

Measuring the size of excitons on isolated phenylene-vinylene chains: From dimers to polymers

Gerwin H. Gelinck,¹ Jacob J. Piet,¹ Bas R. Wegewijs,¹ Klaus Müllen,² Jurjen Wildeman,³ Georges Hadziioannou,³ and John M. Warman¹

¹IRI, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

²Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

³Department of Polymer Chemistry and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

(Received 11 April 2000)

We have determined the excess polarizability of the relaxed first excited-singlet-state S_1 on isolated chains of phenylene-vinylene oligomers and polymers by measuring the transient change in the microwave dielectric constant that occurs on flash photolysis of dilute solutions. The isotropic value of the excess polarizability volume, $\Delta\alpha'(S_1)$, increases from 250 Å³ for a dimer to 960 Å³ for an octamer, and 1600 Å³ for high molecular weight polymers. The value for the isolated polymer is close to that found for the unrelaxed S_1 state in electroabsorption (Stark effect) measurements on solid samples of poly(phenylene-vinylene), indicating that exciton delocalization is not strongly influenced by either post-excitation relaxation of the polymer backbone geometry, or by interchain interactions.

The nature of photoexcitations on conjugated polymer chains is a subject of continuing study and debate.¹⁻⁴ Questions of particular current interest concern the extent of delocalization and the binding energy of the relaxed singlet exciton, S_1 . Such questions are of more than just academic interest since S_1 is the intermediary in molecular electronic devices such as electroluminescent displays⁵⁻⁷ and photovoltaic cells.⁸⁻¹⁰ A parameter directly related to these questions is the polarizability of the exciton, $\alpha(S_1)$, since this is a measure of the effective degree of delocalization and of the dipolar coupling between S_1 and other states within the singlet manifold.

In the past, the polarizabilities of the singlet excited-states of conjugated polymers have been estimated by measuring the Stark effect, i.e., the effect of an applied electric-field on the optical absorption spectrum.¹¹ From such electroabsorption measurements on single crystals of polydiacetylene derivatives, values of the polarizability of the $1B_u$ exciton in the direction of the conjugated backbone within the range 4000 to 8000 Å³ have been determined.¹¹ For solid films of polyphenylene-vinylene values from 2400 to ~ 10 000 Å³ have been reported.¹¹⁻¹³ Polarizabilities determined in this way are related to the vertically excited unrelaxed state in a bulk polymer matrix for which interchain interactions could be important. In this paper, we report measurements of the excess polarizability of the *relaxed* S_1 excited-state on *isolated* phenylene-vinylene chains varying in length from two to several hundred monomer units. The measurements were made by determining the transient change in the dielectric constant of a dilute benzene solution on flash photoexcitation of the molecules.

The molecular structures of the phenylene-vinylene PV oligomers and polymers studied are shown in Fig. 1 and their first optical absorption and emission band maxima are listed in Table I. All of the compounds, including ~ 500 monomer unit polymers could be dissolved in benzene. Low concentration solutions (~ 10 ppm or 10⁻⁴ molar PV units) were investigated under conditions for which no intermolecular

solute aggregation occurred. The solutions were flash photolyzed using single 7-ns, 10-mJ/cm² pulses of 308-nm light from a Lumonics HyperEx 400 excimer laser. The time-resolved microwave conductivity technique (TRMC) was used to monitor the change $\Delta\epsilon'$ occurring in the relative dielectric constant of a solution on flash photolysis.¹⁴⁻¹⁶ Changes in ϵ' as small as 1 ppm could be detected.

A change in ϵ' is related to a change in the polarizability of the solute molecules on photoexcitation, $\Delta\alpha$ by

$$\Delta\epsilon' = [\epsilon' + 2]^2 \Delta\alpha N / 9\epsilon_0. \quad (1)$$

In Eq. (1), N is the concentration of excited molecules and ϵ_0 is the permittivity of vacuum. In the present experiments the transient change in power reflected by a microwave cavity containing the solution, ΔR , was monitored at the upper and lower half-power frequencies of the cavity resonance. The difference between the two transients, $\Delta_{\pm} = \Delta R_{-} - \Delta R_{+}$ is related to $\Delta\epsilon'$ and hence $\Delta\alpha$ by

$$\Delta_{\pm} = C\Delta\epsilon' + Dd\Delta\epsilon'/dt \quad (2a)$$

$$= [\epsilon' + 2]^2 \Delta\alpha [CN(t) + D\{dN(t)/dt\}] / 9\epsilon_0 \quad (2b)$$

with C and D determined by the characteristics of the cavity resonance. The differential term in Eq. (2), which leads to an oscillatory component in the Δ_{\pm} transients, results from a nondissipative change in the energy stored in the cavity when ϵ' changes. Typical transients are shown in Fig. 2 for the da-PVn series of oligomers.

The time dependence of the concentration of excited states $N(t)$ was calculated by a convolution procedure that included the laser pulse shape, the incident light intensity and solute optical density, and the lifetime of the relaxed S_1 excited state. The last parameter was determined by time-resolved fluorescence measurements using the 0.8-ns pulse from an LN1000 nitrogen laser and a 150 ps risetime channel-plate photomultiplier. The lifetimes determined are listed in Table I and are considered to be accurate to within

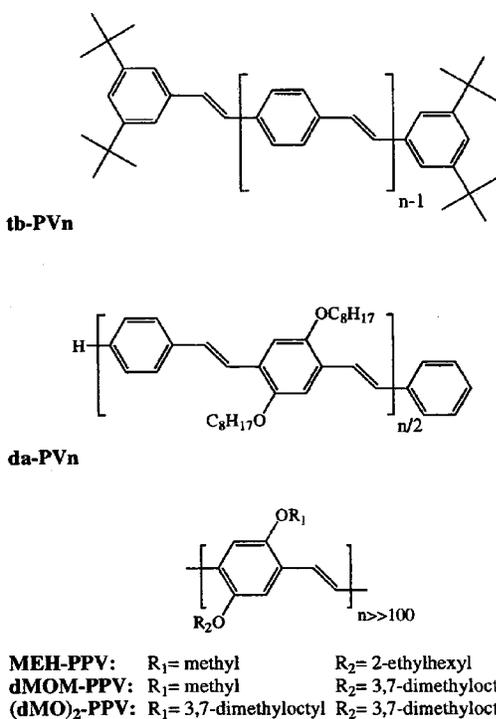


FIG. 1. Molecular structures of the phenylene-vinylene oligomers and polymers studied.

± 50 ps. Examples of fits to the experimental $\Delta\epsilon'$ transients from which $\Delta\alpha$ was determined, are shown in Fig. 2.

Since the molecules are orientated randomly in solution, $\Delta\alpha$ is the isotropic value of the polarizability, i.e., $\Delta\alpha = (\Delta\alpha_{xx} + \Delta\alpha_{yy} + \Delta\alpha_{zz})/3$. Its magnitude is most conveniently discussed in terms of the excess polarizability volume, $\Delta\alpha' = \Delta\alpha/4\pi\epsilon_0$ in units of \AA^3 . The values determined for the excess polarizability volume of the singlet exciton denoted $\Delta\alpha'(S_1)$ are listed in Table I for all of the compounds studied. For both series of oligomers, $\Delta\alpha'(S_1)$ increases with increasing chain length from approximately 250 \AA^3 for the dimers up to a value close to 1000 \AA^3 for the longest oligomeric chains. A further substantial increase to

TABLE I. The fluorescence decay time τ_{FL} , excess polarizability volume $\alpha'(S_1)$, volume of the PVn backbone V_m , first absorption band maximum E_{AB} , and the 0,0 band emission maximum E_{FL} .

Compound	τ_{FL} (ps)	$\alpha'(S_1)^a$ (\AA^3)	V_m^b (\AA^3)	E_{AB} (eV)	E_{FL} (eV)
tb-PV2	980	300 \pm 50	438	3.43	3.12
tb-PV3	950	530 \pm 70	597	3.20	2.88
tb-PV4	740	810 \pm 100	756	3.07	2.76
tb-PV5	670	930 \pm 120	915	3.00	2.70
da-PV2	1000	250 \pm 40	438	3.18	2.79
da-PV4	800	660 \pm 80	756	2.88	2.55
da-PV6	700	900 \pm 110	1074	2.77	2.45
da-PV8	610	960 \pm 130	1392	2.72	2.42
MEH-PPV	250	1600 \pm 400		2.47	2.20
dMOM-PPV	300	1600 \pm 400		2.47	2.23
(dMO) ₂ -PPV	250	1550 \pm 400		2.48	2.22

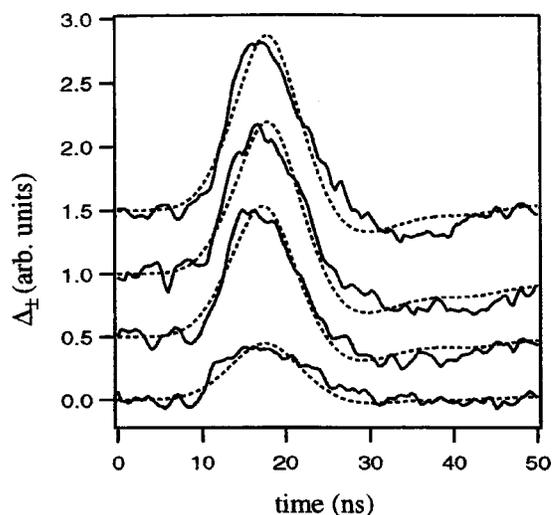


FIG. 2. FP-TRMC difference transients, Δ_{\pm} [see Eq. (2a)], proportional to the change in the dielectric constant on photoexcitation of dilute benzene solutions of the da-PVn oligomers with $n=2, 4, 6,$ and 8 from bottom to top. The base lines of the transients are displaced vertically for clarity. The dotted curves are calculated fits from which the exciton polarizability is determined using Eq. (2b) and measured fluorescence decay times of 1.00, 0.80, 0.70, and 0.61 ns, respectively. The noise level corresponds to a change in the relative dielectric constant of 0.5×10^{-6} .

1600 \AA^3 is found on going to the high molecular weight polymers. These values are orders of magnitude larger than the polarizabilities of ground-state molecules similar in size to the phenylene-vinylene unit, e.g., $\alpha'(S_0) \approx 10 \text{\AA}^3$ for benzene.

Since the exciton polarizability is expected to be highly anisotropic and aligned mainly along the conjugated chain (z axis), the value of $\Delta\alpha'(S_1) = 1600 \text{\AA}^3$ found for the polymers corresponds to $\Delta\alpha_{zz}'(S_1) \approx 4800 \text{\AA}^3$. This is within the range of z axis polarizability values, from 2400 to 10 000 \AA^3 , previously determined by electroabsorption measurements on solid PPV films.¹¹⁻¹³ We conclude from this that the degree of delocalization of the singlet exciton does not change substantially on relaxation from the vertically excited state and that interchain interactions in the bulk solid have only a minor influence, if any, on exciton delocalization.

Using a semiclassical hydrogen atom model Horvath Bässler, and Weiser,¹² derived the relationship $\alpha'(S_1) \approx 4R^3$ for the polarizability volume of a singlet exciton of orbital radius R . This indicates that the polarizability volume should be an approximate measure of the actual volume enclosed by the exciton wave function. In view of this, we compare in Table I the present measured values of $\Delta\alpha'(S_1)$ with the actual molecular volumes of the conjugated backbones of the oligomers V_m . As can be seen, $\Delta\alpha'(S_1)$ and V_m are in fact similar in magnitude. This could be taken to indicate that the exciton wave function is delocalized over almost the entire phenylene-vinylene chain even for the longest oligomers. In the case of the polymers the value of $\Delta\alpha'(S_1) = 1600 \text{\AA}^3$ can be compared with the volume of a single PV unit of 159 \AA^3 . This would suggest that the exciton wave function is delocalized over approximately 10 monomer units. This is in agreement with previous estimates within the range 10 ± 5 based on trends in the optical properties.¹⁷⁻²¹

Rather than taking the polarizability to be a measure of the spatial extent of an exciton as suggested by the semiclassical approach, it should more correctly be discussed in terms of the dipolar coupling with other available quantum states as given by²²

$$\alpha(S_1) = 2 \sum_{n \neq 1} (|\mu_{1n}|^2 / \Delta E_{1n}) / 3 \quad (3)$$

$$= e^2 \hbar^2 \sum_{n \neq 1} \{f_{1n} / \Delta E_{1n}\} / m_e. \quad (4)$$

In Eq. (3), μ_{1n} is the transition dipole moment, f_{1n} the oscillator strength, ΔE_{1n} the energy difference between S_1 and the state n , e , and m_e are the charge and mass of the electron, and \hbar is the Planck constant/ 2π . From Eqs. (3) and (4) it can be concluded that the large polarizabilities measured in the present work are a consequence of strong dipolar coupling of

the relaxed singlet exciton to an upper state or states lying close in energy. The polarizability is, therefore, expected to be related to the exciton binding energy, which is a parameter of considerable interest and discussion at present.^{2-4,23,24} Theoretical calculations similar to those presented recently for polythiophene,²⁵ aimed at quantifying this relationship are underway and will be the subject of a future publication.

We would like to acknowledge Professor A. B. Holmes and Dr. D-H. Hwang (University of Cambridge, UK) and Dr. E. G. J. Staring and Dr. H. F. M. Schoo (Philips Research Laboratories, The Netherlands) for providing the polymeric materials, and Dr. P. van Hutten for helpful discussions. This investigation was supported by the Netherlands Organization for Scientific Research Chemical Sciences Division and Priority Program for Materials.

-
- ¹Primary Photoexcitations in Conjugated Polymers: Molecular Exciton versus Semiconductor Band Model, edited by N. S. Sariciftci (World Scientific, Singapore, 1997).
- ²J. L. Brédas, J. Cornil, and A. J. Heeger, *Adv. Mater.* **8**, 447 (1996).
- ³J. L. Brédas, J. Cornil, D. Beljonne, D. A. Dos Santos, and Z. Shuai, *Acc. Chem. Res.* **32**, 267 (1999).
- ⁴A. Köhler, D. A. Dos Santos, D. Beljonne, Z. Shuai, J. L. Brédas, A. B. Holmes, A. Kraus, K. Müllen, and R. H. Friend, *Nature (London)* **392**, 903 (1998).
- ⁵J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature (London)* **347**, 539 (1990).
- ⁶D. Braun and A. J. Heeger, *Appl. Phys. Lett.* **58**, 1982 (1991).
- ⁷R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, and W. R. Salaneck, *Nature (London)* **397**, 121 (1999).
- ⁸G. Yu and A. J. Heeger, *J. Appl. Phys.* **78**, 4510 (1995).
- ⁹J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Nature (London)* **376**, 498 (1995).
- ¹⁰T. J. Savenije, J. M. Warman, and A. Goossens, *Chem. Phys. Lett.* **287**, 148 (1998).
- ¹¹G. Weiser and Á. Horváth, in *Primary Photoexcitations in Conjugated Polymers: Molecular Exciton versus Semiconductor Band Model*, (Ref. 1, Chap. 12).
- ¹²A. Horvath, H. Bässler, and G. Weiser, *Phys. Status Solidi*, **B173**, 755 (1992).
- ¹³M. Leiss, S. Jeglinski, Z. V. Vardeny, M. Ozaki, K. Yoshino, Y. Ding, and T. Barton, *Phys. Rev. B* **56**, 15 712 (1997).
- ¹⁴J. M. Warman, W. Schuddeboom, S. A. Jonker, M. P. de Haas, M. N. Paddon-Row, K. A. Zachariasse, and J-P. Launay, *Chem. Phys. Lett.* **210**, 397 (1993).
- ¹⁵J. M. Warman, G. H. Gelinck, J. J. Piet, J. W. A. Suykerbuyk, M. P. de Haas, B. M. W. Langeveld-Vos, R. A. J. Janssen, D-H. Hwang, A. B. Holmes, M. Remmers, D. Neher, K. Müllen, and P. Bäuerle, *Proc. SPIE* **3145**, 142 (1997).
- ¹⁶G. H. Gelinck, Ph.D. thesis, Delft University of Technology, Delft University Press, 1998.
- ¹⁷U. Rauscher, H. Bässler, D. D. C. Bradley, and M. Hennecke, *Phys. Rev. B* **42**, 9830 (1990).
- ¹⁸B. Tian, G. Zerbi, R. Schenk, and K. Müllen, *J. Chem. Phys.* **95**, 3191 (1991).
- ¹⁹R. Mahrt, J. Yang, A. Greiner, and H. Bässler, *Makromol. Chem., Rapid Commun.* **11**, 415 (1990).
- ²⁰H. S. Woo, O. Lhost, S. G. Graham, D. D. C. Bradley, R. H. Friend, C. Quattrocchi, J. L. Brédas, R. Schenk, and K. Müllen, *Synth. Met.* **59**, 13 (1993).
- ²¹A. Schmidt, M. L. Anderson, D. Dunphy, T. Wehrmeister, K. Müllen, and N. R. Armstrong, *Adv. Mater.* **7**, 722 (1995).
- ²²P. W. Atkins and R. S. Friedman, *Molecular Quantum Mechanics*, 3rd ed. (Oxford University Press, Oxford, England 1997), Chap. 12.
- ²³S. F. Alvarado, P. F. Seidler, D. G. Lidzey, and D. D. C. Bradley, *Phys. Rev. Lett.* **81**, 1082 (1998).
- ²⁴A. J. Heeger, in *Primary Photoexcitations in Conjugated Polymers: Molecular Exciton versus Semiconductor Bond Model*, (Ref. 1, Chap. 2).
- ²⁵J. W. van der Horst, P. A. Bobbert, M. A. J. Michels, G. Brocks, and P. J. Kelly, *Phys. Rev. Lett.* **83**, 4413 (1999).