Structure formation in doped discotic polymers and low molar mass model systems

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Structure formation in doped discotic polymers and low molar mass model systems

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Doping of low molar mass materials or polymers, possessing disc-like units, with electron acceptors leads to the stabilization of columnar discotic phases or even to the induction of such phases in compounds which either display a nematic discotic phase or only an amorphous phase in the absence of the electron acceptor. The induced columnar phase corresponds frequently to a hexagonally ordered one. We have observed, however, in addition the induction of new columnar phases such as the rectangularly ordered (D_{ro}) and the columnar nematic phase (N_c). The enhancement of the tendency towards the formation of columnar phases is a consequence of electron acceptor–electron donor complex formation. Using a model proposed by de Jeu to describe the induction of smectic phases by complex formation we are able to account qualitatively for the experimental findings.

1. Introduction

The macroscopic properties of matter are controlled to a great extent by their state of order. The presence or absence of a centre of symmetry, for instance, has a direct counterpart in the absence or presence of ferroelectricity or second harmonic generation of light [1, 2]; the presence of long range translational order as well as the dimension of the long range order $(d = 1, 2, 3)$ have a direct impact on the electric or thermal properties [1, 3]. It is for this reason that we want to be able to induce characteristic structures with well-defined translational symmetry and point symmetry in matter at will. The finding has been in the past that we can achieve this particularly well in low molar mass systems and also in polymer systems both in the fluid state or the glassy state by constructing the molecules in such a way that they display liquid-crystalline phases [4–7].

Experience has shown that one important parameter controlling structure formation is the shape of the molecule or molecular groups. Anisotropic attractive interactions increase the tendency towards liquid-crystalline phase formation, the interaction strength determines the thermodynamic stability of the various liquid-crystalline phases with respect to each other and in particular with respect to the isotropic melt. Today we know a large number of phases which are primarily controlled by shape, such as calamitic phases (rod-like shape), discotic phases (disc-like shape) [8] or sanidic phases (board-like shape) [9]. More recently it has become apparent that

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new opportunities arise as far as structure formation is concerned if associated liquid crystals are considered [10–13]. These systems are characterized by the fact that site–site interactions occur, such as for instance hydrogen bonding or strong dipole–dipole interactions, which lead to associations at a molecular level. These associations enhance the tendency towards structure formation or they compete with the tendency of uncomplexed molecules towards structure formation. An example of the first case is the discotic columnar phase formed by non disc-like diols [12] and an example of the second case is the smectic antiphase or the reentrant phase formed by compounds carrying strong longitudinal dipoles [13].

This paper is concerned with discotic associated liquid crystals where the association is controlled by charge transfer interactions. Such interactions are induced by adding electron acceptors of various chemical structures and various strengths to low molar mass or polymer compounds containing flat disc-like units, which act as electron donors. The electron acceptors considered here are flat but they are not able to display discotic phases, at least in the accessible temperature range. The usual observation when adding a non-liquid-crystalline compound to a liquid-crystalline compound is that the liquid-crystalline phase is strongly destabilized and vanishes finally as the concentration of the non-liquid-crystalline additive is further increased [5]. We have shown in previous publications that doping leads to a totally different behaviour in low molar mass and polymeric compounds containing planar disc-like units with electron acceptors. It gives rise to the following effects [14–16]:

stabilization of existing columnar phases;
induction of columnar phases in systems showing nematic discotic phases;
induction of columnar phases in amorphous polymers; where the induced phases
    may be spatially ordered (discotic columnar) or disordered (columnar nematic).

The origin of such effects is evidently the formation of charge transfer complexes, as apparent from the strong colour changes accompanying the mixing. The colour changes are identical in the isotropic melt and in the induced or stabilized discotic phases so that we have to conclude that complexes exist also at elevated temperatures well within the isotropic melt. This paper is concerned with an analysis of the thermodynamic and structural features of such doped systems and with a theoretical analysis of these properties on the basis of models taking complex formation into account [17].

2. Experimental

The disc-like compounds were mixed in solution (THF) with the low molecular weight non-mesogenic electron acceptor 2,4,7-trinitrofluorenone (TNF). The concentration of TNF was varied up to 54 mol%. For higher acceptor concentrations no homogeneous mixtures were obtained after evaporation of the solvent.

The samples were analysed thermally by polarizing microscopy using a Leitz polarizing microscope equipped with a Mettler hot stage FP 82 and by DSC investigations employing a Perkin Elmer DSC 4 (heating rate $20 \, K \, min^{-1}$). For the X-ray structural analysis we used a Kratky small angle compact camera, a flat film camera for oriented samples and a wide angle X-ray goniometer (Siemens D 500) for unoriented samples. The linewidth of selected reflections obtained for unoriented samples was analysed, after corrections for the intrinsic broadening due to the experimental set up, with respect to the correlation length using the Scherrer equation. Macroscopically aligned polymer samples were obtained by a procedure described

elsewhere in more detail [9, 16]. It consists of the induction of a unidirectional flow in the viscoelastic state as controlled by a planar pressure along direction 3 on a sample which was allowed to flow only in direction 1 due to a wall confinement along the direction 2 (see figure 1). Previous investigations revealed that this deformation tends to align discotic columns along direction 3 and the remaining crystallographic axes along directions 1 and 2 for main chain polymers.

3. Experimental results

3.1. *Stabilization of a hexagonal ordered columnar phase*

Figure 2 displays the dependence of the transition temperature of the hexagonally ordered phase of the low molar mass discotic compound H5T (see figure 3 (*a*)) as a function of the concentration of the electron acceptor TNF (see figure 3 (*b*)). It is apparent that the transition temperature displays a maximum at about 50 mol% of the two components; the transition temperature is increased by as much as 140 K. An interesting finding to be discussed in more detail later is that the transition enthalpy decreases, in a non-discontinuous fashion, with increasing concentration of the acceptor (see figure 4), the transition entropy varies approximately in a similar fashion.

Figure 5 reveals that both the intracolumnar distance and the intercolumnar distance decrease with increasing acceptor concentration, at least up to about 50 mol%. This happens at an approximately constant density of about $1 \cdot 0 \, g \, cm^{-3}$. This together with the observation of colour changes has to be taken as an indication that mixed stacks are formed, in agreement with X-ray results [16, 18]. Table 1 compares the experimentally obtained density with the calculated values, based either on the assumption of mixed stacks or on the assumption that the acceptor is incorporated between the stacks at some unspecified location. The comparison between experimental results and the predictions of the two models shows without any doubt that the electron acceptors are incorporated in the stacks, i.e. the columns.

An interesting piece of information comes from an analysis of the width of the X-ray reflections for doped and undoped systems: real crystals and real translationally
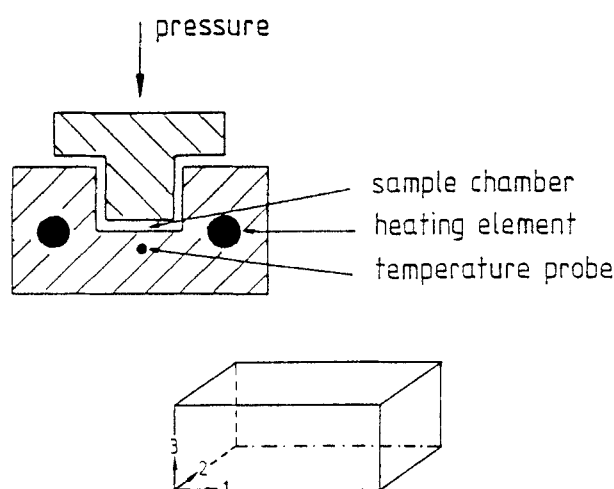

Figure 1. Experimental technique used to obtain monodomain textures in columnar discotic systems. 3, direction of pressure; 2, direction of wall confinement; 1, direction of flow.
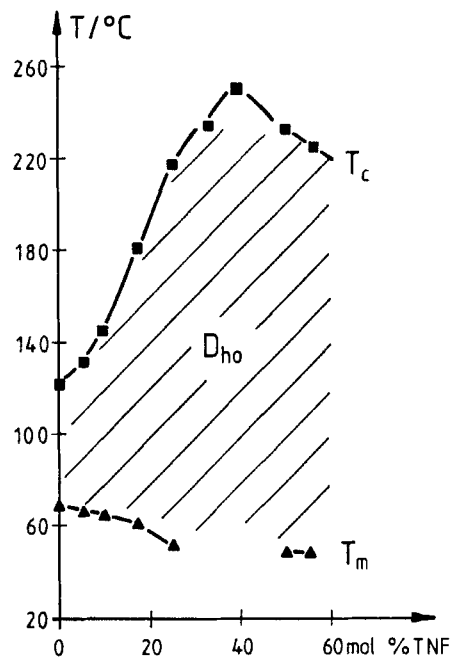
Figure 2. Phase diagram for mixtures of H5T and TNF.

R = C₅H₁₁

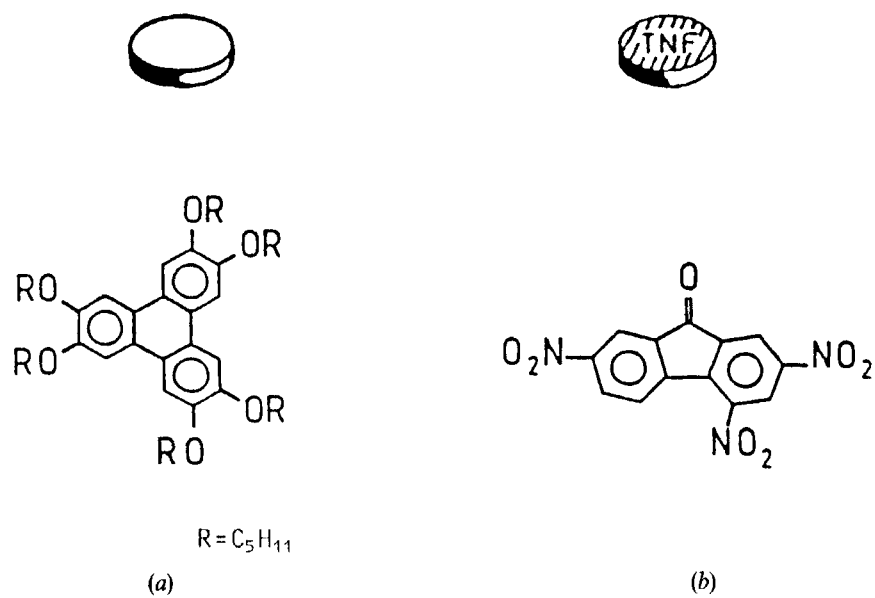(a)   (b)

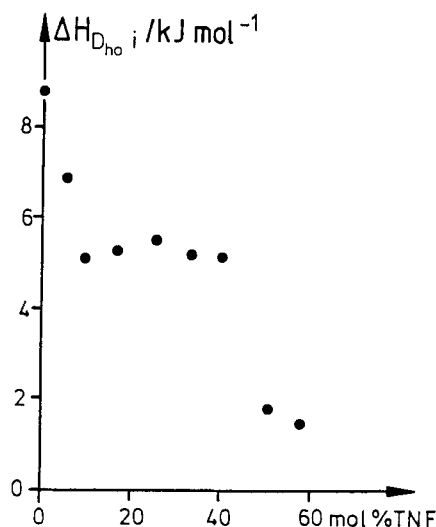Figure 3. Chemical structure of the compounds H5T (a) and TNF (b).

Figure 4. Variation of the transition enthalpy in mixtures of H5T and TNF with the TNF concentration.

ordered liquid crystals are characterized by the presence of imperfections such as a limited crystal size or various kinds of defects [4, 19, 20, 22] and these imperfections give rise to a broadening of the X-ray reflections. Using the Scherrer equation [19]

$$L = 0.9\lambda / W_{1/2} \cos \theta$$

it is possible to derive information on an effective correlation length L along a specific direction and on their temperature dependence. Figures 6(a) and (b) show the results obtained from the intercolumnar reflections and the intracolumnar reflections as a function of the concentration of the dopant for two different temperatures. Displayed is the correlation length within the columns and perpendicular to the columns and thus also the number N of correlated structural units.

It is apparent first of all that the intercolumnar correlation length is considerably increased by doping whereas the intracolumnar effect is only weak. A temperature increase results in a decrease of both the intracolumnar and the intercolumnar correlation length (see figure 6(a) and (b)). The decrease is, however, stronger for the intracolumnar correlation length. A limited correlation length, as reported earlier, may originate from fluctuations controlled by the curvature elastic properties of the liquid-crystalline phase [4, 22]. High resolution electron microscopical studies have furthermore shown that the hexagonal arrangement of columns is frequently disturbed by small displacements of the discs in the individual planes perpendicular to the column axis [23]. A more detailed study on the kind of imperfections present would require the analysis of many orders of the reflections [20], which is usually not possible for the liquid-crystalline phases because of the limited number of reflections present, and of their tails which requires a high resolution technique. In any case, doping leads to an enhancement of the structural perfections.

In addition to TNF other types of electron acceptors were also used as dopants. It is sufficient to state here that they give rise to similar features. The acceptors differ mainly with respect to the magnitude of the shift of the transition temperature [16].

The phenomenon of stabilization of the hexagonal columnar phase by electron acceptors is not limited to low molar mass discotics. Figure 7 shows the chemical
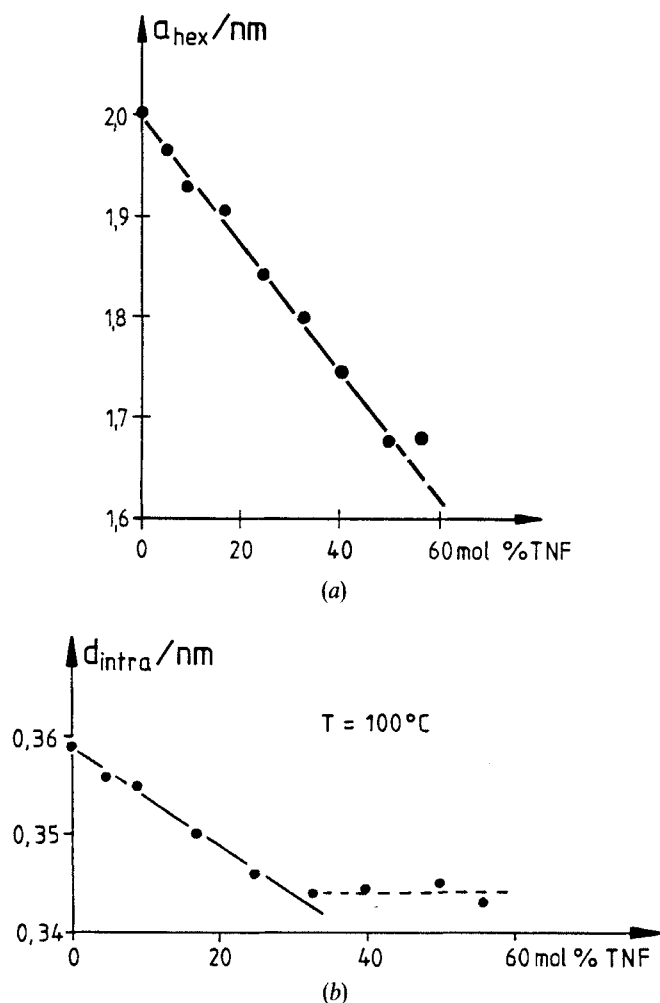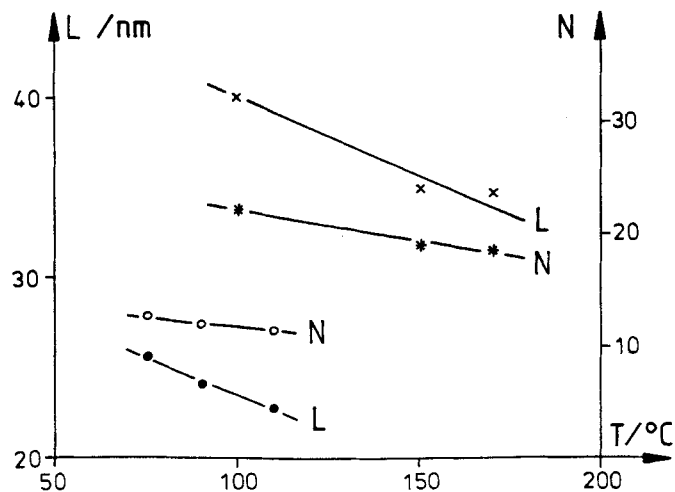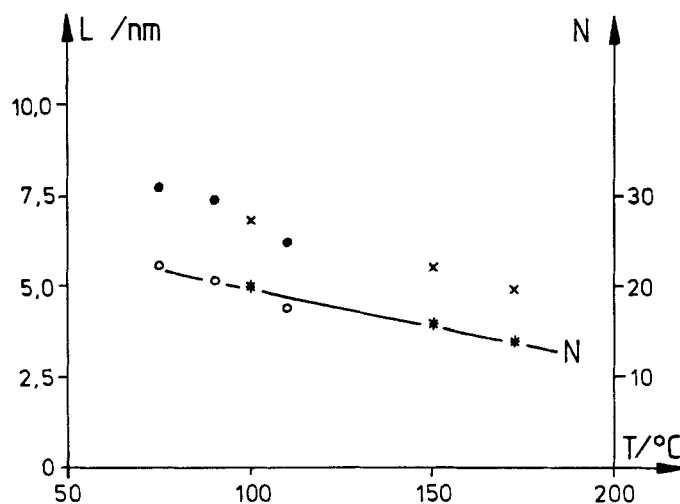
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Figure 5. Dependence of intercolumnar (a) and intracolumnar (b) distances in mixtures of H5T and TNF on the TNF concentration.

Table 1. Densities of mixtures of H5T and TNF. Comparison of experimental (ρ_{exp}) data with those calculated for mixed stacks (ρ_1) and separated stacks (ρ_2).

| H5T/TNF	ρ_{exp}/g cm^{-3}	ρ_1 (22°C)/g cm^{-3}	ρ_1 (100°C)/g cm^{-3}	ρ_2 (100°C)/g cm^{-3}
100/0	—	—	0·99	0·99
95/5	—	—	1·00	1·06
91/9	—	—	1·03	1·13
83/17	—	—	1·01	1·21
75/25	—	—	1·03	1·38
67/33	1·07	1·03	1·02	1·46
60/40	1·09	1·05	1·03	1·72
50/50	—	—	1·04	2·08
44/56	—	—	1·00	2·26

Figure 6. Dependence of intercolumnar (a) and intracolumnar correlation length (b) and of the number N of correlated structural units on temperature for H5T (●, ○) and a mixture 75/25 H5T/TNF (×, *).

structure of a set of main chain liquid crystalline polymers containing disc-like units and spacers of various length. The polymer possessing a spacer length n of 10 displays a hexagonally ordered columnar phase in the undoped state. Doping with TNF leads to a strong enhancement of the thermal stability of this phase [16].

3.2. Induction of a columnar in a system displaying a nematic discotic phase

The phase diagram of the discotic compound N6 [21] (see figure 8), i.e. the transition temperatures as a function of the TNF concentration is shown in figure 9. It is apparent from X-ray and calorimetric studies that the nematic discotic phase is destabilized and a hexagonal ordered columnar phase is induced as the concentration
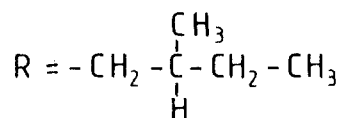
$$n = 10, 14, 20$$

$$R = -CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH_2 - CH_3$$
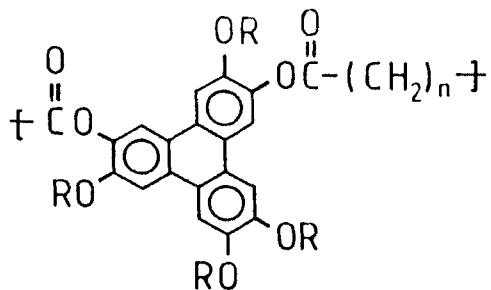
Figure 7.   Chemical structure of the amorphous polymers P1n.
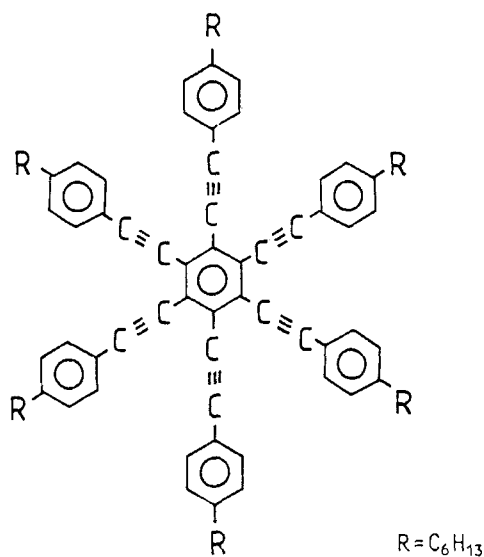
$$R = C_6H_{13}$$

Figure 8.   Chemical structure of N6 [21].

of TNF increases. The stabilization of the columnar phase increases up to a concentration of about 50 mol% of the electron acceptor and decreases again as the concentration of TNF is further increased. This behaviour is similar to that discussed previously for the variation of the columnar transition temperature of doped H5T. This does not hold for the variation of the clearing enthalpy with concentration, which increases from zero (no columnar phase formation) up to a concentration of about 50 mol% TNF above which it levels off [16]. Finally, it has to be mentioned that both the intracolumnar and the intercolumnar distances decrease linearly with increasing TNF concentration. The structural data and the density data are consistent with the formation of mixed stacks (see table 2) [16].
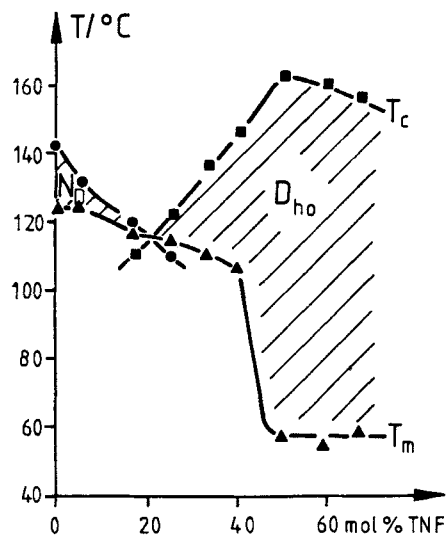
Figure 9. Phase diagram of mixtures of N6 with TNF.

Table 2. Densities of mixtures of N6 and TNF. Comparison of experimental data (ρ_{exp}) with those calculated for mixed stacks (ρ_1) and separated stacks (ρ_2).

N6/TNF	$\rho_{exp}/g\,cm^{-3}$	$\rho_1\,(22°C)/g\,cm^{-3}$	$\rho_1\,(120°C)/g\,cm^{-3}$	$\rho_2\,(120°C)/g\,cm^{-3}$
75/25	—	—	0·95	1·26
67/33	—	—	0·91	1·31
60/40	—	—	0·86	1·35
50/50	1·07	0·82	0·81	1·62
44/56	1·08	0·75	0·74	1·79
33/67	—	—	0·68	2·05

$R = (-CH_2-CH_2-0-)_2-CH_3$

EO5: $R_1 = -CO-CH_3$

EO6: $R_1 = R$
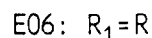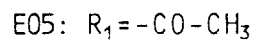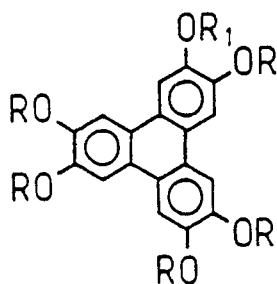
Figure 10. Chemical structures of the compounds EO5 and EO6.

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3.3. *Induction of classical columnar phases in non-discotic compounds*

The phase diagram for mixtures of TNF and EO5 and EO6 (see figure 10) are displayed in figures 11 (*a*) and (*b*). The X-ray investigations reveal that the undoped donors do not display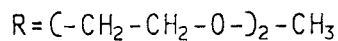 any discotic phase. Adding a small amount of TNF induces a hexagonal ordered columnar phase which is stabilized by increasing acceptor concentration up to 30 mol%. The clearing temperature decreases again as the THF concentration is further increased. The systems EO5/TNF and EO6/TNF differ from those discussed earlier in that the maximum stability of the columnar phases are shifted to smaller concentrations of the electron acceptor, in the range of 20 to 30 per cent. Apart from this the systems considered here behave as described previously, i.e. the enthalpy and entropy of the transition increase more or less linearly with increasing acceptor concentration again up to 30 per cent and level off at higher values. In addition we again find in close similarity to the cases described earlier that the intercolumnar distances decrease linearly with increasing amount of TNF (see figure 12), whereas the intracolumnar distance is approximately independent on the presence of TNF.
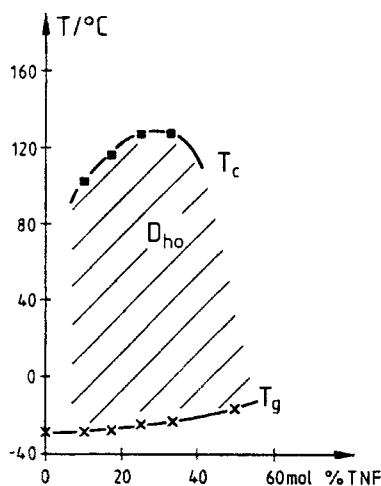
(*a*)
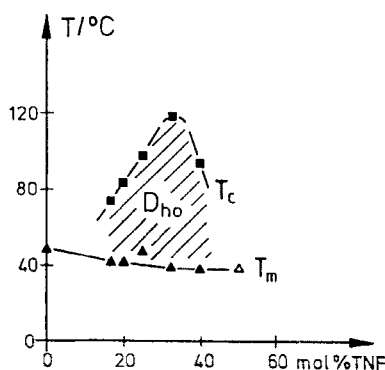
(*b*)

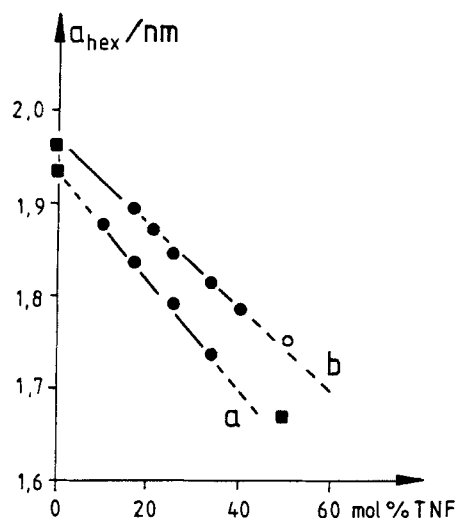Figure 11. Phase diagram for mixtures of EO5 (*a*) and EO6 (*b*) with TNF.

Figure 12. Dependence of intercolumnar distances for mixtures of EO5 (*a*) and EO6 (*b*) on the concentration of TNF.

3.4. *Induction of novel columnar phases in amorphous polymers*

The addition of electron acceptors to the low molar mass and polymer systems considered previously led to the stabilization/induction of a hexagonally ordered columnar phase. In the following we present results which reveal that it is even possible to induce novel columnar phases which have not previously been observed experimentally. These are the rectangularly ordered columnar phase (D_{ro}) and the columnar nematic phase (N_c). These phases have been observed for the polymers P1*n*, the chemical structures of which are displayed in figure 7, for *n* = 14 and 20, respectively. Both polymers are amorphous in their undoped states.

Figure 13 (*a*) shows the wide angle X-ray diagram both of the undoped polymer P1*n* (*n* = 14) and of the one containing 25 mol% of TNF. Doping leads to the formation of a structure characterized by relatively sharp reflections in the small and one in the wide angle X-ray regime. The wide angle reflection is consistent with an ordered stacking of the disc-like units in columns. The small angle reflections, however, disagree with an assignment in terms of a hexagonal packing of columns. We are, however, able to assign these reflections to a two dimensional rectangular arrangement of the columns.

This is especially apparent from the flat film camera diagrams displayed in figures 14 (*a*) and (*b*). These were obtained for oriented samples obtained by the deformation procedure described in the experimental section. The diagrams were taken with the X-ray beam travelling along the three directions defined macroscopically, i.e. pressure, flow, confinement (see experimental section). These X-ray diagrams give a direct image of selected projections of the reciprocal lattice: they clearly indicate the existence of a two dimensional rectangular lattice (see figure 15) with equal size of the two lattice parameters and of a one dimensional lattice along the columns. The reflections can be attributed as follows: A_1: (100), (010) etc.; A_2: (110) etc. in the small angle regime and B: (001) in the wide angle regime. H corresponds to the halo formed by the flexible spacer units. Based on the analysis of the density we can conclude that again mixed stacks are formed (see figure 15).

A much more disordered structure than that described is induced by TNF in the polymer P1*n* with *n* = 20. This is apparent from figures 13 (*b*) and 16 which show both
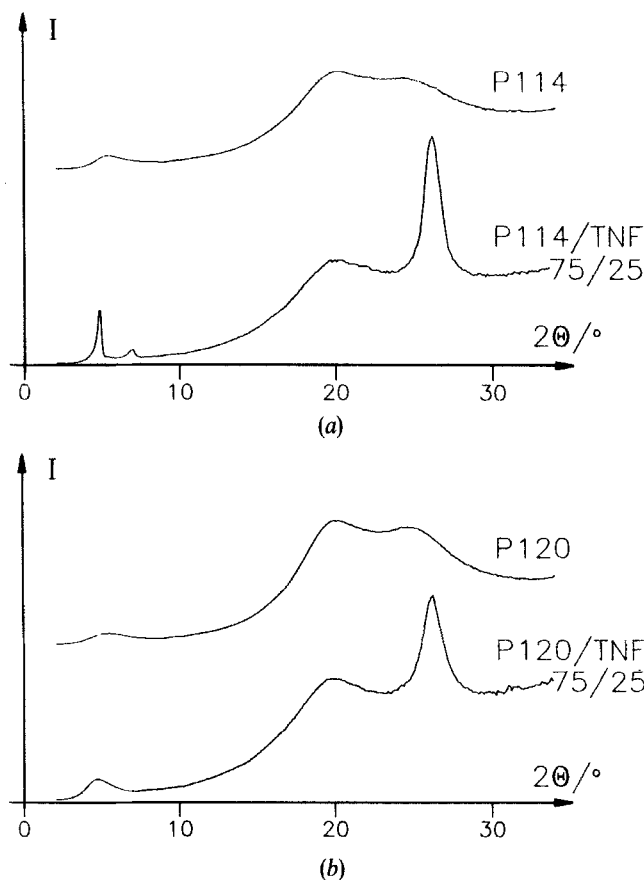
Figure 13. (*a*) Wide angle X-ray powder diagram of the undoped and doped polymer P1*n* (*n* = 14). (*b*) Wide angle X-ray powder diagram of the undoped and doped polymer P1*n* (*n* = 20).

the powder diffraction data and the data obtained on oriented fibres. We observe one narrow wide angle reflection, indicative of an ordered packing of disc-like units in a column but also a very broad rather halo-like reflection in the small angle regime. These findings taken together indicate the presence of columns, the packing of which is characterized by a short range order, in agreement with the flat camera results shown in figure 16 for a sample with a fibre symmetry. The corresponding structural model for the columnar nematic phase is shown in figure 17. We concede that the assignment is not beyond any doubt. Unfortunately we were not able to induce a texture which is characteristic of the nematic phase, namely a schlieren texture, for such a polymer. However we have recently reported X-ray results identical to those shown in figure 16 for various low molar liquid-crystalline systems [24,25]. These systems have the benefit of the formation of the corresponding schlieren texture which proves the columnar nematic discotic state beyond any doubt.

4. Theoretical model for the induction of discotic phases by charge transfer interactions

This section is concerned with an analysis of the origin of the strong effects of doping on structure formation and thermodynamic properties of systems containing
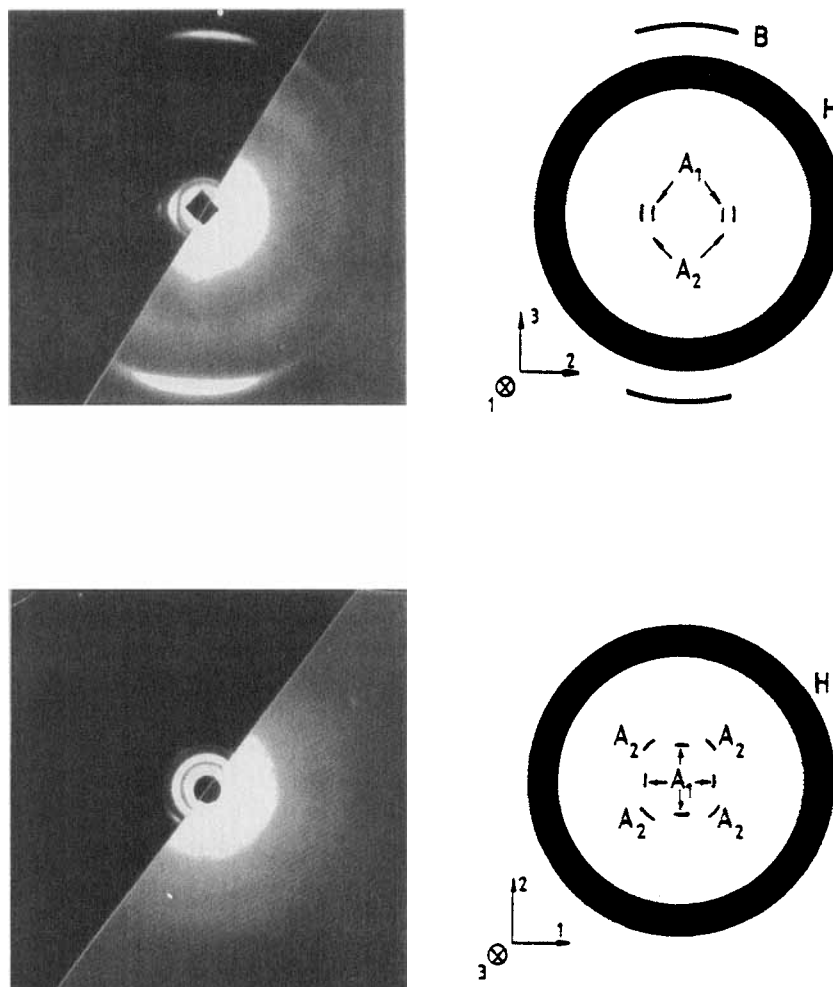
Figure 14. Flat camera diagrams obtained for the oriented sample of doped P1n (n = 14). Beam along direction 1 (upper diagrams) and along direction 3 (lower diagrams).
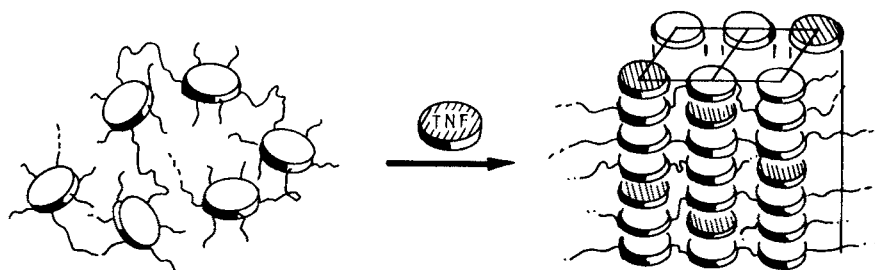

Figure 15. Proposed structural model (discotic rectangular ordered: D_{ro}) for the doped polymer P1n (n = 14).
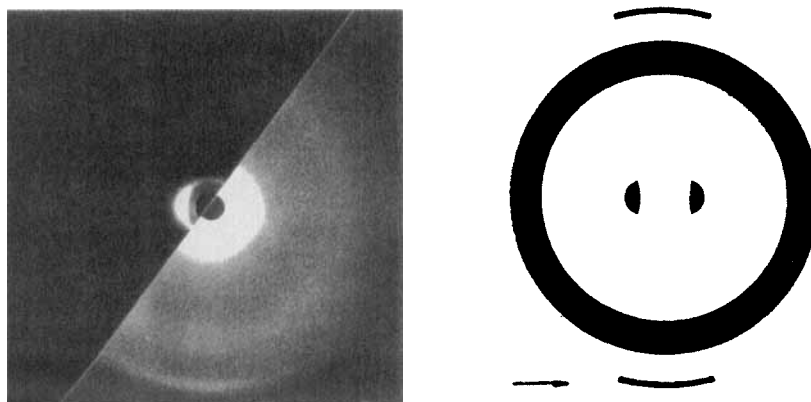
Figure 16. Flat camera diagram obtained for a fibre of the polymer P1n ($n=20$). Beam perpendicular to fibre direction.
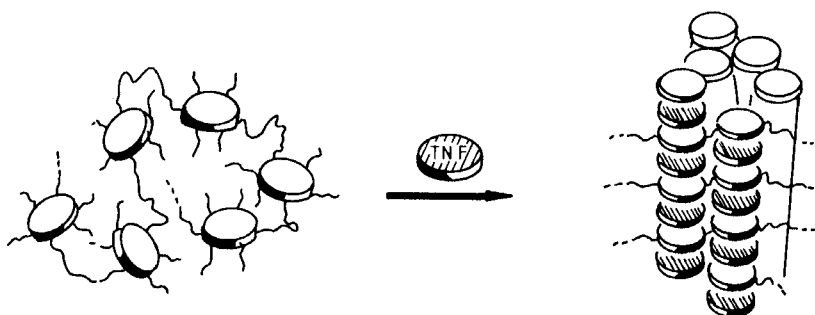

Figure 17. Structural model (discotic columnar nematic: N_c) for the doped polymer P1n ($n=20$).

disc-like units. The analysis proceeds in two steps. First the general molecular field theory for the formation of columnar phases in unassociated liquid crystals will briefly be introduced in order to show the close similarity between the McMillan treatment of the smectic A phase [26] and the treatment of columnar phases [27]. This allows us then to adopt the modification of this theory, which has been proposed by de Jeu *et al.* [17] in order to describe the induction of smectic phases due to molecular associations, for the case of the induction of columnar phases by associations.

The molecular field treatment of the formation of columnar phases (we consider here just the hexagonal one) follows closely the molecular field treatment of the smectic phase. The pair potential is averaged in the spirit of the molecular field approach to obtain the single particle potential

$$V_1(x, y, \cos \theta) = -V_0(1 + (\cos (\mathbf{Ar}) + \cos (\mathbf{Br}) + \cos (\mathbf{Cr}))P_2(\cos \theta),$$

where V_0 is the interaction strength, **A, B, C** the primitive vectors of the two dimensional hexagonal lattice formed by the columns and where a spatial interaction parameter a is given, in close analogy to the McMillan treatment of the smectic phase, by

$$a = 2 \exp(-2r_0/3a_{\mathrm{hex}})^2,$$

where a_{hex} is the lattice constant. The self-consistent analysis shows that the parameter a controls the relative stability of the nematic and the columnar phase [27] and that the parameter V_0 controls the absolute stability of the nematic phase relative to the isotropic. Now in order to be able to explain the experimental results described here we might assume that either the magnitude of the interaction strength V_0 is increased due to the presence of charge transfer interactions, or the magnitude of the interaction parameter a or both. It is, however, apparent at once that we cannot explain the induction or stabilization of the columnar phases along this route. An increase in the magnitude of V_0 will stabilize both the nematic and the columnar phase, which is in contradiction to results to be presented later. The parameter a also does not lend itself to variations since it is controlled by geometry to a first approximation, not by the magnitude of the interaction strength. So it seems that theoretical routes developed for non-associated liquid crystals fail to account for the experimental results.

De Jeu *et al.* [17] were able to account for the induction of smectic phases in rod-like systems due to charge transfer interactions by assuming that the binary mixtures, electron donor, electron acceptor, actually contained three species: acceptor A, donor D and complex C

$$A + D \overset{K}{\leftrightarrow} C.$$
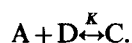
Depending on the magnitude of the EDA interaction and thus on the magnitude of the equilibrium constant K the case of full complexing ($K = \infty$), of no complexing ($K = 0$) and any intermediate state can be specified and treated. De Jeu *et al.* introduced interactions AA, DD, AD, CC, AC, AD, derived within the molecular field approach an expression for the thermodynamic potential and obtained the equilibrium phases on the basis of a variational analysis. Figure 18 shows characteristic examples for the dependence of the stability of the smectic phase on the magnitude of the EDA interaction W_0 for various cases of the mutual interactions between A, D and C. This figure also contains the variation of the concentration of complexes with composition again for various choices of mutual interaction energies [17].
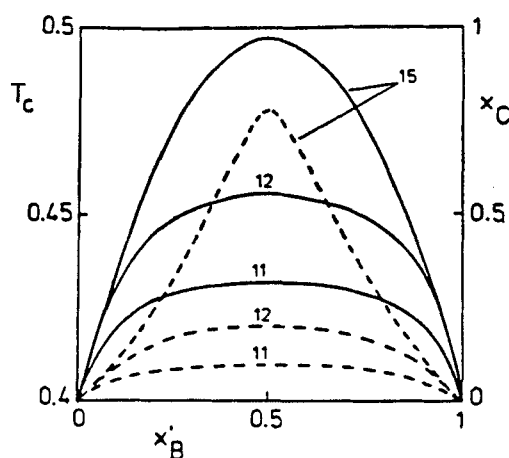

Figure 18.   Results of the model calculations by de Jeu *et al.* [19] on the stability of the induced phase for various magnitudes (parameter of the plot) of the EDA interaction strength. T_c signifies a reduced temperature, x_c is the concentration of complexes and x_B of the dopant.

These results can readily be adopted for the stabilization/induction of the columnar phases because of the strong similarity of the molecular field treatment of smectic and columnar phases. It is quite apparent that the predictions shown in figure 18 agree qualitatively with the experimental findings. The phase stability is predicted to pass through a maximum at intermediate concentrations, the stability enhancement increases with increasing interaction strength of the CT complexes. Accepting this model we are to draw some further conclusions. One conclusion is based on the fact that we often observe that the maximum stability occurs at a concentration of about 40–50 mol% electron acceptor despite the fact that the electron acceptor does not display discotic phases whereas the donor does. This seems to suggest according to the treatment by de Jeu *et al.* that the strength of the EDA complex is very large compared to the mutual interactions between A, D and C. The concentration of complexes is high in this case. It seems furthermore that the linear variation of the intracolumnar and intercolumnar distance with the TNF concentration is controlled by the concentration of complexes present and their structural features: smaller intracolumnar and intermolecular distances due to their intrinsic configurations. Finally, it seems that the variation of the heat of transition between the columnar and the isotropic phase is controlled by the mutual interactions between A, D and C and not at all by the EDA-interaction W_0. It is, therefore, not surprising that the heat of transition remains small even for strong EDA interactions and that it may increase or decrease with increasing electron acceptor concentration, depending on the sign and magnitude of the various mutual interactions.

So, in conclusion, it has become apparent that we are able to control structure, formation and thermodynamic properties of low molar mass and polymer systems containing disc-like molecular groups to a great extent and that we are able to account for this effect qualitatively on the basis of a model taking complex formation into account.

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