

## Structural transformations of even-numbered $n$ -alkanes confined in mesopores

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The  $n$ -alkanes  $C_{12}H_{26}$ ,  $C_{14}H_{30}$ , and  $C_{16}H_{34}$  have been imbibed and solidified in mesoporous Vycor glass with a mean pore diameter of 10 nm. The samples have been investigated by x-ray diffractometry and calorimetric measurements. The structures and phase sequences have been determined. Apart from a reduction and the hysteresis of the melting-freezing transition, pore-confined C12 reproduces the liquid-triclinic phase sequence of the bulk material, but for C16 an orthorhombic rotator mesophase appears that in the bulk state is absent for C16 but well known from odd-numbered alkanes of similar length. In pore-confined C14 this phase shows up on cooling but not on heating.

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### I. INTRODUCTION

The  $n$ -alkanes ( $C_nH_{2n+2}$ , abbreviated Cn) of intermediate length form lamellar crystals. In the fully ordered state at low temperatures the odd-numbered alkanes exist in the orthorhombic phase with the molecules perpendicular to the layers (see Fig. 1), whereas the even-numbered alkanes show phases of lower symmetry, triclinic or monoclinic, with the molecules tilted away from the layer normal [1]. Close to melting mesophases appear which still have the translational symmetry of crystals but in which the rotational degrees of freedom of the molecules about their long axis are partially or completely disordered [1,2], the most prominent being the rotator phase ( $Fmmm$ , orthorhombic). According to Sirota and Herhold the odd-even effect in the crystal structures and phase transition temperatures is closely related to the stability [for  $n$  even ( $\geq 22$ ) and  $n$  odd], metastability ( $n=20, 22$ ), or transient appearance [even  $n$  ( $\leq 18$ )] of the rotator phase [3]. In cooling runs a monolayer of the rotator phase already forms a few K above bulk freezing (an effect known as “surface freezing”) at the liquid-vapor interface [5] which then serves as nucleus for bulk crystallization. The lifetime of the transient  $R$  phase has been reported to be several seconds for C16 and a few minutes for C18 before the material transforms into the stable triclinic modification [3,4]. Analogous observations have been made for emulsified C16 droplets with a diameter of 33  $\mu\text{m}$  [6]. In smaller droplets (with diameters down to 125 nm) there is evidence for a stable  $R$  mesophase for C18 but not for C16. Leaving the short-lived transient state aside, the melts of C18 and of the shorter even-numbered alkanes directly freeze into the fully ordered triclinic solid [1]. C20 is special in the sense that it is the shortest even- $n$  alkane that shows a rotator phase, but only on cooling, whereas on heating it melts directly out of the triclinic phase [2].

We have recently started an investigation of alkanes embedded in mesoporous glasses with pore diameters of 10 nm [7]. Pore-confined C19 shows the phase sequence liquid- $L$ -rotator phase- $R_f$ -“crystalline” low- $T$  phase  $C$  known from the bulk system, except for a minority  $R_H$  state (rhombohe-

dral) in coexistence with the liquid right at the freezing-melting temperature and a downward shift of the transition temperatures  $T_{L-R_f}$  and  $T_{R_f-C}$ . Furthermore, both transitions show hysteresis with respect to heating and cooling. Similar effects on the transition temperatures are known for many other pore fillings [8,9], including small molecules such as He [10], Ar [11], CO,  $N_2$  [12], and  $H_2O$  [13], suggesting that pore confinement favors less ordered phases with respect to more ordered phases. In the present paper we examine the behavior of the even-numbered  $n$ -alkanes C12, C14, and C16.

### II. EXPERIMENT

Vycor glass (code No. 7930, Corning Glass Works) with a porosity of 30% is imbibed with the alkane melts. The structure of the mesoporous host can be described as a network of three-dimensional (3D) randomly oriented, connected pores with relatively uniform diameter  $d \sim 10$  nm [14]. In Fig. 1 a ray-tracing illustration of the matrix with a somewhat exaggerated tortuosity of the pores in comparison to real Vycor is depicted. The samples are mounted in a closed cell that is attached to the cold plate of a closed-cycle refrigerator. They are investigated by means of standard x-ray powder diffractometry employing coupled  $2\Theta$ - $\Theta$  scans with the Cu  $K\alpha$  x-ray beam reflected from the face of a Vycor tablet. Powder patterns have been taken as a function of temperature  $T$  on both cooling and heating, with  $T$  steps down to 1 K at phase

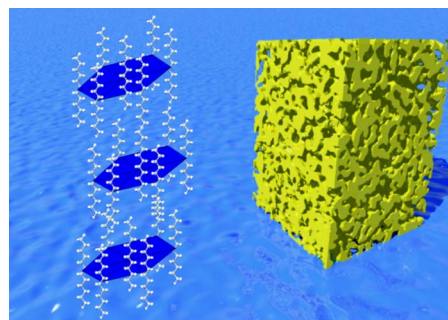


FIG. 1. (Color online) Schematic view of an  $n$ -alkane crystal (left) and a ray-tracing illustration of mesoporous Vycor (right).

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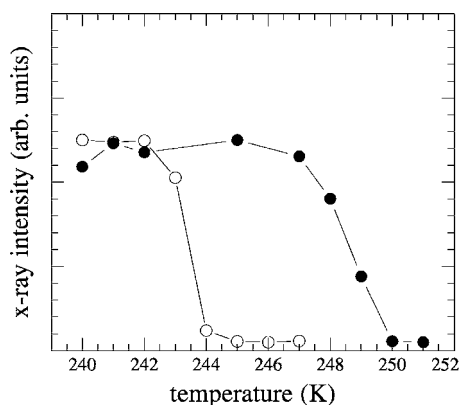


FIG. 2. The temperature dependence of the integrated intensity of a group of Bragg reflections of C12 in Vycor, on both cooling (○) and heating (●).

changes. Recording a powder pattern ( $5^\circ < 2\theta < 40^\circ$ ) took several hours; the waiting time for  $T$  equilibration when changing from one  $T$  to the next was 1/2 h. Thus the experiment only gives information on stable or at least long-lived structural states. The x-ray diffraction patterns will be presented as plots of the scattered intensity versus the modulus of the scattering angle  $2\Theta$  (top axis) and the modulus of the scattering vector  $q$ ,  $q=4\pi/\lambda \sin(\Theta)$  (bottom axis), where  $\lambda$  corresponds to the wavelength of the x rays,  $\lambda=1.542 \text{ \AA}$ . For C14 and C16 complementary differential scanning calorimetry (DSC) scans have been taken with a heating and cooling rate of 0.5 K/min.

### III. RESULTS

Pore-confined C12 freezes at  $T_f=243 \text{ K}$  and melts at  $T_m=249 \text{ K}$  as can be seen from Fig. 2 which shows the  $T$  dependence of the integrated intensity of a group of Bragg peaks for both cooling and heating. The melting temperature of the bulk system is 263.6 K [1]. The powder pattern of the solid regime is shown in Figs. 3 and 4. There are no changes of this pattern with  $T$  that suggest a solid-solid transition. The comparison to the pattern of the bulk triclinic solid which has been calculated from the structural data of Ref. [15] indicates that the structure of pore-confined solid C12 is identical to that of the bulk counterpart, apart from a line broadening due to the finite size of the pore-confined nanocrystallites. Thus the phase sequence liquid-triclinic of the bulk system is not changed. The coherence length, as extracted from the width of the Bragg peaks while properly taking into account the instrumental resolution, was determined to  $12(\pm 1) \text{ nm}$ .

Figure 5 shows diffraction data on pore-confined C16. Solidification (at 273 K) and melting (at about 281 K) are apparent from the pertinent changes of the diffraction pattern. In the liquid state the pattern is dominated by the broad first maximum of the structure factor whereas in the solid state Bragg peaks show up. The bulk melting temperature is 291.2 K. The pattern of the solid state starts out as a two-peak-pattern, with the second peak having the form of a shoulder sitting on the high- $q$  wing of the first peak, and

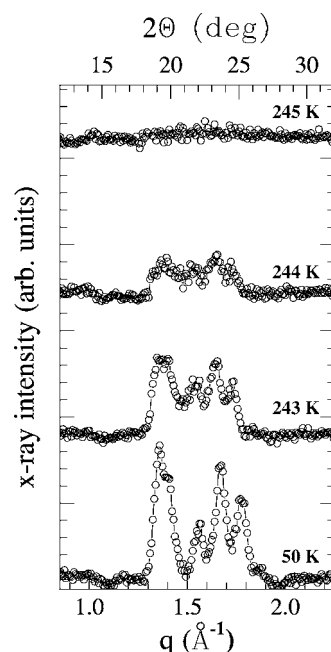


FIG. 3. Diffraction patterns on C12 in Vycor at selected temperatures.

changes to a four-peak pattern at lower  $T$ . The crossover temperature is about 260 K on cooling and 270 K on heating.

The two components of the two-peak pattern are centered at  $1.49$  and  $1.63 \text{ \AA}^{-1}$ . This is what is expected for  $q$  values of the principal in-plane reflections (110) and (200) of the orthorhombic rotator phase  $R_I$  [2]. At lower  $T$  the pattern approaches but does not really reach the pattern of the triclinic state. Three of four stronger diffraction peaks are consistent with the reflections (010)/(011), (100), and (111) of the triclinic structure; the peak centered at  $1.49 \text{ \AA}^{-1}$  is not. This peak is still at the position of the strong (110) reflection of the  $R_I$  phase and is also somewhat broader, due to an admixture of the weaker triclinic (101) reflection. Obviously pore-confined C16 settles at low  $T$  in a state of triclinic-

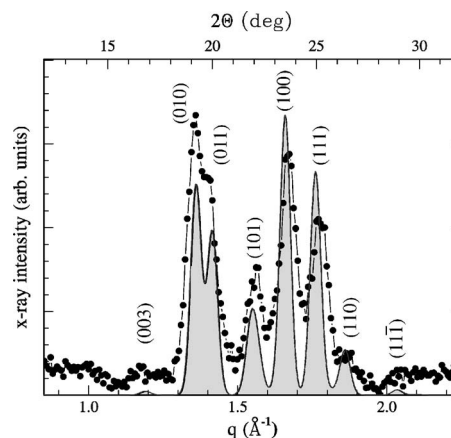


FIG. 4. The diffraction pattern of C12 in Vycor at 50 K in comparison with a powder pattern of bulk C12 (triclinic) calculated from the structural data of Ref. [15].

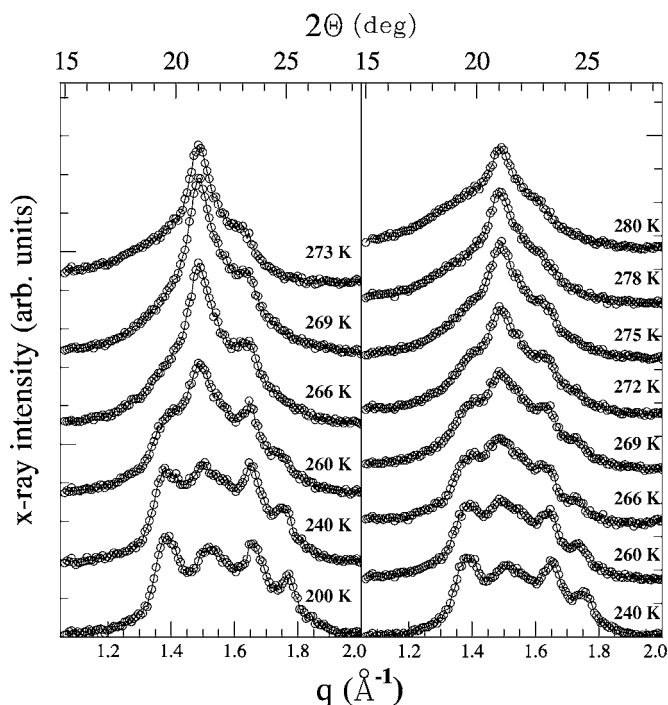


FIG. 5. Diffraction patterns of C16 in Vycor at selected temperatures on both cooling (left) and heating (right).

orthorhombic coexistence. One expects, of course, that the  $R_I$  minority component eventually transforms at low  $T$  into the “crystalline” herringbone phase, but the intensities of the extra reflections of this phase are too weak to be detected.

Thus the phase sequence is liquid- $R_I$ - $R_I$ /triclinic coexistence. The stable intermediate  $R_I$  phase is an extra feature of the pore-confined system. The sequence as such is reversible with respect to cooling and heating but the transition temperatures show thermal hysteresis.

The DSC data (Fig. 6) confirm the values of  $T_f$  and  $T_m$  of the diffraction experiment. On the other hand, there is no evidence in these data for a partial  $R_I$ -triclinic transformation. This may be due to the fact that the latent heat of this transformation is distributed over a broad  $T$  interval, which is in fact suggested by the diffraction data.

The diffraction results (Fig. 7) on pore-confined C14 are in a sense intermediate to those on pore-confined C16 and C12. On cooling the two-peak profile of the rotator phase  $R_I$  appears at  $T_f=263$  K (the bulk melting temperature is 279 K); below 259 K the system shows  $R_I$ -triclinic coexistence that eventually below about 250 K purifies into the triclinic single phase state. On heating the  $R_I$  phase is suppressed and the pore filling melts directly from the triclinic state at 267 K. Nevertheless, the behavior on heating is peculiar. At the end of the cooling run the triclinic reflections are relatively broad; the (010)/(011) doublet is, for instance, not resolved. This suggests that the triclinic crystallites are small in size and/or heavily strained, perhaps due to the presence of  $R_I$  residues. During the heating cycle the peaks sharpen and stay so up to the melting point at 269 K. The crystallites obviously grow in size and built-in strains relax. This ripening occurs at about 260 K which is roughly the temperature of the  $R_I$ -triclinic phase transformation of the

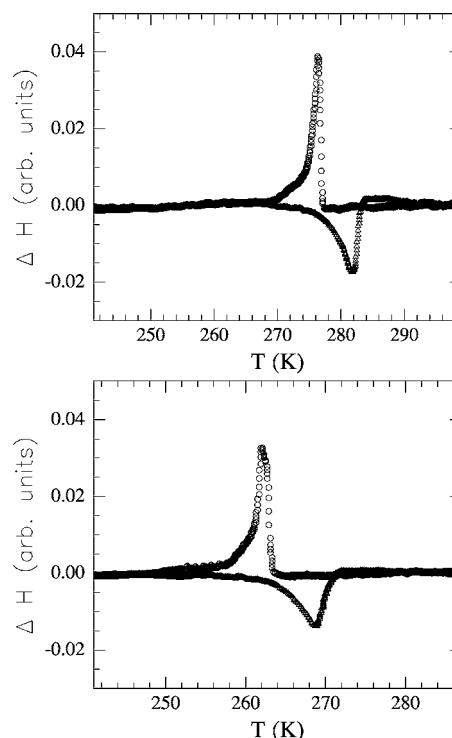


FIG. 6. Differential scanning calorimetry data on C16 (upper panel) and C14 (lower panel) on both cooling ( $\circ$ ) and heating ( $\Delta$ ).

cooling cycle—that is, in a  $T$  range of appreciable thermal agitation. Thus the phase sequence is liquid- $R_I$ -triclinic on cooling and triclinic-liquid on heating, and one has to distinguish between the quenched and annealed versions of the triclinic state. With respect to the appearance of the  $R_I$  phase,

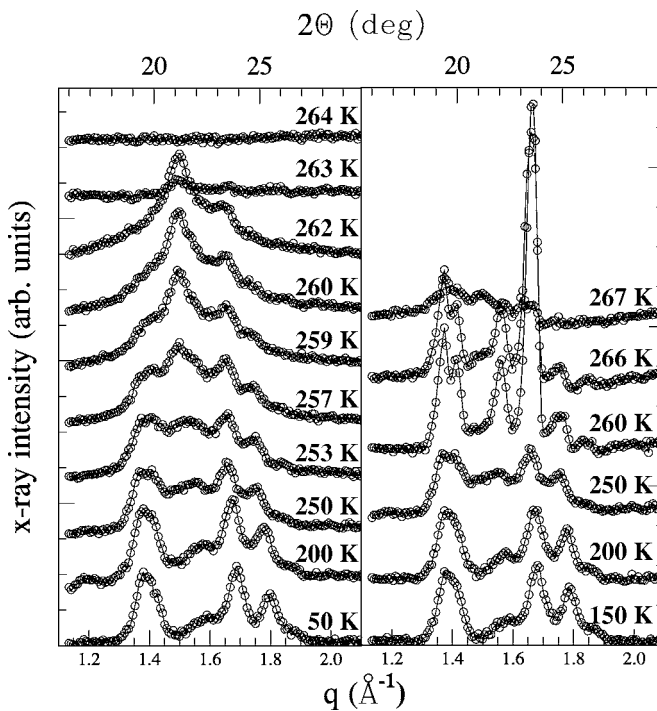


FIG. 7. Diffraction patterns of C14 in Vycor at selected temperatures on both cooling (left) and heating (right).

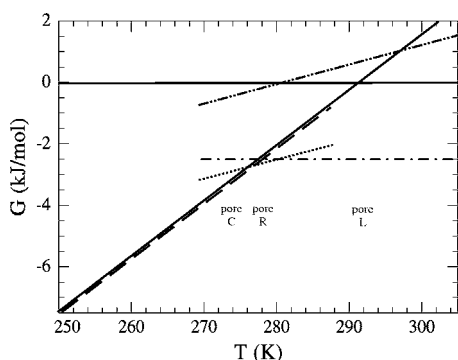


FIG. 8. Schematic diagram of the Gibbs energy  $G$  of C16 as function of temperature for both the bulk and pore-confined state, relative to the bulk liquid ( $G_L^{\text{bulk}}=0$ ). The bulk  $C$  phase is shown by a solid line, the hypothetical bulk  $R$  phase as a dash-double-dotted line, the pore liquid as a dash-dotted line, the pore  $C$  phase as a dashed line, and the pore  $R$  phase as a dotted line.

the sequence is irreversible. When the heating cycle is stopped prior to melting and the sample is cooled down again, the reflections remain sharp.

As for C16, the diffraction and the DSC data agree on the values of  $T_f$  and  $T_m$  (Fig. 6). The long wing of the freezing anomaly of the DSC experiment that extends down to about 250 K may be related to the gradual  $R_I$ -triclinic transformation.

In the  $R_I$  phase of pore-confined C14 and C16 only the two strongest in-plane reflections could be detected. The (00 $l$ ) layering reflections are absent, in agreement with the situation for the pore-confined odd-numbered alkane C19. This means that the lamellar arrangement is suppressed or at least heavily perturbed. Note that already mean-square displacements of the molecules in the direction normal to the lamellae of 1 or 2 Å wash out the modulation of the electron density in this direction. In the triclinic state with tilted molecules, however, the mere existence of the mixed reflection (111) proves that the lamellar arrangement is still intact.

#### IV. DISCUSSION

In the bulk state of even-numbered alkanes, stable rotator phases no longer exist for  $n < 20$ . In the pore this stability limit is shifted to  $n < 14$ . In fact, pore-confined C14 shows exactly the phase sequence of bulk C20, with the rotator phase existing on cooling but being inaccessible on heating. The question of course arises whether the  $R_I$  mesophase and the pore-confined state in general is stable, metastable, or long-lived unstable. From an experimental point of view the diffraction patterns do not change with time over isothermal waiting periods of several days.

In order to explore the question of stability we refer to the phase diagram of Fig. 8, which shows the Gibbs energy  $G = H - TS$  of the liquid  $L$ , the rotator  $R$ , and the triclinic crystalline phase  $C$  of C16 as function of  $T$  for both the bulk and pore-confined state. We assume that the enthalpies  $H$  and the entropies of the three phases do not vary with  $T$  and the entropy of a given phase is the same in the bulk and pore-confined state.  $G_L^{\text{bulk}}$  serves as zero reference.  $G_C^{\text{bulk}}$  is known

from experimental data on the melting temperature and the heat of fusion of C16.  $G_R^{\text{bulk}}$  is constructed from an extrapolation of the transition temperatures and latent heats of other alkanes (even  $n$ ,  $n \geq 20$ , and odd  $n$ ) that do show a  $R_I$  rotator phase [1]. The Gibbs energies of the pore-confined phases are displaced with respect to their bulk counterparts,  $G_A^{\text{pore}} = G_A^{\text{bulk}} - \Delta_A$ ,  $A = C, R, L$ . For the liquid state,  $\Delta_L$  is positive; the pore liquid is stable with respect to the bulk liquid outside the pores as can be seen from the fact that a drop of liquid is sucked into the pores, due to the attractive interaction between the molecules and the pore walls. The pore solid also benefits from this interaction but it has to pay an extra price in form of strains, defects, grain boundaries that are required to match the solid to the pore geometry. If we assume that C12 stays in the pores upon solidification into the  $C$  phase for thermodynamic reasons and not due to kinetic barriers for the extrusion of the solid,  $\Delta_C$  should be lower than  $\Delta_L$ , but still positive.  $\Delta_L$  is unknown for the alkanes of the present study, but a rough idea can be obtained from C8 where the vapor pressure at the melting point is still large enough to allow us measurements of an adsorption isotherm which gives direct information on  $\Delta_L$ ,  $\Delta_L \approx 2500 \text{ J mol}^{-1}$ . Using this value,  $\Delta_C$  can then be estimated to be of the order of  $100 \text{ J mol}^{-1}$  from the shift of the  $C$ - $L$  melting transition of C16 upon pore confinement,  $T_{C-L}^{\text{pore}} - T_{C-L}^{\text{bulk}} = (\Delta_C - \Delta_L) / S_{C-L}$ , where  $S_{C-L}$  is the entropy change at the  $C$ - $L$  transition. This is further evidence that the pore-confined  $C$  solid is stable, but only marginally so.

Whether the  $R$  solid is stable in the pores depends on the value of  $\Delta_R$ . It is reasonable to assume that  $\Delta_R$  is intermediate to  $\Delta_C$  and  $\Delta_L$ . It turns out that  $\Delta_R$  has to be practically equal to  $\Delta_L$  in order to arrive at a stable  $R$  phase in the pores, but its  $T$  range of existence is very small. See the phase diagram of Fig. 8, which is based on the choice  $\Delta_C = 100$ ,  $\Delta_R = \Delta_L = 2500$  in units of  $\text{J mol}^{-1}$ . Analogous considerations of C14 and C12 show that the pore-confined  $R$  phase of these alkanes cannot be stabilized for any  $\Delta_R \leq \Delta_L$ . In case  $\Delta_R$  and  $\Delta_L$  are equal there should be no shift of the  $R$ - $L$  melting temperature by pore confinement and in fact the example of C19 which melts from the  $R$  phase shows that this is almost so [7]. (In bulk C16 the  $R$ - $L$  transition is not accessible because of the appearance of the  $C$  phase; see Fig. 8.) The equality of  $\Delta_R$  and  $\Delta_L$  suggests furthermore that the  $R$  solid can be easily matched to the pore geometry, very much like the liquid, with little extra energy cost, due to the high level of intrinsic disorder. Indeed rotator phases are occasionally called “plastic” since they can be extruded by pressures much smaller than required for completely ordered phases [16].

The discussion in terms of  $G$ ,  $T$  phase diagrams gives hints as to the stability of the phases involved but fail to reproduce the  $T$  width of the  $R$  phase of C16 let alone the appearance of the  $R$  phase of C14 on cooling and the  $R$ - $C$  coexistence of C16 at low  $T$ . We think that structural gradients across the pores have to be considered. The molecule-substrate potential decays with the distance from the pore walls; hence the state of the pore filling next to the pore walls is different from the state in the pore center, including the possibility of a radial arrangement of coexisting phases. For the solidification of Ar in porous glass we could explain

most of the pertinent experimental observations in terms of a simple thermodynamic model that is based on the idea that the solidification takes place in the pore center, but that there is a shell of liquid between the solid core and the pore walls, the thickness of which decreasing slowly with decreasing  $T$  [17]. Such a model could also explain the  $R$ - $C$  coexistence in pore confined C16, with the  $C$  phase in the pore center surrounded by a matching layer of the  $R$  phase. The fact that the diffraction pattern of C16 does not change anymore below about 260 K simply means that this state is frozen in below this temperature and that the thermal energy is no longer sufficient to drive the phase transformation.

As to the appearance of the  $R$  phase of C14 on cooling we cannot present a convincing argument. One could think of undercooling in the sense that the  $C$  phase cannot nucleate in the pore center because of a lack of nucleation sites or refer alternatively to the transient  $R$  phase of Ref. [3] as a vehicle for the further growth of a metastable  $R$  phase rather than for the growth of the stable  $C$  phase.

In more general terms one can argue that the tortuous character of the pore network of Vycor and rough pore walls act as sources of random strain fields that stabilize the disordered  $R$  phase and thereby lower the temperature of the  $R$ - $C$  transition. It is conspicuous that the rotator phase that

appears in the pore-confined state is the  $R_I$  phase, the prototypic rotator phase of the odd-numbered bulk alkanes, and not one of the tilted rotator phases of the even-numbered bulk alkanes. Whether a phase of the alkane-layered crystals is tilted or not can be understood on the basis of packing considerations combined with the symmetry of the molecule. The mirror plane of the odd-numbered alkanes perpendicular to the long axis of the molecule calls for no tilt, whereas the inversion symmetry of the even alkanes tolerates finite tilt angles. Disorder of almost any kind makes odd and even molecules appear equivalent. This is in particular obvious for the case of orientational disorder with respect to rotations about the molecular axis. If disorder destroys the lamellar arrangement, as appears to be the case in pores, the question of tilt is irrelevant.

In summary, we have shown that pore confinement stabilizes the rotator mesophases, such that they appear even in C14 and C16 where they are absent in the bulk state.

#### ACKNOWLEDGMENTS

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