Interplay of Thermochromicity and Liquid Crystalline Behavior in Poly(*p*-phenyleneethynylene)s: $\pi-\pi$ Interactions or Planarization of the Conjugated Backbone?

Tzenka Miteva,[†] Liam Palmer,[‡]
Lioba Kloppenburg,[‡] Dieter Neher,[§] and
Uwe H. F. Bunz*,[‡]

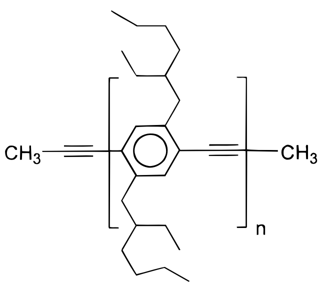
Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208, Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55021 Mainz, FRG, and Institut für Physik, Universität Potsdam, Am Neuen Palais 10, 14469 Potsdam, FRG

Received July 27, 1999
Revised Manuscript Received November 1, 1999

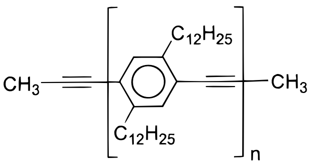
In this communication we wish to report upon the interplay between liquid crystalline (LC) and thermochromic behavior of dialkyl-substituted poly(*p*-phenyleneethynylene)s (PPEs; **1**, **2**) in thin solid films.

PPEs[1,2] are rigid conjugated polymers.[3,4] Due to the presence of the triple bond, the barrier of rotation of adjacent phenyl rings with respect to each other is low. Theoretical calculations and physical measurements have determined this barrier in diphenylacetylene to be less than 1 kcal/mol.[5] Such a barrier of rotation suggests that in solution *any* dihedral between two phenyl rings can be assumed.[6] In the solid state that is not the case, because the USC group[7] and others have shown that PPEs form sanidic−lamellar[2d] LC[7b] phases, in which rotation around the triple bond is restricted and a planar arrangement of the conjugated backbones with concomitant interchain $\pi-\pi$ stacking is observed. Side-chain crystallization reinforces the packing of the main chains which—as in all aromatic systems—is predominantly driven by attractive electrostatic interactions.[8] A detailed study of dialkyl-PPEs in solution showed that aggregate formation is accompanied by a dramatic shift in their UV/vis spectra.[9a,b] In the aggregated state (induced by addition of nonsolvent methanol) a narrow, red-shifted band, centered at approximately 440 nm, was observed. This solvatochromic effect points to a distinct order−disorder transition in dialkyl-substituted PPEs.[10]

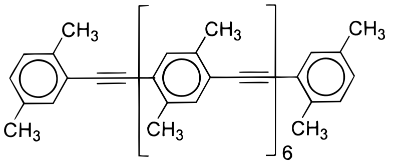
The melting of an LC into the isotropic state is an order−disorder transition, which offers an elegant approach to study the effect of ordering and intermolecular interactions on the optical properties of PPEs. An important question is whether thermotropic LC[7b] behavior and observation of the aggregate band in PPEs are congruent; i.e., will changes in behavior of both occur at identical temperatures? Congruent behavior would suggest that both effects are linked. We noticed that opaque-yellow films of **2** (degree of polymerization, $P_n = 87$, $M_w/M_n = 3.7$; for complete characterization of sample see Table 1, entry 31, in ref 1b) turn almost transparent−colorless when heated (Figure 1a,b). Concomitantly, fluorescence changes from green to blue (Figure 1c). Variable temperature UV/vis spectroscopy (Figure 2) of films of **1** and **2** shows that the disappearance of the aggregate band concurs with their transition from the LC state into the isotropic phase. While at room temperature in **1** the band at 436 nm is prominent, it disappears at 190 °C and the obtained spectrum resembles that of **1** in dilute solution. PPE **2** ($P_{\boldsymbol{n}} = 2.0 \times 10^2$, $M_w/M_n = 3.9$; for complete characterization of sample see Table 1, entry 11, in ref 1b) shows the same qualitative features, but the aggregate band has vanished at 130 °C. Because thin films are examined, a small shoulder of the aggregate band always is preserved, even at elevated temperatures. The inset in Figure 2 shows the ratio of the $I_{\text{aggregate band}}/I_{\text{principal absorption}}$. In both cases a monotonically decreasing curve results as a function of temperature. A similar behavior is observed in the temperature-dependent luminescence spectra of **1** (see Figure 3). However, the effect of isotropization is not as dramatic in the luminescence as it is in the absorption spectrum, and even at 200 °C, the fluorescence of **1** still displays a considerable contribution from the band centered at 500 nm, suggestive of excimer[9c,d] formation in the excited state. DSC examination of **1** and **2** *shows that the LC−isotropic transition occurs at 190 °C for **1** and at 120 °C for **2***. These are the temperatures (±10 °C) at which the respective aggregate band of **1** and **2** disappears.



1



2



3

Two different explanations could be responsible for the observation of an aggregate-band in PPEs. (a) Either this is a single-molecule effect and the planarization of the PPE backbone leads to improved conjugation with a lower band gap, or (b) the aggregate band is a charge transfer-type $\pi-\pi$ stacking of the backbones, which occurs by electronic communication of (many different), well-aligned neighboring chains. In both cases planarization of the PPE chains plays a central role. In scenario a, planarization (induced by the LC phase) is the cause for the band, while in case b planarization is a necessary but not sufficient condition for its occurrence. Only the electronic interaction of many conjugated chains (by virtue of $\pi-\pi$ stacking) would then lead to the aggregate band.

In a landmark paper, Wudl[10a] has shown that in poly(3-alkylthiophene)s, which display substantial rotational barriers, single-chain planarization is responsible for

---

* To whom correspondence should be addressed.
[†] Max-Planck-Institut für Polymerforschung.
[‡] The University of South Carolina.
[§] Universität Potsdam.

10.1021/ma9912397 CCC: $19.00

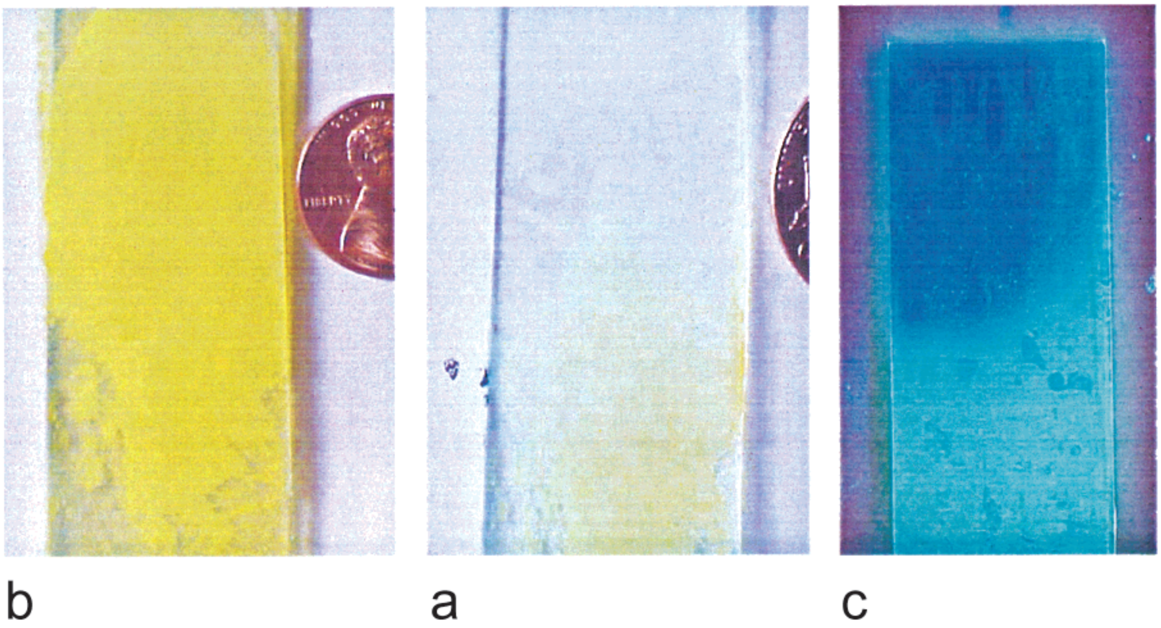


Figure 1. (a) Thin film of PPE **2** at enhanced temperature on top of a hot plate. To make the effect more clear, partial side illumination with a hand-held UV/vis lamp is turned on. (b) Same film at room temperature. (c) Fluorescence of PPE **2**. Thin film of **2** on a hot plate under UV/vis illumination. The upper part is >140 °C while the lower part is approximately 60 °C.

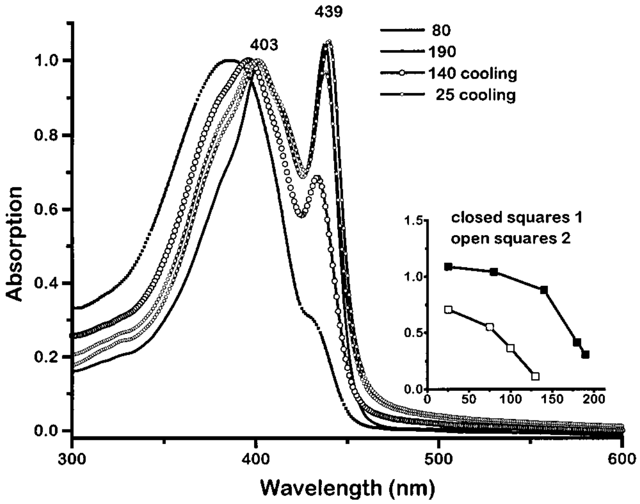


Figure 2. Temperature-dependent UV/vis spectra of a thin film of **1** on a quartz substrate. The inset shows the ratio of the band observed at 439 nm to that at 403 or 387 nm in dependence of the temperature. The upper graph displays the values obtained for **1**, while the lower line is obtained from a similar study for **2**.

their distinct thermochromism, but it is a priori not determined if the same force is in effect in PPEs, i.e., whether their HOMO−LUMO gap is dependent upon the twist angle between the benzene rings or whether the rotationally symmetric alkyne group leads to an angle-independent HOMO−LUMO gap.

A series of semiempirical (PM3) calculations[11] was performed on the model compound **3**,[13] in which methyl groups mimic the alkyl chains in **1** or **2**. Geometry optimization leads to a global minimum in which the PE chain assumes a planar conformation and all methyl groups are located trans to each other. In this conformation a $\lambda_{\max}$ of 631 nm is calculated.[12] If every other benzene ring is rotated by 90°, $\lambda_{\max}$ drops to 539 nm, corresponding to an increase in transition energy $\Delta E = 0.34$ eV. (Figure 4; AM1, 645, and 546 nm; $\Delta E = 0.35$ eV). These calculations are of high qualitative value and suggest strongly that the dihedral angle between the benzene rings influences the size of the HOMO−LUMO gap in PPEs. Planarization will lead to a red shift of $\lambda_{\max}$.

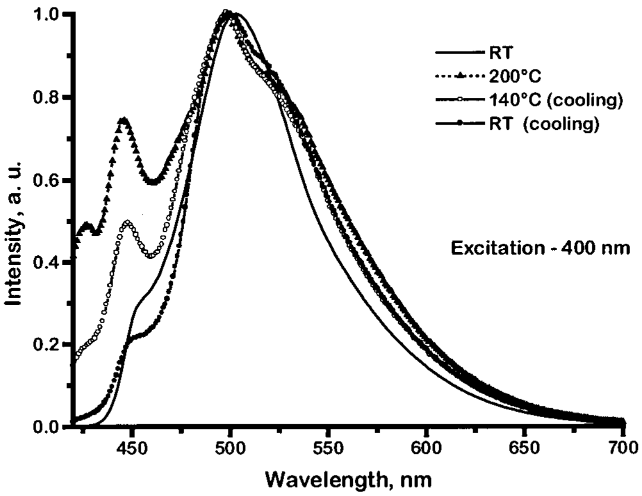


Figure 3. Temperature-dependent fluorescence spectrum of **1**.

The observed shift of 55 nm (384 nm to 439 nm **1** and **2**) corresponding to 0.41 eV is in good agreement with the results of the calculations, considering that they do not take into account electron−electron interaction in the excited state. Additionally, we should note that not all benzene rings in PPEs in solution will be oriented perpendicular to each other. *The occurrence of the aggregate bands in **1** and **2** can thus be satisfactorily explained by simple planarization of the conjugated backbone*, which is induced by the ordering of the molecules entering the LC phase. The absorption in PPEs would thus better be described as aggregate-induced band, instead of aggregate band, because it mirrors the electronic properties of *one* PE chain. A similar case, where planarization has a huge influence on the absorption spectrum is Scherf's ladder polymer in which a poly(*p*-phenylene) backbone undergoes a

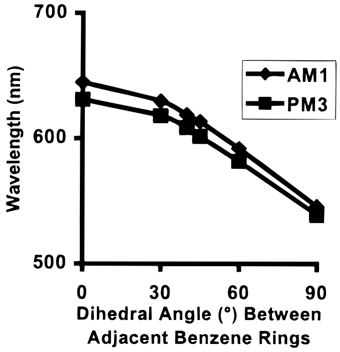


Figure 4. Dependence of the HOMO−LUMO gap (values given in nm) in **3** with respect to the dihedral angle between adjacent benzene rings.

dramatic red shift and band narrowing upon forced planarization.[13]

According to *Ockham's Razor* it is—at least at the moment—not necessary to invoke charge-transfer-type interchain interactions for the observed behavior but planarization alone seems to be a satisfactory explanation for the observed optical properties. In conclusion, we have been able to show the first example of a conjugated polymer (PPEs **1**,**2**) where a pronounced thermochromism in the proximity of the order−disorder transition in the solid state (liquid crystalline to the isotropic phase) has been established. It is explained by conformational changes of the conjugated backbone at this transition. We predict that this behavior will be found in other conjugated polymers in near future.

In another vein the PPEs compare and complement nicely Moore's[2a−c] *meta*-PEs in which desolvation-induced folding into helical structures leads to a hypsochromic shift in their UV/vis spectra. In comparison to biological systems, Moore's *meta*-PEs can be related to the tim barrel motif,[14] *while PPEs would be an analogue to β-sheets found in fibroin,[15] the predominant silk protein.*

Acknowledgment. This work was supported by NSF CHE: 9814118 (PI Bunz) and the Research Corporation. We thank Dr. D. Lupo (Sony) and Prof. Ullrich Scherf (MPI) for helpful discussions.

References and Notes

(1) (a) For high-molecular weight PPEs via alkyne metathesis see: Kloppenburg, L.; Song, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **1998**, *120*, 7973. (b) Kloppenburg, L.; Jones, D.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4194. (c) Weiss, K.; Michel, A.; Auth, E.-M.; Bunz, U. H. F.; Mangel, T.; Müllen, K. *Angew. Chem.* **1997**, *36*, 506. (d) For PPEs via Pd methodology see: Mangel, T.; Eberhardt, A.; Scherf, U.; Bunz, U. H. F.; Müllen, K. *Macromol. Rapid Commun.* **1995**, *16*, 571. Li, H.; Powell, D. R.; Hayashi, R. K.; West R. *Macromolecules* **1998**, *31*, 52. (e) Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157. (f) Ofer, D.; Swager, T. M.; Wrighton, M. S. *Chem. Mater.* **1995**, *7*, 418. (g) Giesa, R.; Schulz, R. C. *Makromol. Chem.* **1990**, *191*, 857. (h) Pang, Y.; Li, J.; Hu, B.; Karasz, F. E. *Macromolecules* **1998**, *31*, 6730. (i) While high molecular weight PPEs have been reported by the Pd-catalyzed coupling reactions, it is necessary to use highly activated, acceptor-substituted diiodides.[4]

(2) For *m*-PEs and their conformational behavior see: (a) Nelson, J. C.; Saven, J. G.; Moore, J. S.; Wolynes, P. G. *Science* **1997**, *277*, 1793. (b) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402. (c) Young, J. K.; Moore, J. S. In *Modern Acetylene Chemistry*; Stang, P., Diederich, F., Eds.; VCH: Weinheim, Germany, 1995; p 417. (d) Rodriguez-Prada, M.; Duran, R.; Wegner, G. *Macromolecules* **1989**, *22*, 2507.

(3) (a) *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley: New York, 1998. (b) Kraft, A.; Grimsdale, A. C.; Holmes,A. B. *Angew. Chem.* **1998**, *37*, 402. (c) Höger, S.; McNamara, J. J.; Schricker, S.; Wudl, F. *Chem. Mater.* **1994**, *6*, 171. (d) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430. (e) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (f) Diederich, F. *Angew. Chem.* **1999**, *38*, 1350. (g) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1994**, *27*, 739.

(4) Cotts, P. M.; Swager, T. M.; Zhou, Q. *Macromolecules* **1996**, *29*, 7323. Zhou, Q.; Swager, T. *J. Am. Chem. Soc.* **1995**, *117*, 12593.

(5) (a) Experimental Measurement of the rotational barrier of tolane: Okuyama, K.; Hasegawa, T.; Ito, M.; Mikami, N. *J. Phys. Chem.* **1984**, *88*, 1711. (b) Calculation: Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 3970.

(6) The average twist angle in **1**−**3** is thus determined by a Boltzman distribution. Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, England, 1986.

(7) (a) Bunz, U. H. F.; Enkelmann, V.; Kloppenburg, L.; Jones, D.; Shimizu, K. D.; Claridge, J. B.; zur Loye, H.-C.; Lieser, G. *Chem. Mater.* **1999**, *11*, 1416. (b) Kloppenburg, L.; Jones, D.; Claridge, J. B.; zur Loye, H.-C.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4460.

(8) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303. Dougherty, D. A. *Science* **1996**, *271*, 163.

(9) (a)Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655. (b) Fiesel, R.; Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Scherf, U.; Bunz, U. H. F. *Macromol. Rapid Commun.* **1999**, *20*, 107. (c) Conwell, E. *Trends Polym. Sci.* **1997**, *5*, 218. (d) Jenekhe, S. A.; Osaheni, A. *Science* **1994**, *265*, 765.

(10) (a) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci. B* **1987**, *25*, 1071. (b) For a more recent example, see: Gonzalez-Ronda, L.; Martin, D. C.; Nanos, J. I.; Politis, J. K.; Curtis, M. D. *Macromolecules* **1999**, *32*, 4558.

(11) AM1 or PM3 level, utilizing Spartan Pro for PC, on a 450 MHz Pentium III computer running on Windows NT.

(12) An alkyl-substituted octameric PE has been made by Tour, and its λ_{max} in solution was determined to 376 nm. While the absolute value does not match with high precision, the obtained number is in fair agreement with the experiment. Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem.* **1994**, *33*, 1360. Huang, S. L.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 4908.

(13) (a) Scherf, U.; Müllen, K. *Macromol. Chem. Rapid Commun.* **1991**, *12*, 489. (b) For an excellent review, see: Scherf, U. *Top. Curr. Chem.* **1999**, *201*, 163.

(14) Stryer, L. *Biochemistry*; W. H. Freeman: New York, 1995.

MA9912397