

# Polymer Dispersed Discotics: Structure, Dynamics, and Optoelectronic Properties

A. Bayer, J. Kopitzke, F. Noll, A. Seifert, and J. H. Wendorff\*

*Department of Chemistry and Materials Science Center, Philipps University, Marburg, Germany*

*Received August 22, 2000; Revised Manuscript Received January 31, 2001*

**ABSTRACT:** Discotic liquid crystalline materials characterized by the spontaneous formation of columns within the fluid phase display a set of interesting optoelectronic properties directly related to the state of order. The dispersion of such columnar discotics in solid polymer matrices results in geometric confinement effects controlling both the structure of the mesophase and dynamical properties related to transport properties. The confinement causes a reduction of the longitudinal and the transverse spatial correlation lengths which, in turn, gives rise to strong modifications of the absorption and emission properties as well as electronic transport processes.

## I. Introduction

Optoelectronic properties of organic materials such as absorption and photo- and electroluminescence as well as the transport of charge carriers and optical excitations are known to depend strongly on the molecular state of order.<sup>1</sup> The spatial disorder characteristic of amorphous materials is known to give rise, for instance, to localized transport states, the energy and distance of which are subjected to a distribution. Assuming the presence of such distributions, Bässler et al. were able to account for the experimentally observed temperature and field dependence of charge carrier mobilities in organic amorphous materials including amorphous polymers and guest host systems.<sup>2–6</sup>

The transition from the short range order characteristic of perfectly amorphous materials to the more regular though noncrystalline order displayed by liquid crystalline materials has been found to lead to significant changes both in electronic transport processes and in excitation and emission properties. It has been reported, for instance, for discotic materials, in particular triphenylene derivatives, that the formation of a hexagonal columnar phase from the isotropic melt leads to an increase of the hole mobility by at least 2 orders of magnitude.<sup>7</sup> Another finding was that the transition from the hexagonal to a more highly ordered plastic columnar state increases the mobility even more, by about 1 order of magnitude in this case.<sup>8–10</sup>

The formation of the columns may furthermore give rise to a significant blue shift of the absorption maximum, a shift which has been attributed to strong interactions between the excited disk-shaped molecules along the columns. Using quantum chemical calculations, Markovitsi et al. were able to correlate the magnitude of the blue shift with the number of molecules within the columns interacting with each other.<sup>11,12</sup>

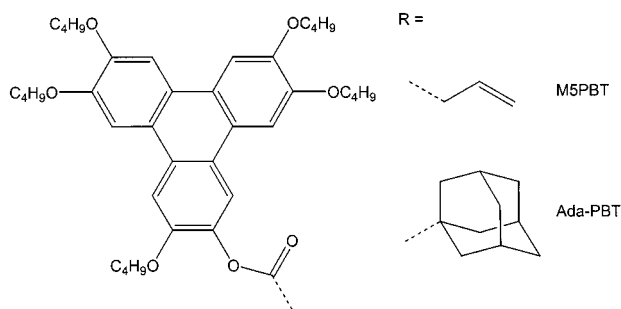
Columnar discotics have been shown to be of particular interest for applications in areas such as light-emitting diodes<sup>10,13–15</sup> or photoconductors, and it might be important for such applications to be able to control their optoelectronic properties and transport properties in a broad range. One expectation is that both excitation and emission properties but also electronic transport properties should depend strongly on the perfection of the liquid crystalline order and in particular on the

magnitude of the correlation length along the columns and perpendicular to them. X-ray studies have revealed that the correlation length along the columns within the bulk state amounts typically to about 15–20 nm as far as triphenylene systems are concerned and that these values do not vary strongly with temperature.<sup>10,16</sup>

One effective way to control the correlation length at a fixed temperature consists of subjecting the discotic material to geometric confinement effects. The influence of geometric confinements on the state of order and on the molecular dynamics of liquid crystals has been the subject of a considerable number of investigations.<sup>17–27</sup> The findings based on theoretical considerations and experimental results are that thermodynamic, structural, and dynamic properties are strongly modified due to confinement effects. In fact, we were recently able to show that structure and molecular dynamics of columnar discotics can be strongly varied by introducing the materials into narrow pores provided by porous glasses.<sup>28</sup> Yet for technical application involving thin films the use of porous glasses meets with considerable difficulties. Such glass–discotic hybrid films tend to scatter light and are rather brittle, and the achievement of a complete filling of the narrow pores leads to further problems. It was for this reason of considerable interest to find modified routes toward geometrically confined discotics.

The route which has recently been exploited by us and which will be reported in this contribution is based on a fine dispersion of the discotic materials in a solid transparent polymer matrix. The preparation of thin films takes place via spin-coating of a solution containing both the polymer matrix and the discotic materials. The spin-coating procedure is in this case characterized by the rapid removal of the solvent, the induction of phase separation, and the freezing in of an intermediate nonequilibrium state. Depending on the spin-coating conditions, the concentration of the discotic material relative to the polymer matrix, and subsequent annealing conditions, one is able to control the degree of dispersion of the discotic materials in a broad range extending from a molecular dispersion all the way up to phase-separated structures in the micrometer range with corresponding variations of structural, dynamic and—most important—optoelectronic properties.

### Scheme 1. Chemical Structure of the Triphenylene Derivatives



## II. Experimental Section

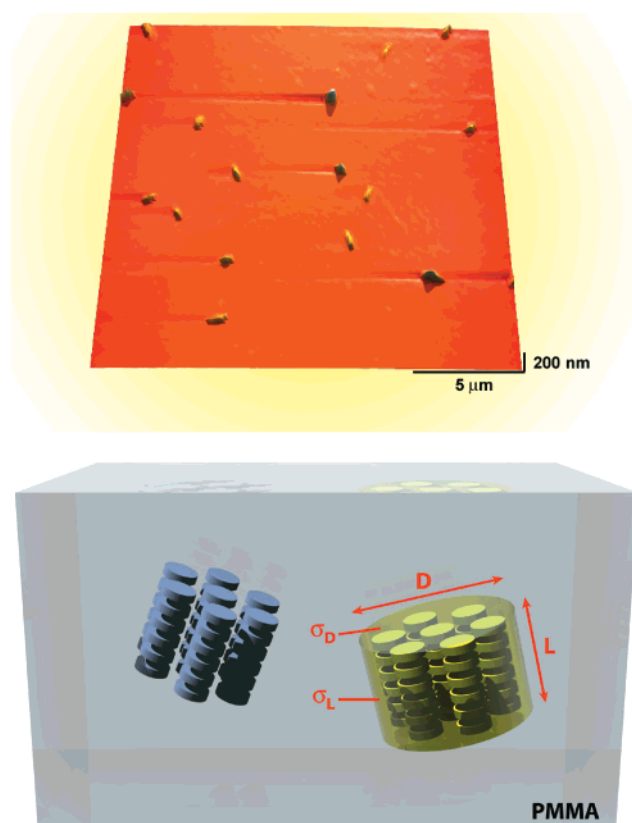
The triphenylene derivatives used for the investigations are shown in Scheme 1; the asymmetrically substituted triphenylenes are characterized by the following phase sequences: g  $-43$  °C Col<sub>hp</sub>  $78$  °C Col<sub>ho</sub>  $188$  °C i ( $\omega$ -pentaenoyl-PBT, M5PBT) and g  $75$  °C Col<sub>hp</sub>  $168$  °C Col<sub>ho</sub>  $188$  °C i (Ada-PBT), respectively. The symbols denote the character of the states which are observed: g = glass, Col = columnar, hp = hexagonal plastic, ho = hexagonal ordered, and i = isotropic phase. The synthesis has been described previously.<sup>29</sup> Solutions of the triphenylene compounds and the amorphous polymers poly(methyl methacrylate) (PMMA) or poly(carbonate) in chloroform as solvent were used for spin-coating thin films.

To perform structural, dielectric, and optical investigations, the polymer concentration amounted typically from a few wt % up to 20 wt % relative to the solvent, and the concentration of the discotic material ( $\omega$ -pentaenoyl-PBT and Ada-PBT, respectively) amounted from 0.3 to up to 30 wt % relative to the amount of polymer present. The films studied had a thickness in the range between 100 nm and a few micrometers in general. To prepare light-emitting diodes, films were spin-coated on indium–tin oxide coated substrates. A thin aluminum layer was vacuum-evaporated as top electrode. The Ada-PBT was predominantly selected for optical investigations because of its brighter luminescence and M5PBT for dielectric studies due to the larger dipole moment relative to Ada-PBT. Previous investigations have shown that both discotic materials show the same phase behavior in confined geometries and that the optical spectra are qualitative very similar in the bulk material.

The X-ray analysis was performed using a Siemens D-5000 wide-angle goniometer, and the dielectric investigations involved a Hewlett-Packard impedance analyzer 4284A ( $10^2$ – $10^9$  Hz). The sizes of the structures were measured by means of optical microscopy, using a Zeiss Axiotech 100HD microscope and a ProgRes 3008 digital camera with a resolution of  $1996 \times 1450$  pixels. AFM investigations were performed using a TopoMetrix Explorer with a  $2 \mu\text{m}$  scanner. Absorption studies were carried out using a Perkin-Elmer Lambda 9 spectrometer with a spectral resolution of about 2 nm. Steady-state fluorescence and excitation spectra were recorded with a Shimadzu spectrofluorometer RF-1502 with a resolution of about 15 nm.

## III. Results and Discussion

**Structure of the Dispersed Discotics.** The spin-coated films turned out to be optically transparent for all concentrations as long as the films were not annealed at temperatures well beyond the glass transition temperature of the polymer. Using optical microscopy and AFM studies, it became apparent that the transparent films with a thickness of some micrometers are characterized by very small dispersed discotic regions having the shape of cylinders. The diameter was typically in the range of 200–300 nm and the length of the same order of magnitude. No such structures were apparent in the 100 nm thick films, indicating possibly a molecular dispersion (see below). Annealing above the glass



**Figure 1.** Dispersion of discotic regions in the solid polymer matrix (example: Ada-PBT in PMMA): (a, top) AFM results; (b, bottom) schematic diagram.

transition temperature of the matrix polymer gave rise to the formation of cylindrical structures where the dimensions increased with increasing concentration of the discotic material. The length varied between 800 and 1000 nm and the diameter between 200 and 400 nm. Figure 1a displays characteristic results on the morphology as obtained from AFM investigations.

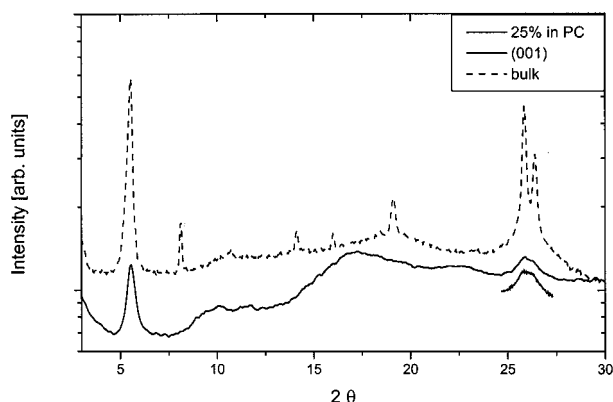
This is a rather surprising result since the general finding as far as binodal phase separation is concerned is that droplets tend to be formed within the matrix at least as far as isotropic materials are concerned. In fact, droplets are also formed if one of the phases is nematic as obvious from a large amount of research on so-called PDLC (polymer dispersed liquid crystals) designed for display applications.<sup>17,18</sup> In all these cases droplets are displayed whatever the preparation mode and the liquid crystalline phase involved.<sup>30</sup> It thus seems that the formation of a columnar phase during phase separation gives rise to special effects, namely, the deviation of the phase-separated discotic aggregates from the spherical shape. The nucleus controlling phase separation will probably have the shape of a disk characterized by two different types of surfaces and corresponding interfacial energies as shown schematically in Figure 1b. Nucleation theory<sup>31</sup> predicts for such a disklike nucleus that the critical height  $h^*$  and the critical radius  $r^*$  are given by

$$h^* = 2\sigma_D T / \Delta H_f \Delta T$$

and

$$r^* = 2\sigma_L T / \Delta H_f \Delta T$$

where  $\sigma_D$  and  $\sigma_L$  are the interfacial energies of the top



**Figure 2.** X-ray scattering diagram of the discotic material confined in the solid matrix and in the bulk nonoriented state (example: Ada-PBT, room temperature).

and side of the disk,  $T_i$  is the clearing temperature, and  $\Delta H_i$  is the corresponding clearing enthalpy. Using the experimental values ( $T_i = 461$  K,  $\Delta H_i = 25.7$  J/g,  $\Delta T = 163$  K) and estimates for  $\sigma_D$  and  $\sigma_L$  based on values of interfacial energies of aromatic and aliphatic components relative to PMMA<sup>32</sup> (about  $2.5$  and  $7.5 \times 10^{-2}$  N/m), we obtain the following critical dimensions of the nucleus:

$$r^* = 5.5 \text{ nm} \quad h^* = 16.5 \text{ nm}$$

This is well below the range which we are currently able to resolve. After the nucleation process this nucleus will grow in the shape of a cylinder as long as discotic material is available in its neighborhood. The equilibrium shape and size will depend on the amount of discotic material present in the dispersed phase and the ratio of the surface free energies of the top and side planes. Minimizing the interfacial energy

$$E_{\text{surf}} = 2\pi R^2 \sigma_D + 2\pi RL \sigma_L$$

with respect to the diameter  $D$  and the length  $L$  of the cylinder, we obtain

$$L/D = \sigma_D / \sigma_L$$

This shows that the ratio of the length to the diameter is controlled by the ratio of the interfacial energies, and we have to conclude that the ratio is of the order of 2–3 in the case considered here. This is reasonable in view of the chemical nature of the side groups defining  $\sigma_L$  and of the core defining to a large extent  $\sigma_D$  (see above). In fact, the same ratio is obtained for the critical size of the nucleus. The expectation is that a variation of the matrix will effect the ratio considerable. We currently perform such studies.

The X-ray diagram characteristic of the polymer dispersed system containing the discotic material is displayed in Figure 2. It is obvious, first of all, that the diagram contains a very distinct reflection resulting from a hexagonal packing around a scattering angle of  $6^\circ$ . An amorphous halo and superimposed on the halo a broad reflection originating from a regular packing along the columns appear in the range of scattering angles from  $15^\circ$  to  $27^\circ$ . Concentrating on the hexagonal reflection, at first, it is obvious that the diagram resembles the one found for the bulk material as also apparent from Figure 2. The bulk material displays hexagonal reflections at smaller scattering angles, and

the hexagonal lattice constant amounts to  $1.89$  nm. A closer inspection reveals, however, that the dispersion in the matrix polymer gives rise to changes. One is that the width of the main reflection is increased relative to the bulk material.

This increase of the width of the reflections indicates a reduction of the effective correlation of the hexagonal lattice relative to the bulk value. We will use the Scherrer equation<sup>33</sup> to obtain information on the correlation length

$$L = \frac{0.9 \lambda}{\text{fwhm} \cos(2\Theta)}$$

where  $L$  is the correlation length,  $\lambda$  the wavelength of the radiation used, fwhm the width of the reflection at half-maximum, and  $2\Theta$  the scattering angle. From this approach we obtained a reduction from about  $26.6$  nm (bulk value) to  $17.7$  nm. We should keep in mind that we used a rather simplified analysis by considering just the width at half-maximum. Nevertheless, it is interesting that a geometric confinement taking place on a scale of the order of several  $100$  nm has an effect on a spatial order extending only over several  $10$  nm.

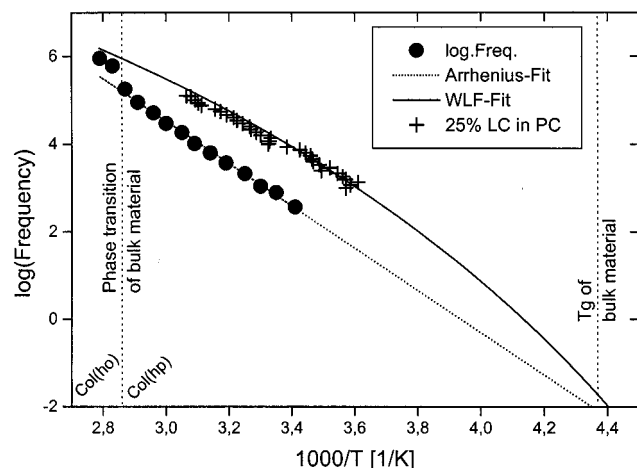
The X-ray diagrams of the confined and the bulk materials differ also in the range of larger scattering angles. Here we observe for the bulk material a doublet reflection superimposed on the amorphous halo and just one broad reflection for the confined discotic state. The doublet is a signature of the plastic columnar state as reported previously.<sup>34</sup> This highly ordered columnar phase is characterized by a three-dimensional registry of the two-dimensional columnar packing and the intracolumnar packing as obvious from the occurrence of mixed reflections ( $hkl$ ). The long-range translational order resembles thus the one of a real crystalline state. Yet NMR and dielectric studies have revealed that the molecules are able to rotate around the columnar axes, a process which freezes in at a glass transition.<sup>34</sup>

For the confined material we observe in the same temperature range a rather broad reflection resulting from a regular packing of the disklike molecules along the columns for the bulk material as found for the hexagonal ordered state ( $\text{Col}_{\text{ho}}$ ). It is thus apparent that the confinement tends to cause a destruction of the plastic columnar phase ( $\text{Col}_{\text{hp}}$ ) and the induction of the less ordered  $\text{Col}_{\text{ho}}$  phase. This result is not totally unexpected since previous studies have revealed that the formation of the plastic columnar phase may be easily suppressed by incorporation of the LCs into nanoporous glasses.<sup>28</sup> Yet a critical size of the dispersed discotics exists above which the plastic columnar state is formed. The results show that it is not the length but rather the diameter and thus the curvature of the dispersed regions which controls the phase formation: a hexagonal ordered state is formed for diameters up to  $300$  nm and a plastic columnar state for diameters above about  $350$  nm.

The dispersion of the discotic material in a solid polymer leads thus to significant modifications of the columnar structure: the plastic columnar phase may be destroyed and thus the three-dimensional registry. The expectation is that these effects will have a strong impact on molecular dynamics and optical properties.

**Dielectric Studies on the Glass Relaxation.** The dielectric relaxation studies performed on the confined material revealed the presence of a glass relaxation process. Figure 3 displays the frequency temperature





**Figure 3.** Activation diagram of the dielectric relaxation of the discotic material in the confined state and in the bulk state (example: M5PBT in PC, PC was chosen to avoid contributions of the  $\beta$ -relaxation of PMMA).

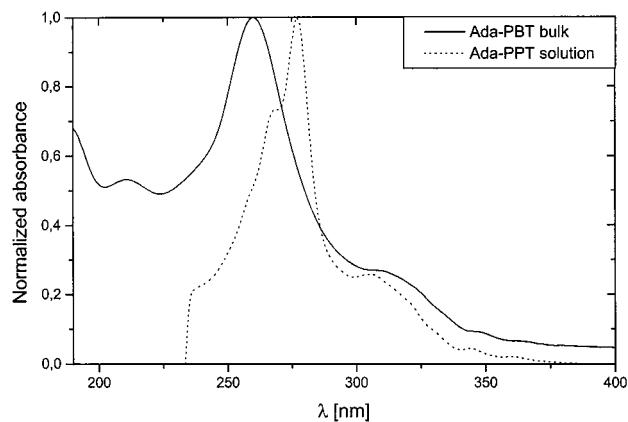
characteristic of the glass relaxation process. This relation can be represented on the basis of the WLF behavior:<sup>35</sup>

$$\log \frac{\omega}{\omega_0} = \frac{C_1(T - T_0)}{C_2 + (T - T_0)}$$

where  $T_0$  is the reference temperature (chosen in the following as the static  $T_g$ ) and  $\omega_0$  the corresponding relaxation frequency. The WLF parameters are close to the ones found on the average for amorphous organic glasses, and for columnar discotics, they turned out to be  $C_1 = 13.4$  and  $C_2 = 4.7$  K, respectively.<sup>36</sup> Furthermore, the location of the quasi-static glass transition temperature agrees with the one found by dielectric studies for the bulk material.

These results differ, nevertheless, from the ones obtained for the bulk material. The bulk material has been found to correspond in the plastic columnar state to a strong glass with a thermally activated relaxation behavior rather than to display a WLF behavior (fragile glass).<sup>37</sup> This is a very unusual result. In general, confinement effects are discussed in terms of shifts of phase transition or glass transition temperatures. No report exists, to our knowledge, describing changes of the character of the glass transition. Figure 3 showing the dielectric relaxation data also for the bulk material reveals this difference. The reason for this change in the character of the glassy state obviously is that the confinement destroys the plastic columnar phase (see X-ray results above) and induces a hexagonal columnar phase. Such a phase, in turn, is known to correspond to a fragile glass. Similar results were reported by us for discotics located in narrow pores of porous glasses.<sup>28</sup> The conclusion is that the confinement influences structural and relaxation processes very strongly. It is expected that these strong changes are also reflected in optical properties.

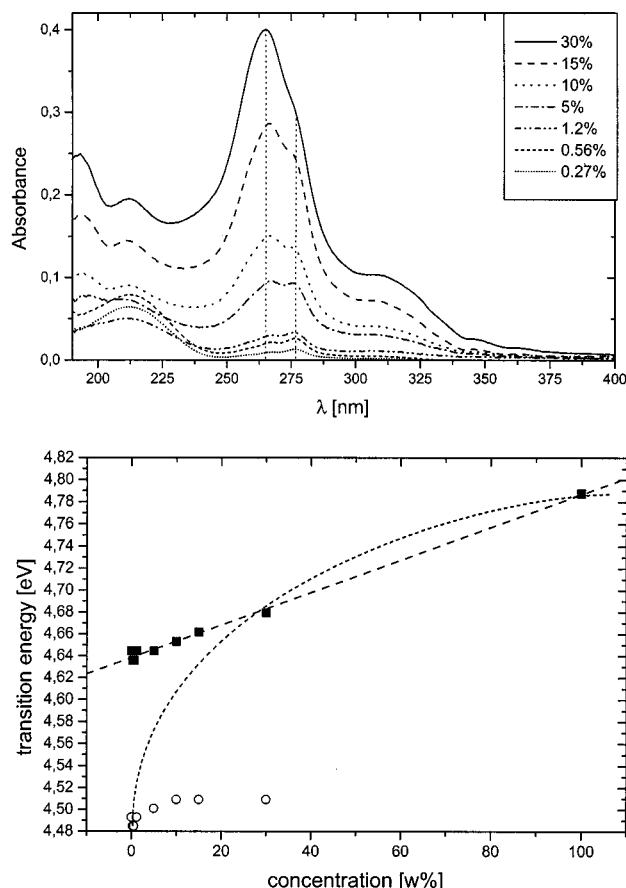
**Absorption and Emission Properties.** At first we will consider the absorption spectra of the dispersed materials, and we will compare them with the one of the bulk material in the columnar plastic state. The UV-vis maximum of the bulk material considered here (Ada-PBT) is characterized by a blue shift compared with the one found for solutions. This is obvious from the absorption spectra found for solutions and for the



**Figure 4.** Absorption spectra of the bulk discotic material and of the solution (chloroform) (Ada-PBT).

ordered bulk material displayed in Figure 4. A blue shift of this kind has been attributed to strong exciton interactions leading to collective excited states along the columns as apparent from quantum chemical calculations.<sup>11</sup> According to these calculations performed on symmetrical triphenylenes, the magnitude of the shift depends on the state of organization in particular on the number of excited molecules interacting within a column. In the spirit of these quantum chemical calculations, a tentative conclusion would be that the number found for the plastic columnar state of the discotic materials considered here is probably well above 10. In fact, the correlation length as determined by X-ray investigations yielded values of the order of 15–20 nm along the columns corresponding to a number of structurally correlated molecules of the order of 40–60.<sup>10,16</sup>

Next we consider the absorption spectra of the polymer dispersed discotics. The results are displayed in Figure 5 for different concentrations leading to different degrees of dispersion. It is apparent that the spectra obtained for films with lower concentrations of the discotics are very similar to the ones found for solutions, indicating a fine dispersion approaching even a molecular dispersion. With increasing concentration there are two significant changes: first, it is obvious that there is an exchange of the relative intensities of the two major vibronic bands (attributed to  $v_4 = 0$  and  $v_4 = 1$ ) of the  $S_0 \rightarrow S_4$  transition, and second, a slight blue shift of both vibronic bands occurs (Figure 5b). The final state found for the larger aggregates is an absorption behavior resembling the one of the bulk material where the  $v_4 = 0$  vibronic band is too weak to be visible. These changes are apparently related to the increasing aggregate sizes of the dispersed material at higher concentrations. The observed behavior is not in full agreement with the expectations based on the model calculations discussed above. We had expected a rather continuous shift of one of the electronic transition amounting to about 18 nm (also schematically shown in Figure 5b) but not strong changes in the relative intensities of the vibronic bands. The real shift of the electronic transition at constant vibronic band probably due to the increase of the correlation length amounts, however, only to 9 nm whereas the redistribution of the intensities of the vibronic bands attribute an additional apparent shift of about 9 nm. The discussed changes in the UV-vis spectra as a function of the size of the aggregates are—to our knowledge—shown for the first time. We tentatively attributed the changes in the intensity of the vibronic bands to slight changes in the



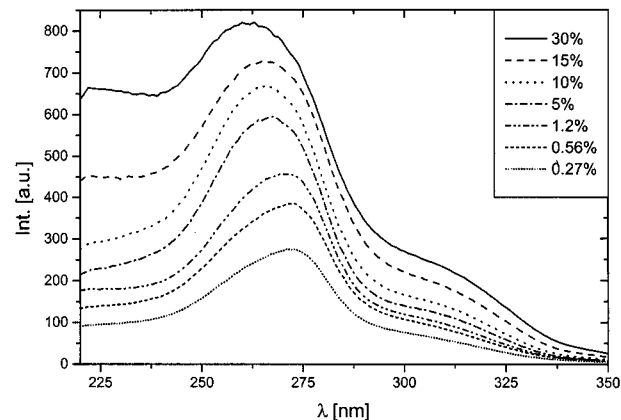
**Figure 5.** (a, top) Absorption spectra of the dispersed discotic material (Ada-PBT in PMMA). (b, bottom) Energetic shift of both vibronic bands  $\nu_4 = 0$  [○],  $\nu_4 = 1$  [■], linear fit [---], expected behavior on the basis of the model calculations cited above (schematic) [···].

anharmonic potentials of the ground and excited states such as slight relative displacements.

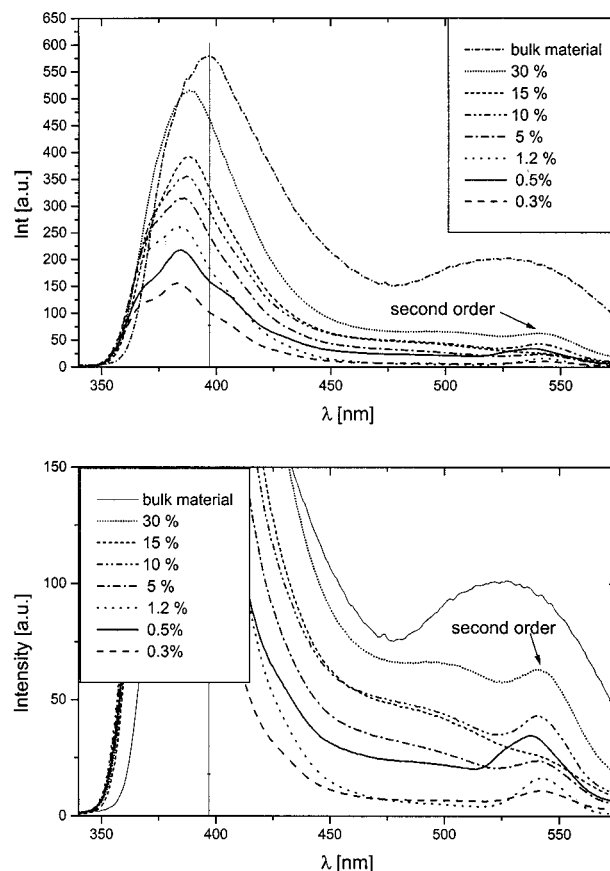
Finally, the absorption spectra of the annealed samples—with concentrations higher than 5 wt % showing coarser dispersed structures—are identical to the one of the bulk material. In any case it is apparent that it is not the transition from the hexagonal ordered to the plastic columnar state happening with increasing sizes of the dispersion which affects the absorption behavior but rather the size of the aggregates.

Rather similar results were obtained for excitation studies. We registered in this case the fluorescence at a given wavelength of emission as a function of the excitation wavelength. The observation is that the locations of the excitation curves correspond rather closely to the ones of the absorption spectra; i.e., we observe a blue shift as the dispersion of the discotic material becomes coarser. The interpretation is similar to the one given for the absorption spectra.

Finally, we will discuss the impact of the geometric confinement on the fluorescence spectra of the discotic materials. For bulk materials in the plastic columnar phase we find that the fluorescence is red-shifted compared to the one found in solution,<sup>38</sup> the shift amounting to about 10 nm (Figure 7) from 385 to 395 nm. The dispersion of the discotic material in the polymer film causes a blue shift of the emission maxima relative to the bulk value, the spectra approaching thus the ones found for solutions. The emission spectrum is characterized in this case by a fine structure apparently



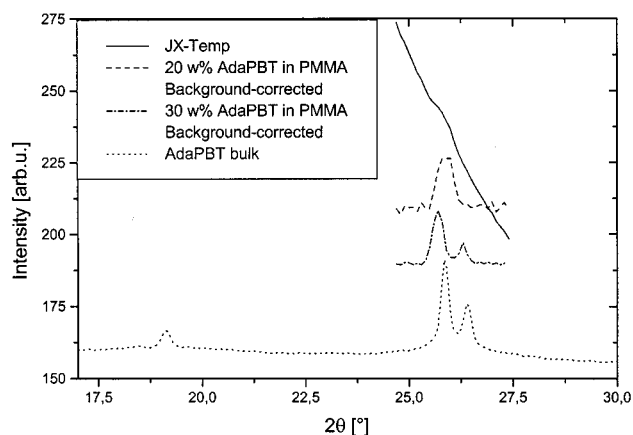
**Figure 6.** Excitation spectra of the dispersed discotic material.



**Figure 7.** (a, top) Fluorescence spectra of the dispersed discotic material as well as of the bulk material. (b, bottom) Comparison of the spectra in the higher wavelength range, detected after 2 min of irradiation (Ada-PBT in PMMA).

related to vibronic contribution. Such a fine structure has also been observed for solutions. This may be taken as an indication for the presence of a molecular dispersion with the polymer acting as a solid solvent. Yet we observe similar spectra for the phase-separated systems. An increase of the size of the dispersion causes a reduction of the fine structure of the emission band but no shift of the location of the emission band; i.e., the emission band remains located at 385 nm. The location of the band is thus a function of the phase structure ( $\text{Col}_{\text{hp}}$ ) and the fine structure a function of the size of the aggregate.

Actually, for symmetrically substituted hexaalkoxy-triphenylenes it is known that there is no such shift



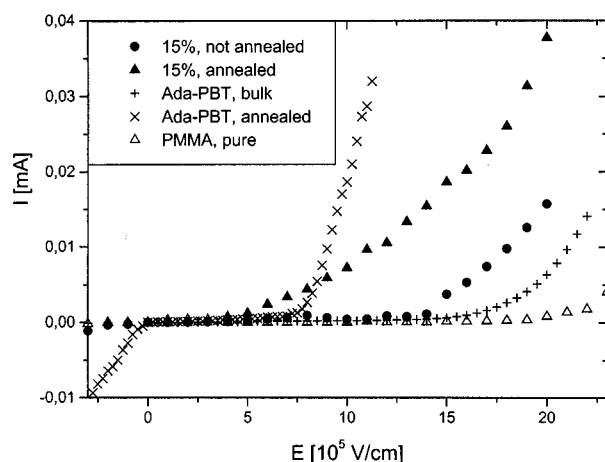
**Figure 8.** Comparison of the X-ray scattering diagrams of the discotic material confined in the solid matrix (20 and 30 wt %) and in the bulk (Ada-PBT in PMMA).

between the emission maxima (385 nm) of the solution and the bulk displaying also the  $\text{Col}_{\text{ho}}$  phase. The only difference is the absence of vibronic progressions in the case of the bulk spectrum.<sup>39</sup> Now, the locations and shapes are very similar in this case to the spectra detected by us. The conclusion thus is that it is the destruction of the plastic columnar phase taking place within the small domains in the confining polymer film which is the origin of the blue shift of the fluorescence spectrum relative to the bulk material. In fact, we have shown above that the dispersion of the discotics leads to columnar assemblies displaying the  $\text{Col}_{\text{ho}}$  phase. The  $\text{Col}_{\text{hp}}$  phase of the bulk material is almost completely suppressed as apparent from X-ray analysis (Figure 2).

We provide further evidence for this interpretation using thin films with enhanced concentrations of the discotic material. The X-ray data of the dispersed systems with 20 and 30 wt % are compared with the one of the bulk material in Figure 8. It is obvious that the structure of the film containing the higher concentration resembles the one of the bulk whereas the other displays a  $\text{Col}_{\text{ho}}$  phase. On the other hand, the finding is that the 30 wt % sample displays an emission spectrum identical to the one of the bulk material whereas the 20 wt % samples shows a blue-shifted spectrum. Again, the controlling influence of the phase structure on the emission properties is apparent.

A most interesting feature as far as the emission of the bulk material displaying the plastic columnar state is concerned was the growth of a second low-energy emission band as a function of the irradiation time. This has been reported by us previously.<sup>38</sup> No such growth was observed for triphenylenes having very similar chemical structures yet which did not display the plastic columnar state but rather the hexagonal columnar phase. The local structure seems to be the origin of this effect. Our tentative explanation therefore was at that time that the growth of the second emission band results from the favorable formation of dimers caused by strong interactions between excited pairs of molecules which in turn act as a new channel for the relaxation of the excitation. This interpretation was based on the finding that the plastic columnar state favors a dimer formation already in the ground state of the molecules.

Accepting this assumption, we concluded that the destruction of the specific order induced by the confinement effects should reduce the tendency toward dimer formation in the ground state and thus also the one



**Figure 9.** Diode characteristics of LEDs of two different concentrations of dispersed material as well as of pure polymer and of pure discotic, respectively (Ada-PBT).

toward dimer formation in the excited state.<sup>38</sup> In fact, we find here for the polymer dispersed systems that the emission spectra for smaller concentrations, i.e., for systems displaying the hexagonal ordered state, do not change as a function of the time for irradiation times at irradiation energies comparable to the ones used for the bulk materials. We observe a weak signal of the high-energy emission only for higher discotic concentrations; it decreases with smaller concentrations, i.e., with smaller dispersed LC structures (Figure 7b). This is a strong hint that the structural arrangement taking place within the column may effect the emission properties strongly.

**LED Applications.** Finally, we will consider the diode characteristics of the dispersed materials compared to that of bulk discotic material and pure matrix polymer which are displayed in Figure 9. It is obvious that the pure matrix polymer does not contribute to the injection and charge carrier transport in any significant way and that the shapes of the curves as well as the onset voltages differ from the ones of the bulk discotic material in LEDs.<sup>10,15</sup> The onset voltage is rather high for the finely dispersed state. Yet, it decreases strongly after annealing the device at temperatures well above the glass transition temperature of the matrix polymer. This may be interpreted in terms of the formation of larger columnar discotic assemblies, which are responsible for an enhanced charge carrier transport. In fact, after annealing we observe cylindrical structures with the length of several hundred nanometers which is obvious from AFM studies. These findings stress again the important role of the columnar state on injection and transport properties.

The particular behavior of the diode characteristic in the negative voltage regime of the annealed bulk LED has been described previously.<sup>40</sup> The origin of this effect is still a matter of discussion, and it has been speculated that it is related to the homeotropic orientation of the columns relative to the substrate which occurs after annealing of the bulk material. We observe no current in this regime in the case of the dispersed systems. It may thus be assumed that such a homeotropic orientation is suppressed in the dispersed state. Unfortunately, the greenish-white emission of the polymer dispersed LED was too weak to record an electroluminescence spectrum.

The advantage of LED applications of PDLC systems discussed here compared to the bulk discotic material

is obvious. Annealing of the bulk material results in the orientation of the columns which reduces the onset voltage yet causes a rather rough surface. LEDs containing PDLCs show almost the same onset voltages but flat surfaces. This should lead to a much easier handling in devices. To obtain for our current experimental setup a sufficient electroluminescence intensity, we have to optimize the concentration of the discotic material.

#### IV. Conclusions

The dispersion of the columnar discotic material in a solid polymer matrix causes significant changes in structural and dynamic properties of the discotic material. Such a dispersion can be used to modify absorption and emission properties of the discotic material due to geometric confinement effects. Thin films which are optically transparent can be obtained via spin-coating. These are of interest in optical applications such as organic light-emitting diodes.

#### References and Notes

- (1) Mott, N. F.; Davies, E. A. *Electronic Processes in Non-crystalline Materials*; Clarendon Press: Oxford, 1971.
- (2) Borsenberger, P. M.; Pautmeier, L.; Bässler, H. *J. Chem. Phys.* **1991**, *94*, 5447.
- (3) Bässler, H. *Phys. Status Solidi B* **1993**, *175*, 15.
- (4) Borsenberger, P. M.; Bässler, H. *J. Chem. Phys.* **1991**, *95*, 5327.
- (5) Bässler, H. *Phys. Rev. Lett.* **1987**, *58*, 767.
- (6) Bässler, H. In *Disorder Effects on Relaxation Properties*; Richert, R., Blumen, A., Eds.; Springer-Verlag: Berlin, 1994; p 485.
- (7) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, H. *Nature* **1994**, *371*, 141.
- (8) Simmerer, J.; Glösen, B.; Paulus, W.; Kettner, A.; Schuhmacher, P.; Adam, A.; Etzbach, K. H.; Siemensmeyer, K.; Wendorff, J. H.; Ringsdorf, H.; Haarer, D. *Adv. Mater.* **1996**, *8*, 815.
- (9) Ochse, A.; Kettner, A.; Kopitzke, J.; Wendorff, J. H.; Bässler, H. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1757.
- (10) Kopitzke, J.; Wendorff, J. H. *Chem. Unserer Zeit* **2000**, *4*.
- (11) Marguet, S.; Markovitsi, D.; Millié, Ph.; Sigal, H.; Kumar, S. *J. Phys. Chem. B* **1998**, *102*, 4697.
- (12) Markovitsi, D.; Germain, A.; Millie, Ph.; Lecuyer, P.; Gallos, L. K.; Argyrakis, P.; Bengs, H.; Ringsdorf, H. *J. Phys. Chem.* **1995**, *99*, 1005.
- (13) Christ, Th.; Stümpflen, V.; Wendorff, J. H. *Makromol. Chem. Rapid Commun.* **1997**, *18*, 93.
- (14) Stapff, I. H.; Stümpflen, V.; Wendorff, J. H.; Spohn, D. B.; Möbius, D. *Liq. Cryst.* **1997**, *23*, 613.
- (15) Lüssem, G.; Wendorff, J. H. *Polym. Adv. Technol.* **1998**, *9*, 443.
- (16) Fimmen, W.; Kettner, A.; Kopitzke, J.; Ruland, W.; Wendorff, J. H. *Tagungsband der 25. Freiburger Arbeitstagung* 1999.
- (17) Golemme, A.; Zumer, S.; Allender, D. W.; Doane, J. W. *Phys. Rev. Lett.* **1988**, *61*, 1937.
- (18) Crawford, G. P.; Zumer, S., Eds.; *Liquid Crystals in Complex Geometries formed by Polymer and Porous Network*; Taylor, Francis: London, 1996.
- (19) Crawford, G. P.; Stannarius, R.; Doane, J. W. *Phys. Rev. A* **1991**, *44*, 2558.
- (20) Crawford, G. P.; Allender, D. W.; Doane, J. W. *Phys. Rev. A* **1992**, *45*, 8693.
- (21) Iannacchione, G. S.; Crawford, G. P.; Zumer, V.; Doane, J. W.; Finotello, D. *Phys. Rev. Lett.* **1993**, *71*, 2595.
- (22) Liu, G.; Li, Y.; Jonas, J. *J. Chem. Phys.* **1991**, *95*, 6892.
- (23) Miyamo, K. *Phys. Rev. Lett.* **1979**, *43*, 51.
- (24) Schwalb, G.; Deeg, F. W. *Phys. Rev. Lett.* **1995**, *74*, 1383.
- (25) Iannacchione, G. S.; Mang, J. T.; Kumar, S.; Finotello, D. *Phys. Rev. Lett.* **1994**, *73*, 2708.
- (26) Naji, L.; Kremer, F.; Stannarius, R. *Liq. Cryst.* **1998**, *24*, 363.
- (27) Panarin, Y.; Aliev, F. M.; Rosenblatt, C. *Phys. Rev. Lett.* **1998**, *81*, 2699.
- (28) Glösen, B.; Kopitzke, J.; Wendorff, J. H. *Liq. Cryst.*, in press.
- (29) Kettner, A. PhD Thesis, Marburg, 1998.
- (30) Drazic, P. S. *Liquid Crystal Dispersion*; World Scientific: Singapore, 1995.
- (31) Wunderlich, B. *Macromolecular Physics II*; Academic Press: New York, 1973.
- (32) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
- (33) Guinier, A. *X-Ray Diffraction*, 2nd ed.; Dover Publications: Mineola, 1994.
- (34) Glösen, B.; Heitz, W.; Kettner, A.; Wendorff, J. H. *Liq. Cryst.* **1996**, *20*, 627.
- (35) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
- (36) Angell, C. A. *J. Non-Cryst. Solids* **1991**, *131*, 13.
- (37) Glösen, B.; Kettner, A.; Kopitzke, J.; Wendorff, J. H. *J. Non-Cryst. Solids* **1998**, *241*, 113.
- (38) Bayer, A.; Hübner, J.; Kopitzke, J.; Oestreich, M.; Rühle, W.; Wendorff, J. H. *J. Phys. Chem. B*, accepted.
- (39) Markovitsi, D.; Rigaut, F.; Mouallem, M.; Malthête, J. *Chem. Phys. Lett.* **1987**, *135*, 236.
- (40) Christ, Th.; Geffarth, F.; Glösen, B.; Kettner, A.; Lüssem, G.; Schäfer, O.; Stümpflen, V.; Wendorff, J. H.; Tsukruk, V. *Thin Solid Films* **1996**, *302*, 214.

MA001470G