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The influence of geometric confinement on the state of order and on the glass relaxation process was investigated for a triphenylene derivative able to display a highly ordered plastic columnar phase in the bulk. The compound was incorporated into porous glasses—characterized by a narrow size distribution—with average pore diameters of 20, 7.5, 5 and 2.5 nm. The X-ray diagrams revealed the presence of a hexagonal order, yet the lattice spacing is significantly reduced with decreasing pore size and the reflections become broad. The X-ray doublet reflection, superimposed on the halo which is characteristic for the bulk plastic columnar phase, is absent in all cases. It is replaced by a single broad intracolumnar reflection which indicates that the confinement destabilizes the plastic phase in favour of the hexagonal ordered phase. A further observation is that the intracolumnar correlation length is reduced with decreasing pore size. The confinement was furthermore found to cause a transition from a strong glass (bulk material) to a fragile glass former, obviously induced by the structural modification.

1. Introduction

The influence of geometric confinement on the state of order and on the molecular dynamics of liquid crystals has been the subject of many investigations [1–11]. The findings based on theoretical considerations and experimental results are that thermodynamic, structural and dynamic properties are strongly modified by confinement effects. It has been reported, for instance, that confinement leads to the formation of nematic or smectic surface layers within the isotropic phase, and to a shift of the isotropic–nematic phase transition from first to second order. Furthermore, it is known that confinement may cause a shift of the relaxation time of order parameter fluctuations or may give rise to anchoring transitions. Investigations on confinement effects are not only of interest with respect to basic science: polymer dispersed liquid crystals and liquid crystalline gels are examples of cases where confinement effects take place to various degrees and where technical applications are obvious [1, 2, 12, 13].

The research on confinement effects in the area of liquid crystals has focused on calamitic systems, predominantly on nematic and smectic phases. Various types of material controlling confinement have been evaluated, among them polymer dispersed systems [1, 2], organic and inorganic filters with well defined cylindrical parallel pores [3, 4], porous glasses with a narrow pore size distribution, but random orientations of the cavities [5, 10] and also silica aerogels with irregularly shaped cavities of different sizes.

We expect strong confinement effects also for discotic materials [14], and in particular for columnar discotics if the pore sizes approach the diameter of the disc-shaped molecules. We envision that the confinement effect will not be limited in this case to molecular dynamics, structural and thermodynamic properties, but also to optoelectronic properties. It has been reported in the literature that the formation of columns and the packing of the columns in space, as well as the intrinsic order within the columnar phases have a strong effect on the absorption and emission spectra and on the mobility of charge carriers [15–18]. Our final aim is the control of such optoelectronic properties via confinement effects. As a first step we have investigated the structure formation of columnar discotics in porous glasses as well as their molecular dynamics. We have selected for such investigations triphenylene derivatives, since in the past most of the optical studies were performed on such materials. We have chosen a triphenylene derivative which displays a highly ordered plastic columnar phase characterized by a three-dimensional lattice and molecules which are able to rotate around the columnar axis [19, 20]. The

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hexagonal spacing of the columns is slightly below 2 nm in this case. We selected porous glasses with average pore sizes in the range 2.5 to 20 nm so that the geometrical restrictions are quite severe: only 2 up to about 100 columns should be able on average to penetrate into the pores.

2. Experimental

The material considered was the asymmetrically substituted triphenylene shown in the scheme. It is characterized by the following phase sequence: T_g − 43 Col_{hp} 78 Col_{ho} 188 I (°C).

Porous glass was obtained from Geltech Inc., USA with pore sizes of 20, 7.5, 5 and 2.5 nm. The glass was provided as cylinders with a diameter of 0.5 cm from which thin slices were obtained using a diamond string saw. The slices were filled in an ultra high vacuum at elevated temperatures by a procedure that has been described previously [10]. Volatile impurities were removed by annealing the thin slices in vacuum for two days at elevated temperatures. The surfaces of the thin slices were purified by removing the material located outside the pores using sharp cutting edges.

The temperatures and enthalpies of the phase transitions were determined by differential scanning calorimetry (Perkin-Elmer DSC 7) at a heating rate of 10 K min⁻¹. The structure was analysed by X-ray scattering studies at the Cornell High Energy Synchrotron Source (CHESS). The beamline was equipped with a 2D detector; the sample was fixed into a Mettler hot stage to control the temperature and the diffraction patterns were obtained in transmission using wavelength of 1.033 Å. For the dielectric studies, both sides of the disc-shaped porous glass sample filled with the triphenylene derivative were covered with aluminium foil and mounted between the gold plated brass electrodes of the capacitor. The dielectric investigations were performed using a Solartron-Schlumberger frequency response analyser FRA 1260 with a Novocontrol active sample cell BDC-S $(10^{-2} - 3 \times 10^6 \, Hz)$ and a Hewlett Packard impedance analyser 4284A $(10^2–10^9 \, Hz)$.
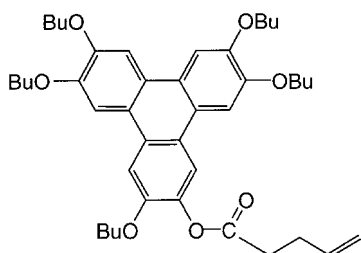
3. Results and discussion

3.1. *Degree of filling*

The porous glasses are characterized by volume fractions of pores ranging from 0.48 (2.5 nm pores) to 0.70 (7.5 nm pores) and finally to about 0.75 (20 nm pores). Using the weight of the thin slices prior to and after the filling procedure we could establish that the pores were filled nearly completely with the discotic compound, even in the case of the 2 nm pores. The surface films turned out to be very thin. We nevertheless removed these traces with the sharp edge of a cutting device so that the amount of material not being confined was negligible (see experimental part). AFM investigations performed on the unfilled and filled glasses led to the same conclusion.

3.2. *X-ray analysis*

For comparison, we will first consider the X-ray diagram of the unoriented bulk material. It displays reflections at smaller scattering angles (about $2\theta = 5°–15°$) originating from a hexagonal packing, as apparent from figure 1. The hexagonal lattice constant amounts to 1.89 nm.

At larger scattering angles ($2\theta = 26°$) we observe a doublet reflection superimposed on the amorphous halo. This doublet is a signature of the plastic columnar state, as reported previously [19, 20]. This highly ordered columnar phase is characterized by a three-dimensional registry of the two-dimensional columnar packing and the intracolumnar packing, as is obvious from the occurrence of mixed reflections ($h\,k\,l$). The long range translational order therefore resembles that 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 the glass transition [19, 20].
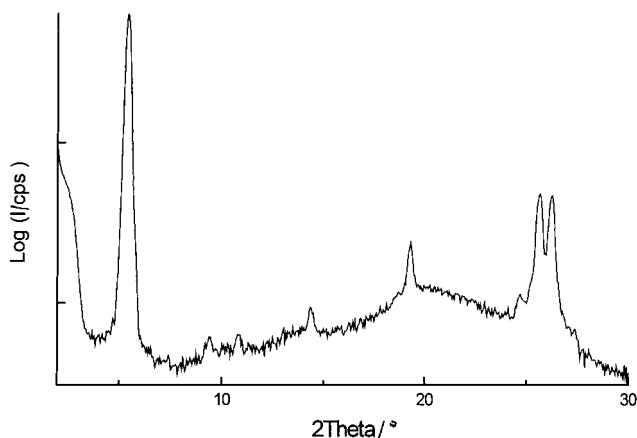

Figure 1. X-ray diagram of the bulk material (ω-undecenoyl-pentabutoxytriphenylene) at room temperature (the scattering angles are given for a wavelength of radiation λ = 1.542 Å).

Scheme. Triphenylene derivative studied.

The X-ray diagrams characteristic of the porous glasses containing the discotic material within the pores are displayed in figures 2(*a*) and 2(*b*) for two different pore sizes. It is obvious that the diagrams all contain reflections at smaller scattering angles resulting from hexagonal packing. In fact, the system with a pore diameter of 20 nm displays higher order hexagonal reflections (see inset of figure 2) quite similar to the case of the bulk material. Yet decrease of the pore diameter gives rise to two changes: the location of the main reflection is shifted to large scattering angles and the width of the reflection increases strongly.

The table displays the corresponding decrease of the hexagonal spacing with decreasing pore size. The value observed for the 20 nm pores corresponds to the bulk value, that found for the 7.5 nm pores is somewhat
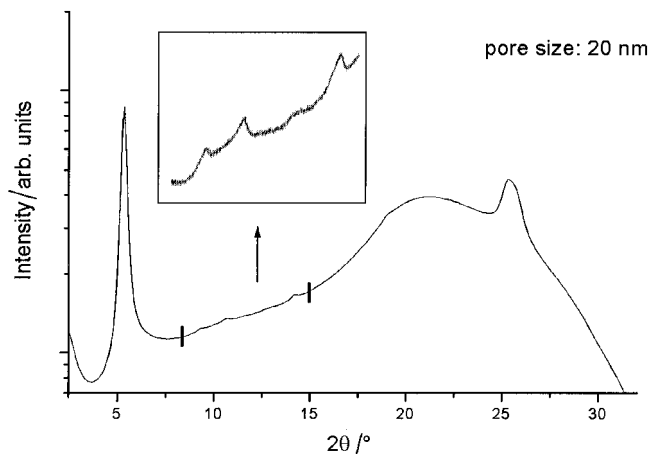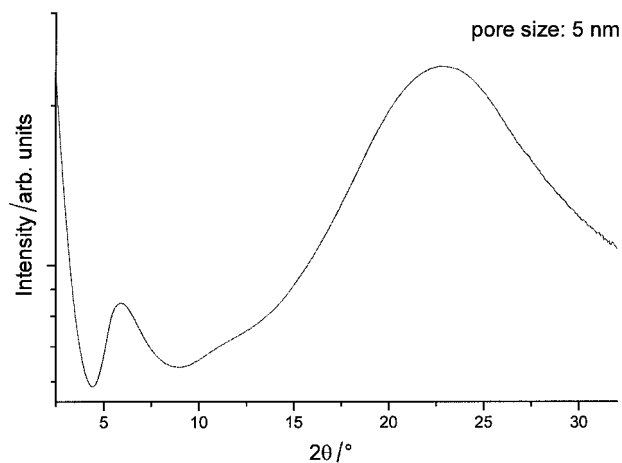
Table. Variation of the intercolumnar distance, the width of the intercolumnar reflections, and the correlation length, with the pore size of the porous glass (see the text).

Pore size/nm	Intercolumnar distance/Å	FWHM/°	Crystallite size/nm
20	16.3	0.35	22.3
7.5	16.2	1.00	8.3
5	14.9	1.90	4.2
2.5	14.3	2.05	3.9

reduced, and the values are strongly reduced by as much as 15% for the smaller pores. In view of the small compressibility of fluids it seems reasonable to assume that the density is not increased by the confinement, so that we have to conclude that the confinement gives rise to a considerable interpenetration of neighbouring columns in the way shown schematically in figure 3. This overlap thus allows a dense packing of the columns even for the case of a mismatch between the space requirements of the columns and the space provided by the pores.

The strong increase of the width of the reflections with decreasing pore size (see the table) is not unexpected, since the decreasing pore size will reduce the effective correlation length of the hexagonal lattice. We used a very simple approach to obtain information on the correlation length which is based on the Scherrer equation [21]:

$$L = \frac{0.9\,\lambda}{\text{FWHM}\cos(2\theta)}$$

where L is the correlation length, λ the wavelength of the radiation used, FWHM the width of the reflection at half height and 2θ the scattering angle. Using this approach we obtained the values displayed in the table. It is obvious that the correlation length agrees surprisingly well with the pore diameter with the exception of the glass with 2 nm pores. A distribution of pore sizes caused particularly by the junction of pores may be one reason for the discrepancy. We should also keep in mind that we used a rather simplified analysis by considering only the width at half maximum.

Next we will consider the scattering diagram observed for larger scattering angles. The halo originating from the disordered packing of the side groups is present in all cases. Superimposed on it is a rather broad reflection resulting from a regular packing of the disc-like molecules along the columns, as discussed for the bulk material. The surprising findings are, however, first that we observe a singlet rather than a doublet and second that this reflection is suppressed for smaller pore sizes (figure 2). It is thus apparent that the confinement causes a destruction of the plastic columnar phase. DSC investigations did not show any sign of a transition from a plastic to the

(*a*)

(*b*)

Figure 2. X-ray diagrams obtained for the discotic material in pores of two sizes taken at room temperature (note that the glass contributes to the halo).
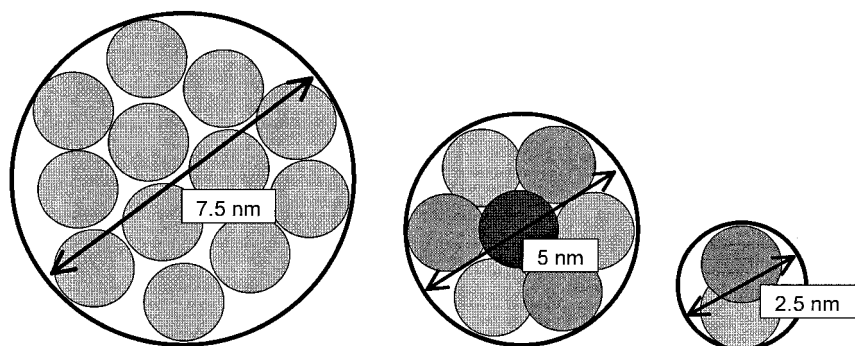
Figure 3. Schematic drawing of pore filling.

hexagonal phase as in the case of the bulk material. This result is not totally unexpected since previous studies [22] had revealed that the formation of the plastic columnar phase may be easily suppressed by doping with electron acceptors even at small concentrations, or by temperature variation (occurrence of a re-entrant behaviour). Cooling of the systems to about 0°C did not lead to the appearance of the plastic phase at a lower temperature, although the intracolumnar reflection became broader (see figure 4). This may be an indication of the formation of a Col_{hp} phase at still lower temperatures.

More surprising was the observation that the regular intracolumnar packing is destroyed by the confinement. Our interpretation is that the increasing interpenetration of the columns enforced by the decreasing pore sizes causes the intracolumnar packing to become less dense, which in turn causes a destruction of the regular packing.

In summary, the confinement leads to significant modifications of the columnar structure: the plastic columnar phase is destroyed, the intracolumnar packing becomes disordered (Col_{hd}) and the columns are forced to interdigitate. The expectation is that these effects will have a strong impact on the thermodynamic properties and molecular dynamics.

3.3. *Thermal properties*

The DSC investigations revealed that the phase transition temperatures are significantly influenced by the confinement. This is obvious from the DSC traces displayed in figure 5. We observe two well separated endothermic peaks for the sample with 200 nm pores located at about 165 and 180°C. Both peaks appear at lower temperatures compared with the clearing peak for the bulk material. The endothermic peak located at lower temperatures has the same asymmetrical shape as that observed for the bulk material, whereas the smaller higher temperature peak is less broad and more symmetric. The total enthalpy of transition summed over both peaks corresponds approximately to the value expected from the bulk measurements. The observation is that the low temperature peak is strongly reduced as
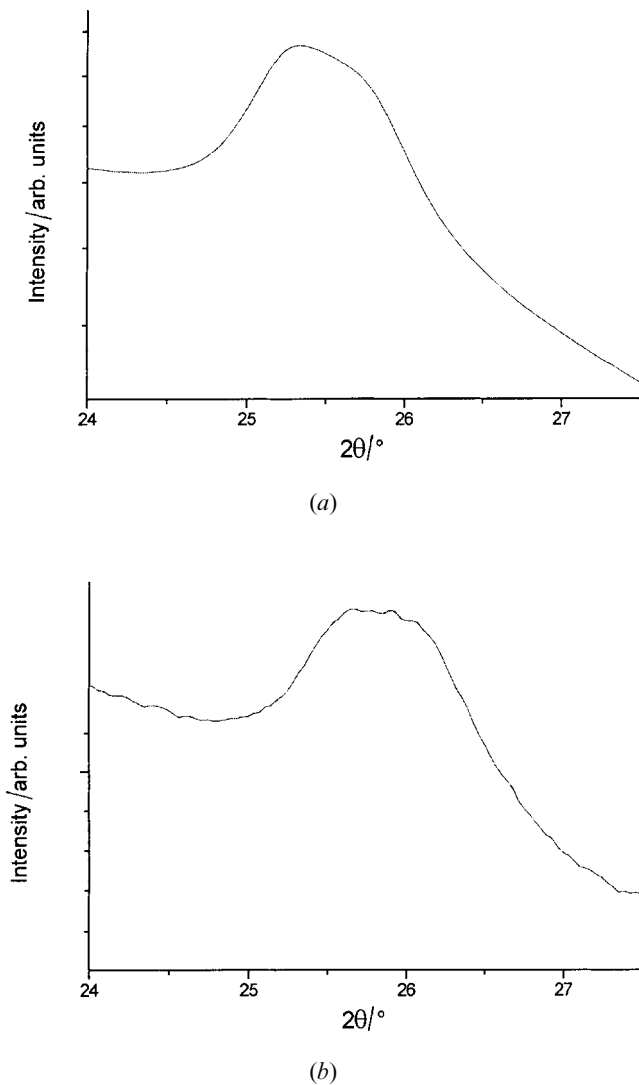

(*a*)

(*b*)

Figure 4. X-ray diagrams: (*a*) intracolumnar reflection at room temperature and (*b*) at about 0°C (sample confined in pores of 20 nm diameter).

the pore sizes decrease: we observe only the small high temperature peak for a pore size of 7.5 nm. We attribute the low temperature peak therefore to the bulk-like, yet
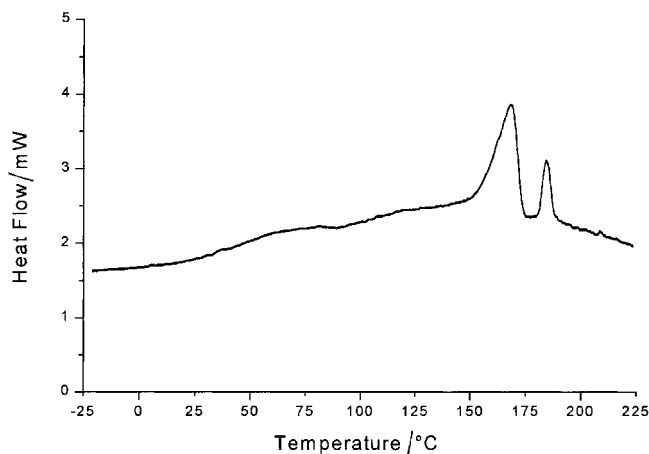
Figure 5.   DSC diagram of the sample confined in pores with a diameter of 20 nm.

disturbed material in the centre of the pores (melting point depression: 23 K) and the higher temperature peak to the columns close to the walls. It is known from the literature that the two regions are well separated [23]. The DSC traces obtained for all of the confined materials do not reveal the presence of a glass transition, in contrast to the case of the pure discotic compound.

### 3.4. *Dielectric studies on the glass relaxation*

Dielectric relaxation studies performed on the confined material did however reveal the presence of a glass relaxation process, as apparent from figure 6(*a*). Figure 6(*b*) displays the frequency versus temperature characteristic of the glass relaxation process. It is obvious that this relation can be represented very well on the basis of the WLF behaviour [24]:

$$\log \omega/\omega_0 = C_1(T - T_0)/[C_2 + (T - T_0)]$$

where T_0 is the reference temperature (chosen in the following as the static T_g) and ω_0 the corresponding relaxation frequency.

We extracted the following parameters from this diagram: C_1 13.4, C_2 84.7°C and T_g −46°C. The C_i values are close to those found on average for amorphous organic glasses and for columnar discotics [24, 25] and the location of the glass transition temperature is close to that found by dielectric studies for the bulk material. It may seem therefore as if the freezing-in process is not modified to any significant degree by the geometric confinement as far as dynamic features are concerned.

Yet, the results of the dielectric relaxation studies are nevertheless surprising. The bulk material has been found not to follow a WLF behaviour (fragile glass) due to its plastic columnar phase, but rather to correspond to a strong glass [26], i.e. the glass relaxation is thermally activated. Figure 6(*b*) displays the dielectric relaxation
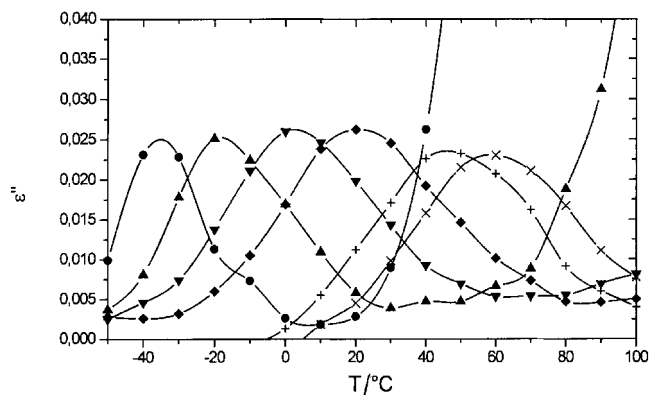
(*a*)
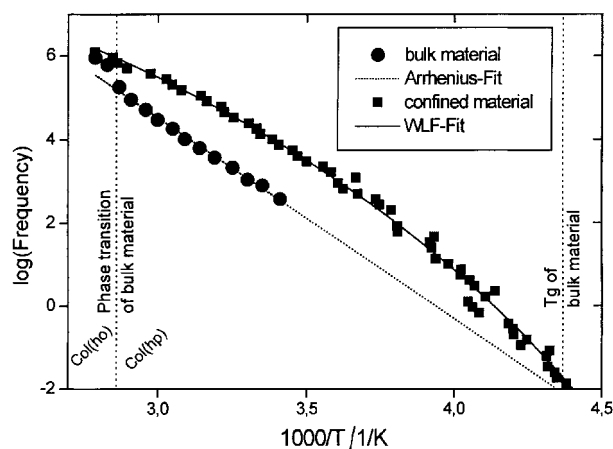
(*b*)

Figure 6.   (*a*) Dielectric loss curves for the confined material (porous glass, pore diameter 20 nm): −●− 0.28 Hz; −▲− 25 Hz; −▼− 675 Hz; −◆− 7.5 kHz; −+− 110 kHz; −×− 0.3 MHz: (*b*) frequency–temperature relation for the bulk (●) and the confined material (■).

data obtained for the bulk material. The confined material on the other hand behaves as a fragile glass [25], the activation diagram corresponding to WLF behaviour. The reason 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. This is, to our knowledge, the first time that a transition from a strong to a fragile glass due to confinement effects has been reported.

To conclude, it has become obvious that confinement influences structural, thermodynamic and relaxation processes very strongly. The expectation is that these strong changes are also reflected in optical properties, as well as electronic transport properties; corresponding studies are currently being performed.

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