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Induced G phase through intermolecular hydrogen bonding: X. Crystallization kinetics study on two structural isomers†

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A comparative systematic crystallization kinetics study has been carried out on two distinct novel liquid crystalline isomers, DBA:R:DBA and DBA:H:DBA (where DBA = *p-n*-decyloxybenzoic acid, R = resorcinol and H = hydroquinone) using differential scanning calorimetry. The kinetics experiment is performed from the crystal G phase (kinetophase), which is a common induced phase in both compounds. The molecular mechanism and dimensionality of crystal growth are studied from the Avrami exponent n while the characteristic crystallization time (t^*) at each crystallization temperature is deduced from the individual plots of log t vs. ΔH.

1. Introduction

It is now well established that a large majority of polymorphic transformations, and transformations involving simple decomposition into two phase regions, are described by a nucleation and growth process in which the nuclei of a new phase are first formed at a particular rate in the form of small domains followed by their aggregation at a faster rate resulting in the formation of layered domains. A completely different, much more complicated mechanism is found to occur in liquid crystal systems involving intermolecular hydrogen bonding, due to the low bond activation energies of the non-covalent interactions [1, 2]. To understand such a nucleation mechanism and related phenomena, the study of the crystallization kinetics by a calorimetric method is now widely used.

In recent years, hydrogen bonding has gained prominence in self-organization via molecular aggregation in liquid crystal systems [3–7]. Despite playing a crucial role in the induction of new phases in mesogenic systems [8–10], it has been observed that these non-covalent interactions, with their low bond activation energies, have a profound influence on the rate of crystallization and the related nucleation mechanism. The present communication deals with a systematic crystallization kinetics study on two novel liquid crystalline compounds involving hydrogen bonding with different proton donors and acceptors. In continuation of our extensive crystallization kinetics investigations [1, 2] on liquid crystals

involving intermolecular hydrogen bonding, we describe a systematic crystallization kinetics study and the related nucleation process for the two novel liquid crystalline isomers DBA:R:DBA and DBA:H:DBA (figure 1) using *p-n*-decyloxy benzoic acid (DBA) as a common mesogenic moiety.

2. Experimental
2.1. Synthesis and characterization

The synthetic procedure and structural characterization of the compounds DBA:R:DBA and DBA:H:DBA are reported in a previous communication [11]. The growth rate of melting transitions and their corresponding enthalpies at each crystallization temperature were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 system. The DSC scans were
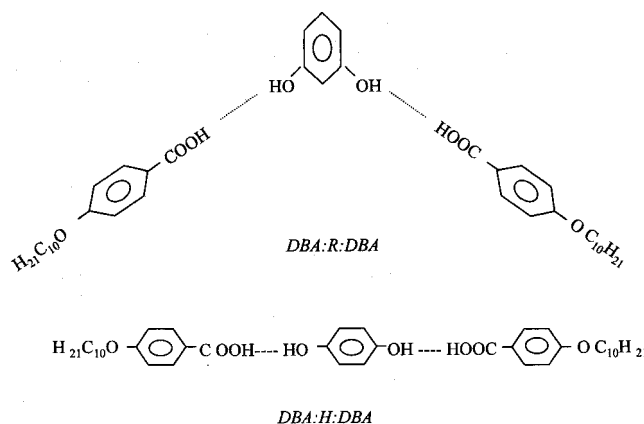

Figure 1. Molecular structures of DBA:R:DBA; DBA:H:DBA.

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† For part IX see Ref. [11].

performed on each member of the present compounds (3–5 mg samples) using aluminium crucibles.

A typical DSC thermal scan for a given sample at each crystallization temperature is described as follows. The sample is heated to its isotropic melt with a scanning rate of 5°C min^{-1} and, after holding for ~2 min for attaining thermal equilibrium, the sample is cooled at the same scan rate to its predetermined crystallization temperature. After holding for a suitable time interval at the given crystallization temperature, the endotherm peaks are recorded while the sample is heated to the isotropic state at 5°C min scan rate. This process is repeated for each of the compounds under present investigation at the corresponding preselected crystallization temperature. In the following text the various phases are denoted as follows: Cr = crystal, G = crystal G, SmA = smectic A, SmC = smectic C, N = nematic, I = isotropic.

2.2. *Selection of thermal range of crystallization temperatures*

The procedure for the thermal selection of crystallization temperatures (CT) is described for DBA:R:DBA as representative. The DSC thermograms of DBA:R:DBA are illustrated in figure 2. On heating, the compound
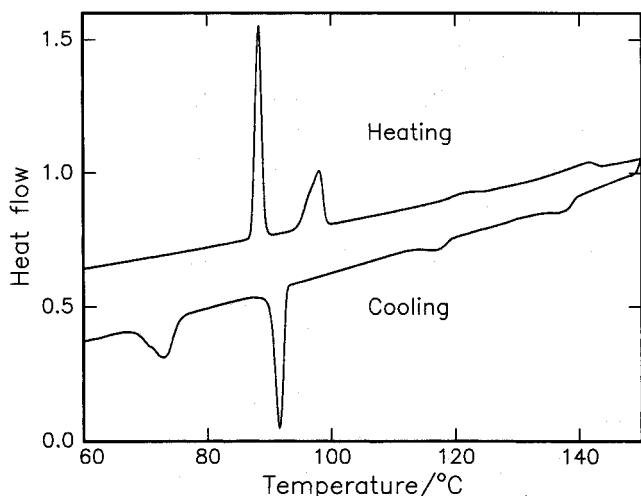

Figure 2. Heating and cooling DSC profiles of DBA:R:DBA.

exhibits transitions at 88.2°C (Cr–G), 97.8°C (G–SmA), 121.1°C (SmA–N) and 141.2°C (N–I) with corresponding enthalpies 62.7, 33.9, 2.7 and 4.1 J g^{-1}, respectively. The cooling exotherm shows distinct transitions at 137.8°C (I–N), 117.2°C (N–SmA), 91.6°C (SmA–G) and 72.9°C (G–Cr) with the corresponding enthalpies, 3.3, 3.1, 31.1 and 22.5 J g^{-1}, respectively. A glance at figure 2 reveals the thermal span of the mesomorphic phases as: $(T_{Cr-G}) - (T_{G-Cr}) = $ ~10°C. Once the phase transition from SmA to G is completed, the kinetics of the crystallization from crystal G could be investigated over the temperature range between T_{Cr-G} and T_{G-Cr}.

3. Results and discussion
3.1. *Phase variants*

The phase variants exhibited by DBA:R:DBA and DBA:H:DBA are identified by their characteristic textures [12] by cooling the isotropic melt using a polarizing thermal microscope. The phase variants and the transition temperatures [11] are summarized in table 1. The transition temperatures of the phases observed through thermal microscopy (TM) are found to be in reasonable agreement with the corresponding DSC thermograms. DBA:R:DBA exhibits N, SmA and crystal G phases while DBA:H:DBA displays N, SmC and crystal G phases.

3.2. *Rate of crystallization*

The method for thermal selection of crystallization temperatures is performed as described in the previous section. The crystallization kinetics relating to phase transition from crystal to melt for each compound is selectively performed at a predetermined crystallization temperature (table 2).

3.3. *DBA:R:DBA*

From DSC thermograms (figure 2), it is deduced that the kinetics of crystallization from the G phase could be investigated over the temperature range 75–85°C. The crystallization kinetics study relating to the transitions from the G phase is selectively performed at 78, 79, 80 and 81°C.

Table 1. Transition temperatures (°C) from TM and DSC [in square brackets] of DBA:R:DBA and DBA:H:DBA complexes. Enthalpy values (J g^{-1}) are given in parentheses. I = isotropic, N = nematic, A = smectic A, C = smectic C, G = crystal G, Cr = crystalline.

Compound	Phase variant	Phase transition			
		I–N	N–A/C/G	A/C–G	G–Cr
DBA:R:DBA	NAG	128.6 [137.8(3.3)]	118.5 [117.2(3.2)]	95.9 [91.6(31.1)]	79.3 [72.9(22.5)]
DBA:H:DBA	NCG	128.8 [120.7(4.7)]	118.5 [109.0(2.34)]	92.3 [90.1(25.0)]	75.2 [71.2(16.4)]

Table 2. Crystallization parameters measured in the crystal G phase of DBA:R:DBA and DBA:H:DBA complexes.

Compound	Crystallization temperature/°C	Crystallization time (t^*)/min	x	n	b
DBA:R:DBA	78	16.0	0.942	0.179	0.6087
	79	32.0	0.948	0.093	0.7247
	80	64.0	0.938	0.044	0.8345
	81	120.0	0.945	0.024	0.8901
DBA:H:DBA	75	4.0	0.986	1.08	0.2237
	76	8.0	0.998	0.85	0.1707
	77	16.0	0.999	0.87	0.896
	78	32.0	0.998	0.20	0.5000
	79	64.0	0.999	0.25	0.3535
	80	120.0	0.991	0.04	0.8257

Typical DSC endotherm profiles for different time intervals at two crystallization temperatures 78 and 81°C are presented in figures 3 and 4, respectively. In figure 3
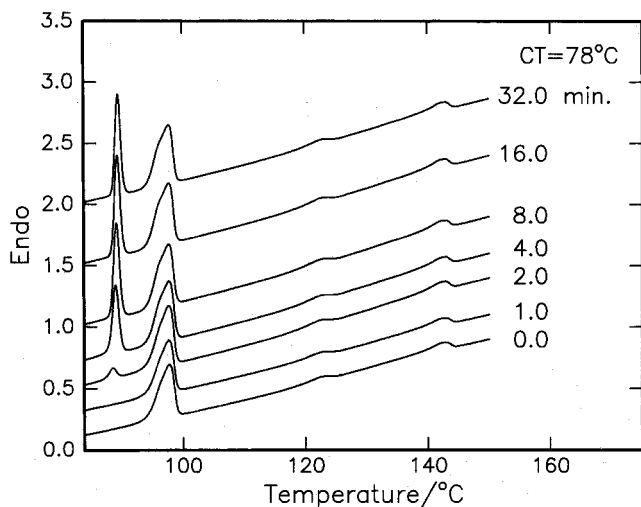
Figure 3. DSC endotherm of DBA:R:DBA at 78°C.
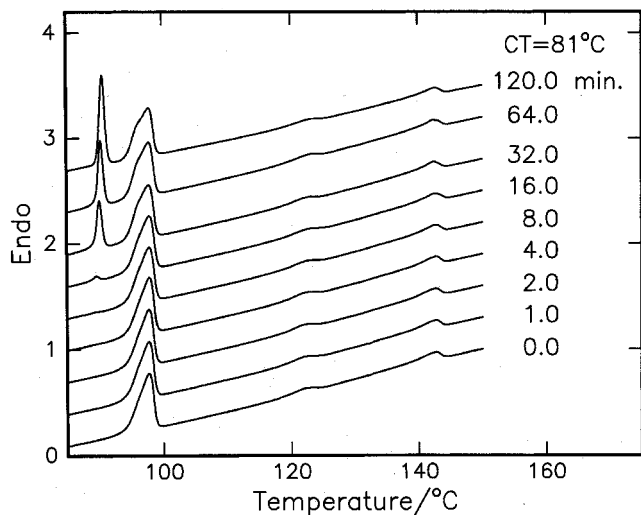
Figure 4. DSC endotherm of DBA:R:DBA at 81°C.

the heating curve recorded immediately at crystallization time $t = 0$ min shows all pertinent transitions except the crystal to melting transition. However, the formation of a melting transition starts as a small peak after holding the sample for 2.0 min at the quench temperature. The growth of this transition is completed and a saturated enthalpy value is attained after 16.0 min. This suggests a slow crystallization mechanism in the complex. A similar trend is observed in the endotherm profiles recorded at 81°C (figure 4). However, a melting transition is first observed after 16.0 min and the completion of its formation is seen after 120.0 min. This clearly suggests that the process of crystallization at 81°C follows a delayed nucleation process.

3.4. *DBA:H:DBA*

The DSC thermogram of DBA:H:DBA is illustrated in figure 5. During heating, the complex exhibits transitions at 88.4°C (Cr–G), 96.2°C (G–SmC), 110.0°C (SmC–N) and 125.2°C (N–I) with heats of transitions, 48.9, 24.2, 1.3 and 7.6 J g^{-1}, respectively. The cooling exotherm

Figure 5. Heating and cooling DSC profiles of DBA:H:DBA.

shows the corresponding transitions at 120.7°C (I–N), 109.0°C (N–SmC), 90.1°C (SmC–G) and 71.2°C (G–Cr) with their enthalpy values 4.7, 2.3, 25.0 and 14.6 J g⁻¹ respectively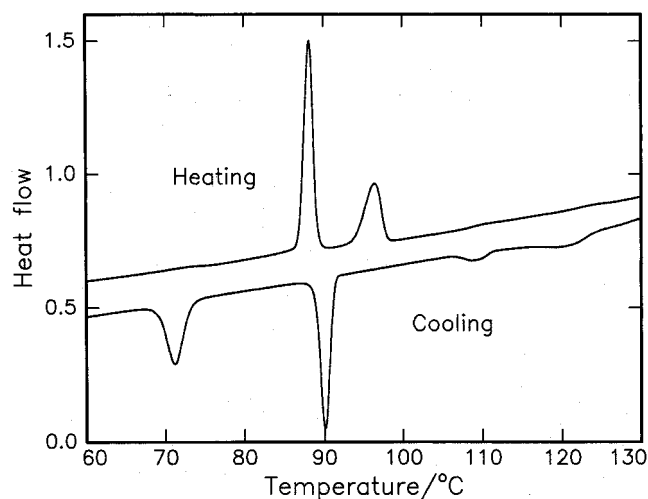. From the above data, it is deduced that the kinetics of crystallization from the kinetophase (crystal-G) could be investigated over the temperature range 75–85°C. The crystallization kinetics relating to the transitions from the G phase is selectively performed at 75, 76, 77, 78, 79 and 80°C.

Figures 6 and 7 illustrate typical DSC endotherm profiles for different time intervals at crystallization temperatures 75 and 80°C, respectively. At a crystallization temperature of 75°C (figure 6) the heating curve recorded with no time delay ($t = 0$ min) shows the absence of a melting transition. However, its appearance is noticed as a small peak after holding the sample for 0.2 min, which suggests a fast crystallization process. The saturated

enthalpy value of the melting transition is attained after holding the sample for 4.0 min. Figure 7 shows a similar trend where the development of a small peak is seen after holding the sample for 8.0 min; the formation of this shoulder reaches a saturated value after 120.0 min. This suggests a delayed nucleation mechanism at 80°C. This slow rate of crystallization with the increased crystallization temperature may be substantiated in terms of the stability of hydrogen bonding towards the number of terminal carbons.

3.5. *Process of crystallization*

The heats of transition for individual transitions for different time intervals have been calculated [13] at each crystallization temperature and the data (table 2) plotted against the corresponding logarithm of time intervals for each compound. Figures 8 and 9 show such plots
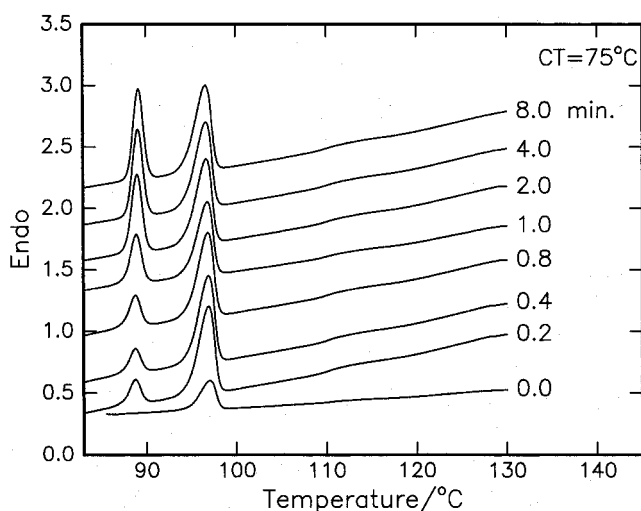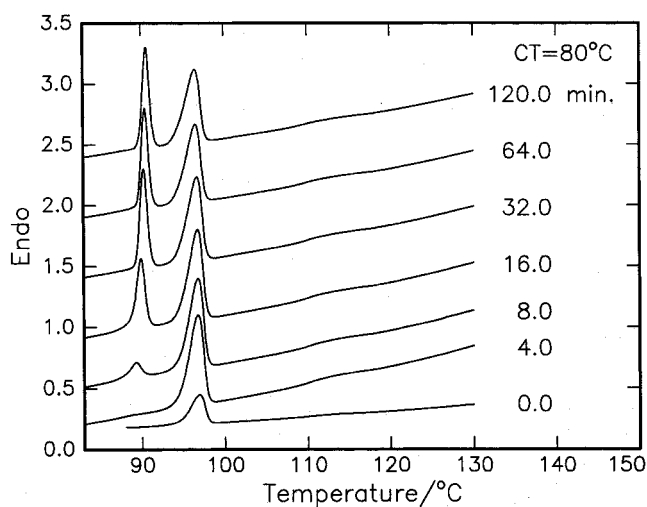

Figure 6.   DSC endotherm of DBA : H : DBA at 75°C.

Figure 8.   Enthalpy vs. log *t* of DBA : R : DBA at 78 and 81°C.
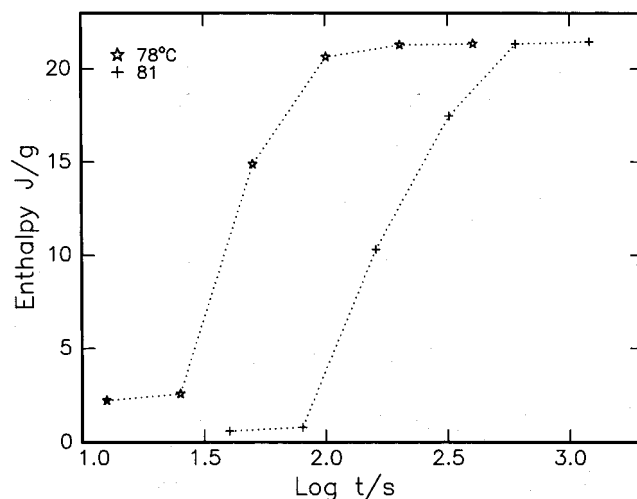

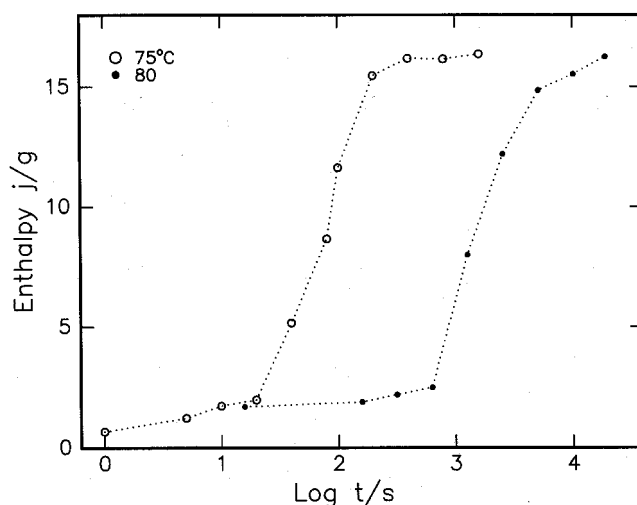Figure 7.   DSC endotherm of DBA : H : DBA at 80°C.

Figure 9.   Enthalpy vs. log *t* of DBA : H : DBA at 75 and 80°C.

for DBA:R:DBA at 78 and 81°C, and DBA:H:DBA at 75 and 80°C. The plots are identical in shape, apart from the shift in the log *t* axis, suggesting the limitations of the rate of crystallization [13, 14]. Moreover, the simultaneous measurement of enthalpy of the crystal G endotherm with time illustrates the effective beginning and end of the crystal formation process, which coincides with that of formation of the melting transition.

The plots of enthalpies of the growing melting transitions vs. log of annealing time at different crystallization temperatures is obtained by shifting the data along the log *t* axis to 81°C for DBA:R:DBA and to 80°C for DBA:H:DBA, the corresponding plots are depicted in figures 10 and 11, respectively. A glance at these master curves clearly suggests that the overall crystallization in both compounds is controlled by a unique nucleation mechanism [14]. If the crystallization kinetics from the
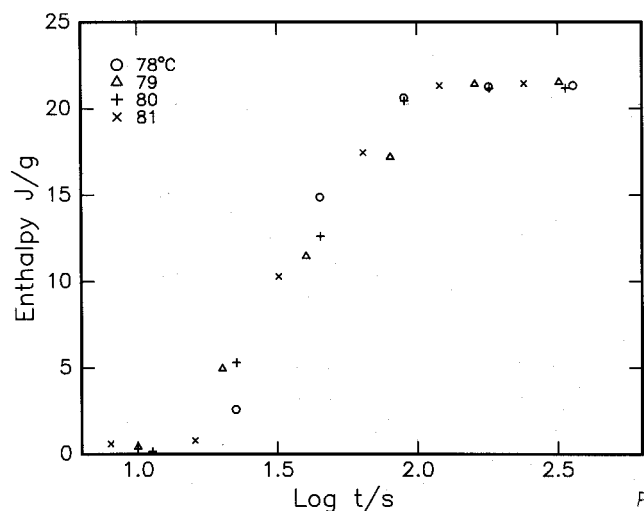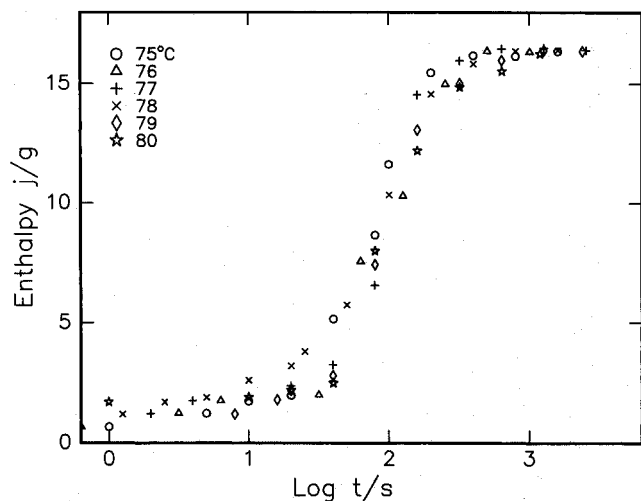
corresponding smectic phase is described by the Avrami equation [15, 16], the data for all the crystallization temperatures will match the single equation

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

where $t^* = b^{-1/n}$. Further, the characteristic time t^* can be determined experimentally since at $t = t^*$, $x = 0.632$. The constants n and b are calculated as reported earlier [13].

As borne out by the data (table 2) the value of the Avrami exponent n varies from 0.02 to 0.17 for DBA:R:DBA, and 0.04 to 1.08 for DBA:H:DBA. This clearly suggests that the mode of nucleation falls in the category of diffusion-controlled transformations leading to a situation similar to first order kinetics, which involves the growth of isolated plates or needles of finite size [17]. The very low n values (below 0.5) indicates the thickening of plates after their edges have impinged upon each other, while the relatively higher values (near to unity) may be attributed to the growth and formation of isolated plates or needles of finite size. Moreover, the possible explanation of the magnitude of n is supplemented either by two-dimensional sporadic nucleation or by growth in three dimensions. The former is compatible with the crystallization process occurring in smectic layers, while the possibility of the latter argument is small [13, 14]. However, predictions on growth dimensionality in the case of low n values require a detailed X-ray investigation.

The magnitude of constant b (table 2), which governs the nucleation mechanism, is unaltered with an order of 10^{-1} for both the compounds under present study. This trend in the magnitudes of b is found to be in good agreement with the reported data for DBA:ACP [1].

Figure 10. Master curves of DBA:R:DBA.

4. Conclusion

A comparative crystallization kinetics study has been performed on two distinct isomers involving hydrogen bonding with *p-n*-decyloxybenzoic acid (DBA) as a common mesogenic moiety. The results confirm the existence of different trends of crystallization behaviour. This clearly suggests a negligible influence of the liquid crystalline DBA moiety on the overall nucleation process. The compounds exhibit a slow rate of kinetics at their final crystallization temperatures. A gradual growth in the melting transition is observed at each crystallization temperature for both compounds. The value of the dimensionality parameter n varies at each crystallization temperature, and these values follow a decreasing trend with increasing temperature. This degree of variation in n suggests an independent nucleation mechanism. This crystallization behaviour may be attributed to sporadic nucleation growth, following an inhomogeneous process of continuous nucleation over a constant time. However,

Figure 11. Master curves of DBA:H:DBA.

the low values of *n* clearly indicate the occurrence of diffusion-controlled transformations in these mesogenic systems, in which nucleation starts as an initial growth of particles in the form of plates or needles of finite size possessing impinged edges.

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