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Ziru He; Yue Zhao; Alain Caille

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# A kinetics study of crystallization from discotic mesophases

by ZIRU HE, YUE ZHAO\*

Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, J1K 2R1,  
Canada

and ALAIN CAILLÉ\*

Centre de recherche en physique du solide, Département de physique,  
Université de Sherbrooke, Sherbrooke, Québec, J1K 2R1, Canada

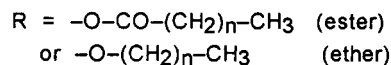
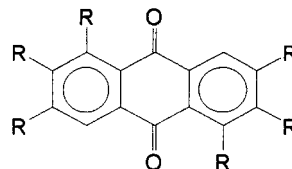
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The polymorphism of hexa-*n*-octanoate of rufigallol (RHO) was used to investigate the crystallization kinetics when starting from two different discotic mesophases, namely, a high-temperature enantiotropic mesophase and a low-temperature monotropic mesophase. In all cases, an Avrami exponent of  $n=3$  was obtained, suggesting two-dimensional sporadic nucleation and growth. Although the same overall mechanism was predicted to operate for all crystallization temperatures investigated, the Avrami constant  $b$  has a temperature-dependence which is different for different starting columnar phases, indicating a strong influence on the rates of nucleation and of growth of the different molecular arrangements of the starting mesophases. Differential scanning calorimetry was used for the studies, supplemented by direct observations through optical polarizing microscopy.

## 1. Introduction

Among the known disc-like molecules which display columnar mesophases [1], ester- and ether-substituted rufigallol [2–4], whose chemical structures are shown below, are distinct by a number of characteristics. Firstly, these molecules have an elongated mesogenic core with a twofold rotational axis of symmetry. Secondly, they exhibit an important polymorphism. Indeed, in the case of hexa-*n*-octanoate of rufigallol (RHO), which is the ester-substituted rufigallol with  $n=6$ , the polymorphism is identified as two columnar mesophases having two-dimensional rectangular lattices of different unit cell sizes and different molecular orientations of the columns [3]. They include an enantiotropic phase on the high-temperature side and a monotropic phase on the low-temperature side, which are hereafter denoted as D1 and D2, respectively. According to the general assignments [5], the enantiotropic D1 phase is the stable phase formed after the melting of the crystal, while the monotropic D2 phase represents a metastable phase which, once formed during the cooling, transforms into the stable crystalline phase upon lowering of the temperature. RHO thus provides a particular molecular system which, under appropriate conditions, could allow for the observation of crystallization from both the metastable and the stable columnar mesophases, and, in particular, to

see if the phase transformation kinetics are affected by the different initial states. With this objective in mind, we have performed kinetics investigations using differential scanning calorimetry (DSC) supplemented by optical polarizing microscopy. In this paper, we report the experimental results and propose a general mechanism for the crystallization process.



## 2. Experimental

The sample of RHO was synthesized following a reported method [2]. A Perkin–Elmer DSC-7 apparatus was utilized for studying the crystallization kinetics. The crystallization rate can be monitored by measuring the development of the crystal endotherm with time. The typical run for a given crystallization temperature was as follows. A sample was held at 140°C in its liquid phase for 5 min to reach equilibrium, and then cooled

\*Author for correspondence.

rapidly to the pre-selected crystallization temperature (actual cooling rate  $\sim 60^\circ\text{C min}^{-1}$ ). After the sample was held at this temperature for a pre-determined time, a heating scan at a rate of  $10^\circ\text{C min}^{-1}$  was recorded. The experiment was then repeated on the same sample for different crystallization times. However, the measurements for each crystallization temperature were carried out on a new sample. The texture and morphology observations were made on a Leitz DMR-P polarizing microscope, using an Instec hot stage for the control of the temperature. As for the DSC, the thin films were first heated to  $140^\circ\text{C}$  for 5 min and then cooled to the observation temperature. When using cold water, a cooling rate of approximately  $10^\circ\text{C min}^{-1}$  could be obtained.

### 3. Results and discussion

Figure 1 displays the cooling curve from  $140^\circ\text{C}$  to  $30^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$  and the subsequent heating curve at the same rate. The known features of RHO phase transitions [2, 3] are reproduced. Upon cooling from the liquid phase, L, the columnar D1 phase first appears at  $T_{L\rightarrow D1} = 126.8^\circ\text{C}$  with a heat of transition of  $13.5 \text{ J g}^{-1}$ , followed by the occurrence of the D1  $\rightarrow$  D2 transformation as indicated by the second exotherm at  $T_{D1\rightarrow D2} = 88.8^\circ\text{C}$  with a heat of transition of  $3.2 \text{ J g}^{-1}$ . Subsequent cooling results in the crystallization at  $T_{D2\rightarrow Cr} = 63.1^\circ\text{C}$  with a heat of transition of  $36.9 \text{ J g}^{-1}$ . When heating the sample, the D2 discotic mesophase is no longer seen indicating the monotropic nature of this phase. The crystal melting endotherm is first encountered at  $T_{Cr\rightarrow D1} = 108.6^\circ\text{C}$ . Its melting heat,  $\Delta H_{Cr\rightarrow D1}$ , is found to be equal to the total of the heats of transition for

D1  $\rightarrow$  D2 and D2  $\rightarrow$  Cr upon cooling, which indicates that the crystalline order achieved through the two steps from the D1 phase during the cooling is lost in a single melting step giving rise to the D1 phase. The D1  $\rightarrow$  L transition takes place at  $T_{D1\rightarrow L} = 131.4^\circ\text{C}$ , the melting heat,  $\Delta H_{D1\rightarrow L}$ , being equal to the heat of transition for L  $\rightarrow$  D1 during the cooling cycle.

On examination of the curves in figure 1, we expected that it would be possible to observe the crystallization process of RHO starting from any one of its two columnar mesophases. Due to the large supercooling of the crystalline phase, being defined as  $T_{Cr\rightarrow D1} - T_{D2\rightarrow Cr} = 45.5^\circ\text{C}$  in figure 1, once the D1  $\rightarrow$  D2 phase transition is completed, the crystallization from D2 could be investigated over the temperature range between  $T_{D1\rightarrow D2}$  and  $T_{D2\rightarrow Cr}$  if the kinetics were not too fast. More interestingly, there is a temperature range before the D1  $\rightarrow$  D2 phase transition which is below the crystal melting temperature  $T_{Cr\rightarrow D1}$ . This means that when a sample, cooled from the liquid phase, is held in this temperature region, a direct transformation from D1 to the Cr phase could also take place. This temperature region can be defined approximately as the interval between  $T_{D1\rightarrow D2}$  and  $T_{Cr\rightarrow D1}$ . However, because of the existing, although very low, supercooling for the D2 phase we found that up to  $93^\circ\text{C}$  the D1  $\rightarrow$  D2 phase transition could occur. Therefore, for all practical purposes,  $T = 94^\circ\text{C}$  is considered as the border separating the two temperature regions for the crystallizations from D1 and D2.

Indeed, the transformation from the D2 mesophase to the Cr phase is easily observed from the DSC measurements. A set of the recorded heating curves illustrating the crystallization kinetics is shown in figure 2 for

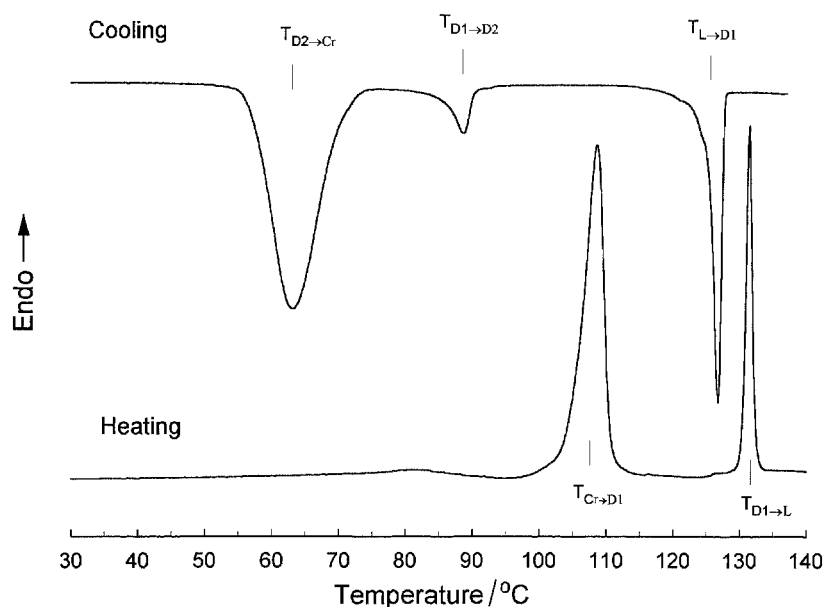


Figure 1. DSC cooling and subsequent heating curves for RHO, recorded at a rate of  $10^\circ\text{C min}^{-1}$ .

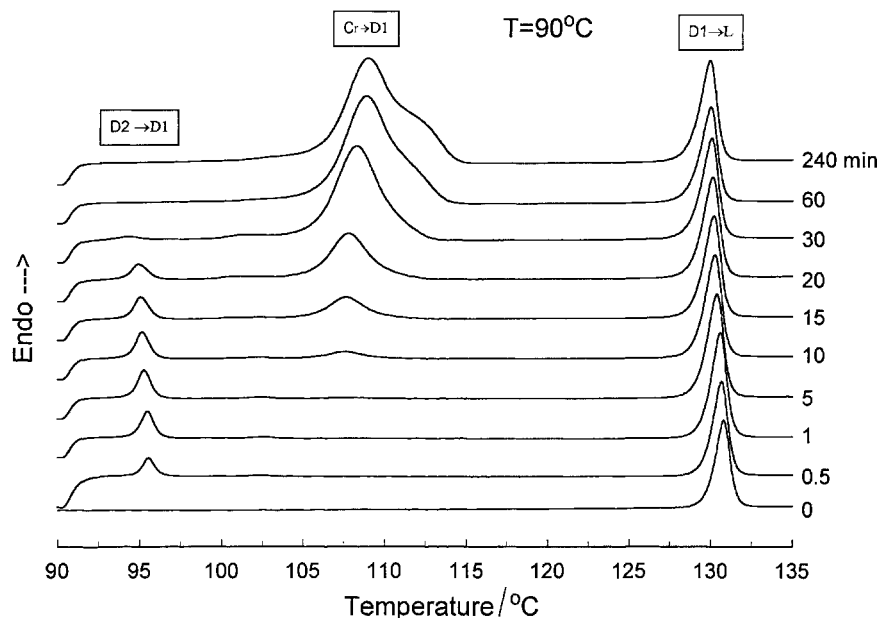


Figure 2. DSC heating curves for RHO annealed in the D2 phase at 90°C for different times between 0 and 240 min as indicated in the figure.

reference. The sample was held at 90°C for the different times indicated in figure 2. As a first approximation, the heating curve with a crystallization time of  $t=0$  min was that recorded immediately following the quenching to 90°C. It can be seen that this curve displays only the D1 melting endotherm, indicating that the D1  $\rightarrow$  D2 phase transition has not yet occurred. The D1  $\rightarrow$  D2 transition kinetics at 90°C are however very fast, since after 0.5 min the D2 melting endotherm is clearly visible at 96°C, in the absence of any crystal melting. No D2  $\rightarrow$  Cr transition has occurred even after 5 min at 90°C. The curve after 10 min shows a small crystal melting endotherm at approximately 106°C, indicating that the crystallization from the D2 phase has started during the 10 min period of time. Once started, the formation with time of a larger and larger crystal fraction from the D2 phase is reflected by a continuing increase of the crystal melting endotherm at the expense of the D2 endotherm. This conversion process appears to be completed after 30 min since the D2 endotherm could no longer be seen after this time. An interesting feature of the crystal melting was noted: in addition to a slight increase in the melting temperature (the peak maximum) with time, which could be attributed to the usual growth of larger and larger crystallites, a new endotherm appears as a shoulder on the high temperature side of the crystal melting endotherm, and becomes more prominent with time. This suggests that the crystalline phase of RHO undergoes a structural evolution with time. At this point we have not conducted experiments in order to exploit and interpret this specific feature.

From the data shown in figure 2, the change with time of the melting heats of the D2  $\rightarrow$  D1 and Cr  $\rightarrow$  D1 transitions can be measured for a given crystallization

temperature. Plotted in figure 3 are the results obtained for two crystallization temperatures in the D2 phase, 77°C and 92°C. Different scales are used for  $\Delta H_{D2 \rightarrow D1}$  and  $\Delta H_{Cr \rightarrow D1}$ . It can be seen that at 92°C, which corresponds to a much smaller supercooling, the crystallization is observable only after a much longer time than at 77°C. However, the two  $\Delta H_{Cr \rightarrow D1} - \log t$  curves have the same shape, being only displaced along the  $\log t$  axis. Moreover, the simultaneous measurement of the melting heats of the D2 endotherm with time shows without ambiguity that the effective beginning and end of the crystal formation process coincide with those of the decay of the D2 phase, illustrating a direct D2  $\rightarrow$  Cr phase conversion. It is also interesting to note that at 92°C even the D1  $\rightarrow$  D2 phase transition can be observed as indicated by the early increase in  $\Delta H_{D2 \rightarrow D1}$  with time. This transition precedes the crystallization from the D2 phase at longer times, as revealed by the beginning of the decrease in  $\Delta H_{D2 \rightarrow D1}$  and the increase in  $\Delta H_{Cr \rightarrow D1}$ . This cannot be seen at 77°C as the D1  $\rightarrow$  D2 transition kinetics are too fast to be observed, being completed during the cooling to 77°C.

The crystallization from the enantiotropic D1 mesophase was also observed at temperatures between 94°C and 105°C, at longer typical times. A set of the heating curves for different crystallization times at 97°C are given in figure 4. No sign of a crystal melting endotherm can be seen before 30 min, the crystal endotherm becoming clear after 60 min and increasing at longer times. Again, a distinct, new broad shoulder develops continuously on the high temperature side of the melting endotherm. The kinetics of the D1  $\rightarrow$  Cr transformation are shown in figure 5 for three temperatures. It is clear

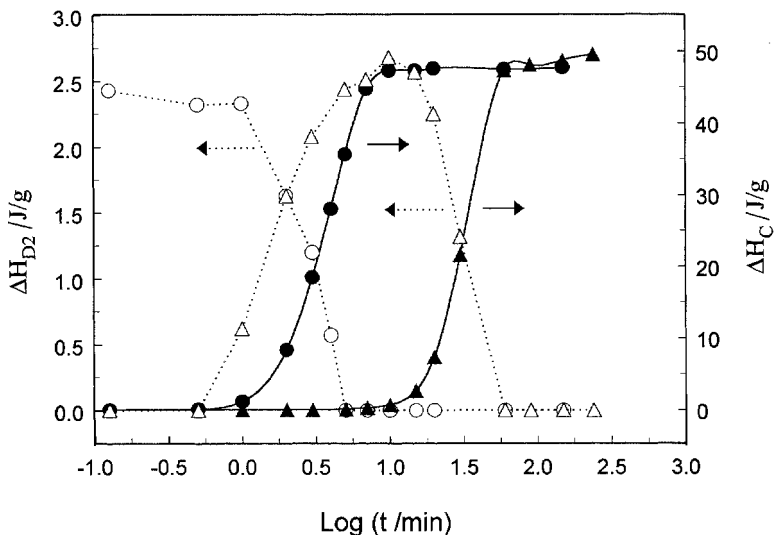


Figure 3. Melting heats of D2 (open symbols) and of the crystalline phase (closed symbols) for RHO as a function of logarithmic annealing time in the D2 phase, at two temperatures: 77°C (○, ●) and 92°C (△, ▲).

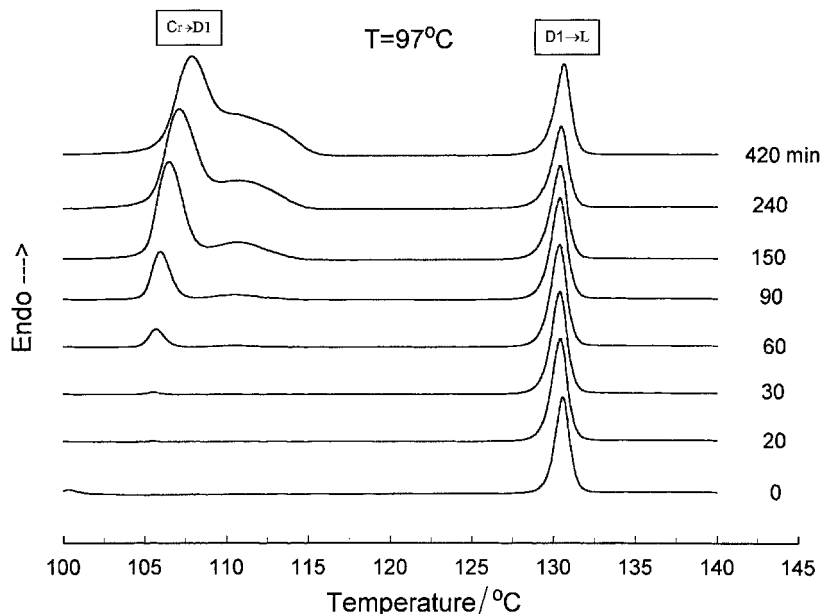


Figure 4. DSC heating curves for RHO annealed in the D1 phase at 97°C for different times between 0 and 420 min as indicated in the figure.

that the curves have the same shape as those in figure 3 for the D2 → Cr phase transformation. Actually, all the crystallization curves can be superposed to construct a master curve. Such a master curve is shown in figure 6, using 97°C as the reference temperature. It contains the data obtained for nine crystallization temperatures covering both D2 → Cr and D1 → Cr transformations, the  $\log t$  shift factor for each temperature being chosen to assure the best superposition of the curves. This result strongly suggests that the same mechanism operates for the crystallization from both D1 and D2. The overall crystallization rate should be controlled by a nucleation rate and the rate of growth of domains which are function of the degree of supercooling and the starting discotic mesophases.

The kinetics of the phase change taking place when a stable lower temperature phase grows out of a mother metastable phase in the form of small domains are controlled by two characteristic quantities: the rate of nucleation of small stable domains of the lower temperature phase and their rate of growth with time. As a first limiting case, nucleation can take place as a homogenous process which is essentially constant over time and appears as a sporadic phenomenon. A second limiting case corresponds to the growth from a pre-determined number of nuclei present at the beginning of the process in the form of defects or impurities in the sample. For a constant rate of growth of the linear dimension of the nuclei, a situation which usually exists for solid-state transformations where the growth occurs

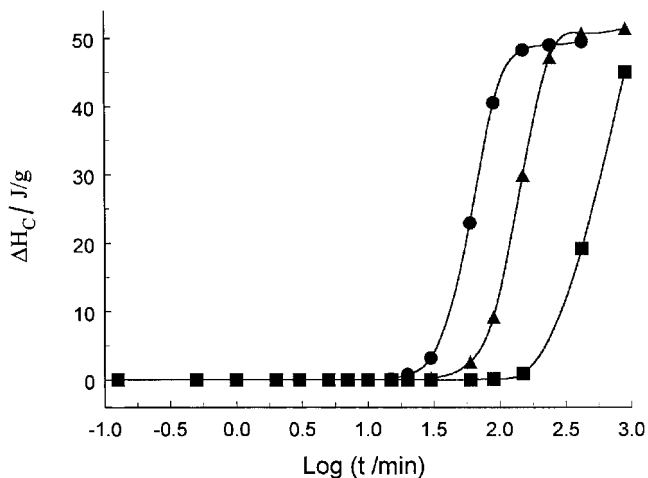


Figure 5. Melting heats of the crystalline phase for RHO as a function of logarithmic annealing time in the D1 phase, at three temperatures: 95°C (●), 97°C (▲) and 100°C (■).

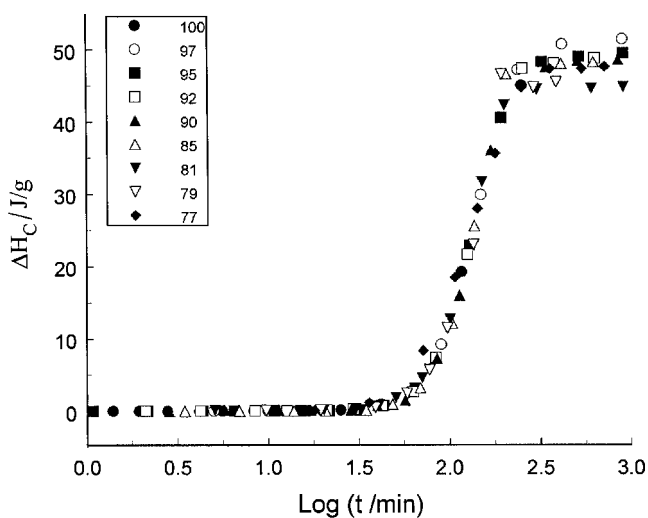


Figure 6. Master curve of the melting heats of the crystalline phase as a function of logarithmic annealing time for nine temperatures, obtained by shifting data along the  $\log t$  axis to the curve of 97°C.

only at the surface of the nuclei without transportation of the molecular species over distances exceeding a fraction of the intermolecular distance, the overall rate of phase transformation depends on the dimensional geometry of the growing domains. The fraction of the transformed volume  $x$ , at a time  $t$  measured since the beginning of the crystallization process, is usually described by the Avrami equation

$$x = 1 - \exp(-bt^n) \quad (1)$$

where the two constants  $b$  and  $n$  depend on the nucleation mechanism and the dimensional geometry of the growing domains. In what follows, the obtained kinetics data are analysed using the Avrami equation. The transformed volume  $x$  at a crystallization time  $t$  is

given by  $\Delta H/\Delta H_0$  where  $\Delta H$  is the crystal melting heat measured at the time  $t$  and  $\Delta H_0$  is the maximum value obtained from the plateau in figure 6.

If the crystallization kinetics from both D1 and D2 are described by the Avrami equation, the data for all crystallization temperatures will match the single equation

$$x = 1 - \exp[-(t/t^*)^n] \quad (2)$$

where  $t^* = b^{-1/n}$ .  $t^*$  is then dependent on the crystallization temperature. This characteristic time  $t^*$  can be determined experimentally since at  $t = t^*$ ,  $x = 0.632$ . From the  $\Delta H_{C \rightarrow D1} - \log t$  curves as shown in figures 3 and 5,  $t^*$  for different crystallization temperatures were obtained and the results are reported in the table. Using these  $t^*$  values, the kinetics data for nine different temperatures were fitted with equation (2) by plotting  $\log[-\ln(1 - \Delta H/\Delta H_0)]$  versus  $\log(t/t^*)$ . The results given in figure 7 show a single straight line for all the crystallization temperatures in both regions of D1 and D2 and for a wide time interval. The straight line drawn in figure 7 is the result of a linear curve fitting through the origin; the slope yields the exponent  $n$  with a value

Table 1. Measured characteristic time  $t^*$  for completing 63 per cent transformation (by volume) from the columnar mesophases to the crystalline phase.

Crystallization temperature/°C	$t^*/\text{min}$
77	4.2
79	7.9
81	14.1
85	21.1
90	27.4
92	36.6
95	72.9
97	158.5
100	562.3

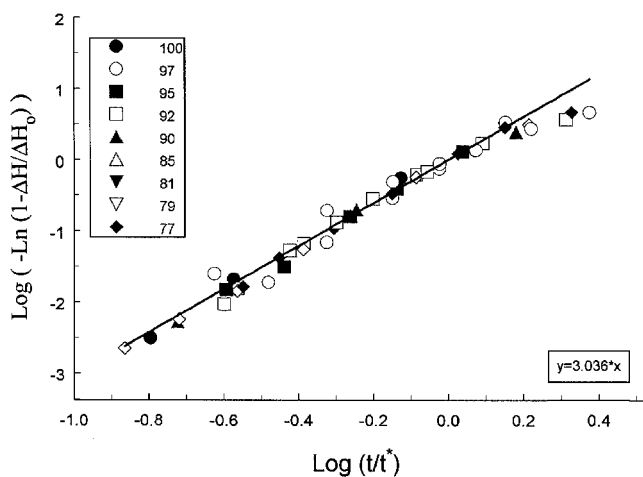


Figure 7. Avrami plots for different crystallization temperatures covering both D1 and D2. See text for details.

of  $3 \pm 0.1$ . It can be noticed that a couple of data points for the longest crystallization times deviate from the straight line. This probably is due to a greater experimental error in the measurement of the crystal melting heats as the melting endotherms are broadened.

For  $n = 3$ , two possibilities exist for the crystallization process: a pre-determined nucleation followed by a growth in three dimensions or a sporadic nucleation and a growth in two dimensions. Even though the first case may not be totally rejected, we propose that, for crystallization from columnar liquid crystal phases, the second case is more probable. We base our conjecture on the existing knowledge of the structural properties of the columnar phases of RHO. Indeed, according to J. Billard *et al.* [3], based on X-ray diffraction data, the two columnar phases D1 and D2 have an organized network of liquid-like columns inscribed on two-dimensional centred rectangular lattices. As depicted schematically in figure 8, D1 has two columns per unit cell, whereas D2 has four (the lattice dimensions are reported in reference [3]). The columns, made of RHO molecules having a rigid core of twofold rotational symmetry, have long-range orientational order in three dimensions, with two different molecular orientations for D1 and three for D2. Both phases exhibit a liquid-like positional order along the columns, with a mean distance of  $5.6 \text{ \AA}$  between two neighbouring molecules. A large part of the melting enthalpy of the crystal phase

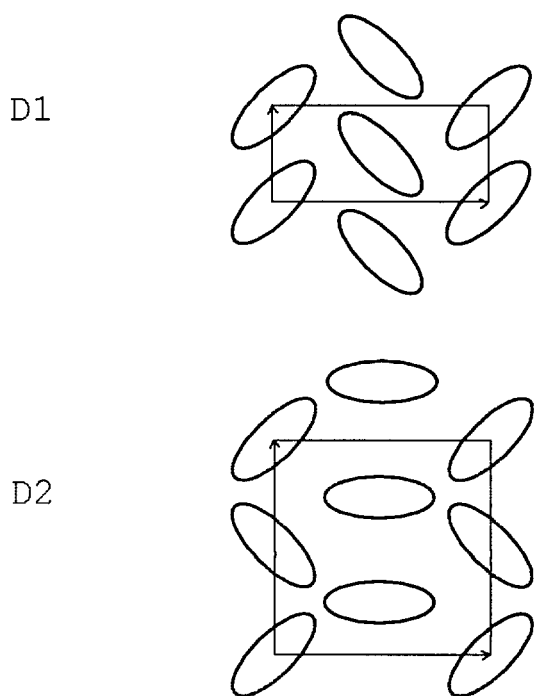


Figure 8. Schematic representation of the two-dimensional lattices of the columns for D1 and D2 phases (reproduced from reference [3]).

of RHO may be attributed [6] to the conformational disordering of the six flexible alkyl chains of the molecules upon entering the discotic phases. Unfortunately, the crystal structure of RHO has not been determined. However we suspect that, as is usually the case for discotic materials [7], the intermolecular distances in the crystal phase are close to the intercolumnar distances of the columnar phases. As a result, it is reasonable to assume that the intermolecular structural changes occurring upon crystallization are being dominated by the intermolecular interlocking of the lower-temperature rigidified and anisotropic ester groups, in particular the double-bonded oxygen of the carboxylate groups which would then be lying out of the anthraquinone plane. Consequently, we argue that a model for the formation of a pseudo-crystal nucleus, based on intra-columnar correlation of the molecular cores, even though it may be only descriptive, has enough links to reality to be useful. Also, the subsequent growth of the crystal domain by intercolumnar correlation of the core positions along the columnar axis describes the most probable route to the crystal state, at least for the dominant aspects as shown above.

As we lower the temperature in the columnar phases, the dominant intermolecular interactions, which are still free to drive the system into a more ordered phase, are between neighbouring molecules inside a column. As a result, over a correlation length  $\xi_0$ , a segment of a column in the supercooled columnar phases acquires an intramolecular and intermolecular structural arrangement typical of the lower temperature crystal phase. This is sketched in figure 9(a) by the succession of hatched rectangles over a length  $\xi_0$  along the columnar direction. This segment serves as a seed for the formation of a pseudo-crystal nucleus in the supercooled D phases. The growth of such an ordered domain to form a stable

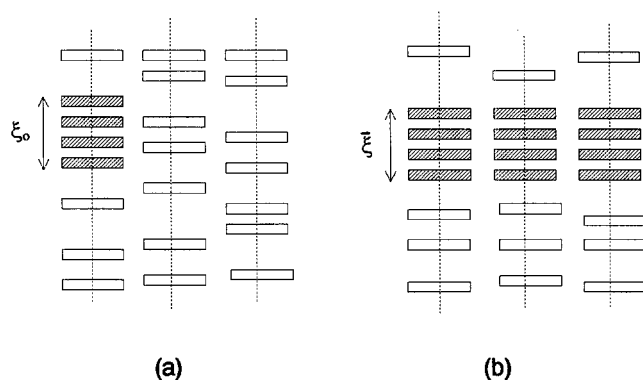


Figure 9. Schematic representation of a two-dimensional nucleation and growth, the molecules in three columns being represented by horizontal rectangles. The hatched molecules have adopted an intramolecular and intermolecular crystal-like arrangement: (a) a seed of extension  $\xi_0$ , and (b) a growing nucleus of extension  $\xi$ .

nucleus takes place by aggregation of molecules of the surrounding columns to form a disk-like pseudo-crystal nucleus of a critical size with their positions in the columnar direction in register. The capture of these molecules by the seed is rendered more effective by a kind of zipper effect for the crystallization of a corona on an existing crystallized disk: indeed, the positional correlation in the plane perpendicular to the columnar direction is both necessary and effective to establish long-range positional order along the columns. Consequently, once a nucleus has reached a critical size, further growth will proceed in a form of a disk by a process of successive addition of molecules from neighbouring columns as illustrated in figure 9(b). The average vertical extension of the disks in the columnar direction  $\xi$  will be affected by the growth mechanism, but it is assumed that  $\xi$  will remain finite and small as compared to the lateral extension. We also understand that regions of typical length  $\xi_0$  appear randomly at all times, at least for times less than the typical time needed for impingement of the domains on each other. These two assertions justify the basic assumptions of both a sporadic nucleation and growth in two dimensions.

Furthermore, under the above conditions for phase transformation, the constant  $b$  in the Avrami equation is given by

$$b = (\pi/3)U^2I\xi \quad (3)$$

where  $I$  is the rate of nucleation and  $U$  is the rate for lateral growth. As  $t^* = b^{-1/n}$  and knowing  $t^*$  and  $n = 3$ , the constant  $b$  for different crystallization temperatures can also be calculated. In figure 10, the logarithmic  $b$  is plotted as a function of the crystallization temperature. The temperature ranges for D1 and D2 are indicated. It is seen that  $b$  has a larger value as the crystallization

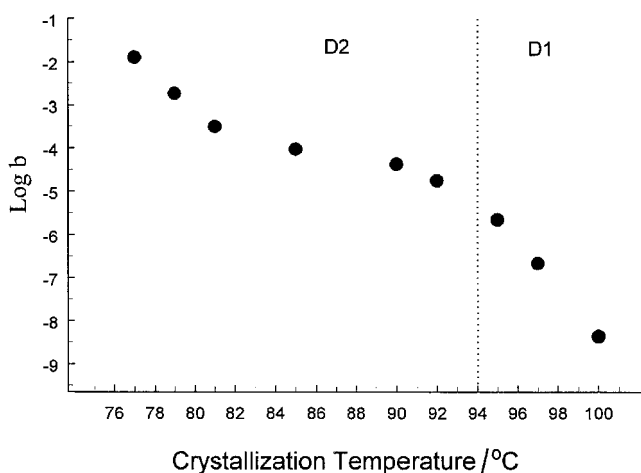


Figure 10. The logarithm of the constant  $b$  (in  $\text{min}^{-3}$ ) as a function of crystallization temperature. The regions of D1 and D2 are indicated.

temperature decreases, or as the supercooling increases. Considering the experimental uncertainties which could be involved in the DSC measurements, no attempt was made to understand the apparent shape of the  $\log b - T$  curve in figure 10. However, what seems to be clear is that crystallization from the D1 phase does not have the same temperature-dependence for the constant  $b$  as compared with crystallization from the D2 phase. Indeed, for the D2 phase, the change in the  $b$  values is about three orders of magnitude over a temperature range of  $17^\circ\text{C}$  whilst when crystallizing from the D1 phase, the variation in  $b$  extends also to about three orders of magnitude for a temperature range of only  $6^\circ\text{C}$ . In other words, as the crystallization temperature is raised, the value of  $b$  lowers much faster in D1 than in D2. Unfortunately, we were not able to gain independent information on the rate of nucleation or the rate of crystal growth. Therefore the exact meaning of this difference in the temperature dependence of  $b$  for crystallization from the two different columnar mesophases remains unexplained. Nevertheless, these results clearly reveal an influence of the starting discotic phase on the overall crystallization behaviour. In the case of RHO, the effects must be related to the different molecular arrangements within the two columnar mesophases, the growth in the form of disks being present in both cases.

It is noted that the Avrami constants obtained in this study are in contrast with those obtained for crystallization from a mesophase other than a discotic phase. For instance, an Avrami exponent of  $n$  being approximately 4 was obtained for a cholesteric-crystalline phase transition [8]. This is also the case for a crystallization from a smectic phase [9], indicating in both cases a sporadic nucleation of spherical domains. The constant  $b$  obtained in our study reaches the order of  $10^{-8} \text{ min}^{-3}$  (for crystallization from D1), which is at least two orders of magnitude smaller than the values of  $b$  reported in the above mentioned studies [8, 9].

The crystallization from the two discotic mesophases was confirmed by direct observations using an optical microscope under crossed polarizers. A set of photomicrographs showing the  $\text{D2} \rightarrow \text{Cr}$  phase transition is presented in figure 11. The typical texture for the D1 phase [2] was first obtained by slowly cooling the sample from the liquid phase to  $120^\circ\text{C}$  (cooling rate =  $1^\circ\text{C min}^{-1}$ ). When the sample was rapidly cooled from  $120^\circ\text{C}$  to  $90^\circ\text{C}$  (cooling rate  $\sim 10^\circ\text{C min}^{-1}$ ), a morphological change in the same area of the film was evident due to the  $\text{D1} \rightarrow \text{D2}$  phase transition. The texture became striated with fine lines lying perpendicular to the long axes of the birefringent regions. The new texture remained unchanged for several minutes as the D2 phase persisted. After 10 min at  $90^\circ\text{C}$ , regions having fine-grained crystalline texture appeared, indicative of the



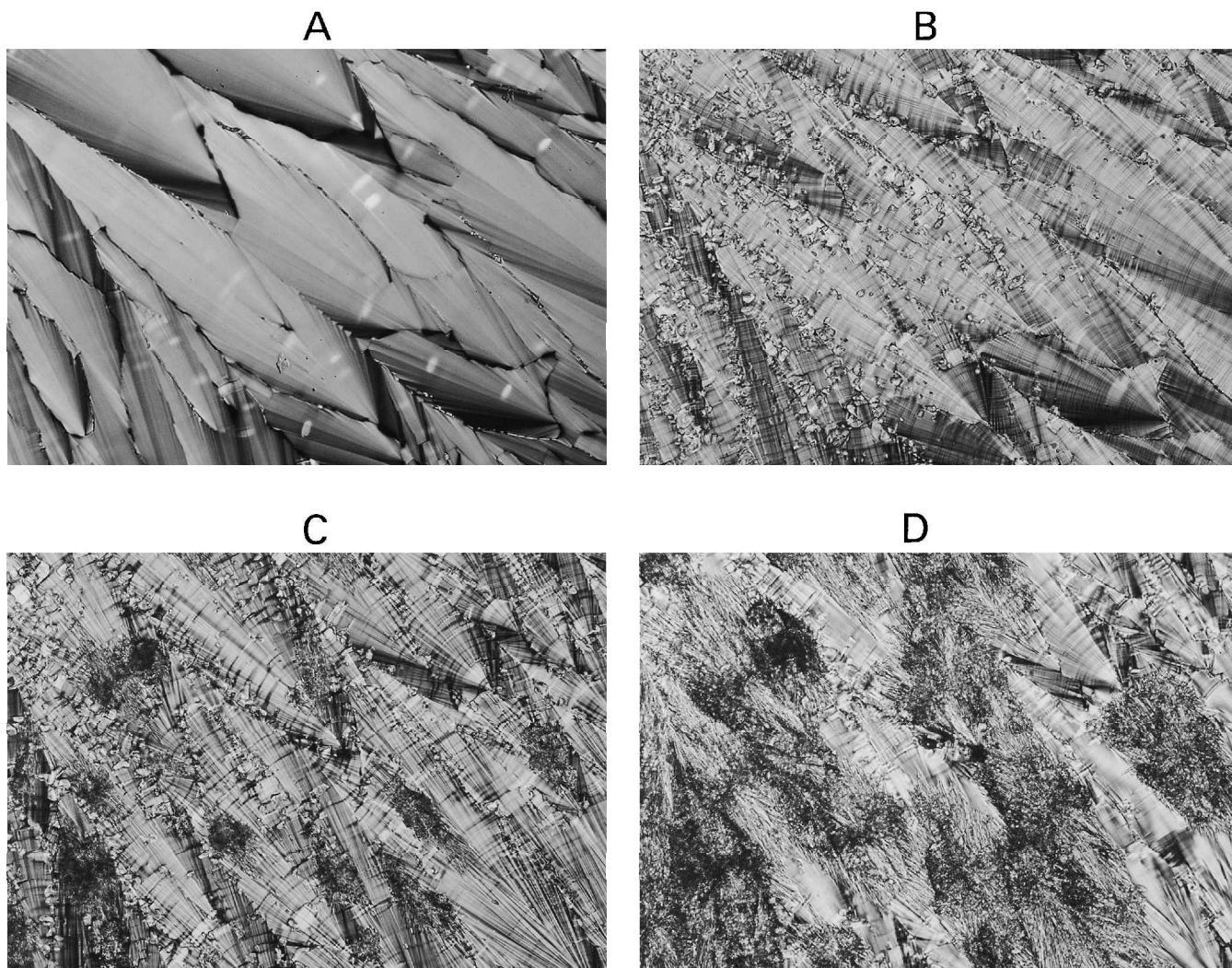


Figure 11. Polarizing photomicrographs of RHO in the D1 phase at 120°C (*a*), then cooled to 90°C for 3 min (*b*), 10 min (*c*), and 40 min (*d*), showing the D1 → D2 and D2 → Cr phase transitions. Magnification: 75×.

D2 → Cr conversion. The grain texture regions increased with time as the D2 phase was continuously converted into the Cr phase. Similar for demonstrating the direct crystallization from the D1 phase, some photomicrographs are shown in figure 12, where the sample was rapidly cooled from 120°C to 97°C. Initially, no morphological change could be seen. Only after 30 min, regions with the grained texture emerged from the texture of D1, and developed with time. Those observations are fully consistent with the results of the calorimetric measurements. No difference in the crystalline texture could be noted with the crystallization from both D1 and D2, and the texture was similar to that observed by quenching the sample from the liquid phase to room temperature. Unlike a crystallization from a liquid state displaying crystallites (often spherulites) emerging from a black background under crossed polarizers, in the case of crystallization from D1 or D2, the birefringent back-

ground and the irregular forms of the crystallized regions, as shown in figures 11 and 12, make it difficult to measure the growth rate of the crystallized domains.

#### 4. Conclusion

The transitions from the two different discotic mesophases to the crystalline phase of RHO were observed by means of differential scanning calorimetry and polarizing microscopy under appropriate conditions. The crystallization rates for a number of crystallization temperatures assessed from the calorimetric measurements indicated that the same overall mechanism operates for the crystallization process starting from the two discotic mesophases. Analysing the kinetics data with the Avrami equation gives rise to a value for the exponent  $n$  of 3. This result suggests a sporadic nucleation of disks for crystallization from a columnar mesophase, in contrast to the reported sporadic nucleation of spheres for

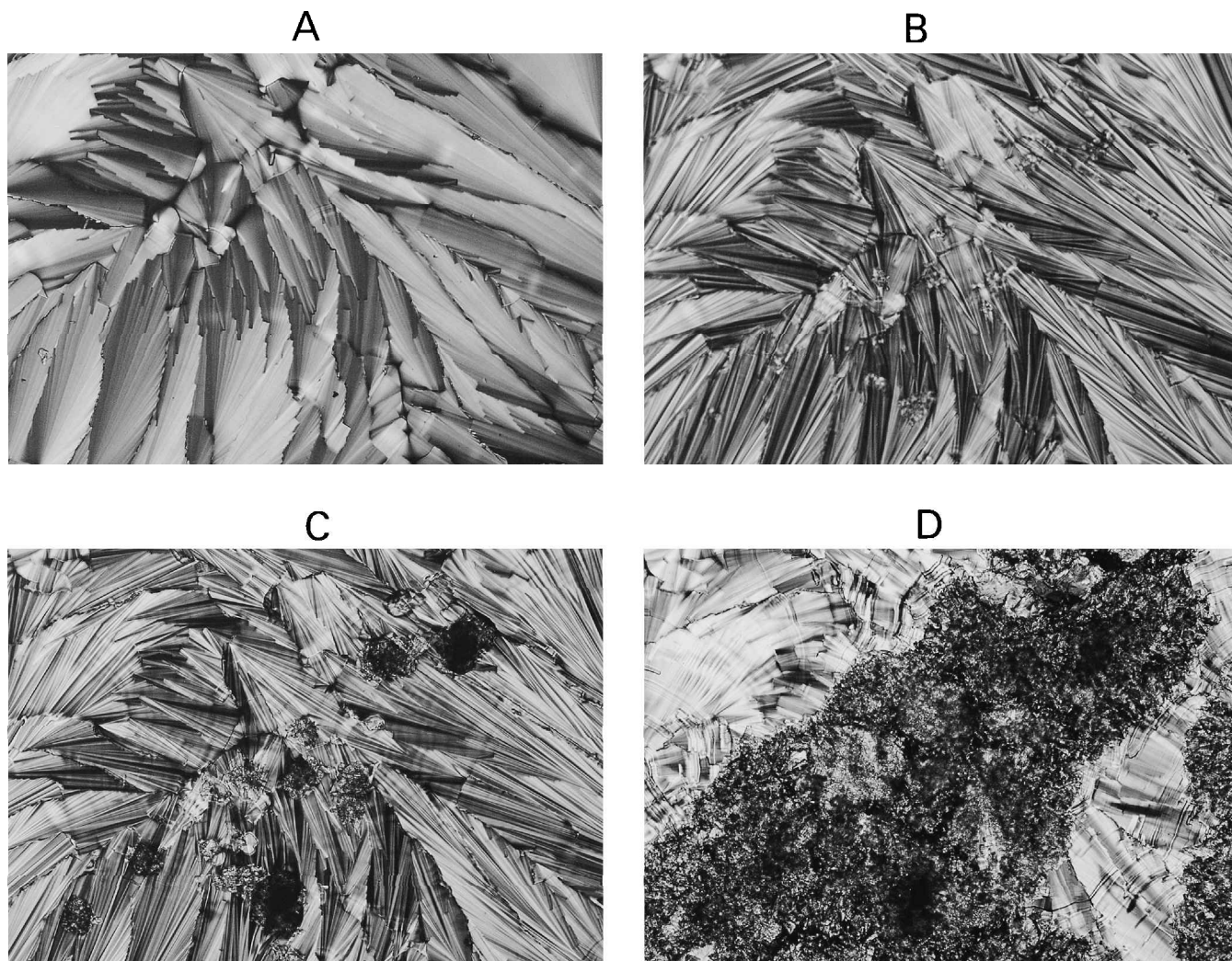


Figure 12. Polarizing photomicrographs of RHO in the D1 phase at 120°C (a), then cooled to 97°C for 30 min (b), 60 min (c), and 240 min (d), showing the D1 → Cr phase transition. Magnification: 75×.

crystallization from either a cholesteric or a smectic phase [8, 9]. The constant  $b$  in Avrami equation, which depends on the rate of nucleation and the rate of growth, is shown to have a different temperature-dependence for crystallization from D1 and D2. This is indicative of the influence on the crystallization rate of the different molecular arrangements in the two columnar phases. Observations using a polarizing microscope confirmed the crystallization from both discotic mesophases, showing no difference in the resulting crystalline texture.

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