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Molecular Engineering of Liquid-Crystalline Polymers: Architecture and Functionalization [and Discussion]

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Molecular engineering of liquid-crystalline polymers: architecture and functionalization

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In the past few years molecular engineering of liquid-crystalline (LC) polymers with respect to molecular architecture and functionalization has become increasingly important. Molecular architecture of LC polymers, i.e. the variation of the arrangement of mesogens, the variation of their shapes (rod, disc, board) and the variation of the polymer backbone, leads to polymers with new LC phases and new properties. Functionalized or dye-containing polymers can be used for a destruction or even the formation of the LC phase by photoreactions as well as for photochromic effects. The induction of discotic phases in amorphous polymers with disc-like mesogens is possible by charge-transfer interactions and opens the accessibility for a wide variety of highly oriented polymer systems.

1. Introduction: self-organization and the formation of supramolecular systems

Order and mobility are two basic principles in Nature. On a molecular level two extreme cases can be found: the perfect order of crystals, in which the molecules exhibit almost no mobility at all, and the disordered state in gases and liquids, which exhibit randomness of highly mobile molecules. Both principles, order and mobility, are combined in liquid-crystalline (LC) phases. Although there are many possibilities for self-organization, the molecular basis is always simple: formanisotropic or amphiphilic molecules make up the simplest building blocks. These already suffice (see figure 1) to construct a broad range of supramolecular systems (Ringsdorf *et al.* 1988) from thermotropic (Kelker 1980; Demus 1984) or lyotropic (Forrest 1981; Tiddy 1980) liquid crystals and the manifold micellar systems up to the highly ordered membranes in liposomes and cells (Degiorgio 1985).

In materials science the significance of liquid crystals and micellar systems has long been known; it is based on the combination of order and mobility in formanisotropic molecules that leads to anisotropic (i.e. direction-dependent) properties of their materials and solutions. From the life sciences we know that no life would be possible without lipids' self-organization into bilayers within the cell membrane. In this case, too, order and mobility are related to the structure of functional units now formed by lipids and proteins. In all cases, the functions of such supramolecular systems formed by aggregation are based on their organization.

This paper is concerned with the molecular engineering of LC polymers. It will not summarize the field. Instead it will only briefly refer to the molecular architecture of polymeric LC systems with its wide variety of shapes and arrangements of mesogenic building blocks.

The discussion will then concentrate on a few examples of functionalization of polymeric liquid crystals. The introduction of functionality into oriented systems is consistent with an existing applied concept of Nature, namely that order, mobility and functionality can always

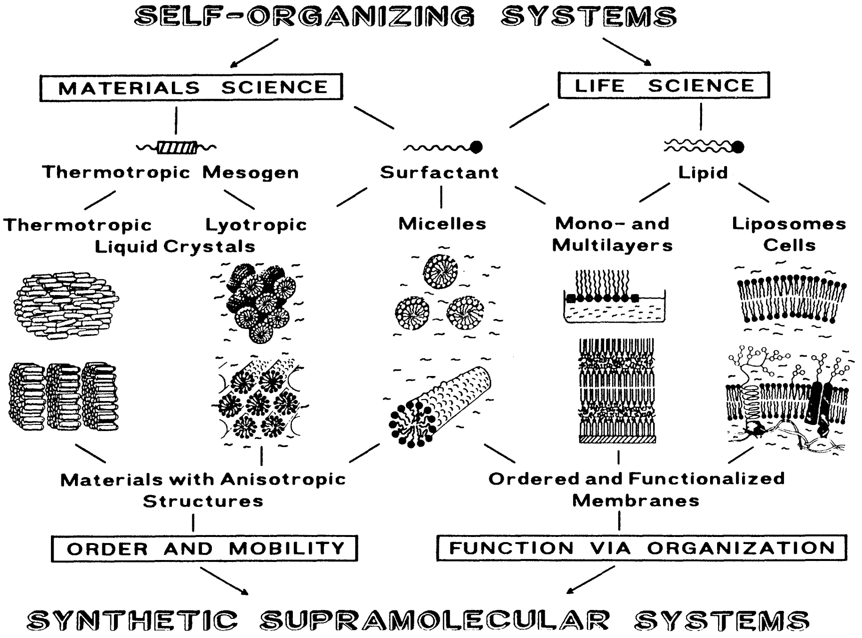

FIGURE 1. Self-organization and supramolecular systems in materials science and life science. The supramolecular structures range from simple nematic liquid crystals to complex biomembranes.

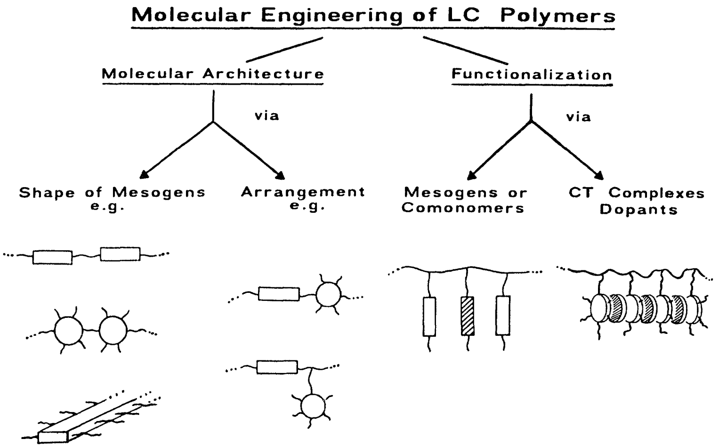

FIGURE 2. Molecular architecture and functionalization are two important aspects in molecular engineering of LC polymers.

be combined. The introduction of functionality into liquid crystals allows the variation of their properties on a wide scale and paves the way to new synthetic supramolecular systems and device construction.

2. MOLECULAR ARCHITECTURE OF POLYMERIC LIQUID CRYSTALS

The development of polymeric liquid crystals (White 1985; Samulski 1985) started with polymers whose stiff main chain as a whole functions as the mesogens. Such polymers form LC phases either in solution (Robinson 1956; Morgan 1977; Kwolek *et al.* 1977; Bair *et al.* 1977;

Panar *et al.* 1977) or in the melt (Jackson *et al.* 1976; Jackson 1980). At present, they are used as high-tensile-strength fibres (e.g. Kevlar®) or as thermoplastically processable, self-reinforcing plastics (e.g. Xydar®, Vectra®, Ultrax®).

Parallel to these industrial developments, numerous studies have been carried out in the area of basic research during the last ten years. They have mainly dealt with the incorporation of rod-shaped mesogenic groups, known from low-molecular-mass (LMM) liquid crystals, into polymers. This incorporation is either carried out by connecting the mesogenic groups via flexible spacers (de Gennes 1975) thus forming semiflexible LC main-chain polymers (Roviello *et al.* 1975) (type A, figure 3) or, as in the case of the LC side-group polymers, by fixing the mesogens via flexible spacers to the polymer backbone (Finkelmann *et al.* 1978; Shibaev *et al.* 1979) (type B, figure 3). Both types of LC polymers were, and still are, intensively investigated. Their structure–property relations are discussed in numerous monographs (Ciferri *et al.* 1982; Gordon *et al.* 1984; Blumstein 1985) and reviews (Blumstein *et al.* 1984; Finkelmann 1987; Varshney 1986).

Starting from the two 'classical' types (A and B in figure 3) several variations of the macromolecular architecture of LC polymers have recently been carried out. On the one hand, it is now possible to also realize discotic phases, as observed in the case of (LMM) liquid crystals, by using side-group polymers of type C (Kreuder *et al.* 1983) or main chain polymers of type D (Kreuder *et al.* 1985, Herrmann-Schönherr *et al.* 1986; Wenz 1985). On the other hand, it is of course also possible to incorporate rod-shaped mesogens in different ways in the polymeric systems; examples are side-group polymers of type E (Hessel *et al.* 1987; Zhou *et al.* 1987; Berg *et al.* 1986) as well as main-chain polymers of type F (Berg *et al.* 1986) both with laterally fixed mesogens. These strange-looking architectures do not prevent the formation of LC phases. As far as polymers of type E are concerned, the limited rotation of the mesogenic groups around their longitudinal axes leads to the formation of biaxial nematic phases (Hessel *et al.* 1985; Hessel *et al.* 1987; Zhou 1987). The third group of structural variations makes use of a well-known principle in polymer chemistry, which is rarely used in the field of LC materials: the combinations of different structural elements and different building principles to design one molecule. This includes the combinations of rod- and disc-shaped mesogens in polymers of type G, H, and I (Kreuder *et al.* 1987; Karthaus 1988) and the combination of the building principles of the classical LC polymers (type A and B) in the combined main-chain or side-

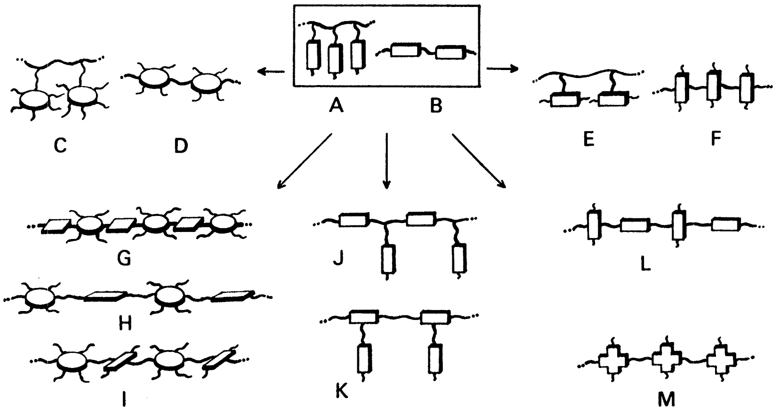

FIGURE 3. Molecular architecture of LC polymers involves the variation of mesogens' shapes (rod-like, disc-like) and the variation of mesogens' arrangement in the polymer.

group polymers of type J and K (Reck *et al.* 1985). Furthermore, polymers with cross-shaped mesogens (type M) (Berg *et al.* 1986) should be mentioned, as well as the idea of combining laterally and terminally connected mesogenic groups (type L), which has not yet been realized.

3. FUNCTIONALIZATION OF LIQUID CRYSTALLINE POLYMERS

There are several routes to functionalize LC polymers as schematically shown in figure 4.

Meanwhile, dye-containing liquid crystals have found wide interest even for polymeric systems (Ringsdorf *et al.* 1986, 1987). By fixing the non-mesogenic dyes covalently to polymer backbones the dye content of LC phases can be increased considerably without loss of mesophase or phase separation.

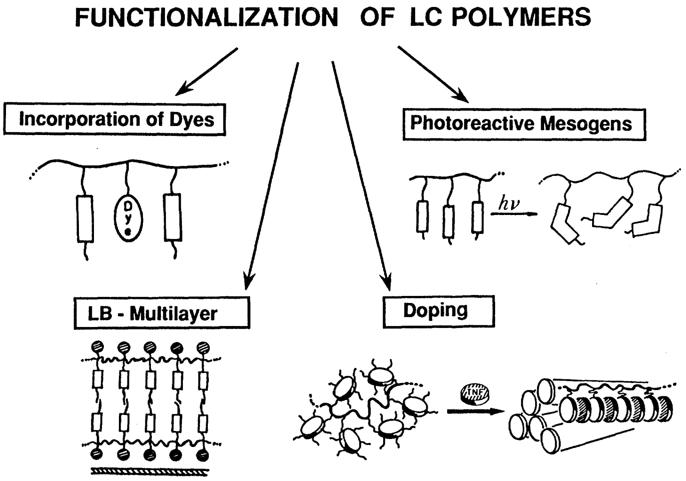

FIGURE 4. Functionalization of LC polymers may be achieved by the incorporation of dyes, the incorporation of photoreactive mesogens, by the Langmuir–Blodgett technique or by doping.

LC polymers with mesogenic units have only been tested lately in attempts to prepare Langmuir–Blodgett (LB) multilayers of higher mobility that are also able to undergo phase transitions reversibly (Schuster 1986; Erdelen *et al.* 1989; Jones *et al.* 1985). This concept should make it possible to orient the domains of LB multilayers by annealing and the use of electric or magnetic fields.

The incorporation of photoreactive groups allows the modification of mesomorphic structures by irradiation. Polymers have been synthesized of which the LC phases can be destroyed or induced upon irradiation (Engel 1988). If photochromic groups are incorporated, the colour of the LC phase may be changed also (Cabrera *et al.* 1987). Polymers containing azobenzene show photoisomerization that one takes advantage of in reversible information storage by holographic methods (Eich *et al.* 1987*a*, *b*).

Another means of functionalizing LC polymers is by doping them with LMM molecules.

4. Functionalization and structural variation of lc polymers by doping

Doping provides an easy way to introduce functionality, i.e. physical properties like colour, polarity, electrical or photoconductivity, into liquid crystals (Kuczynski 1987; Kuczynski *et al.* 1980; Gottarelli *et al.* 1985; Okamoto *et al.* 1983; Stegemeier *et al.* 1987; Ivashchenko *et al.* 1987; Meredith *et al.* 1982). Additionally, doping often brings around some change to mesomorphic structures, making it also a tool for structural variation. Both these effects of doping, that are functionalization or functionalization combined with structural variation, are illustrated in figure 5.

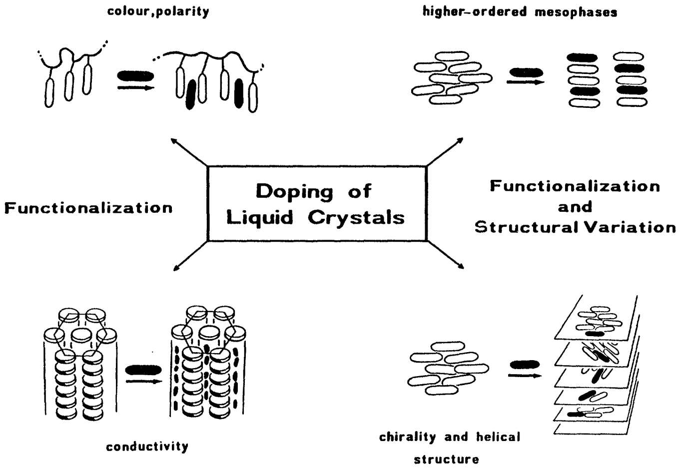

Figure 5. The effects of doping liquid crystals: functionalization or functionalization combined with structural variation. Functionalization involves the introduction of physical properties like colour, polarity or conductivity. Functionalization and structural variation involves both the introduction of physical properties and changes in the mesomorphic structure such as the transition from less-ordered nematic (n) phases to higher-ordered phases with layer arrangement (smectic phases s) or with helical structures (cholesteric phases n*).

As a means of functionalization doping has been used for many lc systems. This refers to calamitic lmm and polymeric liquid crystals and recently also to lmm discotic liquid crystals. The latter were doped with iodine (van Keulen 1987) or $AlCl_3$ (Boden 1988) so as to build up one-dimensional conductors with the charge transport running along the column axes.

To achieve both, functionalization and structural variation doping has been applied as often. It is well known that nematic phases can be transformed to twisted nematic n* (cholesteric) phases with helical superstructures upon adding chiral dopants (Stegemeier *et al.* 1987; Gottarelli *et al.* 1985). In the same way smectic C phases can be transformed to chiral smectic C (S_C^*) phases that are of interest for their ferroelectric properties (Kuczynski 1987; Kuczynski *et al.* 1980; Stegemeier *et al.* 1987).

Furthermore, highly ordered phases with layer structures (smectic phases) may be induced from less ordered (nematic) liquid crystals. This has been realized in mixtures of nematic molecules that differ in polarity (Oh 1977) or that have adapted molecular shapes (Diele *et al.* 1988) or that have electron donor and electron acceptor properties (Petzl *et al.* 1987*a*, *b*). Microphase separation leads to the layer arrangement in the first case, space filling reasons in the second and charge-transfer (ct) interactions in the third case.

ct interactions have further been used by Matsunaga *et al.* (1980, 1985, 1987) to even induce mesophases from non-LC compounds as shown for the calamitic phase type. Polymeric LC phases and discotic liquid-crystalline phases, however, have not yet been induced.

The field of discotic liquid crystals (Chandrasekhar 1977; Destrade 1984) was in particular promising to us for the study of the effect of CT interactions. Most disc-like molecules derive from condensed aromatics that are known for their electron donor properties. Their large, flat, aromatic cores allow strong interaction with aromatic acceptor molecules and tight packing. As a consequence we expected CT complexation not only to add new physical properties to the system but also to influence molecules' order in the LC discotic phase (see figure 6).

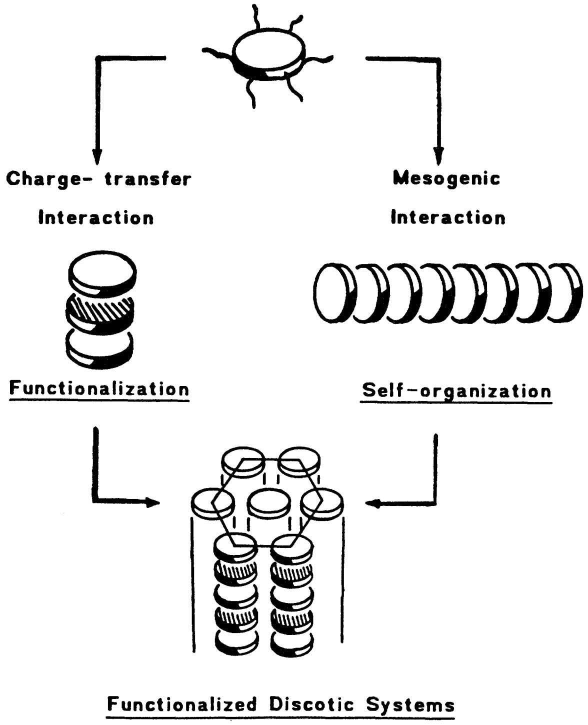

FIGURE 6. The combination of the two ordering principles, CT interactions and mesogenic interactions, leads to functionalized discotic systems with new physical properties (colour, photoconductivity, electric conductivity). It may further lead to the induction of discotic phases in non-LC LMM compounds or polymers with disc-like molecules (see figures 9–12).

Creating a 'preorder' of donor and acceptor molecules in stacks, CT interactions should – when combined with mesogenic interactions between formanisotropic molecules – increase the degree of order within the LC phase and stabilize it. This is what we found for LMM and polymeric discotics. Additionally, it was possible to even induce polymeric and LMM discotic phases from non-LC compounds (Ringsdorf *et al.* 1989; Ebert *et al.* 1989*a*, *b*). These results will be discussed for polymers in the following.

The polymers investigated contain triphenylene ethers as disc-like electron donor molecules. Their synthesis starts from partly etherified mono- or dihydroxy triphenylenes (Kreuder *et al.* 1985) and then follows routine procedures. Main-chain polymers were obtained by melt condensation (Kreuder 1986; Kreuder *et al.* 1985; Karthaus 1988) and side-group polymers by radical polymerization (Kreuder 1986). Molecular masses as determined by gel permeation chromatography (against PS-standards, $CHCl_3$, ultraviolet detection) are between 13000 (**1** in figure 7) and 50000 (**5** in figure 12) for the polycondensates and 380000 (**4** in figure 12) as well as 3800000 (**3** in figure 11) for the side-group polymers. The polymers were doped with aromatic electron acceptors, in particular with 2,4,7-trinitrofluorenone (TNF). Doping was carried out by solution mixing in dichloromethane or tetrahydro-fyrane; the solvent was evaporated and the remaining solid dried *in vacuo* over *ca.* 24 h. The phase behaviour of the samples was characterized by differential scanning calorimetry, polarizing microscopy and X-ray diffraction (small-angle X-ray scattering (SAXS), flat plate camera) of oriented fibres.

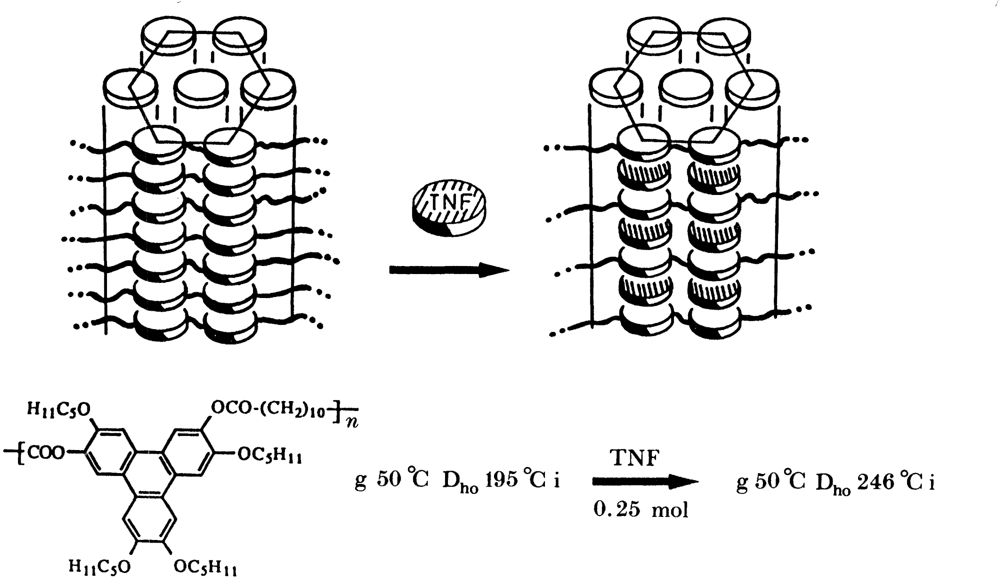

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FIGURE 7. Functionalization of discotic polymers by doping with electron acceptors. The D_{ho} mesophase of the triphenylene-polyester **1** is retained upon doping with TNF and its clearing point is even increased.

4.1. *Functionalization of liquid-crystalline discotic polymers by doping with electron acceptors*

Doping of LC discotic polymers, such as the main-chain polyester **1** in figure 7, involves functionalization. Upon adding the electron acceptor TNF to **1**, CT complexes are formed as evident from the colour change from colourless to deep red (CH_2Cl_2 solution) or black (solid).

The LC phase and also the phase type, D_{ho} (discotic hexagonal ordered), are retained; the clearing temperatures, however, are increased (see table 1). The undoped polyester **1** becomes isotropic at 195 °C and the TNF-doped systems at 246 °C and 245 °C for molar ratios **1**:TNF of 3:1 and 2:1. This is contrary to what is generally found for mixtures of LC polymers with LMM substances that show a rapid fall in clearing temperatures and loss of the mesophase at 3–10% by mass added LMM-component. Whereas the phase type of **1** is not affected by the addition of TNF, the mesomorphic structure, though, is changed. X-ray investigations show that the intracolumnar spacing, i.e. the distance between the molecules within the column, decreases slightly over 0.1 Å† from 3.5 Å of the undoped polyester **1** to 3.4 Å of the TNF-doped polyesters (see table 2 and figure 8). The intercolumnar spacing, i.e. the spacing between the columns in the hexagonal lattice, however, decreases considerably from 20.4 Å of undoped **1** to 18.9 Å and 18.0 Å of TNF-doped **1**. The decrease in the intercolumnar spacing becomes

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† 1 Å = 10^{-10} M = 10^{-1} nm.

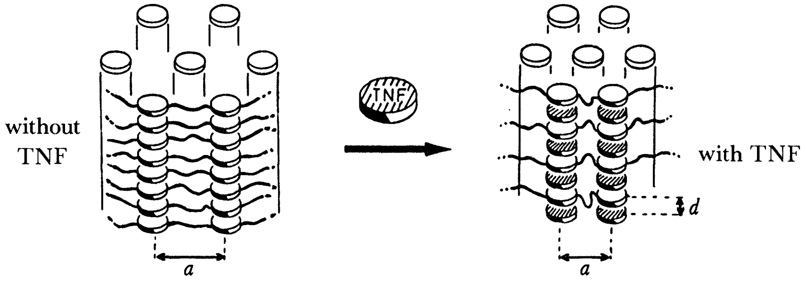

FIGURE 8. Mesomorphic structure of the main-chain polyester **1** in the doped and undoped state. The X-ray data show that the intercolumnar spacing *a* of the D_{ho} mesophase decreases with rising TNF content. The intracolumnar spacing *d* is only slightly affected by the addition of TNF.

larger the more TNF is added, yet the density remains the same. Calculating the density from the X-ray data (table 1) gives the measured values (1.00 g cm^{-3}) if one assumes that nearly all TNF molecules are inserted right into the columns and not located between them.

TABLE 1. DOPING OF THE DISCOTIC MAIN-CHAIN POLYESTER **1** WITH TNF

(Phase transition temperatures and mesomorphic structures for various molar ratios 1:TNF.)

			spacing/Å		
polymer	molar ratio polymer:TNF	transition temperatures[a]/°C	within the column (±0.03 Å)	between the columns (±0.3 Å)	halo (±0.1 Å)
1	—	g 50 D_{ho} 195 i	3.50	20.4	4.1
1	3:1	g 50 D_{ho} 246 i	3.41	18.9	4.2
1	2:1	g 50 D_{ho} 245 i	3.41	18.0	4.2

[a] D_{ho} is discotic hexagonal ordered.

For LMM discotic compounds (hexapentyloxytriphenylene, hexaethyloxycarbonylmethylenoxytriphenylene) we also observed a decrease in the intercolumnar spacing (at constant density) upon doping with TNF; the relation between the intercolumnar spacing and added TNF could be established as linear here (Ebert *et al.* 1989*a*, *b*).

4.2. *Functionalization and induction of discotic phases in non-liquid-crystalline polymers*

Doping of the non-LC main-chain polyester **2** with TNF adds functionality (CT complexation) to the system and, furthermore, induces discotic columnar phases from a previously non-LC polymer (see figure 9).

The diagram in figure 10 represents the influence of the TNF concentration on the phase behaviour of the **2**–TNF mixtures; transition temperatures are listed in table 2 together with the X-ray data. As shown, discotic columnar phases can be induced up from TNF contents as low as 20 mol.%. Clearing temperatures as well as glass transition temperatures slightly decrease with rising TNF concentration so that the phase width stays constant up to 50 mol.% TNF.

X-ray investigations have proved a D_{ho} structure of the mesophase for molar ratios of **2** and TNF of 1:1 and 2:1. Interestingly, the intercolumnar spacings found were extremely large. The values as high as 26.6 Å and 26.9 Å do not allow any contact between the alkyl chains of triphenylene molecules in neighbouring columns (the cross section of hexapentyloxy triphenylene in its fully extended form is 23–24 Å). Density measurements give identical values

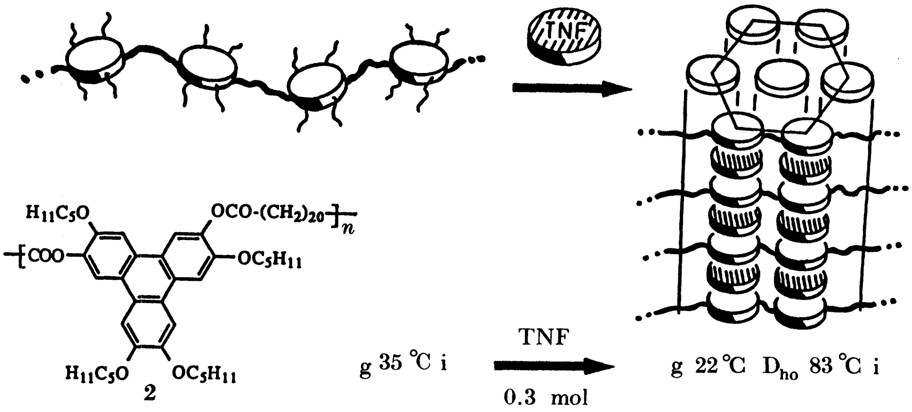

FIGURE 9. Functionalization and induction of discotic main-chain polymers by doping with electron acceptors. The amorphous polyester **2** (g 35 °C i) becomes LC upon doping with TNF. At a molar ratio **2**:TNF of 2:1 the LC D_{ho} phase ranges from 22 °C to 83 °C. The TNF acceptor molecules are not only located in the columns (as pictured here) but also in the intercolumnar spacing (see text).

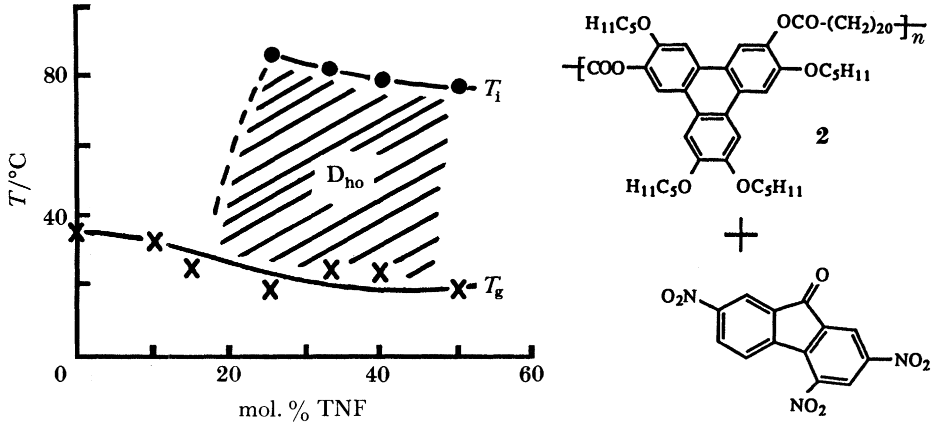

FIGURE 10. The influence of the TNF concentration on the phase behaviour of the amorphous main-chain polyester **2**. An LC phase is induced in mixtures with more than 20 mol. % TNF.

TABLE 2. INDUCTION OF DISCOTIC PHASES IN THE AMORPHOUS MAIN-CHAIN POLYESTER **2** BY DOPING WITH TNF

(Phase transition temperatures and mesomorphic structures for various molar ratios 2:TNF.)

			spacing/Å		
polymer	molar ratio polymer:TNF	transition temperatures[c]/°C	within the column (±0.03 Å)	between the columns (±0.3 Å)	halo (±0.1 Å)
2	—	g 35 i	—[a]	—[a]	—[a]
2	9:1	g 32 i	—[a]	—[a]	—[a]
2	5:1	g 25 i	—[a]	—[a]	—[a]
2	3:1	g 20 $D_?$ 85 i	—[b]	—[b]	—[b]
2	2:1	g 22 D_{ho} 83 i	3.40	26.9	4.4
2	1:1	g 17 D_{ho} 76 i	3.41	26.6	4.4

[a] Non-oriented diffuse reflections.

[b] Only the Bragg spacings are known: 3.4 Å, 21.6:15.5 Å, 4.4 Å. The spacings between the columns cannot be calculated because the phase type $D_?$ is still unknown.

[c] g is glass transition; i is isotropic; $D_?$ is columner phase; D_{ho} is discotic hexagonal ordered.

of 1.04 g cm^{-3} for the undoped amorphous polymer **2** and the discotic TNF-doped polymeric systems. No drop in density was found as expected for the mixtures if TNF molecules were inserted in the columns mostly. This provides good reason to assume that considerable amounts of TNF molecules are uncomplexed and located in the intercolumnar spacing (Ringsdorf *et al.* 1989). Investigations are in progress to quantify the amount of TNF located in and between the columns by ^{2}H nuclear magnetic resonance (NMR) spectroscopy. It is interesting to note that no such large intercolumnar spacings were found for any TNF-doped LMM discotic phase of triphenylene molecules (Ebert *et al.* 1989*a*, *b*).

To widen the field of discotic phase induction by means of doping, non-LC side-group polymers such as **3** were also tested with TNF. Again, discotic columnar phases could be induced as shown for the polymethacrylate in figure 11.

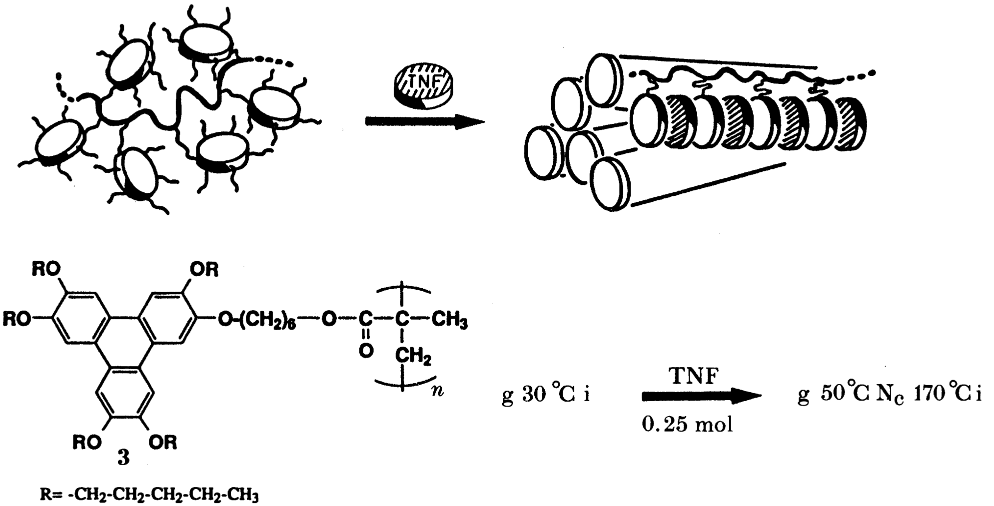

FIGURE 11. Functionalization and induction of discotic side-group polymers by doping with electron acceptor molecules. The amorphous polymethacrylate **3** (g 30 °C i) yields an LC nematic columnar (N$_C$) phase upon doping with TNF.

Table 3 contains the glass transition and clearing temperatures of mixtures with various molar ratios polymer:TNF for the polymethacrylate **3** and the polyacrylate **4** (see figure 12) that also displays discotic columnar phases.

TABLE 3. INDUCTION OF DISCOTIC PHASES IN THE AMORPHOUS SIDE-GROUP POLYMERS **3** AND **4** BY DOPING WITH TNF

(Phase transition temperatures and mesomorphic structures for various molar ratios polymer:TNF.)

			spacing/Å		
polymer	molar ratio polymer:TNF	transition temperatures[b]/°C	within the column (±0.03 Å)	between the columns (±0.3 Å)	halo (±0.1 Å)
3	—	g 30 i	—[a]	—[a]	—[a]
3	3:1	g 50 N$_C$ 170 i	3.42	19.1	4.6
3	2:1	g 50 N$_C$ 195 i	3.40	19.0	4.6
4	—	g −6 i	—[a]	—[a]	—[a]
4	9:1	g −6 i	—[a]	—[a]	—[a]
4	4:1	g 10 N$_C$ 47 i	3.40	19.2	4.1
4	3:1	g 10 N$_C$ 88 i	3.40	19.0	4.2

[a] Non-oriented diffuse reflections.

[b] g is glass transition; i is isotropic; N$_C$ is nematic columnar.

The type of the induced discotic phase is different from the D_{ho} phase of the TNF-doped main-chain polyesters **1** and **2**. Detailed X-ray analyses (SAXS) confirms a nematic columnar (N_C) phase (Ringsdorf *et al.* 1989). This phase type has not been found for thermotropic liquid crystals yet, but only for lyotropic LMM systems (Boden *et al.* 1986). In the N_C phase columns are no longer positionally ordered as in the D_{ho} phase, but still orientationally. This type of N_C phase has not occurred in TNF-doped LMM discotic systems (Ebert *et al.* 1989*a*, *b*), which again points at some differences in induced polymeric and LMM discotic phases. It seems as if the induction in polymeric systems allows a wider variation of mesomorphic structures leading also to less-ordered phases like the N_C phase.

4.3. *Functionalization, induction of discotic phases and induced compatibility in polymer blends*

For an incompatible mixture of non-LC electron donor polymers doping with electron acceptors like TNF involves functionalization, the induction of discotic columnar phases and additionally induces compatibility (see figure 11). The polymers **4** and **5** are incompatible at a molar ratio of 1:1 and are both not LC. In contrast, their mixture with TNF in the molar ratio 1:1:1.2 proves to be a compatible polymer blend with a nematic columnar phase between 13 °C and 89 °C. It is interesting to note that the individual systems **4**–TNF and **5**–TNF do not show any LC phase at the molar ratio 1:0.6. The system **4**–TNF is phase separated and the **5**–TNF system is amorphous.

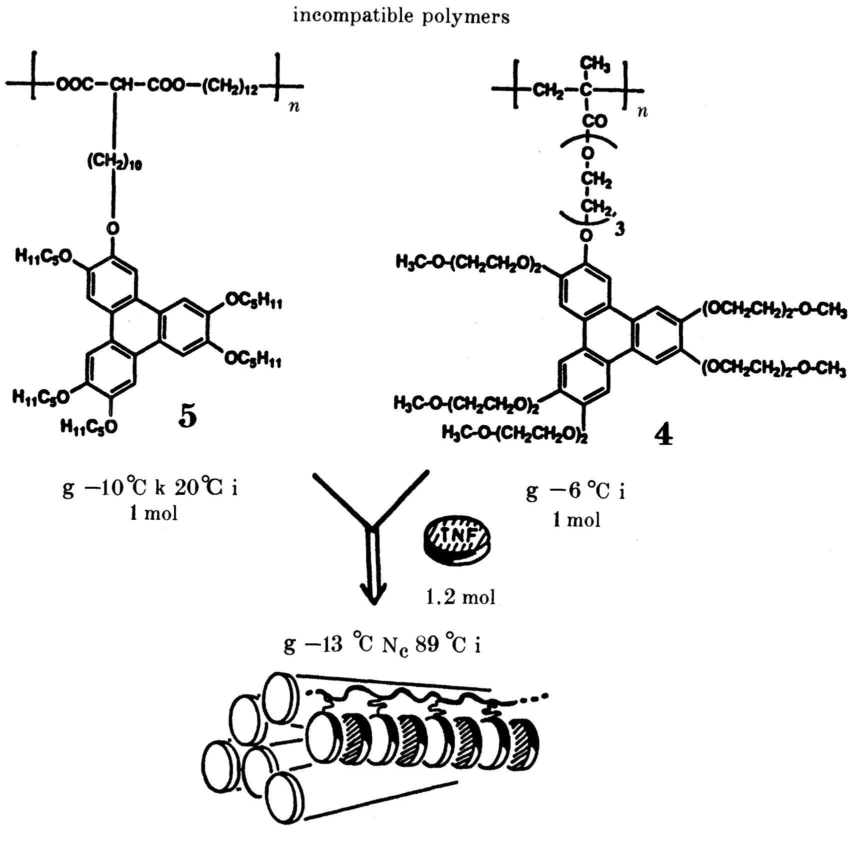

FIGURE 12. Functionalization, induction of discotic phases and induced compatibility in polymer blends by doping with electron acceptor molecules. The incompatible polymers **4** and **5** form, if mixed in a 1:1 molar ratio with 1.2 mol TNF, a compatible discotic polymer blend.

4.4. *Short-term outlook*

Doping with LMM acceptors opens a variety of opportunities for discotic polymers and LMM compounds also. For discotic polymers doping makes them more easily accessible, and especially from a wider variety of starting materials. Mesomorphic properties such as phase type and structure or clearing temperatures can be varied by the choice of polymer (main-chain polymer, side-group polymer), the miscibility ratio and by the choice of electron acceptor molecule. Further perspectives lie in the approach to compatible discotic polymer blends. And last not least, the introduction of CT interactions by doping provides an easy way to functionalized discotic polymers, making the method interesting to physics and application also, e.g. in the field of conductive or photoconductive LC systems.

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Discussion

P. Hodge (*Chemistry Department, University of Lancaster, U.K.*). Mr Ringsdorf pointed out that the photoisomerization of *trans*-azobenzene mesogens to their *cis*-isomers destroys the liquid-crystal character. With appropriate azo compounds the isomerization to the *cis*-isomer might result in the formation of a discotic mesogen. Would he like to comment on this?

The discotic mesogens generally contain side arms. What is known about the number of side arms that are required and how long need they be?

H. Ringsdorf. This is an interesting and funny idea: in principle, the molecular architecture of liquid crystals might allow the formation of a discotic mesogen of the *cis*-isomer of a highly substituted azo compound. This phase formation would require a 100% conversion to the *cis*-isomer. Due to the photostationary equilibrium and the thermal back reaction, this condition can hardly be fulfilled. In addition, the rotation around the nitrogen–carbon bond may prevent the proper packing.

Depending on the size and geometry of the disc-like core, the number of side chains may be three (Lattermann 1987), four (Ohta *et al.* 1988), five (Morris *et al.* 1988), six (J. Billard *et al.* 1978) or eight (Zimmermann *et al.* 1988). The length of the side chains again depends strongly on the core. Normally, 4–10 carbon atoms are required: shorter chain length leads to core crystallization, too long side chains lead to side chain crystallization.

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