geometry used to probe the oriented blend resulted in a modulated noise signal at 2Ω of roughly 2 μV at 4 kV.

We emphasize that the polarized photoluminescence presented in Ref. 1 and the EFM spectra presented below were measured on precisely the same sample. The tensile drawn films were approximately 1 m in length and individual segments demonstrated excellent reproducibility in all optical measurements. Identical measurements were carried out on two independently prepared samples with good qualitative reproducibility; however the anisotropy in EFMS and photoluminescence were somewhat different for the two samples: (60:1 vs 150:1 for EFMS and 30:1 vs 60:1 for PL). The data presented in detail here and in Ref. 1 are representative of the sample with the highest anisotropy.

III. THE POLARIZATION DEPENDENCE OF $-\Delta T/T$

We first examine the polarization dependence of the measured nonlinear response, $-\Delta T/T$, with respect to the applied electric field. The objective is to demonstrate that the observed polarization dependence is related to the magnitude of the off-axis component of the dominant ground state (G) to excited state (${}^kB_u$) transition dipole moment.

The nonlinear wave equation describes the propagation and generation of electromagnetic fields in the system due to the the applied dc electric field perturbation and the incident optical field, and is therefore the most general description of electro-optic phenomena, describing both electroabsorption and electroreflectance. In this analysis we will focus exclusively on the field-induced absorption; the corresponding expressions for the electroreflectance can be obtained by applying the appropriate boundary conditions. For the electroabsorption measurements on the oriented MEH-PPV/PE blend, the applied dc electric field is along the drawing axis, henceforth referred to as the X axis, and the optical polarization makes an angle of θ with respect to the electric field. Using the definitions of the complex linear dielectric function, $\tilde{\epsilon} = 1 + 4\pi\chi^{(1)} = N_0^2$, and the complex linear refractive index, $N_0 = n_0 + i\kappa_0$, the nonlinear wave equation describing the modulation of the optical field, $\mathbf{E}(k,\omega)$, by the applied dc electric field, $\mathbf{F}(\Omega)$, can be written as

$$\frac{\partial^2}{\partial z^2}\mathbf{E}(k,\omega,z) + \left[k_0 N(\omega;2\Omega)\right]^2\mathbf{E}(k,\omega,z) = 0, \tag{1}$$

where $k_0 = \omega/c$ is the free space wave vector of the optical field, and $N = N_0 + \Delta N$ is the complex refractive index in the presence of the applied dc electric field,

$$\begin{aligned} N^2(\omega;2\Omega) &= 1 + 4\pi\chi_{IL}^{(1)}(\omega)\ (\hat{\theta}\cdot\hat{I})(\hat{\theta}\cdot\hat{L}) \\ &\quad + 4\pi\chi_{IJKL}^{(3)}(\omega,0,0) \\ &\quad \times (\hat{\theta}\cdot\hat{I})(\mathbf{F}\cdot\hat{J})(\mathbf{F}\cdot\hat{K})(\hat{\theta}\cdot\hat{L})\ e^{i2\Omega t}. \end{aligned} \tag{2}$$

In writing Eq. (2), we have used the experimental observation that the electroabsorption line shape tends to resemble a positive derivative of the unperturbed absorption coefficient. This dictates that the subscripts I and L refer to the matrix elements associated with the optical field and J and K refer to matrix elements associated with the applied dc electric field.[12]

In order to extract information pertaining to the microscopic electronic structure of the individual MEH-PPV conjugated polymer chains from the polarization dependence of the field-induced absorption, we must define the relationship between the macroscopic and the microscopic linear and nonlinear susceptibility/polarizability tensors. The linear susceptibility is defined in terms of $\alpha_{il}^{(1)}(\omega)$, the microscopic linear polarizability

$$\chi_{IL}^{(1)}(\omega) = \frac{1}{V}\,\alpha_{il}^{(1)}(\omega), \tag{3}$$

where V is the average volume per MEH-PPV conjugated polymer chain. A similar expression relates the macroscopic nonlinear susceptibility to $\gamma_{ijkl}^{(3)}(\omega:\omega,\Omega,\Omega)$, the microscopic third-order nonlinear polarizability

$$\chi_{IJKL}^{(3)}(\omega:\omega,\Omega,\Omega) = \frac{1}{V}\,\gamma_{ijkl}^{(3)}(\omega:\omega,\Omega,\Omega). \tag{4}$$

In Eqs. (3) and (4) the upper-case subscripts refer to the macroscopic coordinate system of the oriented sample and the lower-case subscripts refer to the microscopic coordinate system of the individual conjugated polymer chains. Because of the high degree of orientation of the MEH-PPV polymer chains within the polyethylene matrix, the microscopic and macroscopic coordinate systems approximately coincide. Note that because of the dilution factor we have neglected all local-field correction factors which are easily shown to be of order unity.

The polarization dependence of the unperturbed transmission is given by

$$\begin{aligned} T(\theta) &= T_{\parallel}\cos^2(\theta) + T_{\perp}\sin^2(\theta) \\ &= I_0\left[\cos^2(\theta)\ e^{-\alpha_{\parallel}d} + \sin^2(\theta)\ e^{-\alpha_{\perp}d}\right], \end{aligned} \tag{5}$$

where d is the sample thickness, and

$$\begin{aligned} \alpha_{\parallel}(\omega) &\equiv k_0\,\frac{1}{n_0}\,\frac{4\pi}{V}\,\mathrm{Im}\{\alpha_{xx}^{(1)}(\omega)\}, \\ \alpha_{\perp}(\omega) &\equiv k_0\,\frac{1}{n_0}\,\frac{4\pi}{V}\,\mathrm{Im}\{\alpha_{yy}^{(1)}(\omega)\}, \end{aligned} \tag{6}$$

are the absorption coefficients for optical polarization parallel and perpendicular to the polymer chain axis.

The modulated component of the transmission is found by inserting both Eqs. (3) and (4) into the nonlinear wave equation and integrating over the sample thickness. The polarization dependence of the relative measurement, $-\Delta T/T$, is then given by[13]

$$-\frac{\Delta T}{T} = d\,\frac{T_{\parallel}\Delta\alpha_{\parallel}\cos^2(\theta) + T_{\perp}\Delta\alpha_{\perp}\sin^2(\theta)}{T_{\parallel}\cos^2(\theta) + T_{\perp}\sin^2(\theta)}, \tag{7}$$

where

$$\begin{aligned} \Delta\alpha_{\parallel}(\omega) &\equiv k_0\frac{1}{n_0}\frac{4\pi}{V}\mathrm{Im}\{\gamma_{xxxx}^{(3)}(\omega,\Omega,\Omega)\}F^2(\Omega), \\ \Delta\alpha_{\perp}(\omega) &\equiv k_0\frac{1}{n_0}\frac{4\pi}{V}\mathrm{Im}\{\gamma_{yxxy}^{(3)}(\omega,\Omega,\Omega)\}F^2(\Omega), \end{aligned} \tag{8}$$

are the field-induced absorption coefficients for optical polarization parallel and perpendicular to the polymer chain axis.

In practice, the chains of an oriented sample are never perfectly aligned, but rather fall within a range of angles about the drawing axis. We define the angle, ϕ_{mos}, of the mosaic spread of a system of N_c chains to be

$$\tan(\phi_{\rm mos}) = \frac{1}{N_c}\sum_{i=1}^{N_c}\left|\frac{\hat{y}_i\cdot\hat{X}}{\hat{x}_i\cdot\hat{X}}\right| = \frac{1}{N_c}\sum_{i=1}^{N_c}|\tan(\phi_i)|, \tag{9}$$

where $\hat{X}$ is the unit vector along the macroscopic drawing axis and $\hat{x}_i$ and $\hat{y}_i$ are the unit vectors parallel and perpendicular to the long axis of the ith polymer chain. By measuring the ratio of $-\Delta T/T$ for optical polarization parallel and perpendicular to the draw axis in oriented materials we obtain a convolution of the mosaic spread of the polymer chains and the magnitude of the off-axis component of the dominant G to ${}^kB_u$ transition dipole moment

$$\rho \equiv \frac{\Delta T/T(90^\circ)}{\Delta T/T(0^\circ)} \approx \frac{\Delta\alpha_\perp}{\Delta\alpha_\parallel} + \frac{T_\parallel}{T_\perp}\tan^2(\phi_{\rm mos}). \tag{10}$$

Since the applied dc electric field is fixed along the drawing axis, the ratio $\Delta\alpha_\perp/\Delta\alpha_\parallel$ is a direct measurement of the angle, ϕ_d^p, of the G to ${}^kB_u$ transition dipole moment with respect to the conjugated polymer axis

$$\frac{\Delta\alpha_\perp}{\Delta\alpha_\parallel} = \frac{{\rm Im}\{\gamma^{(3)}_{yxxy}(\omega,\Omega,\Omega)\}}{{\rm Im}\{\gamma^{(3)}_{xxxx}(\omega,\Omega,\Omega)\}} = \frac{|r_\perp|^2}{|r_\parallel|^2} \equiv \tan^2(\phi_d^p), \tag{11}$$

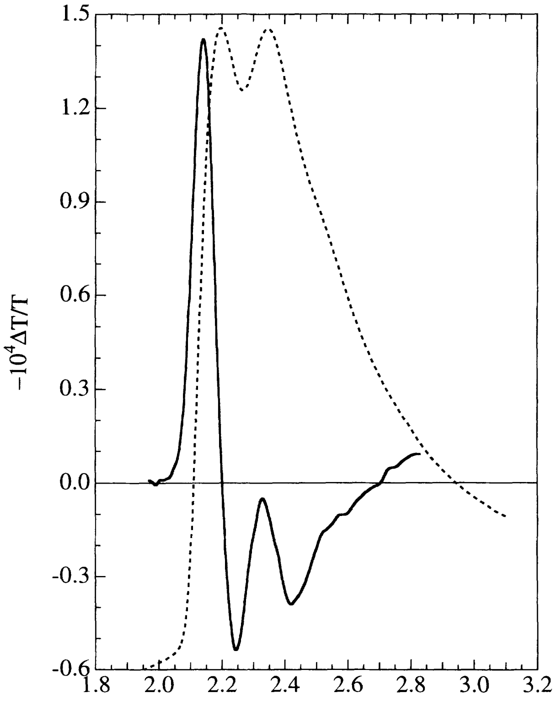

FIG. 1. The 80 K absorption and electroabsorption spectra for an *oriented* (× 50) thin film of MEH-PPV/PE for optical and electric field polarization parallel to the drawing axis. The applied field strength is 40 kV/cm (amplitude). The ratio of the field-induced absorption maximum at 2.14 eV to the minimum at 2.24 eV is 3:1, indicating that the intrinsic line shape is highly asymmetric. The line-shape asymmetry is clearly evident in the linear absorption spectrum as well.

where the off-axis component of the transition dipole moment is defined as

$$\mathbf{r}_\perp = \langle {}^kB_u|\mathbf{y}|G\rangle = \int d\mathbf{r}\ \psi^\dagger_{{}^kB_u}(\mathbf{r})\ \mathbf{y}\ \psi_G(\mathbf{r}). \tag{12}$$

By analyzing the polarization dependence of the fluorescence excitation spectrum and the decay of fluorescence polarization anisotropy, Hudson and coworkers[14–16] have demonstrated that the off-axis transition dipole moment of several finite polyenes is as large as 15°.

IV. EXPERIMENTAL RESULTS

In Fig. 1 we show the 80 K absorption and electroabsorption spectra of an oriented, free-standing film of MEH-PPV/PE for optical and electric field polarization parallel to the draw axis, and an applied field strength of 40 kV/cm. The magnitude of the field-induced absorption was found to be linear in the intensity and scaled quadratically with the applied dc electric field. The electroabsorption line shape of the oriented blend resembles the first energy derivative of the unperturbed absorption spectrum, and is independent of the magnitude of the

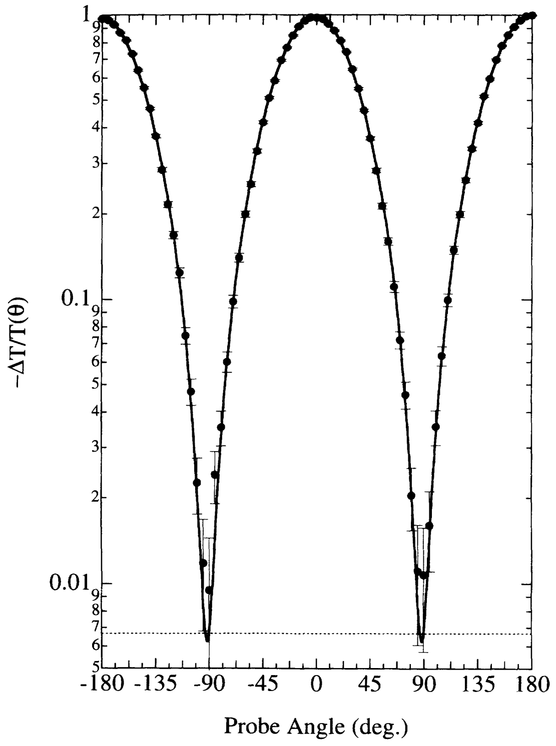

FIG. 2. The polarization dependence of the field-induced absorption with respect to the optical field for the oriented MEH-PPV/PE blend. The solid line is a fit to Eq. (7). Note that over the entire spectral range investigated, the perpendicular component of the field-induced absorption was not detectable; the error bars reflect the noise level of the experimental apparatus, which was approximately 2 μV. The fitting parameters demonstrate a polarization anisotropy in the field-induced absorption in the oriented blend in excess of 150:1.

applied electric field up to the maximum field applied, 40 keV/cm. At higher voltages, a corona discharge was observed emanating from the platinum wires.

The figure demonstrates that the absorption and electroabsorption line shapes of the oriented blend are highly asymmetric. The onset of the nonlinear absorption is extremely sharp and crosses zero only twice; once at 2.20 eV and again at 2.70 eV. The ratio of the field-induced absorption maximum at 2.14 eV to the minimum at 2.24 eV is approximately 3:1. It is straightforward to show that the electroabsorption line shape for a system with a symmetric density of states will have a maximum to minimum ratio of 1:1.

The data presented in Fig. 1 should be contrasted with the electroabsorption spectra of disordered and nonoriented PPV,[17] PTV,[18] and of single crystals of DCH-PDA,[19,20] all of which exhibit broad field-induced absorption onsets, maximum to minimum ratios of approximately 1:1, and several zero crossings. A detailed analysis of the MEH-PPV/PE electroabsorption line shape will be presented in a subsequent publication.[21]

Figure 2 shows the polarization dependence of the field-induced absorption measured at 2.14 eV with respect to the optical field, the circles are the data, and the solid line is a fit to Eq. (7). Note that over the entire spectral range investigated, the perpendicular component of the field-induced absorption was not detectable; the error bars reflect the noise level of the experimental apparatus, which was approximately 2 μV at 4 kV applied bias. From the fit and Eq. (10), we find that $\rho^{-1} > 150 : 1$. Hence, the polarized electroabsorption data demonstrate a field-induced nonlinear refractive index anisotropy in excess of 150:1, the largest ever reported.[22]

V. RESULTS AND DISCUSSION

A. The off-axis transition dipole moment and excited state delocalization

In Fig. 3 we show the molecular structure of *trans*-stilbene. It is clear from the symmetry of this planar π-conjugated molecule that the transition dipole moment is predominantly polarized along the long axis of the molecule, which bisects the centers of the two phenyl rings.[23] The effect of the ethylenic unit is to rotate the angle of the transition dipole moment away from the molecular axis and towards the axis of the double bond, which results in an off-axis component of the transition dipole moment.[24] Using polarized ir and uv-vis absorption spectroscopy, Uznanski, Kryszewski, and Thulstrup[11] demonstrated that the $\pi-\pi^*$ transition dipole moment of *trans*-stilbene makes an angle of approximately 20° with respect to the long axis of the molecule. In the following analysis, we shall assume that the off-axis dipole moment of the MEH-PPV repeat unit is equivalent to that measured in *trans*-stilbene.

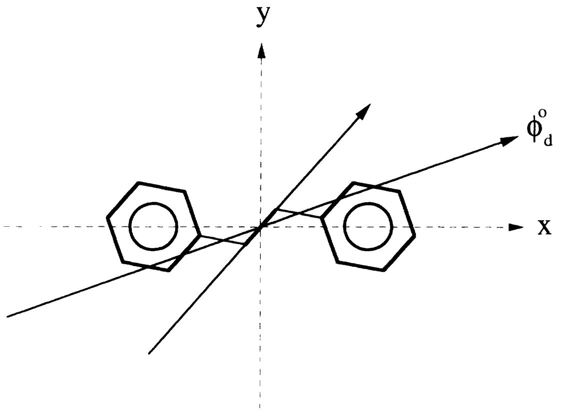

FIG. 3. The molecular structure of *trans*-stilbene. The effect of the ethylenic unit is to rotate the angle of the transition dipole moment away from the molecular axis and towards the axis of the double bond, which results in an off-axis component of the transition dipole moment (Ref. 24). The measured angle of the transition dipole moment is labeled by ϕ_d^0 (See Ref. 11).

In Fig. 4(a) we show one possible conformation of the conjugated polymer MEH-PPV, where the macroscopic chain axis bisects every phenyl ring. Since the off-axis component of the transition dipole moment for each repeat unit will add constructively, the maximum polarization anisotropy for this conformation is identical to that of oriented *trans*-stilbene, which has been measured[11] to be more than an order-of-magnitude smaller than the anisotropy shown in Fig. 2. Hence, it becomes apparent that the observed polarization anisotropy of the photoluminescence and field-induced absorption *requires* that the off-axis component of the transition dipole moment fluctuate about the macroscopic chain axis in such a manner as to approximately sum to zero over the spatial extent of the excited-state wave function.

In Figs. 4(b) and 4(c) we show two additional conformations of the conjugated polymer MEH-PPV, which differ by virtue of the relative orientation of the adjacent vinylene linkages. Because of the low potential energy barrier,[25–27] the solution polymerization of MEH-PPV,[28] and the elevated-temperature gel-processing of the MEH-PPV/PE blend,[1] rotational defects of this type are assumed to be randomly distributed throughout the polymer chain, and "frozen in" by the polyethylene matrix prior to stretching. Hence, within our model for the geometric structure of MEH-PPV oriented in PE, there is no correlation in the absolute angular orientation of the double bond in the vinylene linkage with respect to the macroscopic chain axis.

The geometric structure of the sp^2 hybridized orbitals suggests that a line bisecting the centers of the second and third rings in the two conformations makes an angle of $\pm\phi_g$ with respect to the macroscopic chain axis. If we assume, to a first approximation, that all the bond lengths are equal, the magnitude of this geometric angle is

$$\phi_g = \tan^{-1}\left[\frac{\sqrt{3}}{9}\right] \approx 11^\circ. \tag{13}$$

If the energy eigenstates are localized within a "stilbenelike" repeat unit, defined from the center of one phenyl ring to another, the transition dipole moment will make an angle $\phi_d^{o} + \phi_g$ with respect to the macroscopic chain axis, where $\phi_d^{o} \approx 20°$ is the angle of the off-axis transition dipole moment of the "stilbenelike" repeat unit. This would result in a maximum anisotropy for any optical measurement of $\cot^2(\phi_d^{o} + \phi_g) \approx 3$, again clearly inconsistent with experiment.

In the conjugated polymer PPV and its derivatives, the angle of the off-axis transition dipole moment is directly related to the spatial extent of the excited-state wave function; a highly delocalized wave function will average over many of the configurations shown in Fig. 4, resulting in a much smaller off-axis component for the transition dipole moment. By treating the off-axis component of the transition dipole moment as a "random walk" in one-dimension, we find an expression for the angle of the off-axis transition dipole moment of the conjugated polymer, ϕ_d^{p}, as a function of the excited-state localization length, N_{uc}:

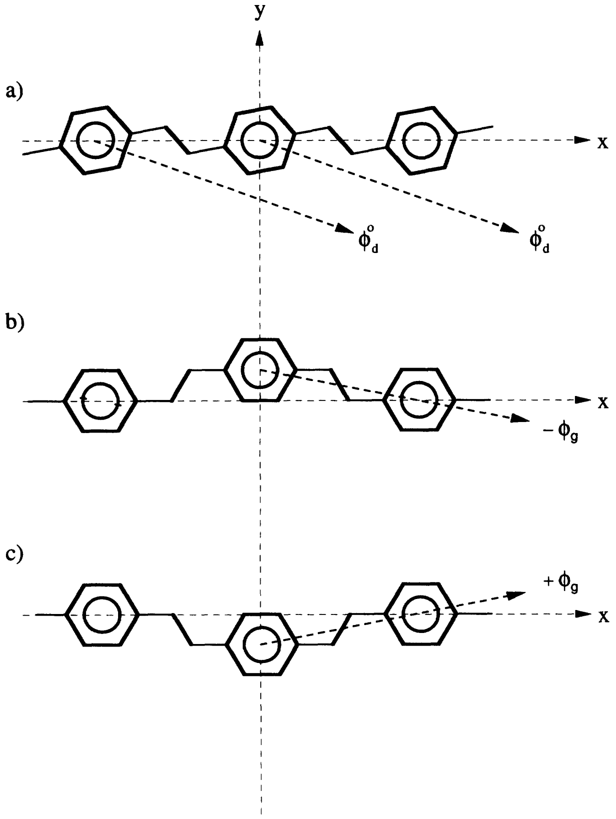

FIG. 4. (a) One possible conformation of the conjugated polymer MEH-PPV, where the macroscopic chain axis bisects every phenyl ring; the side groups have been suppressed for clarity. Since the off-axis component of the transition dipole moment for each repeat unit will add constructively, the maximum polarization anisotropy for this conformation is identical to that of oriented *trans*-stilbene, which has been demonstrated (Ref. 11) to be more than an order-of-magnitude smaller than the anisotropy measured for the oriented blend. Two additional conformations of the conjugated polymer MEH-PPV are depicted in (b) and (c). The magnitude of the off-axis component of the transition dipole moment is a function of the spatial extent of the excited state wave function which averages over the two conformations, which are assumed to be randomly distributed throughout the sample. If the excited state wave function is localized within the unit cell, the transition dipole moment makes an angle $\phi_d^{o} + \phi_g \approx 30°$ with respect to the macroscopic chain axis, which would yield a maximum anisotropy of 3:1 in the measured optical spectra.

$$\tan(\phi_d^{p}) = \frac{1}{\sqrt{N_{uc}}} \tan(\phi_g + \phi_d^{0}). \qquad (14)$$

As indicated in Eq. (10), the observed anisotropy of an oriented sample, ρ, is related to the magnitude of the off-axis transition dipole moment, ϕ_d^{p}, and the mosaic spread, ϕ_{mos}, of the conjugated polymer chains with respect to the drawing axis. A simple rearrangement yields an expression for the localization length of the excited-state wave function:

$$N_{uc} = \frac{\tan^2(\phi_g + \phi_d^{0})}{\tan^2(\phi_{\mathrm{obs}}) - (T_{\parallel}/T_{\perp}) \tan^2(\phi_{\mathrm{mos}})}. \qquad (15)$$

In deriving Eq. (15) we have used the following relation:

$$\rho \equiv \tan^2(\phi_{\mathrm{obs}}) = \tan^2(\phi_d^{p}) + \frac{T_{\parallel}}{T_{\perp}} \tan^2(\phi_{\mathrm{mos}}). \qquad (16)$$

B. The spatial extent of the excited-state wave function in the oriented blend

The polarization dependence of the field-induced absorption in the oriented blend indicates that $\phi_{\mathrm{obs}} \approx 4.5°$. If we assume that the isolated MEH-PPV chains are perfectly aligned with respect to one another [i.e., $\phi_{\mathrm{mos}} = 0$], and that the transition dipole moment of an individual unit cell is polarized with an angle of $(\phi_d^{0} + \phi_g) = \pm 30°$ with respect to the macroscopic chain axis, Eq. (15) yields $N_{uc} > 50$. Thus, the measured anisotropy of the electroabsorption signal in the oriented blend suggests that the instantaneous energy eigenstates are extended over a minimum of 50 unit cells, corresponding to roughly 400 Å. This value is well into the optical saturation regime, where both the energy gap and the ratio of $\chi^{(3)}$ to $\chi^{(1)}$ are independent of the conjugation length,[8,9] and are therefore consistent with the extremely sharp absorption onset and well-defined vibronic structure observed for the oriented MEH-PPV/PE blend (see Fig. 1 and Ref. 1).

A similar analysis applied to the polarization anisotropy of the photoluminescence[1] suggests that the vibrationally-relaxed excited state of the luminescent polaron-exciton is delocalized over a minimum of 20 unit cells, corresponding to roughly 160 Å. Note, however, that spectral differences in the polarized photoluminescence spectrum[1] suggest that the perpendicular component of the photoluminescence originates from residual disordered MEH-PPV in the blend. Furthermore, since the electro-optic response is proportional to $\chi^{(3)}$, the magnitude of the field-induced absorption is far more sensitive to the conjugation length than the photoluminescence. As a consequence, the polarization anisotropy of the photoluminescence originating on the ordered conjugated segments is greatly underestimated. We therefore caution against interpreting the smaller localization length inferred from the polarized photoluminescence spectrum as a measure of lattice relaxation.

The preceding numbers represent lower limits of the spatial extent of the energy eigenstates, since an increase in the mosaic spread of the individual MEH-PPV chains within the polyethylene matrix will tend to decrease the measured anisotropy. This trend is shown in Fig. 5, where we plot the localization length of the instantaneous excited state as a function of the mosaic spread. It is apparent that a mosaic spread of 9° would require the instantaneous energy eigenstates to be infinitely delocalized over the polymer chain. Note that a mosaic spread of 9° would be comparable to the best published results for an oriented conjugated polymer.[27,29–32]

The similarity of Eqs. (6) and (8) suggests that the polarized absorption spectrum should provide an identical measurement of the off-axis component of the transition dipole moment of the instantaneous excited state. In practice, an accurate determination of the absorption polarization anisotropy is difficult due to the scattering losses of the tensile drawn films, hence, only a lower limit (which is an order of magnitude smaller than that observed in the electroabsorption spectrum) can be obtained. Independent of the scattering losses, different values for the polarization anisotropy of the absorption and electroabsorption spectra are expected, since the electro-optic response is proportional to $\chi^{(3)}(\omega,0,0)$ and $\chi^{(3)}$ has been demonstrated both theoretically[7–9] and experimentally[10] to depend strongly on the localization length of the energy eigenstates. Hence, EFMS probes only the longest and most ordered conjugated segments in a given sample. In contrast, the linear susceptibility, $\chi^{(1)}(\omega)$, is primarily a function of the π-electron density, and is therefore largely independent of the conjugation length. As a consequence, polarized absorption spectroscopy probes the entire conjugation length distribution, including the residual fraction of MEH-PPV in the polyethylene matrix which has been demonstrated to be nonoriented and severely disordered.[1] Therefore, the physical mechanisms probed by polarized electroabsorption spectroscopy are more directly related to the intrinsic electronic properties of the pristine material, and are, therefore, more relevant to existing theoretical models which do not account for disorder.

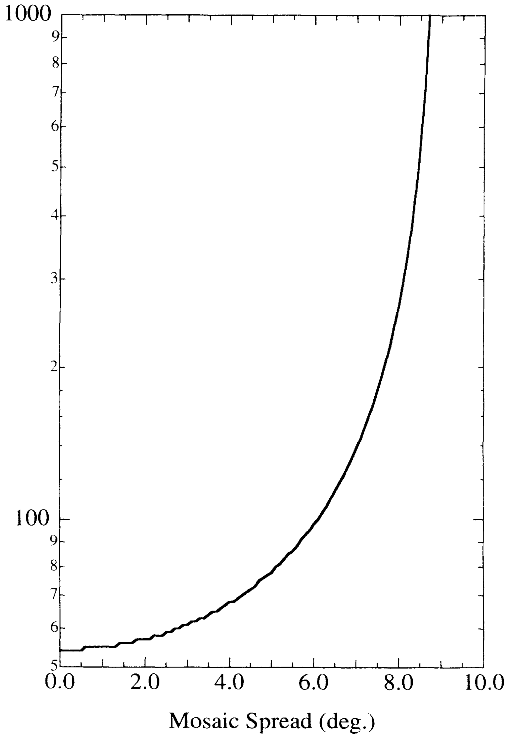

FIG. 5. The instantaneous excited state localization length as a function of the mosaic spread. It is apparent that a mosaic spread of 9° would require the instantaneous energy eigenstates to be infinitely delocalized over the polymer chain.

C. Exciton or band-states?

The observed polarization anisotropy of the electroabsorption and photoluminescence demonstrate unambiguously that the excited-state wave functions in highly-ordered MEH-PPV are delocalized over many repeat units. The question remains as to whether these excited states are best described as band states or tightly bound excitons delocalized as a result of translational symmetry. Although the polarization studies alone provide no direct measure of the exciton binding energy, the large polarization anisotropy in conjunction with the clearly asymmetric absorption and electroabsorption line shapes provide a strong argument against a large Coulomb binding energy. If the low-lying excitations in MEH-PPV were dominated by the Coulomb interaction, momentum conservation in the center-of-mass coordinate would require that only the $K_{\mathrm{ex}} = k_e + k_h = 0$ excitons would couple to the optical field.[33] As the exciton binding energy is increased, oscillator strength is transferred from the continuum and higher lying bound exciton states to the lowest discrete exciton state.[34] In the limit of large Coulomb binding energy there becomes only one dominant dipole allowed transition from the ground state (i.e., to the ^1B_u exciton),[34] and hence the absorption and electroabsorption line shapes will appear symmetric. Symmetric absorption and electroabsorption line shapes are observed in the conjugated polymer dicarbazolylhexadiyne (DCH)-polydiacetylene,[19,20] where the first optically allowed transition is known to be a bound exciton. It is clear from Fig. 1 that both the absorption and electroabsorption line shapes in the oriented MEH-PPV/PE are highly asymmetric. Although one might argue that the observed line-shape asymmetry in the oriented blend is a manifestation of disorder[35] or a distribution of conjugation lengths, this interpretation is clearly inconsistent with the sharp absorption onset, well defined vibronic structure, and the large polarization anisotropy of the field-induced absorption and the photoluminescence.

The analysis of the polarized absorption, photoluminescence, and electroabsorption spectra in structurally ordered MEH-PPV indicates that the intrinsic energy eigenstates are highly delocalized, and that the joint density of states is unambiguously asymmetric. Since the spatial extent of the instantaneous excited-state wave functions encompasses some 400 π-electrons, it seems reasonable to suggest that the asymmetric line shape is the characteristic signature of a one-dimensional band structure. In Ref. 1 the absorption line shape was shown to be accurately described by a square-root singularity broadened by 0.040 eV, and we have recently modeled the electroabsorption spectrum of the oriented blend using the very same Gaussian-broadened square-root singularity in the joint density of states. The details of the electroabsorption line-shape analysis are to be published separately.[21]

VI. CONCLUSIONS

We have demonstrated that the polarized electroabsorption and photoluminescence spectra of stretch oriented MEH-PPV/PE are both strongly anisotropic, with polarization ratios in excess of 150:1 and 60:1, respectively. Using the published results for the off-axis transition dipole moment of *trans*-stilbene, we have demonstrated that the observed polarization anisotropy in the field-induced absorption in dilute oriented blends of MEH-PPV in polyethylene requires that the instantaneous excited-state wave function extends over a minimum of 50 unit cells, corresponding to 400 Å. These results imply that the asymmetric line shape observed in the absorption and electroabsorption spectra of the oriented MEH-PPV/PE blend is an intrinsic property of the ordered π-electron system, and that the optical properties of the material are not dominated by disorder or a distribution of conjugation lengths.

The analysis of the polarized absorption and electroabsorption spectra in structurally ordered MEH-PPV in PE indicates that the intrinsic energy eigenstates are highly delocalized, and that the joint density of states is unambiguously asymmetric, consistent with the square-root singularity predicted for an interband transition in a quasi-one-dimensional π-electron system.

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