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Eutectic mixtures with plastic columnar discotics: molecular structure, phase morphology and kinetics of phase separation

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We report the properties of eutectic mixtures of triphenylenes displaying a highly ordered columnar phase with a low molar mass non-discotic compound. Such highly ordered triphenylenes display large charge carrier mobilities which are strongly controlled by the state of order in the discotic phase. The motivation was to establish how the state of order—molecular order, phase morphology, temperature ranges of phase stabilities and macroscopic orientational order—can be influenced by mixing. The studies reveal that the molecular order, in particular the mutual arrangement of the columns and the intracolumnar order, are unaffected by dilution of the discotic compound, whereas the phase morphology and the kinetics of phase separation change significantly with dilution. Rod-shaped discotic domains with a hexagonal cross-sectional area are formed via a nucleation process and the rods grow linearly as a function of time. Both the pure discotic phase as well as the discotic domains forming during phase separation can be macroscopically ordered by orientation layers.

1. Introduction

Columnar discotic liquid crystals display a set of unique optical and electric properties, discotic triphenylenes providing well known examples. The one-dimensional mobility of charge carriers along the columnar direction is unusually large [1–3]. Such properties are of potential interest for applications in areas such as photoconductivity, organic light emitting diodes, field effect transistors or solar cells [4–8]. The transport of charge carriers is known to occur in such systems via hopping between localized electronic states located at the individual disc-like molecules. The assumption is that the energy of such states is subjected to a distribution which can be modelled in terms of a Gaussian distribution with a width σ [9–15]. Using analytical calculations and Monte Carlo simulation it was shown that a direct correlation exists between the model parameter σ/kT and the mobility: the smaller σ the larger the mobility. Based on quantum mechanical calculations using the density functional approach (DFT) it was predicted that electronic properties controlling the mobility such as, for example, the site energies, and the electronic overlap between neighbouring molecules, depend very strongly on internal structural features such as the intracolumnar distance, molecular twist or longitudinal fluctuations, i.e on the degree of spatial order [16].

Thus it is important to have means to allow such structural features to be controlled over a broad range. In fact, we have shown that the introduction of dipoles, which enhances fluctuations of the electric potential at constant spatial structure, or the introduction of specific lateral substituents in asymmetrically substituted triphenylenes, give rise to strong variations of the mobility and its temperature and field dependence [3, 11]. A further approach investigated by ourselves consisted of applying a hydrostatic pressure to the discotic system. The findings were that the pressure induces, of course, a reduction in molecular distance but at the same time causes structural transitions towards a more disordered state and a decrease in the spatial correlation length [17, 18]. The effect of pressure on electronic properties proved to be rather small, as evident from a shift of the absorption edge by only 0.06 eV for a pressure of 10 kbar.

Further theoretical predictions were that confinement effects causing a restriction in the longitudinal length of the columnar aggregates would favourably affect the mobility [13, 14]. Experimental studies were performed on discotics dispersed in glassy polymers [19]. It was observed that a phase separation took place leading to tiny rod-like particles dispersed in the glassy polymer matrix. The absolute sizes were found to depend in this case on the composition of the starting ternary solutions and the thermal history. In all cases the opto-electronic properties were found to depend on the state of dispersion.

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The disadvantage of these heterogeneous systems, in which structure formation starts from a polymer solution containing a given amount of triphenylene, is that the formation of the phase separated regions is accompanied by evaporation of the solvents and the onset of the glass transition of the polymer. This makes both the control of the structure formation process as well as its detailed analysis highly complex. In this paper we investigate a different approach, the mixing of chemically different compounds. Mixing liquid crystalline phases is known to give rise to a broad range of structural variations such as the induction of novel phases or the stabilization of a given phase [20–24]. We consider here mixtures of columnar discotic systems, in particular systems exhibiting the highly ordered plastic columnar phase, with a low molar mass non-discotic compound. In principle it should be much easier in such systems to understand and to control the formation of discotic regions dispersed in a non-discotic environment. We used two discotic model systems, one able to crystallize and one able to form an ordered glass at lower temperatures. We wished to know (i) whether the intracolumnar packing is disturbed in such mixtures, (ii) if the shapes of the phase separated regions are spherical as in phase separating isotropic fluids or reflect the columnar order, and (iii) whether we could impose a macroscopic orientation onto the phase morphology via substrate effects.

2. Experimental

2.1. *Model compounds*

3,6,7,10,11-Pentabutoxytriphenylene-2-yl-(1-adamantenoylmethanoate) (AdaPBT) and 2,3,6,7,10,11-hexabutoxytriphenylene (HBT) were chosen as discotic model compounds, both displaying the more highly ordered plastic columnar phase. The chemical structures of the two compounds are shown in figure 1. AdaPBT becomes glassy and HBT crystalline at room temperatures. The phase sequences are:

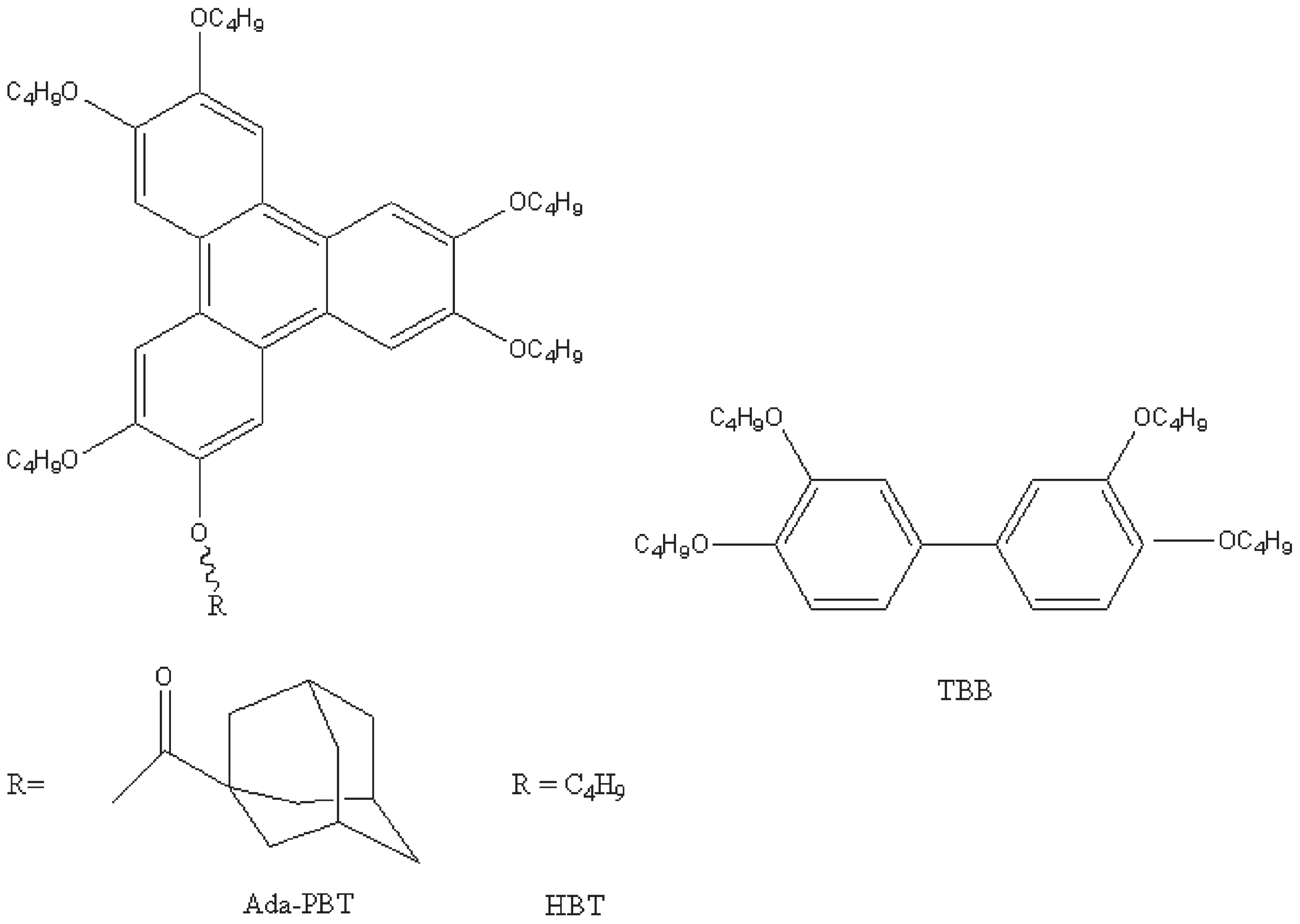

Figure 1. Chemical structure of the compounds used in the mixtures.

$$\text{Ada} - \text{PBT} : \text{I} \overset{187^\circ\text{C}}{\longleftrightarrow} \text{Col}_{\text{ho}} \overset{168^\circ\text{C}}{\longleftrightarrow} \text{Col}_{\text{hp}} \overset{80^\circ\text{C}}{\longleftrightarrow} \text{g}$$

$$\text{HBT} : \text{I} \overset{146^\circ\text{C}}{\longleftrightarrow} \text{Col}_{\text{hp}} \overset{90^\circ\text{C}}{\longleftrightarrow} \text{Cr}$$

The second non-discotic compound used for these studies was TBB which transforms from the isotropic to the crystalline phase at 93°C.

2.2. *Analysis of phase diagrams and phase morphology*

The phase diagrams were determined (i) by differential scanning calorimetry, employing a DSC821 (Mettler-Toledo), with heating and cooling rates of $10\,\text{K}\,\text{min}^{-1}$, and (ii) by polarizing microscopy using a Leitz Laborlux 12 Pol S equipped with a Mettler FP 82 hot stage. The kinetics of phase separation were analysed using the same microscopy.

2.3. *Structure analysis*

Wide angle X-ray scattering using a Siemens D 5000 wide angle goniometer equipped with a heating cell was used to analyse the effect of mixing on both the intracolumnar and intercolumnar order.

3. Experimental results and discussion

3.1. *Mixtures AdaPBT/TBB*

We will discuss first the results obtained for the model mixtures AdaPBT/TBB. The phase diagram as obtained from DSC as well as from polarizing microscopy is shown in figure 2. The temperature of the transition from the columnar discotic phase to the isotropic phase decreases continuously as the concentration of the non-discotic compound TBB is increased in the mixtures. The hexagonal columnar phase is stable only in a limited range of concentrations of TBB, and a plastic columnar phase is the only stable phase for higher TBB concentrations. Finally the formation of the plastic columnar state becomes strongly inhibited as its glass transition is approached. The melting temperature of the crystalline component TBB, on the other hand, is reduced with increasing concentration of component AdaPBT for small concentrations and stays constant for higher concentrations. The crystallization temperature is also essentially constant at all concentrations of AdaPBT with the exception of the smaller values and is located about 20 K below the melting temperature.

The phase diagram is clearly characteristic of eutectic behavior: the two components are miscible within the isotropic phase and become immiscible within the discotic phases on one side and in the crystalline phase on the other side of the diagram. It is not surprising that the crystalline phase of component TBB does not tolerate the component AdaPBT to an appreciable extent, since the molecular shapes and thus the intermolecular interactions are different and since crystalline states tend to be very specific. On the other hand, one might have assumed that the fluid and much less ordered discotic columnar state of component AdaPBT might tolerate the component TBB to a certain extent. Examples are known in the literature for limited miscibility even of purely rod-like molecules with discotic ones. This clearly is not the case in the mixtures considered here, even for lower concentrations, as apparent from the DSC analysis and the X-ray investigations to be discussed in more detail later.

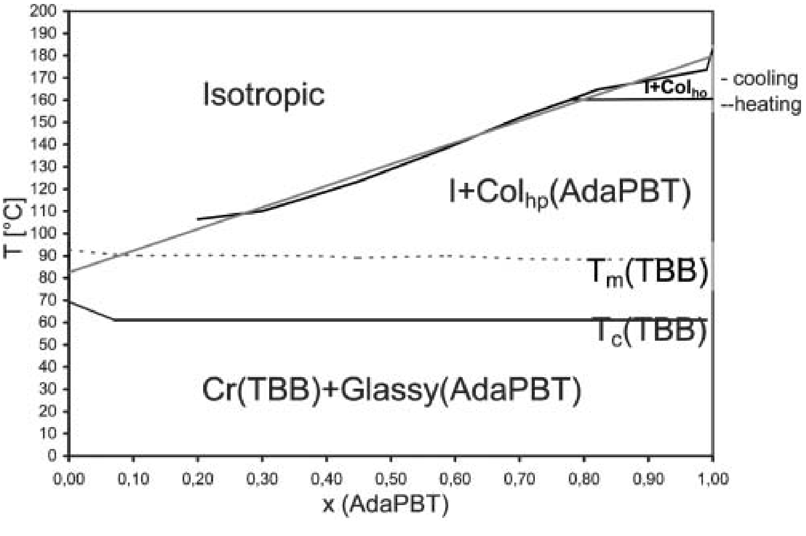

Figure 2. Phase diagram of the mixtures of AdaPBT and TBB. T_m=melting temperature, T_c=crystallization temperature.

The DSC analysis gives information not only on the location of the transition for the crystalline or discotic columnar phase to the isotropic melt, but also on the transition enthalpies and thus the transition entropies. The analysis shows that the transition enthalpies are subject to considerable fluctuations yet seem to be constant if reduced to the actual amount of the compound present in the mixtures. Thus either the phase separation yields the pure discotic phase and crystalline phase of TBB, or the concentration of the second components within the discotic or crystalline state are in any case negligibly small. Similar conclusions may be drawn from the results of X-ray scattering investigations.

3.2. *X-ray results*

Wide angle X-ray scattering was performed on the pure components and on the mixtures, choosing the concentration of the components as a parameter. The pure discotic component displays, within the hexagonal and plastic discotic columnar state at smaller scattering angles, a set of X-ray reflections arising from the two-dimensional hexagonal packing of the discs. The plastic columnar state is characterized by a doublet reflection superimposed on an amorphous halo, and the hexagonal columnar phase by one asymmetric peak at this position, both arising from the intracolumnar packing of the disc-shaped molecules [25, 26]. Figure 3 shows that all the mixtures display at lower temperatures similar X-ray patterns which resemble closely that of the pure component AdaPBT. The location of the peaks are not subject to shifts and the relative intensities of the peaks remain about constant. The structure is thus not disturbed, for example, by the incorporation of the crystalline TBB component. This interpretation is in agreement with that based on the DSC data discussed already. Previous studies have revealed that the plastic columnar phase is highly sensitive to the incorporation of foreign molecules such as, for example, electron acceptors [27]. One apparent feature is that the peak width increases slightly with increasing concentration of the crystalline component TBB, i.e. with increasing concentration of the solvent. Ordered columnar regions with a reduced spatial correlation length obviously form at higher dilution within the solutions.

3.3. *Phase morphologies*

To learn more about eutectic behaviour, and in particular about the phase morphology arising from a superposition of phase separation and discotic structure formation, we have performed cooling and heating experiments using the polarizing microscope. For the pure component AdaPBT we observe a transition from the dark field characteristic of the isotropic phase to a birefringent texture, as shown in figure 4 (*a*), at a given temperature (see phase diagram in figure 2). Such a dendritic texture is characteristic of the columnar state and has been modelled, for example, on the basis of the aggregation model of Witten and Sander [28, 29]. The crystallization of the pure TBB, on the other hand leads to the texture shown in figure 4 (*b*).

In the mixtures containing low TBB concentrations the field of observation displays increasing anisotropic regions with an approximately circular shape located within an isotropic environment as the temperature is decreased. At the eutectic temperature the remaining isotropic melt is transformed over a narrow temperature range, clearly due predominantly to the crystallization of the crystalline compound TBB. All these observations are in agreement with a eutectic type of phase

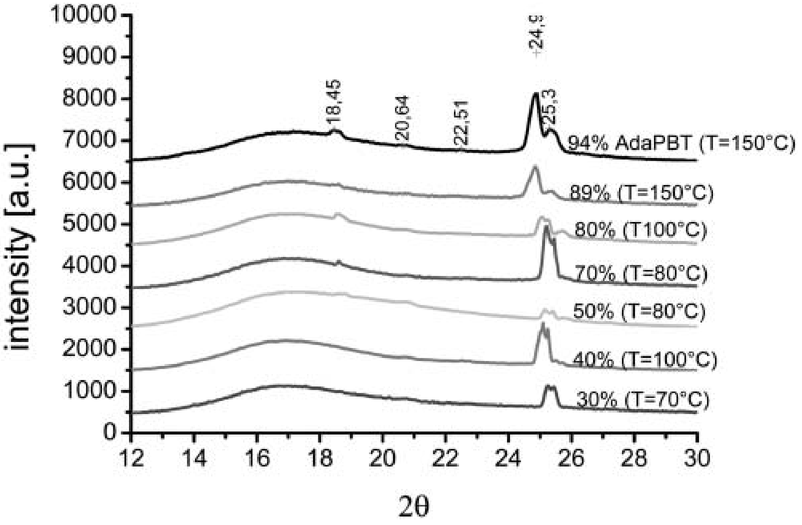

Figure 3. X-ray profiles of mixtures of AdaPBT and TBB.

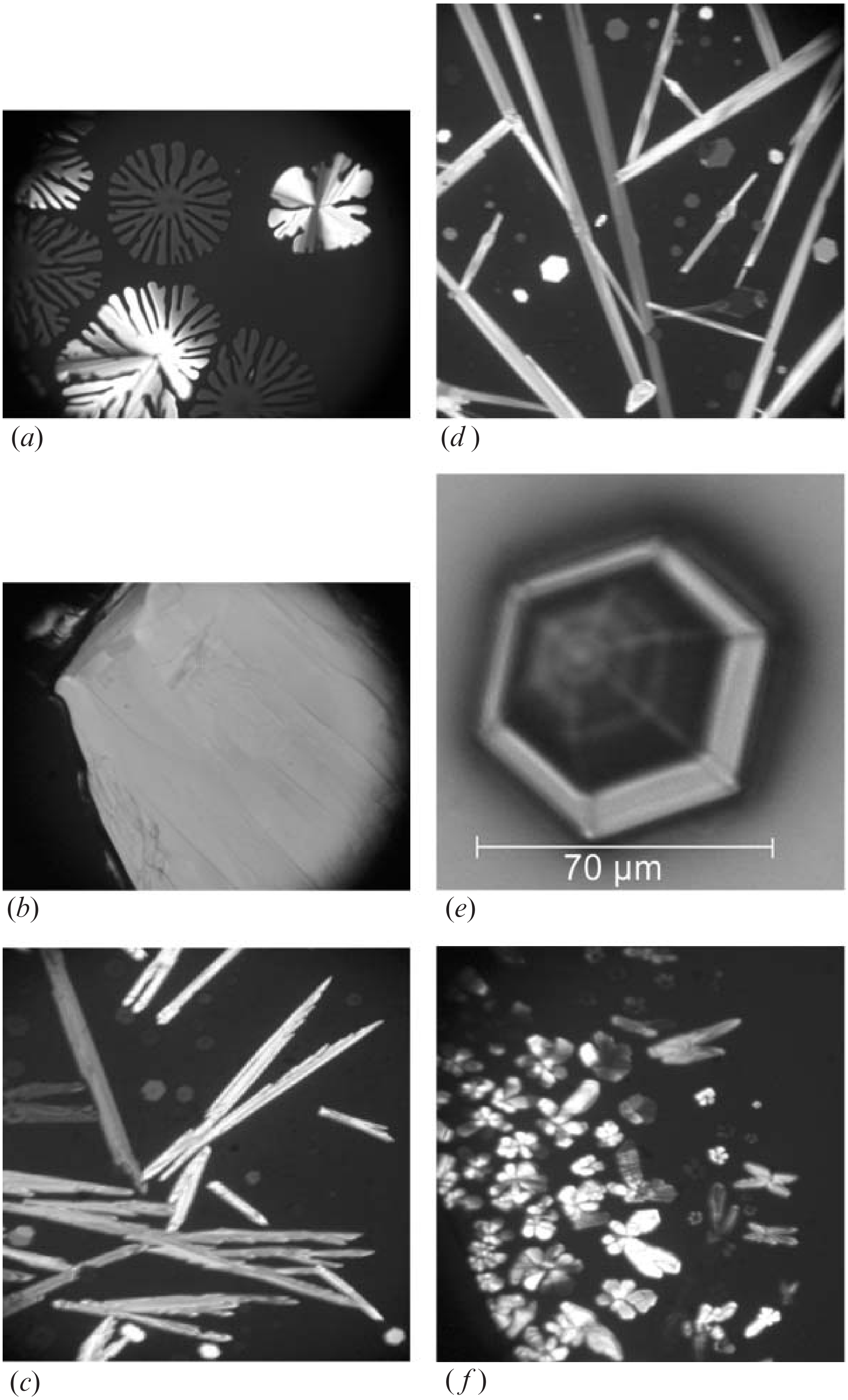

Figure 4. Phase morphologies for the pure compounds and various mixtures: (*a*) AdaPBT at 187°, (*b*) TBB at 90°C, (*c*) AdaPBT/TBB ratio 60:40 at 129°C, (*d*) AdaPBT/TBB ratio 42:58, (*e*) AdaPBT/TBB ratio 50:50, (*f*) AdaPBT/TBB ratio 71:29 at 146°C.

diagram with a eutectic temperature of 90°C and eutectic concentration of approximately 5% AdaPBT.

The character of the phase morphology, however, is not constant in the mixtures but depends on its composition. The surprising feature is the growth of a birefringent rod-like phase morphology within the still fluid and isotropic matrix for AdaPBT mixtures containing rather high TBB concentrations. Figures 4 (*c*) and 4 (*d*) reveal such rod-shaped domains as observed with the polarizing microscope. The cross-sectional area of the rod-shaped dispersed phase is not circular but rather assumes a hexagonal shape, as clear in figure 4 (*e*). It is well known from the literature that energy minimization processes taking place in ordered yet mobile systems may give rise to shapes differing from spherical or circular ones. The hexagonal cross-section clearly reflects the 2-d hexagonal packing of the columns. This suggests that the columns may be oriented parallel to the disc-normal. In fact we have previously found that a dewetting process of triphenylene systems taking place for thin films on solid substrates tends to give rise to pits of hexagonal cross sectional area [30].

Such rod-like dispersed regions have also been observed for triphenylene systems in blends with polymers and, as discussed already, were of considerable interest for optoelectronic applications [19]. Thus it seemed interesting to learn more about the underlying growth process. For this purpose we have studied the growth of the rod-shaped regions both for a given temperature, i.e. for a given supercooling as a function of time, and for different values of supercooling. The results are shown in figure 5 (*a*). The findings are that the rods start as very short entities and grow linearly as a function of time at approximately constant diameter. The diameter of the rods was of the order of 50 μm, a typical growth rate was of the order of 0.2 μm s^{-1} amounting to a deposition rate of one discotic molecule per ms, and the total length of the rods approached values of more than 1 mm. A further observation was that the number of rods that grow was constant. Finally experiments revealed that the growth rate increased as the supercooling increased, figure 5 (*b*).

All these features may be explained to a first approximation in terms of a simple nucleation model as applied to condensation processes, phase separation in blends, or polymer crystallization to mention just a few examples [31]. The basic idea is that the formation of the higher ordered phase takes place via small nuclei which originate from statistical fluctuations and which can grow if this leads to a reduction of the total free enthalpy. Unfavourable free enthalpy terms arise from the surface of such nuclei and it is for this reason that the nuclei can grow only if their dimensions become larger than certain critical values. These may be calculated from the nucleation theory and depend, for example, on the absolute values of the surface free energy for the different surfaces of the nuclei.

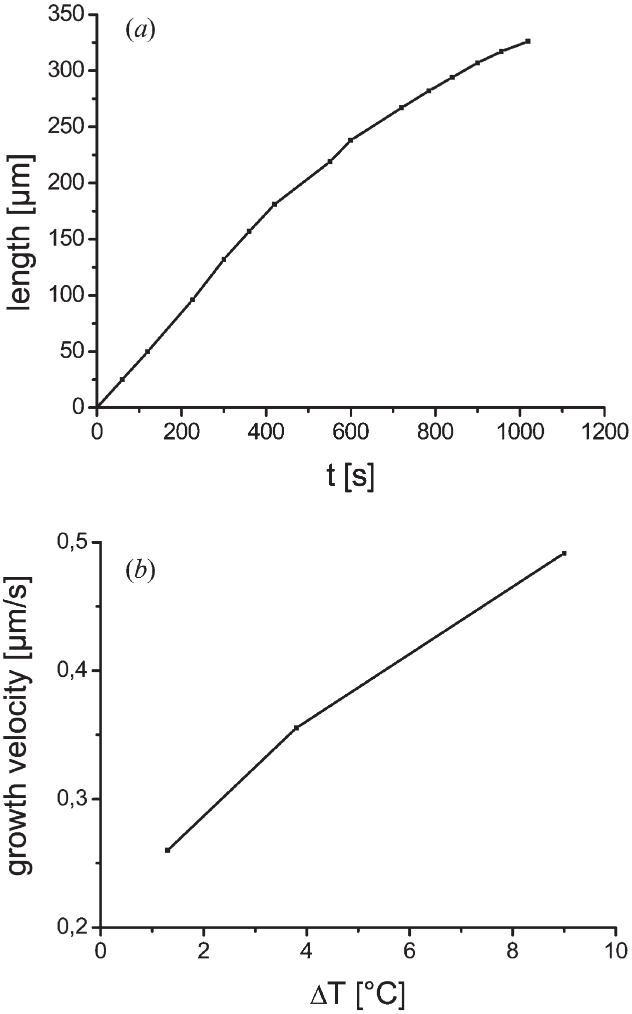

Figure 5. (*a*) Linear growth of rods for mixtures at $T=132.2°C$ and an AdaPBT/TBB ratio of 50:50. (*b*) Linear growth of rods as a function of undercooling.

It has been reported in the literature that columnar discotics have a tendency to exhibit columnar stackings within the isotropic state either in the melt or in solution. These stacks are, of course, subject to statistical fluctuations and are not thermodynamically stable. They become so, however, at lower temperatures, below the isotropic columnar transition temperature, and may serve in this case as disc-shaped nuclei for lateral and longitudinal growth. Therefore we tentatively assume for the case considered here a disc-shaped nucleus with a hexagonal cross sectional area of thickness L. To facilitate the calculations we approximate the shape of the nucleus to a

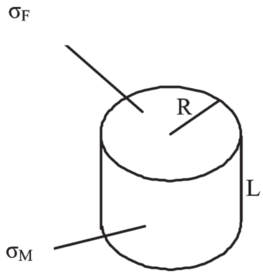

Figure 6. Model for nucleation of phase separated regions in discotic mixtures.

circular one (figure 6) with a radius R (average radius for the hexagonal cross sectional area). The analysis yields critical dimensions which depend inversely on the supercooling:

$$R^* = (2\sigma_M T_m/\Delta H)/\Delta T$$

$$L^* = (2\sigma_F T_m/\Delta H)/\Delta T$$

The disc-shaped nucleus may grow in the radial as well as in the longitudinal direction. Now, in the case of polymer lamellae it is well known that the thickness stays constant (as controlled by the critical dimension L^*) and radial growth takes place. It seems to a first approximation that in our case the situation might be that the radius is constant, as controlled by the critical value R^*, while the length grows giving rise to the formation of rods.

If the growth is nucleation-controlled, the length will increase linearly with time; it will depend on the square root of time if it is diffusion controlled. Thus on the basis of our observation of a linear growth in time we have to conclude that the growth of the rods is nucleation controlled, i.e. a constant additional length element is added for a given time element by the formation of a new nucleation layer on top of the growing front. The constant radius is, in terms of the nucleation model and typical interfacial energies of organic materials, unusually large. Our intepretation is that actually a liquid crystal transition cannot be supercooled to a significant degree as far as nucleation is concerned.

Now, as the concentration of the compound TBB is reduced in the blends, we observe a continuous modification of the phase morphology as shown in figures 4 (*c*) and 4 (*f*). The surface of the rods becomes rough as the TBB concentration is reduced, and branching occurs although with low probability with decreasing TBB concentration, until finally at still lower TBB concentrations branching controls the phase separation process, figure 4 (*a*). To interpret these findings it is important to point out that a nucleated growth may give rise to smooth growth fronts as described so far, or to fractal ones depending on details of the growth mechanism. Branching will take place during the longitudinal growth of the rods if secondary nuclei grow along the cylinder walls and this seems to be the situation for intermediate TBB concentrations. The phase separated domains approach a circular shape yet this shape seems to be characterized by undulations. In any case the phase separation process is still controlled by the presence of the 2-d hexagonal lattice defined by the packing of the columns.

3.4. *Mixtures HBT/TBB*

These mixtures differ from those discussed in the previous section in that the discotic phase of HBT is transformed into a crystalline phase rather than to a glassy state at lower temperatures. The studies to be

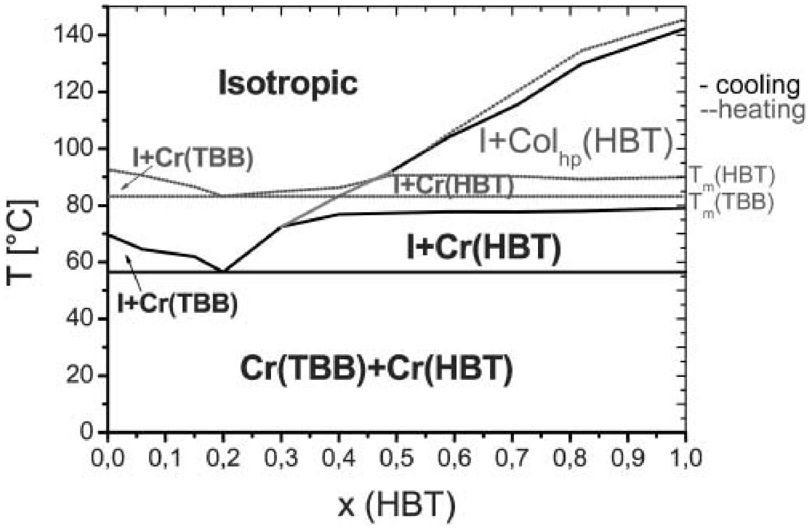

Figure 7. Phase diagram of mixtures of HBT and TBB. T_m=melting temperature.

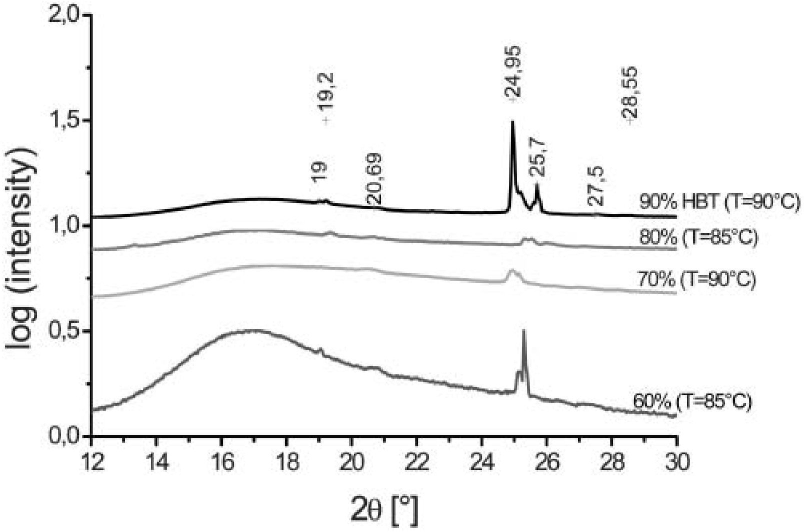

Figure 8. X-ray patterns of mixtures of HBT and TBB.

discussed revealed that most of the features relating to the phase diagram, structure formation and phase morphology are similar to those described already for the mixtures of AdaPBT and TBB. It is for this reason that the discussions will be rather brief.

The phase diagram is shown in figure 7. Eutectic behaviour is observed, indicating a complete miscibility of the two components in the isotropic phase and immiscibility in the ordered phases. The transition temperature of the discotic phase into the isotropic phase is decreased continuously with increasing TBB concentration. The transition temperature between the crystalline and the discotic phase does not vary with composition. This is not surprising since the discotic phase separated regions are composed of the pure component (as apparent from DSC studies and X-ray studies to be discussed later) and thus crystallize or melt, respectively, at identical temperatures for all mixtures. The TBB melting and crystallization temperatures are reduced with increasing HBT concentration until finally crystallization is suppressed.

The X-ray diagrams shown in figure 8 reveal that the plastic columnar phase is exhibited even at very high concentrations of TBB in the mixtures, as the characteristic wide angle X-ray doublet reflection is present in all mixtures at elevated temperatures. The position of the doublet does not depend on composition, i.e. the intracolumnar order is not disturbed.

The blends of HBT with TBB also display a rod-shaped phase morphology for higher concentrations of TBB. The cross-sectional area is hexagonal and the growth process and growth kinetics are similar to those reported previously: spectrally, nucleation of rods, linear growth of the rods, and increasing growth rates

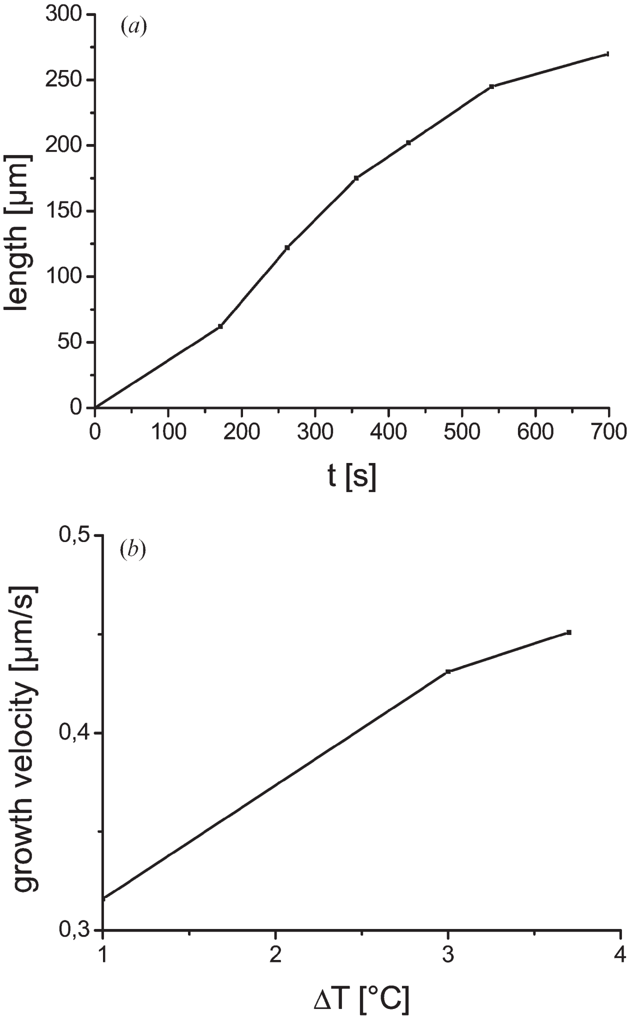

Figure 9. (*a*) Linear growth of rods for mixtures at $T=104°C$ and an HBT/TBB ratio of 60:40. (*b*) Linear growth of rods as a function of undercooling.

with increasing supercooling, see figure 9. Finally branching begins to dominate the phase separation process as the TBB concentration is reduced. These findings show that features of the phase separation processes described are quite general.

3.5. *Macroscopic orientation of the rod-shaped domains*

The phase separation process described already in some detail was clearly controlled by the presence of the 2-d hexagonal columnar packing in the emerging discotic phase. Since liquid crystalline structures have a tendency to become oriented on a macroscopic level if in contact with an orientation layer we investigated the effect of such a layer on the phase morphology. As an orientation layer we used a thin highly oriented PTFE film which was previously coated onto a glass substrate. Figure 10 (*a*) reveals the effect of such a layer on the texture of the pure discotic compound, and figure 10 (*b*) shows the formation of rod-shaped discotic domains. The fractal growth of the discotic structure of the pure component is strongly affected by the orientation

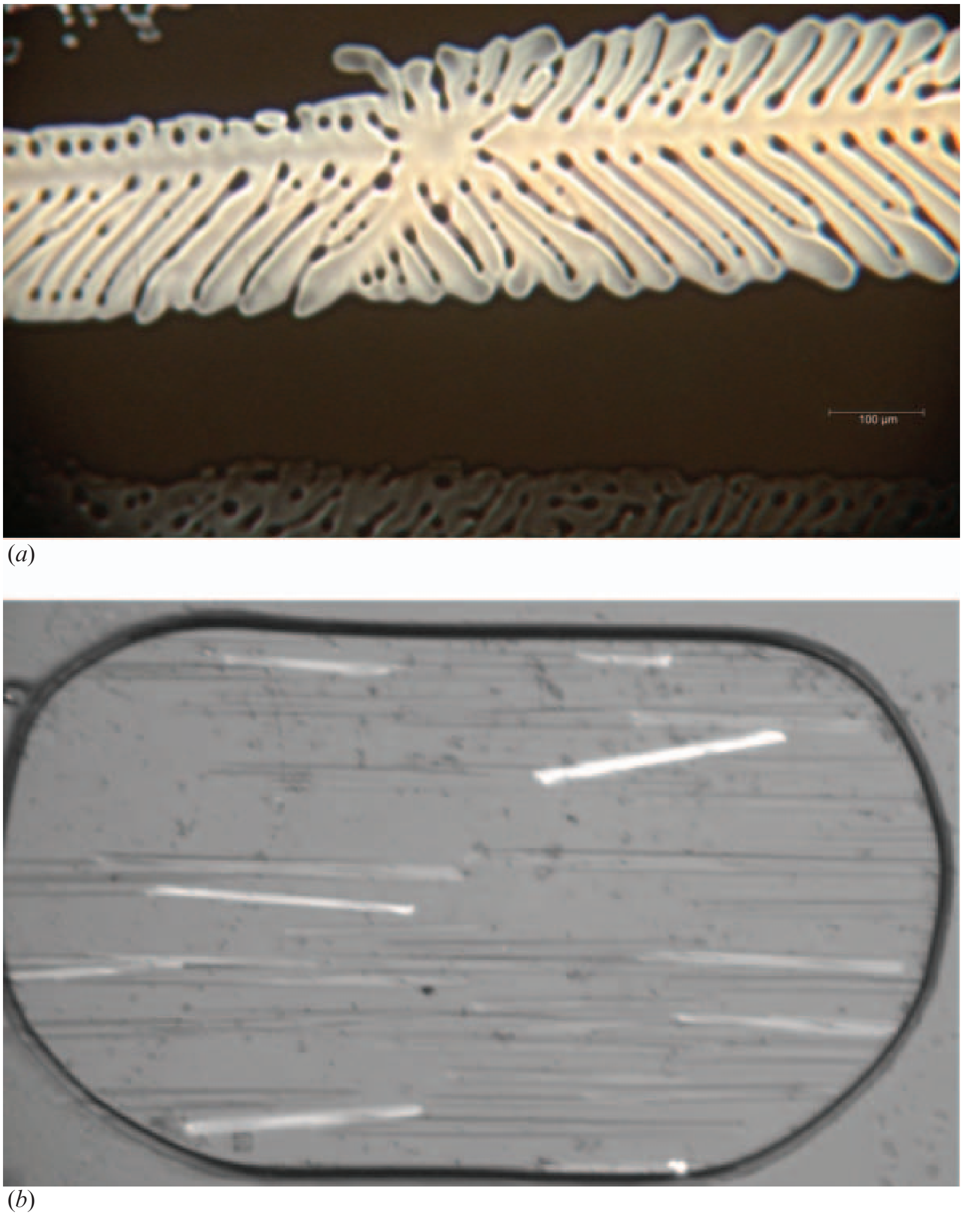

Figure 10. (*a*) Texture formation of HBT grown on a PTFE orientation layer. (*b*) Orientation of rods induced by phase separation of blends of AdaPBT/TBB on a PTFE orientation layer.

layer, and the rod-shaped domains are oriented along the rubbing direction. Thus, the effect of an orientation layer on the discotic mixtures discussed here is surprisingly strong. We used dichroic absorption investigations to learn more about the internal structure of the oriented rods. The results are shown in figure 11.

The absorption values parallel and perpendicular to the rubbing direction are different. Taking into account the fact that the transition dipole moment is oriented within the plane of the disc-shaped triphenylene, we are able to calculate an overall orientation parameter S as:

$$S = \frac{E_{\parallel} - E_{\perp}}{E_{\parallel} + 2E_{\perp}} \cdot \left(1 - {}^{3}\!/_{2} \sin^2 \Theta\right)^{-1}$$

giving a value of 0.6. It is controlled both by the internal orientational order within the domains and the orientational distribution of the domains.

4. Conclusions

Mixing columnar discotics with a low molar mass non-discotic compound gives rise to rod-shaped phase

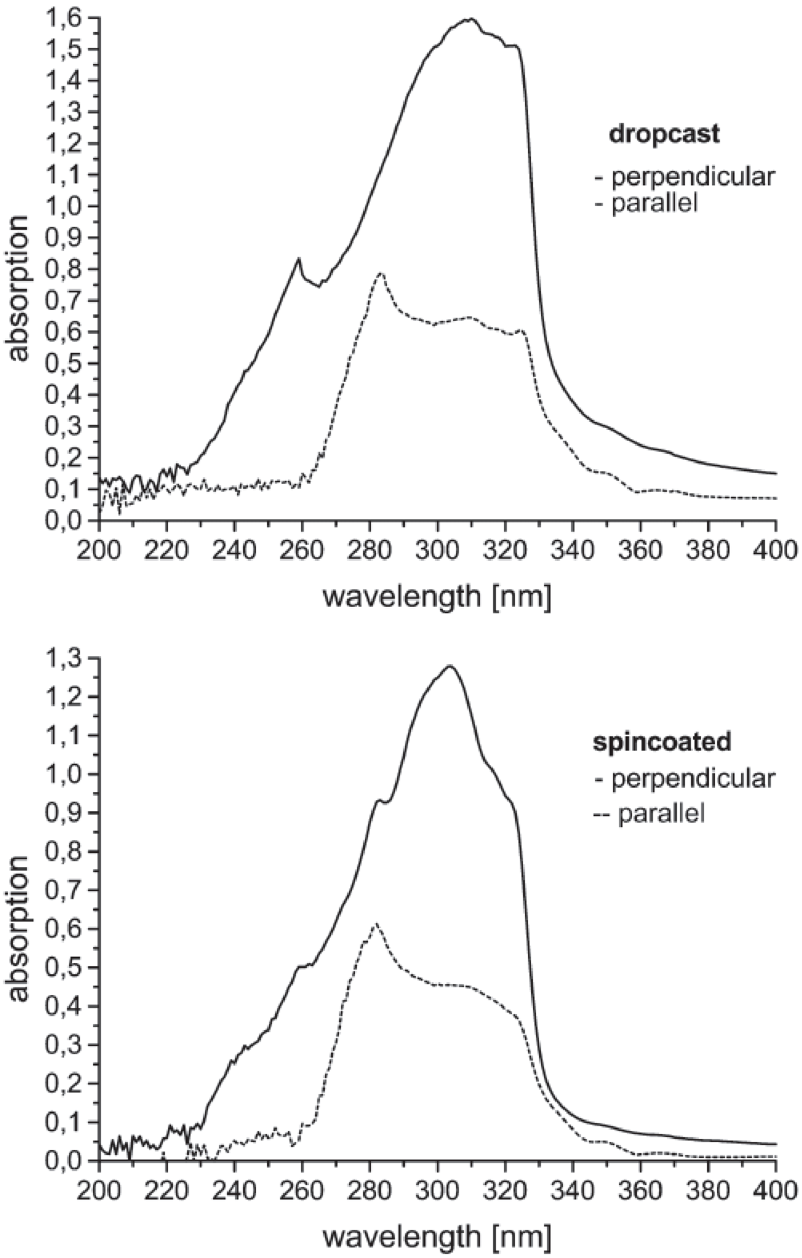

Figure 11. Absorption studies on blends oriented using a PTFE layer.

separated discotic domains having a hexagonal cross-sectional area. The columns are oriented predominantly along the rod-axis. Such areas may be of considerable interest for opto-electronic applications. Because an oriented layer can be used to orient all these areas along a given direction. The removal of the surrounding matrix poses no problem. It can be removed at a temperature where it melts leaving the rods intact.

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