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Dendrite-like texture growth in the nematic liquid crystal phase of 4-*n*-heptyl- and 4-n-octyl-oxybenzoic acids aligned by a polyimide coating

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An oriented dendrite-like texture is reported, appearing at a definite temperature in the nematic phase range of 4-*n*-heptyl- and 4-*n*-octyl-oxybenzoic acids (HOBA and OOBA), aligned by rubbed polyimide and preceding the smectic C phase, on cooling. Two preferred directions with respect to the 'easy' axis are indicated in the dendrites grown of HOBA and OOBA. We discuss a possible mechanism, at molecular and supramolecular levels, for this dendrite growth; and assume that the building 'blocks' of the dendrites are oligomers, or mixture of oligomers with 'free' closed and open dimers, constituting a detached crystalline layered state (named by us SmX, a smectic state intermediate between the N_1 ordinary nematic and SmC phases). The study of the dynamics of the dendrite growth demonstrates a scaling relationship typical for non-equilibrium systems. The observed dendrites can be considered as patterns formed in complex non-linear dissipative systems, driven outside of equilibrium.

1. Introduction

The growth of crystals from their supercooled melt is a most interesting pattern-forming phenomenon. A spectacular and practically important growth mode observed in nature is dendrite or needle generation [1, 2]. This non-equilibrium crystal growth, resulting in complex pattern morphologies such as dendrites, has been intensively studied both theoretically [3, 4] and experimentally [5–12].

Dendrites at a smectic B (SmB)–smectic A (SmA) liquid crystal interface have been observed [6], and dendritic smectic seeds nucleating spontaneously in the nematic (N) liquid crystal phase have also been reported [8, 13]. The special features, as well as the advantages of studying smectic–nematic or SmB–SmA interfaces, compared with crystals (e.g. metals) growing into its melt are: with both phases being fluids, the material parameters have similar values on both sides of the interface, both phases are anisotropic [2] and the anisotropies of the material parameters strongly affect the pattern formation.

The molecules that constitute the liquid crystals for which dendrite growth was observed are usually considered in a first approximation to be rigid rods. The influence of temperature on the structure of the liquid crystal molecules, and in turn on the dendrite pattern growth, is a new effect, which we have observed in 4-*n*-heptyl- and 4-*n*-octyl-oxybenzoic acids, HOBA and OOBA, respectively. To date there are no reports concerning dendrite growth in liquid crystal systems displaying nematic and smectic C phases. Pattern growth is also interesting since HOBA and OOBA show mesomorphic behaviour only because of the presence of a sufficiently high concentration of dimers, formed via hydrogen bonds. The dimers can be closed (centrosymmetric, with two hydrogen bond, symmetry C_{2v}) or open (with just one hydrogen bond) [14, 15]. The dimerization (with energy $20.05\,\mathrm{kJ\,mol^{-1}}$ [15]) depends on the temperature, implying a dimer–monomer concentration variation. Due to the temperature variation of the dimer–monomer concentration, different properties of the N phase at high and low temperatures have been reported [16–19]. These experiments demonstrated that in the N phase of HOBA and OOBA a temperature exists, usually indicated as T^*,

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which divides the N temperature range into high temperature N_1 (with macroscopic properties of conventional nematics, e.g. MBBA, PAA) and low temperature N_2 (with smectic-like character). Strong textural changes and strong Rayleigh light scattering was detected at the temperature of the N_1–N_2 transition (T^*) [16, 19].

Herbert [20], using DSC and NMR measurements, measured the phase transition temperatures and enthalpies of the 4-*n*-alkyloxybenzoic acids for homologues with chain length n between 2 and 16. According to this investigation the homologues with $n \leqslant 6$ (propyl to hexyl) display only a nematic phase; those with $7 \leqslant n \leqslant 13$ (heptyl to tridecyl) display both smectic C and nematic phases; while the homologues with $13 < n \leqslant 16$ display only a smectic C phase. The experiments, which we present here, clearly show that using polyimide-treated substrates for HOBA and OOBA orientation, at T^* a texture oriented in two preferred directions, with a dendrite form, nucleates spontaneously. This new effect prompts a qualitative and quantitative study of the dendrite growth, which is the purpose of the present work.

2. Experimental and results

2.1. *Materials*

The materials used in this experiment are:

HOBA: Cr-92-SmC-98-N-146-I (°C)

OOBA: Cr-101.1-SmC-108-N-147-I (°C)

The N–SmC phase transition enthalpies of HOBA and OOBA are 10.89 and 1.26 kJ mol^{-1} respectively [20]. We have purified the HOBA and OOBA used in these experiments by re-crystallization.

2.2. *Texture presentation of OOBA and HOBA*

The dendrite textures of HOBA and OOBA were observed through an Olympus polarizing microscope equipped with a hot stage and an automatic temperature control. Commercial liquid crystal cells (from E.H.C., Japan) were used, with thickness $d = 6\,\mu$m and with rubbed polyimide deposited on an ITO surface layer for uniform orientation.

The N phases of OOBA are very well aligned in the planar orientation and are black when viewed between crossed polarizers. At $T = 124$°C on cooling, a texture consisting of a set of dendrites emerges from the N texture (see figure 1). The dendrites grow with two main branches, strictly following two directions forming angles of about 30° and 60° with the 'easy' direction $\mathbf{n}_o$ ($\mathbf{n}$ is the nematic director). The side branches of the dendrites grow parallel to each other and perpendicular to the main branches, but also follow these two preferred directions.

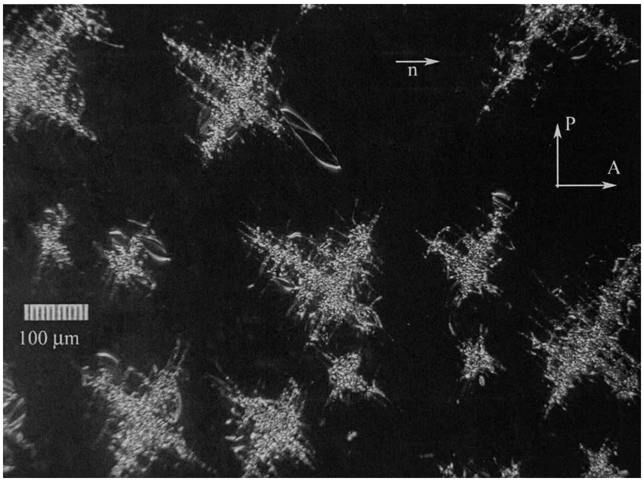

Figure 1. Dendrite emergence in the nematic phase of OOBA crossed polarizers well aligned using a rubbed polyimide coating.

Here we assume that the 'easy' directions imposed on the N phase by the two orienting surfaces are parallel (no imposed twist). The increase of the dendrites on cooling indicates that the percentage of the molecular forms constituting the dendrite structure increases, while that of the N phase decreases in some proportion. Observing the dendrites on a textural level, one can see that inside each dendrite is a polycrystalline grainy structure. This structure seems to be locally disordered, although more 'rigid' than the conventional N structure.

On further cooling of OOBA, the SmC phase appears as a well oriented single local monocrystal (SLM) form, from which one can determine the smectic C tilt angle to be ~45°. We note that the two preferred directions for dendrite growth coincide with the direction of growth of the SmC layers.

On heating, the dendrites decrease in size and finally disappear a few degrees below the nematic–isotropic (I) phase transition. The sizes of the dendrites vary, indicating different rates of propagation of the nematic–dendrite interface, and probably reflects a temperature field distribution. We also found a large hysteresis of the temperature at which dendrites appear (124°C) and disappear (141°C) on cooling and heating, respectively.

The dendrite texture evolution of HOBA is similar to that of OOBA. The dendrite growth again follows two preferred directions. A difference however in their SmC texture formation is seen. The SmC texture formed as SLM cannot be developed in the expected range (~6°C measured by DSC [20]) for HOBA. The HOBA smectic texture grows as SmC drops which are elongated and divided along their long axes by well pronounced sharp lines, probably indicating the layer position. The hysteresis of the dendrites appearing on cooling and disappearing on heating is again very large, ~16°C.

From the differences in the SmC texture formation of HOBA and OOBA, oriented by a polyimide coating, one can conclude that increase in n (i.e. the molecular length) stimulates the formation of a stable smectic C state with a tilt angle ~45°. In homologues with $n>8$ we expect the SmC state, to be fully developed for these surface conditions, and less perturbed by the intermediate (between N_1 and SmC) dendrite texture. Besides the molecular length increase, the other important parameter controlling the dendrite growth, and in turn the SmC texture development, is the surface treatment. To study the role of the surface treatment in dendrite emergence and growth control, we repeated the experiment with the same substances (HOBA and OOBA), and the same experimental geometry, changing only the polyimide (hydrophobic) surface treatment with ITO/glass, SiO/ITO/glass, SiO/glass and PVA/glass surface treatments. The last four treatments usually provide hydrophilic orienting surfaces, implying hydrogen bonding of these surfaces with 'free' monomers and the open dimers. We were unable to observe dendrites using these orienting substrates. Thus the supression of hydrogen bonding of the liquid crystal molecules with the surface in the case of the polyimide coating, could (to some extent) favour the bulk structure transition (indicated by dendrites) in HOBA and OOBA at temperature T^* (transition of the closed dimers into open dimers and in turn into oligomers).

2.3. *Quantitative analysis of dendrite growth*

Here we study the dynamics of the dendrite growth of OOBA. The parameters used in our measurements are: the supercooling $\Delta T = T^* - T$, where T^* is the temperature of the nematic–dendrite texture transition, $T < T^*$. The temperature T^* can be considered as an equilibrium phase transition temperature. This temperature is the same as that at which the texture transition N_1–N_2 occurs (see § 1) and where the nematic conventional texture transforms into a smectic-like texture.

We use also a dimensionless parameter [8] ('distance' from the equilibrium) $\Delta = c_p \Delta T / L$, where c_p is the specific heat per unit volume and L is the latent heat per unit volume of the N_1–N_2 transition with $c_p = 19.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$, and $L = 0.3\,\mathrm{k\,J\,mol^{-1}}$ respectively as measured by DSC [18]. A series of patterns of different size grown at different values of supercooling were studied. Depending on the supercooling, a thermal equilibrium state of the system, is approached where the shape anisotropy of the equilibrium dendrite can be used, by a Wulff construction [5], to estimate surface tension, which is important in dendrite growth. Applying a sufficiently large supercooling ($\Delta T > 0.3$°C), however, spontaneously nucleated seeds appear. At this stage we worked only with the spontaneous nucleation of the dendrites, without using the equilibrium shape. The time passed from the moment of nucleation ('pattern age') was measured. The dendrite pattern normally had the shape of a cross. We accept that dendrite growth means that the four main branches are still observable with intensive side branching. The angle between the main branches is 90° and it is the same for each nucleation centre. We normally obtained a few seeds for measurements.

The dendrites are optically homogeneous. On rotating the sample, extinction of all four main branches and all side branches occurs simultaneously if the crossed polarizers point along the bisectors of the main branches of the growing pattern. This suggests a two-fold symmetry (with two mirror planes), and that the internal organization of all branches of the dendrites is the same. The directions of director **n** outside and inside the dendrites coincide and are along the main branches bisectors, as found using a quartz wedge as compensator. The direction of **n** in the SmC phase is the same as that in the N phase and in the dendrites; the layer planes are at an angle of 45° to this direction, thus coinciding with the dendrite main branches direction.

The dendrite represents the interface between the nematic N_1 and N_2 states. This interface may be considered as a front of the stable phase (N_2, ordered), which propagates into the metastable one (N_1, disordered–supercooled). Following [21] we emphasize that the N_1–N_2 transition can be considered as a weak first order phase transition (large hysteresis of the appearance and disappearance of the dendrites and a comparatively small latent heat, $0.3\,\mathrm{kJ\,mol^{-1}}$ [18]). In addition the theory [21] predicts a nucleation barrier near to the transition, provided the system is supercooled to below the phase transition temperature. Thus an interface occurs and depending on Δ it propagates with velocity v.

In the case of spontaneous nucleation considered here, we measured the velocity of growth of the freely moving dendrite tips. The growth velocity decreases with time, and could be fitted by a power law $v \sim t^{-\mu}$, where μ was in the range 0.52–0.66 for Δ variation between 0.34 and 0.98. The characteristic time dependence of the tip velocity is shown in figure 2, from which the tendency of the growth velocity to be asymptotically constant is seen. This is a generic feature of pattern formation in a non-linear dissipation system driven outside of the equilibrium [22].

It is known that the presence of flow allows the

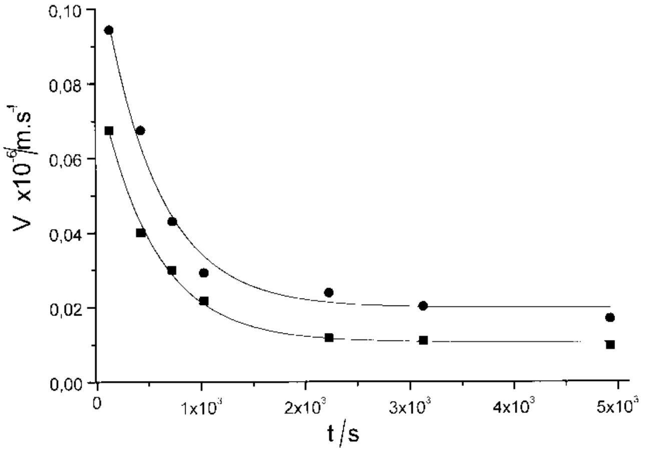

Figure 2. Characteristic time dependence of the growth velocity. ●: $\Delta = 0.58$, $\mu = 0.52$; ■: $\Delta = 0.34$, $\mu = 0.6$.

possibility of instabilities due to the flow itself, in addition to the morphological instabilities normally found in dendrite growth [23]. We observed dendrite growth without flow, i.e. without driving viscous forces.

The disposition of the building 'blocks' in the growing dendrites (seeds), giving a low symmetry (with low energy) state, must be more ordered than in the N_1 matrix, given that the entropy of the growing formation is smaller. Then for this dendrite to grow, some quantity that is generated at the interface between dendrite and nematic N_1 during the supercooling, for example latent heat of the N_1–N_2 transition, must be channelled away from that interface [22, 23].

The supercooled N_1 state can be conserved for a very long time in a metastable state, but within a critical supercooling, for given conditions, a multitude of small smectic clusters (aggregates) appear. The coalescence of these aggregates minimizes the free energy of the system, but the new growing surfaces increase. In this non-equilibrium process [22] the aggregates grown form a continuous layer, which in turn constitutes the interface layer. We can consider the process of the growth of these aggregates and in turn the growth of the dendrite.

Let us separate an elementary unit area on the growing interface wall (between N_1 and the aggregate) in the ξ direction; ξ is perpendicular to the plane of this moving wall. The velocity of the wall growth v is the thickness of the layer, increasing in unit time; then for time dt the interface wall will grow by the layer $d\xi = v dt$. The heat emitted during aggregate growth from the layer with thickness $d\xi$ and unit area is $dQ_1 = c\rho d\xi = c\rho v dt$, where c is the heat of crystallization and ρ is the dendrite density. The condition of heat conservation at a point on the moving interface determines the velocity of the front at that location for a given temperature field [22]. The heat taken away from the unit area interface for dt, is $dQ_2 = \chi(dT/d\xi)\,dt$, where χ is the coefficient of the heat-conductivity of the growing dendrite, and $dT/d\xi$ is the temperature gradient normal to the interface wall. Dendrite formation occurs with a velocity v at condition $dQ_1 = dQ_2$; i.e. at $c\rho v dt = \chi(dT/d\xi)\,dt$, from which $v = \chi/c\rho(dT/d\xi)$.

From this dependence, it follows that the dendrite grows fastest in the direction of maximum temperature gradient, and v decreases as the dendrite density ρ increases. We cannot analyse the exact trend of $v(t, \Delta)$ by this formula for aggregate growth, since we do not take into account parameters important for the dendrite growth, such as surface tension or the kinetic coefficient.

3. Discussion

The temperature dependence of the equilibrium concentration of the closed dimers, open dimers and monomers (calculated by FTIR spectroscopy) has been reported for HOBA [24]. According to this investigation in the nematic range the predominant molecular form is the closed dimer. About 15°C above the N–SmC transition, the monomers disappear and only closed dimers and open dimers remain, as this ratio persists into the SmC phase. We note that FTIR spectroscopy cannot detect the oligomers.

The closed dimers may be presented as derivatives of the monomers, which are linked by two linear hydrogen bonds, figure 3 (*a*). The energy of this bonding is $20.05\,\mathrm{kJ\,mol^{-1}}$ [15] and can be easily destroyed by temperature variation and even by optical or surface effects, when these effects affect the hydrogen bonding energy. Thus the closed dimers can be a stable state, if they are isolated from these external effects, which is not case in the liquid crystal phase. The dimerization is a process of minimizing the hydrogen bond energy (on cooling), while the opposite process—monomerization is connected with a high energy state (on heating). Consequently an intermediate process, energetically favourable under external (temperature in our case) effects, is the opening of the closed dimers; this occurs by rotation about one of the hydrogen bond axes, thus forming open dimers (only one linear hydrogen bond) or at higher energy, 'free' monomers figure 3 (*b*). The open dimers as well as the 'free' monomers are amphiphylic molecular forms (polar heads and hydrophobic tails). They can participate in H-bonding with neighbouring open dimers or with other 'free' monomers. This process leads to a multiplication of the linear hydrogen bonds, thus providing supramolecular forms known as oligomers [25]. A model of this is shown in figure 3 (*c*).

The local orientation of a building unit represented

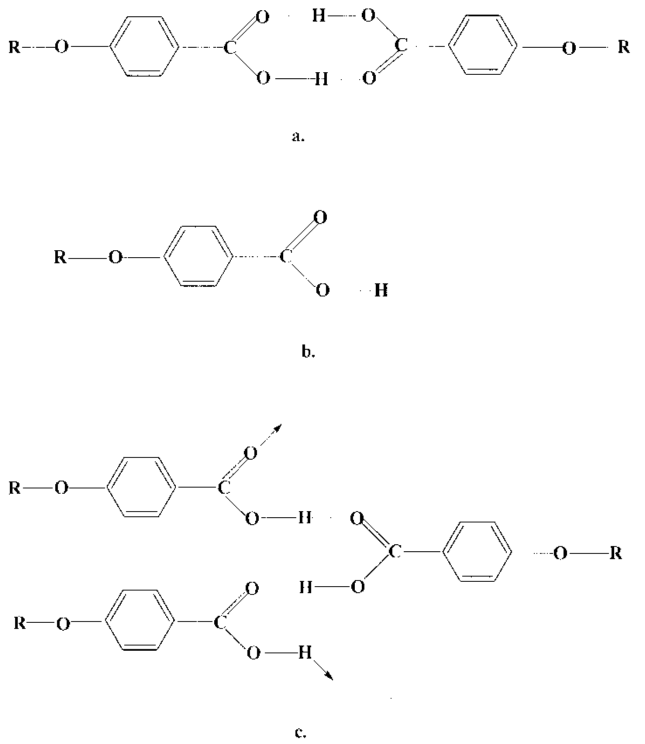

Figure 3. Oligomer development on varying temperature. (*a*) The closed dimer, (*b*) the monomer and (*c*) oligomers.

in figure 3 (*c*) can more or less provide the selection of the microtextural pattern like that of the dendrite. We assume that the polyimide treatment constrains the 'rigid' molecular part, i.e. the benzene rings, to follow the 'easy' direction. This means that the process of multiplication of the linear bonds (oligomerization) seems to be affected by the matrix of the very well aligned nematic phase. In any case, the symmetry C_{2v} of the basic molecular form, closed dimers, changes. It is very important, however, to imagine the disposition of the benzene rings in space. They could be distributed in space as local ordered molecular fragments. In such a disposition, starting with the basic geometry shown in figure 3 (*c*), one can note two directions in the construction of the building blocks, which resemble the preferred directions of the dendrite growth in respect to the easy 'axis', i.e. -30° and 60° (see figure 1). The direction of 60° is half the angle between the C–O and C–O in the dimer ring, which is 120°. The O atom of the C–O bond—see the arrows in figure 3 (*c*)—could form a H-bond not only in the plane of the dimer ring (this plane is not destroyed in the closed dimer), but also in space, meaning with a H of other dimer ring planes situated in other levels.

Such a development of the H-bonding, could promote an oligomerization in which the dimer rings are open, could be parallel each other and coexist with a majority of 'free' closed dimers. Subjected to the influence of the strong smectic order fluctuation (due to the smectic C formation upon cooling) these basic molecular forms minimize the energy of the system by packing in supramolecular smectic-like complexes (aggregates) giving a dendrite texture as an intermediate between that of the conventional nematic (N_1) texture and the SmC texture. This process is underlined in the bulk, as we demonstrated by FTIR spectroscopy, but in very thin samples the surface action cannot be neglected. That is why, depending on the nature of the surface coating, hydrophobic (polyimide) or hydrophilic, one can observe arranged smectic-like 'grains' in dendrite forms or non-arranged 'grains', respectively [16, 19].

Such a smectic-like texture was found by small angle X-ray scattering [19] of a bulk OOBA sample (thin capillary tube without treatment). A layering with a spacing of 3.0 nm (intermediate tilt angle $\omega = 34^\circ$), different from that of the SmC phase of OOBA (tilt angle $\omega = 45^\circ$) was detected below T^*. At this temperature, a N_1–N_2 texture transition (manifested by non-arranged 'grains' in the N_2 state) occurs in the case of samples thinner than 50 μm, oriented between SiO-coated glass plates (evaporation angle α between 66° and 86° and nominal SiO thickness layer δ between 18.3 and 13.4 nm, respectively). A layered smectic-like structure was found [19] by small angle X-ray scattering which we termed smectic X (indicating an unknown smectic-like layered structure), intermediate between the N_1 and the SmC structures; this could be providing the texture of the dendrites. In this sense the N_2 state can be considered as an intermediate smectic-like (SmX) state between the N_1 and SmC phases. Consequently we note that the polyimide hydrophobic surface is a candidate for study of the bulk properties of the peculiar smectic-like state below the T^* temperature, since the surface perturbation on the molecular building block formation, due to the hydrogen bonding of the liquid crystal molecules and the surface, is (to a great extent) suppressed. The complex grain-like texture inside each dendrite (see figure 1), which is highly polycrystalline, may indicate regions of low curvature of the layers. We recall that the planar oriented SmC texture is also polycrystalline, but the single local monocrystals representing homogeneously oriented smectic C are comparatively large [19]. Certainly one cannot imagine the exact constituent complex molecular unit, assumed in figure 3, for such a layered smectic-like state. This is because besides the compact layering of 'free' closed dimers, simple 'free' open dimers as well as oligomers also participate in the selection mechanism of the microtextural pattern generation and growth.

This description of the phenomenon give us the possibility, following the statements in [21–23], to relate the dendrite texture growth to a weak first order transition (N_I–SmX) where the front of the SmX stable state propagates in the metastable N_I state. The large hysteresis of this transition and the comparatively small latent heat measured for OOBA [18], support this conclusion. Thus the dendrite texture, starting below T^* can be viewed as indicating a detached liquid crystal phase.

Extensive further investigations on molecular, supramolecular and macroscopic levels are in progress for understanding the dendrite-like texture of HOBA and OOBA. An X-ray experiment with the possibility of distinguishing the conventional nematic and dendrite oligomeric structure should now be performed.

4. Conclusion

We have studied for the first time the dynamics of growth of an oriented dendrite-like texture in HOBA and OOBA in a homogeneously planar orientation, achieved by rubbed polyimide surfaces. Two preferred directions with respect to the 'easy' axis are indicated in the dendrite growth of HOBA and OOBA. The normal texture (SLM) observed for other surface conditions for HOBA, cannot develop on a polyimide treated surface, and only smectic C droplets appear. OOBA however, although it has a small difference in respect to the molecular length of HOBA, develops a well aligned smectic C (SLM) texture.

We have discussed, at molecular and supramolecular levels, a possible mechanism for the dendrite growth in two preferred directions with respect to the 'easy' axis. We assume that the building 'blocks' of the dendrites are oligomers, or a mixture of oligomers with 'free' closed and open dimers, constituting a detached crystalline layered state (termed by us SmX, a smectic state intermediate between the N_I ordinary nematic and SmC phases), which was reported in [19].

The study of the dynamics of the dendrite growth demonstrates a scaling relationship typical for non-equilibrium systems. The observed dendrites can be considered as patterns formed in complex non-linear dissipative systems, driven outside of equilibrium.

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