RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 58, NUMBER 20 15 NOVEMBER 1998-II

Estimate of the effective conjugation length of polythiophene from its $|\chi^{(3)}(\omega;\omega,\omega,-\omega)|$ spectrum at excitonic resonance

S. Kishino and Y. Ueno
Department of Physics, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

K. Ochiai, M. Rikukawa, and K. Sanui
Department of Chemistry, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan
and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Corporation (JST),
1-4-25 Mejiro, Toshima-ku, Tokyo 171-0031, Japan

T. Kobayashi, H. Kunugita, and K. Ema
Department of Physics, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan
and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Corporation (JST),
1-4-25 Mejiro, Toshima-ku, Tokyo 171-0031, Japan

(Received 14 July 1998)

The spectra of the third-order optical nonlinearity, $|\chi^{(3)}(\omega;\omega,\omega,-\omega)|$, around excitonic resonance in a spin-coated film and a Langmuir-Blodgett (LB) film of polythiophene derivative, poly(3-[2-((S)-2-methylbutoxy)ethyl]thiophene), were measured using the degenerate four-wave-mixing method. The obtained value of $|\chi^{(3)}(\omega;\omega,\omega,-\omega)|$ at the excitonic resonance was $\sim 10^{-7}$ esu, which was the largest value ever obtained in conjugated polymers. From the absorption spectra and $|\chi^{(3)}|$ spectra, the average effective conjugation lengths of the spin-coated film and the LB film were estimated to be approximately 20- and 36-thiophene rings, respectively. [S0163-1829(98)50144-0]

Since polythiophene has a large and fast third-order optical nonlinearity $|\chi^{(3)}|$, it should become a useful material in all-optical devices. Besides its properties with practical applicabilities, polythiophene serves as a model system for understanding the electronic and optical properties of one-dimensional systems with nondegenerate ground states. Excitons in one-dimensional system play an essential role in linear and nonlinear optical properties. The nature of excitons in polythiophene, however, had not been clarified until recently, because the quality of sample characteristics such as the effective conjugation length was not good enough for the investigation of its excitonic features. A recent advance in the synthesis techniques has produced highly ordered poly(3-alkylthiophene) (P3AT), containing almost 100% head-to-tail (HT) coupling of the alkyl sidegroups,[1] and the excitonic structure in HT-coupling P3AT has been clearly determined.[2] Furthermore, enhancements in the third-order optical nonlinearity have been reported for such highly ordered P3AT.[3,4] The enhancements can be interpreted as a result of an increase in the effective conjugation length of the polymer chain. The absolute value of the effective conjugation length in polythiophene, however, has not been reliably measured yet, despite the fact that it is a most important physical quantity to determine optical properties such as the excitonic resonance energy, the transition dipole moment, and optical nonlinearity. The estimated values of the conjugation length vary widely, ranging from 4-thiphene rings[5] to 100-thiophene rings.[4]

In this study, we measured $|\chi^{(3)}|$ spectra of the thin films of a polythiophene derivative, poly(3-[2-((S)-2-methylbutoxy)ethyl]thiophene), with HT coupling [hereafter denoted as P(S)MBET] around excitonic resonance using the degenerate four-wave-mixing (DFWM) method, and estimated an average conjugation length by fitting an absorption spectrum $\alpha(\omega)$ and a $|\chi^{(3)}|$ spectrum to a theoretical model. The reason for using P(S)MBET instead of P3AT is that P(S)MBET is expected to have better regularity than P3AT for reasons which will be mentioned later. We investigated a spin-coated film and a Langmuir-Blodgett (LB) film of P(S)MBET, and found that the average conjugation lengths for the spin-coated film and the LB film were approximately 20-thiophene rings and 36-thiophene rings, respectively.

Since optical properties of polythiophene in the visible region are mainly due to a singlet exciton with odd parity ^1B_u,[2] we only considered the ^1B_u state and its vibronic sidebands in our study. The excitonic transition energy in a molecule with conjugation length N, ω_N, is approximately given by[6]

$$\omega_N = A + \frac{B}{N}, \tag{1}$$

where A and B are constants determined by the band gap of a thiophene monomer, the exciton-transfer energy, and the Coulomb interaction energy. Using several absorption data for thiophene oligomers,[7,8] we get excellent agreement between experimental data and equation (1). The dipole moment of excitonic transition, μ, is proportional to the square root of the conjugation length N.[9,10] Therefore, α and $|\chi^{(3)}|$ of the molecule with conjugation length N are proportional to N and N^2 respectively, i.e.,

$$\alpha_N \propto |\mu_N|^2 \propto N, \tag{2}$$

$$|\chi_N^{(3)}| \propto |\mu_N|^4 \propto N^2. \tag{3}$$

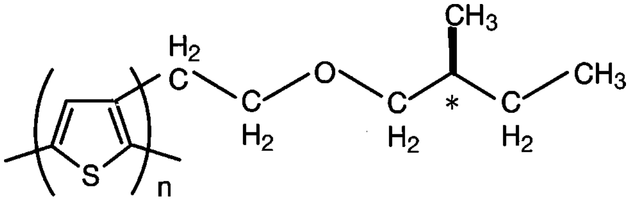

FIG. 1. The chemical structure diagram of P(S)MBET. R-O-R′ is an ether coupling.

This difference in the N dependence is essential for our estimation of conjugation length N.

The chemical structure diagram of P(S)MBET is shown in Fig. 1. The sidechain contains an ether coupling (R-O-R′) in addition to C-C couplings. Oxygen in the ether coupling has only two coupling units, while the C-C coupling has four. Therefore, the ether coupling is less rigid than the C-C coupling, and the sidechain in P(S)MBET is flexible. Thus, this flexibility reduces the repulsion between the sidechains.[11] Consequently, P(S)MBET can be expected to have good regularity with long conjugation lengths. In the present study, P(S)MBET was synthesized by a modified Rieke method,[12] and had a number-averaged molecular weight (M_n) of 1.06×10^4, indicating that there are on average approximate 80-thiophene rings per one molecule. Thin films for optical measurements are prepared by the spin coating and LB methods. The thickness of the spin-coated and LB films are several 10 nm and about 13 nm, respectively.

Figure 2 shows the absorption spectra at room temperature and 8 K of (a) a spin-coated film, and (b) an LB film of P(S)MBET. The structure in these spectra is much better resolved than those in previously reported spectra of highly ordered P3AT,[4] and is as clear as that of an annealed sample.[2] Several peaks can be seen in the structure. The interval energies of these peaks correspond to C=C vibration energy (0.18 eV) and are independent of temperature. We can assign the lowest energy peak to the ^1B_u exciton band and the higher-energy peaks to its vibronic sidebands. The width of each peak corresponds to the distribution of the conjugation length. Each peak becomes clearer and shifts to the lower energy side at low temperature, because the backbone conformation can be made more regular, when the thermal motion of sidechains is suppressed. By comparing the absorption spectra (a) and (b), the LB film appears to have a larger average conjugation length than the spin-coated one.

In DFWM experiments, we used 80-fs pulses from an optical parametric amplifier (OPA) seeded by an amplified mode-locked Ti:Al$_2$O$_3$ laser. The sample was maintained at a low temperature (8 K) in vacuum in order to prevent chemical changes. DFWM experiments were performed using a two-incident-beam configuration. The DFWM signal intensity increased in proportion to the third power of the incident pulse intensity up to $I_{in}\sim$GW/cm^2, which corresponds to the exciton density of $\sim10^{14}$ cm^2. The signal became saturated at higher intensity. $|\chi^{(3)}|$ was estimated from the cubic dependence region considering the absorption and the refractive index dispersion $n(\omega)$, which was approximately determined by the Kramers-Kronig analysis of the absorption spectrum.

$|\chi^{(3)}|$ spectra of P(S)MBET at 8 K are shown in Fig. 3. Although the estimated value of $|\chi^{(3)}|$ has some uncertainty [mainly arising from the approximate determination of $n(\omega)$], we can see clear peaks which are due to one-photon resonance of the exciton and its vibronic sidebands. The peak value of $|\chi^{(3)}|$ are $\sim10^{-7}$ esu, which to our knowledge is the largest value ever obtained in conjugated polymers. In Fig. 3 the absorption spectrum at 8 K is also shown for comparison (the solid curve). We can see that each peak of the vibronic structure in $|\chi^{(3)}(\omega)|$ is located at lower energy than the corresponding absorption peak, as shown by the arrows in Fig. 3. These shifts are caused by the difference in the N-dependence between $\alpha_N(\omega)$ and $|\chi_N^{(3)}(\omega)|$.

We show the precise formulas of $\alpha_N(\omega)$ and $|\chi_N^{(3)}(\omega)|$ at the exciton resonance assuming the exciton system is an ideal two-level system, i.e., an extreme case of the phase-space filling model. This assumption is justified by the fact that we observed no DFWM signal due to two-exciton states (such as a biexciton) and exciton-exciton interactions, which should be observed in the negative time-delay region and/or under perpendicular-configuration excitation.[13] In the ideal two-level model $\alpha_N(\omega)$ and $|\chi_N^{(3)}(\omega)|$ can be expressed as[14]

$$\begin{aligned}\alpha_N(\omega)&=\frac{4\pi\omega_N}{c}\frac{|\mu_N|^2}{\hbar}f(N)\frac{T_2}{1+(\omega-\omega_N)^2T_2^2}\\&\propto\omega_N N f(N)\frac{T_2}{1+(\omega-\omega_N)^2T_2^2},\end{aligned}\tag{4}$$

$$\begin{aligned}|\chi_N^{(3)}(\omega)|&=\frac{4}{3}f(N)\frac{|\mu_N|^4T_1T_2^2}{\hbar^2}\frac{1}{[1+(\omega-\omega_N)^2T_2^2]^{3/2}}\\&\propto N^2f(N)T_2^2\frac{1}{[1+(\omega-\omega_N)^2T_2^2]^{3/2}},\end{aligned}\tag{5}$$

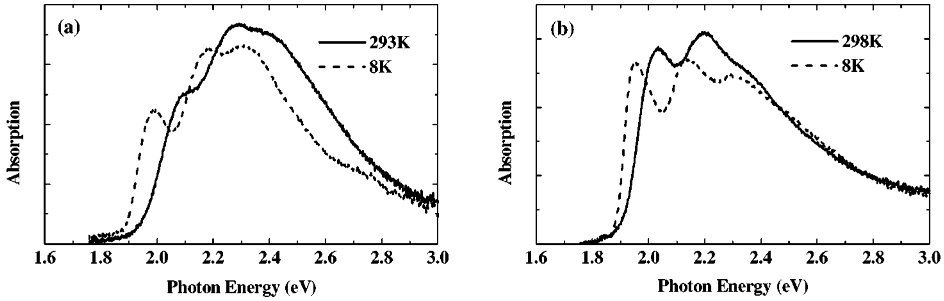

FIG. 2. Absorption spectra of P(S)MBET at room temperature and 8 K for (a) a spin-coated film and (b) an LB film.

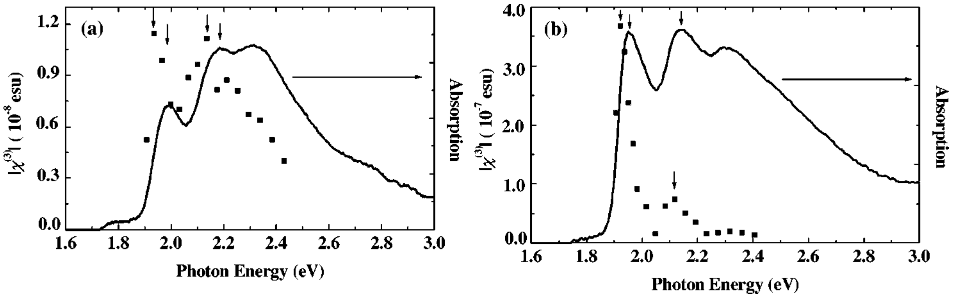

FIG. 3. $|\chi^{(3)}|$ spectra (square dot) of P(S)MBET at 8 K for (a) a spin-coated film and (b) an LB film. Absorption spectra (solid curve) is also shown for comparison. The peaks of $|\chi^{(3)}|$ are located at lower energy side than the absorption peaks (shown with arrows).

where $f(N)$ is the number density of molecules with conjugation length N, and T_1 and T_2 represent the population relaxation time and the dipole dephasing time of the exciton system, respectively. In this model the relationship between $|\chi^{(3)}(\omega)|$ and $\alpha(\omega)$ obeys a scaling law, $|\chi^{(3)}(\omega)| \propto \{\alpha(\omega)\}^{1.5}$, that is consistent with scaling laws proposed for various organic materials.[15,16] Observable spectra $\alpha(\omega)$ and $|\chi^{(3)}(\omega)|$ are obtained by the summation over the range of the value of N, and by adding the contribution of the vibronic sidebands. The contribution ratio of the m-vibronic sideband is determined by the Frank-Condon parameter,[17]

$$F_{m0}=\frac{e^{-S}S^{m}}{m!}, \tag{6}$$

where Huang-Rhys parameter S represents the strength of the electron-phonon interaction.

If we assume that twists, which break conjugation bonds, occur at random positions in a molecule with a constant probability, the number density of the molecule with conjugation length N is given by an exponential distribution,[18,19]

$$f(N)=\frac{1}{N_{ave}}\exp\left(-\frac{N}{N_{ave}}\right), \tag{7}$$

where N_{ave} is the average conjugation length. In order to estimate N_{ave} we fitted the calculated absorption and $|\chi^{(3)}|$ spectra to the experimental ones using Eq. (7). In the fitting procedure, we varied the Huang-Rhys parameter S, A, and B in Eq. (1), and N_{ave}. We used T_2 of the experimental values ($T_2 \cong 30 fs$ at the excitonic resonance, $T_2 \cong 10 fs$ at 1-vibronic sideband and $T_2 \cong 8 fs$ at 2-vibronic sideband) which were obtained from the peak shifts of the time-integral signals of DFWM.

The results of the fit are shown in Fig. 4 (spin-coated film) and Fig. 5 (LB film). We obtained close agreement between the experimental and calculated spectra for $\alpha(\omega)$. Although there is a small discrepancy in $|\chi^{(3)}(\omega)|$, which may be caused by experimental errors and by using our simple model, the calculated spectra resemble the experimental ones in shape. The best fit values of the parameters are listed in the figure captions of Figs. 4 and 5. The fitted values of A and B, which are the same for the spin-coated and LB films, are consistent with absorption data of thiophene oligomer.[7,8] Since the strength of the electron-phonon interaction must vary with conjugation length N, we should use different values of S according to N. To simplify the fitting procedure, however, we used a single value of S. This simplification might also have caused the discrepancy in $|\chi^{(3)}(\omega)|$. It is noted that our best fit value ($S=1.9$) is close to the one for HT-P3AT ($S\sim 2$),[2] and is much larger than that of polyethylene ($S\sim 0.5$).[20] The best fit values of N_{ave} in the spin-coated and LB films are 20-thiophene rings and 36-thiophene rings, respectively. Although these values can be varied to some extent with a slight change of the other fitting parameters, it is certain that they are within the error of ± 3-thiophene rings in the value of N_{ave}. In our calculation, we ignored the spectral width of the laser pulse and the interference of $|\chi_N^{(3)}(\omega)|$ between different N. A more precise calculation including the above effects are in progress, and at the present stage it shows almost similar results as the present calculation.

As shown with the arrows in Fig. 3, the peak-position difference between $\alpha(\omega)$ and $|\chi^{(3)}(\omega)|$ in the spin-coated film is larger than that in the LB film. In our model larger N_{ave} produces a smaller peak shift of $|\chi^{(3)}(\omega)|$. In the case of $T_2 \rightarrow \infty$ and $N_{ave} \gg B/A$, the peak shift, Δ, is easily calculated to be

$$\Delta=\frac{B}{2N_{ave}}\propto\frac{1}{N_{ave}}. \tag{8}$$

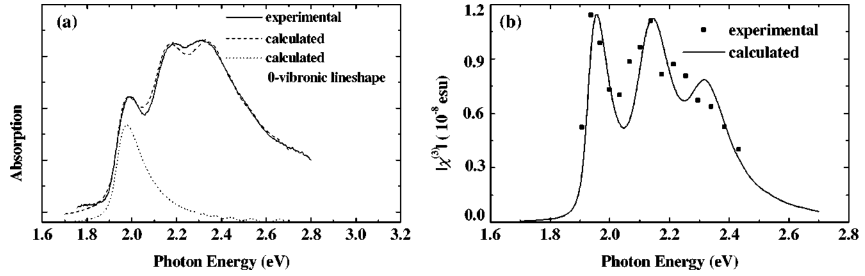

FIG. 4. Fits of (a) absorption spectrum and (b) $|\chi^{(3)}|$ spectrum for a spin-coated film of P(S)MBET. The best fit parameters are $A=1.9$, $B=3.8$, $S=1.9$, and $N_{ave}=20$.

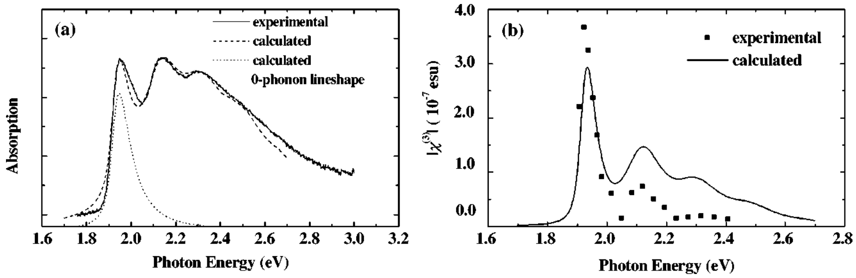

FIG. 5. Fits of (a) absorption spectrum and (b) $|\chi^{(3)}|$ spectrum for an LB film of P(S)MBET. The best fit parameters are $A=1.9$, $B=3.8$, $S=1.9$, and $N_{ave}=36$.

Although a finite T_2 makes Δ larger, the inverse proportionality is approximately valid.

Even though we used the exciton model for the analysis of the data, there are arguments against the exciton model in conjugated polymers. One of the arguments for ruling out the exciton model is the fact that the 0-vibronic transition line shape is well fitted to a broadened square-root singularity as expected for band models in a one-dimensional system. The assertion is that the exciton model should predict symmetric line shape. In our model, however, the exciton transition line shape becomes asymmetric because of the complicated dependence of the excitonic parameters on N. In Figs. 4 and 5, the calculated exciton transition lineshape [0-vibronic component of $\alpha(\omega)$] are shown by dotted curves. If the conjugation length were identical for all molecules in the sample, the exciton lineshape would become symmetric. If the conjugation length is distributed over some range, it cannot be symmetric.

In conclusion, we measured $\alpha(\omega)$ and $|\chi^{(3)}(\omega;\omega,\omega,-\omega)|$ around excitonic resonance in spin-coated and LB films of poly(3-[2-((S)-2-methylbutoxy)ethyl]thiophene), and estimated the average effective conjugation lengths N_{ave}. This is the first time that N_{ave} is estimated from both a linear absorption spectrum and a nonlinear spectrum. Although the distribution function of the conjugation length we used is very simple, the experimental spectra can be well reproduced. Using our model the asymmetric profile of the absorption lineshape is well explained in the framework of the exciton model. Since the effective conjugation length of polymers is not constant, it is important to obtain the distribution function of the conjugation length and its average value for the analysis of optical properties of polymers.

---

[1] R. D. McCllough, R. D. Lowe, M. Jayaraman, and D. L. Anderson, J. Org. Chem. **58**, 904 (1993).

[2] K. Sakurai, H. Tachibana, N. Shiga, C. Terakura, M. Matsumoto, and Y. Tokura, Phys. Rev. B **56**, 9552 (1997).

[3] H. Kawahara, Y. Ueno, N. Abe, S. Kishino, K. Ema, M. Rikukawa, Y. Tabuchi, and N. Ogata, Opt. Rev. **4**, 188 (1997).

[4] T. Bjǿrnholm, D. R. Greve, T. Geisler, J. C. Petersen, M. Jayaraman, and R. D. McCullough, Adv. Mater. **8**, 920 (1996).

[5] J. Kastner, H. Kuzmany, J. Paloheimo, and P. Dyreklev, Synth. Met. **55-57**, 558 (1993).

[6] N. S. Sariciftci, *Primary Photoexcitations in Conjugated Polymers: Molecular Exciton versus Semiconductor Band Model* (World Scientific, Singapore, 1997), p. 62.

[7] M.-T. Zhao, B. P. Singh, and P. N. Prasad, J. Chem. Phys. **89**, 5535 (1988).

[8] H. Thienpont, G. L. J. A. Rikken, and E. W. Mwijer, Phys. Rev. Lett. **65**, 2141 (1990).

[9] E. Hanamura, Phys. Rev. B **37**, 1273 (1988).

[10] E. Hanamura, Phys. Rev. B **38**, 1228 (1988).

[11] L. Belobrzeckaja, G. Bajo, A. Bolognesi, and M. Catellani, Synth. Met. **84**, 195 (1997).

[12] T.-A. Chen, X. Wu, and R. D. Rieke, J. Am. Chem. Soc. **117**, 233 (1995).

[13] J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures* (Springer, Berlin, 1996), p. 78.

[14] R. W. Boyd, *Nonlinear Optics* (Academic Press, San Diego, 1992), p. 202.

[15] C. Bubeck, A. Kaltbeitzel, A. Ground, and M. LeClerc, Chem. Phys. **154**, 343 (1991).

[16] V. A. Shakin, S. Abe, and T. Kobayashi, Phys. Rev. B **53**, 10 656 (1996).

[17] B. Henderson and G. F. Imbusch, *Optical Spectroscopy of Inorganic Solids* (Clarendon, Oxford, 1989).

[18] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953), p. 318.

[19] B. E. Kohler and J. C. Woehl, J. Chem. Phys. **103**, 6253 (1995).

[20] T. W. Hagler, K. Pakbaz, K. F. Voss, and A. J. Heeger, Phys. Rev. B **44**, 8652 (1991).