Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Kranig, Wolfgang , Boeffel, Christine , Spiess, Hans Wolfgang , Karthaus, Olaf , Ringsdorf, Helmut and Wüstefeld, Renate(1990) '^{2}H NMR studies of phase behaviour and molecular motions of doped discotic liquid-crystalline systems', Liquid Crystals, 8: 3, 375 — 388

To link to this Article: DOI: 10.1080/02678299008047354

URL: http://dx.doi.org/10.1080/02678299008047354

LIQUID CRYSTALS, 1990, VOL. 8, NO. 3, 375–388

^{2}H NMR studies of phase behaviour and molecular motions of doped discotic liquid-crystalline systems

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(*Received 1 February 1990; accepted 16 April 1990*)

A discotic triphenylene monomer as well as a dimer and a main chain polymer, all substituted with heptyloxy side groups, were doped with an electron acceptor (2,4,7-trinitrofluorenone (TNF)) to give charge transfer complexes. These doped systems were aligned in a magnetic field, thus proving their liquid crystallinity. ^{2}H NMR measurements show that the electron acceptor molecules are incorporated into the columns built of triphenylene cores. In the charge transfer complex with the triphenylene monomer almost all the electron acceptor molecules stack in the columns even close to the clearing temperature T_I, while for the dimer and especially for the polymer a significant fraction of the TNF molecules exhibits isotropic motion, which is attributed to their location in the region between the columns, already way below T_I. This isotropically distributed part increases on approaching T_I. Fast rotation of the discs around their column axes takes place in the monomer and is quenched in the dimer and the polymer, due to the interlinking of the columns by the spacer. The electron acceptor molecules, on the other hand, exhibit free rotation in all samples, even in the charge transfer complexes with the triphenylene dimer and polymer. In the side group labelled triphenylenes increased ^{2}H NMR spectral narrowing is detected in the charge transfer complex samples compared with the corresponding pure triphenylenes. This indicates higher side group mobility in the doped systems, since the incorporation of TNF molecules increases the spacing between the discotic units.

1. Introduction

Disc-like molecules consisting of a flat rigid core with laterally bound aliphatic side groups exhibit discotic mesophases, where the cores stack together into columns [1–3]. It was shown that polymers with discotic mesogens, either as a part of the main chain, or as side groups attached to the polymer backbone via a flexible spacer, also form discotic liquid-crystalline phases [4–6]. These phases can be ordered macroscopically, either by magnetic fields [7–9] or by mechanical forces [10–12]; this mesophase alignment can be frozen in, resulting in anisotropic glasses or crystals. Recently, Ringsdorf *et al.* showed that discotic liquid-crystalline systems can be doped to form charge transfer complexes. In fact it is even possible to induce discotic liquid-crystalline behaviour by doping amorphous discotic materials [13, 14]. These systems are of a particular interest as they may exhibit interesting material properties in terms of their colour, polarity, photoreactivity and also conductivity or photoconductivity. As the phase behaviour can be adjusted to specific needs in the pure discotic compounds [15] as well as in the doped systems [13, 14] it is important to know the molecular dynamics of the doped systems as we do for the pure substituted triphenylenes [15–19].

^{2}H NMR spectroscopy offers unique possibilities for studying liquid-crystalline phases and the glassy state in terms of their dynamics and the degree of order [20–22]. By selective deuteriation we can study the behaviour of the discotic cores and the electron acceptor molecules independently and we can even detect possible differences in the side group mobility caused by the doping. In this paper, therefore, ^{2}H NMR studies on charge transfer complexes based on heptyloxysubstituted triphenylenes, using 2,4,7-trinitrofluorenone (TNF) as electron acceptor are discussed. A triphenylene monomer as well as its dimer and the corresponding main chain polymer were doped with TNF in a molar ratio of two parts disc/one part TNF to give charge transfer complexes.

2. Experimental part

The compounds studied are listed in the table. The syntheses of the substituted triphenylene compounds are described in [5, 15].

The molecular structure of 2,4,7-trinitrofluorenone (TNF) **1** and the substituted triphenylene compounds **2a**, **3a**, **4a**. Phase transitions temperatures as determined by DSC are also given.

Compound	m	M_n g/mol^{-1}	Transition temperatures/K	
2a			C 337	D_h 362 I
b				D_h 487 I
3a	0		g 325	D_h 420 I
b	0			D_h 473 I
4a	19	17000	g 323	D_h 455 I
b	19	17000†		D_H 453 I

† Value for the undoped polymer.

2.1. *2,4,7 trinitro-perdeutero-fluorenone (1)*

One gramme of perdeutero-fluorenone was added in portions to a stirred mixture of 30 ml of nitric acid (100 per cent) and 10 ml of sulphuric acid (100 per cent) at 273 K. The mixture was warmed to room temperature and stirred overnight. After pouring on ice (200 g) the solid was collected by filtration and dried under reduced pressure. The product was purified by column chromatography (silica gel, hexane/ethylacetate 1/3) giving 1·4 g (yield: 80 per cent) of (1). ^{1}H NMR shows the deuteriation to be 90 per cent.

2.2. *Charge transfer complexes (general procedure)*

A solution of the electron acceptor TNF (1) in dichloromethane (10 mg/ml) was added to a solution of the triphenylene compound (electron donator) in dichloromethane (10 mg/ml) with rapid stirring. The solvent was evaporated and the dark coloured residue was dried under reduced pressure at 353 K for 3 days. Samples of two parts triphenylene disc per molecule (1) were prepared.

For ^{2}H NMR measurements selectively deuteriated triphenylene compounds (ring d_6-, 1,1-d_2- or 3,3-d_2-heptyloxygroups) were prepared [16, 17].

2.3. *Characterization*

All samples were characterized by optical microscopy, DSC and ^{1}H NMR. The molecular weight estimations of the polycondensates are based on GPC with polystyrene as a reference and on ^{1}H NMR end group determination. The ^{2}H NMR spectra were recorded on a Bruker CXP 300 spectrometer via the solid echo technique. The delay time τ between the two pulses was 30 μs. Typically 1000 transients were recorded. Transition temperatures and transition enthalpies were measured on a Mettler DSC 30 with a heating rate of 5 K/min. The textures were studied using a Zeiss Axiophot microscope equipped with a Linkam TMS 90 hot stage. Thin samples were examined between two untreated cover slips.

3. Results and discussion

3.1. *Differential scanning calorimetry*

The thermal data of the compounds studied are presented in the table. For reader convenience the data for the undoped triphenylene compounds are also given. In all cases charge transfer complexes with a molar ratio of two part triphenylene disc/one part TNF **1** were studied. For the undoped pure heptyloxy substituted triphenylenes a pronounced dependence of the clearing temperature T_i on the molecular weight was found [15]. T_i increases from 362 K for the hexaheptyloxy substituted monomer **2a** to 420 K for the dimer **3a** and reaches a plateau value of about 455 K for the polymer **4a**. Doping these compounds with TNF increases T_i substantially for the monomer and the dimer. In fact the dependence of T_i on the molecular weight is reversed. For the 2 : 1 charge transfer complex **2b** prepared from the hexaheptyloxy substituted triphenylene **2a** and TNF, T_i is found to be 487 K. The corresponding doped triphenylene dimer **3b** has T_i of 473 K and for the doped polymer **4b** T_i is observed to be 453 K. This means an increase in T_i for the charge transfer complexes compared to the undoped compounds of 125 K for the triphenylene monomer **2**, of 53 K for the dimer **3** and no increase for the polymer **4** [13, 14].

The values of the specific phase transition enthalpies, ΔH_i, and of the transition entropies per mole disc unit, $\Delta S_{m,disc}$, for the transition from the discotic mesophase to the isotropic phase as detected by DSC are very small compared with the corresponding enthalpies of the pure triphenylenes. While for the undoped triphenylenes **2a**, **3a**, **4a** ΔH_i ranges from 5·5 J/g up to 8 J/g ($\Delta S_{m,disc}$ from 14·1 to 19·9 J/mol disc) [14], for the doped systems **2b**, **3b**, **4b** values of only $\Delta H_i < 0{\cdot}2$ J/g ($\Delta S_{m,disc} < 0{\cdot}7$ J/mol disc) are observed. DSC measurements were performed in a temperature range from 223 K up to 523 K. Neither for the doped samples of the dimer **3b**, nor of the polymer **4b** were glass transitions detected.

3.2. *Optical microscopy*

In figure 1 the mesophase textures of the doped samples of the monomer **2b** (*a*), the dimer **3b** (*b*) and the polymer **4b** (*c*) are shown. The textures were obtained by heating the sample to the isotropic phase and subsequent cooling below T_i with cooling rates as low as 0·2 K/min. The doped monomer **2b** (see figure 1 (*a*)) exhibits mesophase textures typical of highly ordered columnar mesophases [2]. Upon slow

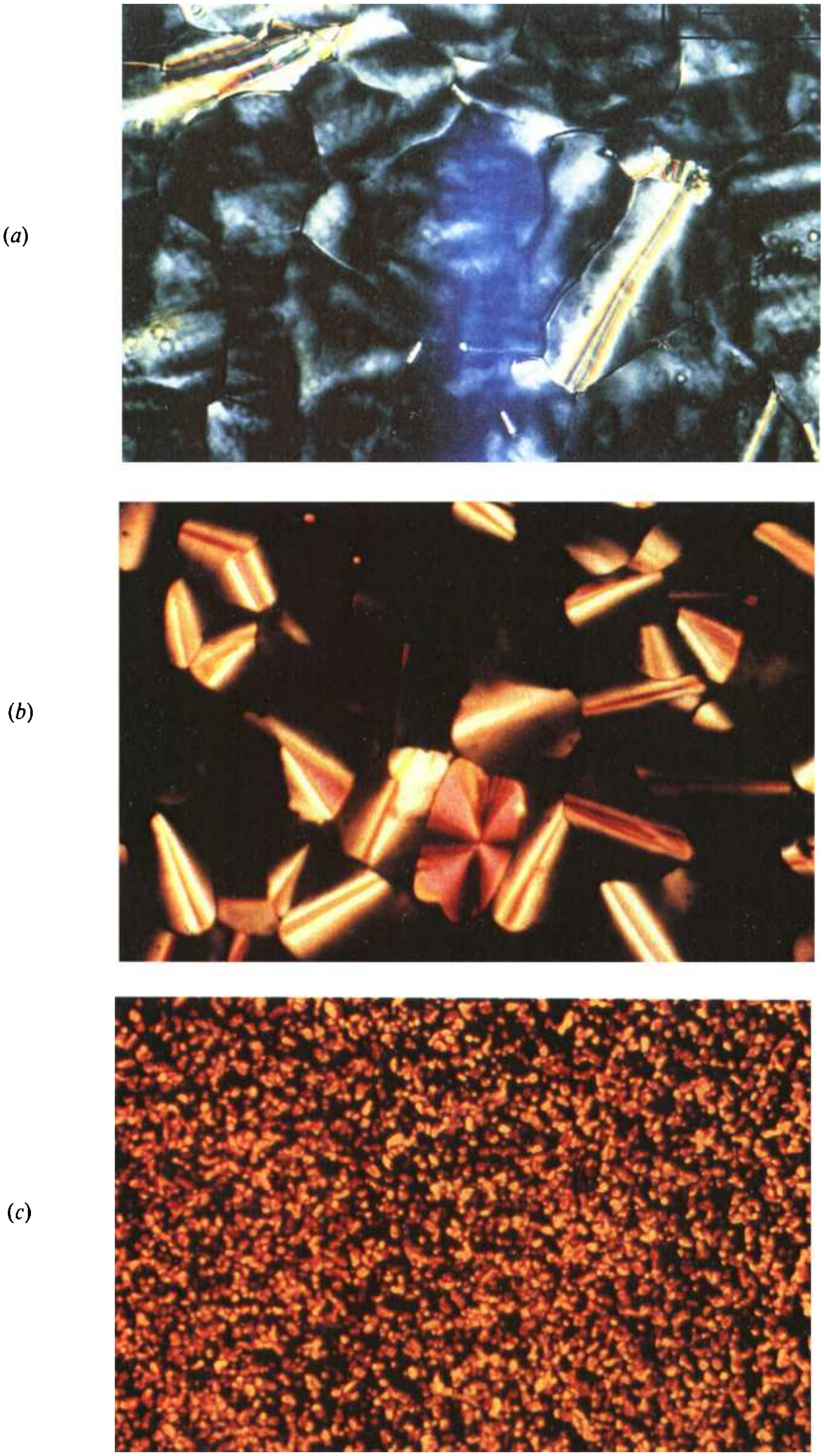


Figure 1. Optical textures for the mesophases of the doped monomer **2b**, the doped dimer **3b** and the doped polymer **4b**. The magnification is the same in all three cases.

cooling from the isotropic liquid phase, defect axes appear and then grow spherolitic like contours, almost not birefringent, thus indicating homeotropic alignment of the columns perpendicular to the cover slips of the sample. Shearing of such an aligned sample in the mesophase results in a very pronounced increase of the birefringence. The size of the contours is dependent on the cooling rate. A lower cooling rate results in larger optical structures. The doped dimer **3b** (see figure 1 (*b*)) exhibits a texture similar to that of the doped monomer **2b** with smaller contours. For the polymer charge transfer complex **4b** textures with extremely small domain areas are observed, but still homeotropic aligned areas with almost no birefringence occur (see figure 1 (*c*)).

3.3. *Columnar packing*

Doping the alkoxylated triphenylene compounds results in the formation of charge transfer complexes. This is indicated by their almost black colour compared to the white colour of the pure triphenylenes. The optical textures show that the columnar mesophase packing of the discs in the triphenylene materials is not destroyed by adding TNF. The large increase of the clearing temperature T_1 on doping the monomer **2a** and the dimer **3a** even leads to the conclusion that the columnar structure is stabilized by adding the electron acceptor [13, 14]. A crucial point is to know where the electron acceptor molecules are located. From X-ray measurements it seems that the TNF molecules can be incorporated into the discotic columnar structure or not, depending on the length of the spacer interlinking the main chain discs [13].

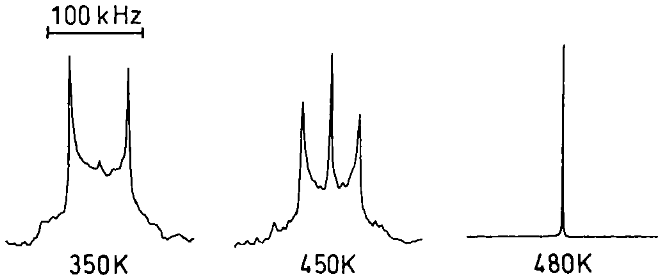


Figure 2. ^{2}H NMR spectra of the dimer **3b**, doped with perdeuteriated TNF at 350 K (left), at 450 K (middle) and at 480 K (right).

^{2}H NMR measurements on charge transfer complexes with perdeuteriated TNF as electron acceptor allow us to prove whether the TNF is incorporated into the columns and in what amount. TNF located in the columns has a reduced mobility caused by the restriction to planar motions, while TNF located outside of the columns can undergo isotropic motions. The spectrum of TNF incorporated into the columns of an unaligned sample is, therefore, expected to be a Pake diagram type pattern reduced in width by a factor of two, due to the planar motions within the columns [20–22], while TNF molecules outside the columns should give a narrow line, due to the isotropic motions. If both cases occur simultaneously the resulting spectrum will be a superposition of broad and narrow components. In figure 2 three spectra for the doped dimer **3b** are shown, at 350 K only a broad Pake pattern, at 450 K well below T_1 a superposition of broad and narrow components and at 480 K (above T_1) a narrow line are observed. This demonstrates that indeed at lower temperatures all TNF molecules are incorporated into columns, while for higher temperatures but still well below T_i isotropic distributed TNF molecules also exist.

In order to quantify the amount of TNF outside the columns figure 3 shows the amount N (in per cent), determined from integral intensities of the two components, of the sharp spectral component due to TNF molecules moving isotropically as a function of temperature for the doped samples of the monomer **2b**, the dimer **3b** and the polymer **4b**. In the monomer **2b** first isotropic parts (> 1 per cent) appear at 475 K (12 K below T_i), in the dimer **3b** at 430 K (43 K below T_i) and in the polymer **4b** already at 360 K, i.e. 93 K below T_i. On approaching T_i the amount of isotropically moving TNF not located in columns increased, above T_i only isotropic TNF was observed.

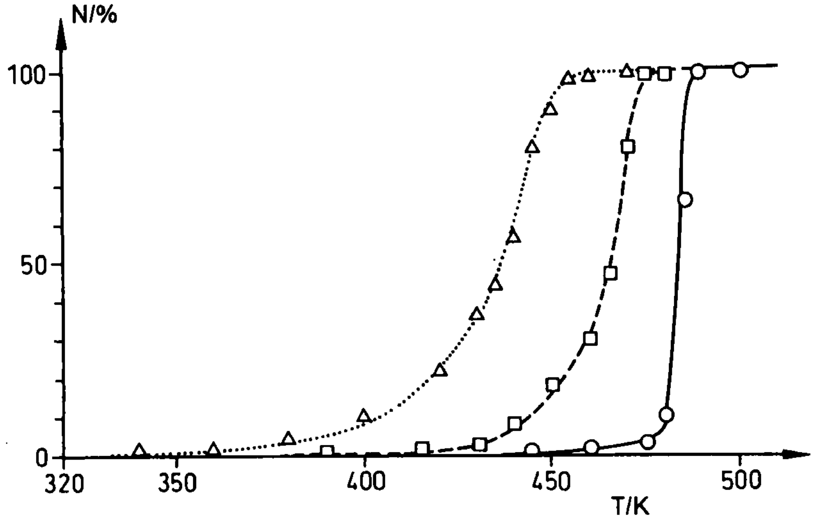


Figure 3. The amount N (in per cent) of TNF not incorporated into the columns for the doped samples of the monomer **2b** (○), the dimer **3b** (□) and the polymer **4** (△) as a function of the temperature.

It is important to know whether this increase of the isotropic fraction as a function of the temperature below T_i means a continuously increasing destruction of the columnar structure of the sample resulting in a biphasic system, or whether an increasing fraction of TNF is expelled from the columns only, ending up in the space between the columns without destroying the columnar structure of the mesophase. As reported in a previous paper [16] the phase transition even for an undoped main chain polycondensate based on heptyloxysubstituted triphenylenes **4a** shows a pronounced pretransitional behaviour occurring within a temperature range of about 30 K, where parts incorporated into the columnar structure and isotropic parts coexist. X-ray measurements and electron microscopy [9] in this temperature range indicate a decrease in the order of the columnar packing rather than biphasic behaviour with separated phases. In order to demonstrate the effect on the columnar structure by doping with TNF figure 4 shows the amount N of the isotropic part (in per cent) of triphenylene main chain discs as a function of temperature, determined by an spectral analysis of ^2H NMR data analogous to that for the TNF dopant molecules described previously.

For the sample **4b** labelled in the side groups the first isotropic parts (> 1 per cent) of the discotic polymer are detected about 35 K below T_i (very similar to the undoped

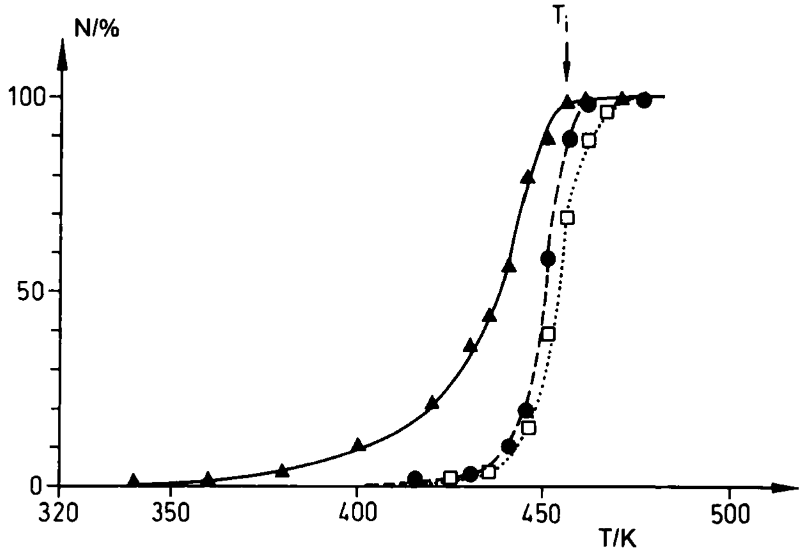


Figure 4. Isotropic parts of polymer **4a** (□) and doped polymers **4b** as a function of temperature (●) show the behaviour of the discs in a sample **4b** with heptyloxy side groups deuteriated in the 1-position, (▲) show the behaviour of TNF electron acceptor in a sample with perdeuteriated TNF.

polymer **4a**) compared with 90 K below T_i for the TNF of the corresponding sample with perdeuteriated TNF. The situation for the dimer **3b** is analogous; first the isotropic parts in the doped dimer **3b**, selectively deuteriated in the 1-position of the heptyloxy side groups were observed 15 K below T_i compared with 50 K below T_i for the sample with perdeuteriated TNF. We conclude therefore that the amount of TNF located in the columns of the doped dimer **3b** and polymer **4b** decreases with increasing temperature, while simultaneously the amount of TNF isotropically located in the space between the columns increases, without causing a continuous destruction of the columnar structure. In agreement with this the textures observed under a polarization microscope did not show biphasic behaviour in the mesophase. It has to be noted that for charge transfer complexes with a molar ratio of one part disc/one part TNF biphasic behaviour is detected on approaching T_i [13].

3.4. *Alignment of the columns and motions of the triphenylene cores*

All compounds studied in these ^{2}H NMR measurements did align in the magnetic field of the spectrometer. This not only proves their liquid crystallinity, but we can also take advantage of this in order to study the motional processes in the charge transfer complexes. To achieve aligned materials the samples were heated up above T_i and subsequently slowly cooled into the discotic liquid-crystalline phase. This results in aligned samples, where the directors of the columns lie in a plane perpendicular to the magnetic field [9, 15]. This alignment can be generated in the doped monomer **2b** as well as in the doped dimer **3b** and polymer **4b**. In the mesophase itself the alignment of the columns is no longer affected by the 7 T magnetic field on the experimental time scale of several hours. Therefore by a goniometer within the probe we can subsequently rotate the sample around an axis perpendicular to the magnetic field, $\mathbf{B}_0$, such that $\mathbf{B}_0$ can form any angle β_0 with the normal to the planar distribution.

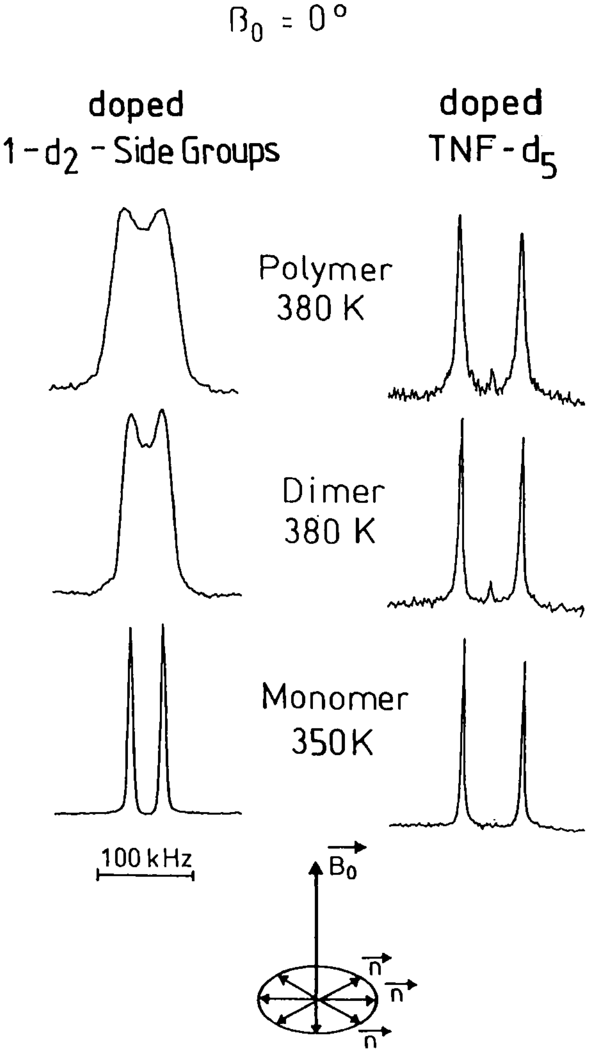


Figure 5. ^{2}H NMR spectra of the aligned doped systems. Left hand column: charge transfer complexes of the monomer **2b**, dimer **3b** and polymer **4b**, all deuteriated in the 1-position of the side groups of the triphenylene core. Right hand column: charge transfer complexes of the monomer **2b**, dimer **3b** and polymer **4b**, all with perdeuteriated TNF as electron acceptor.

For the doped samples of the monomer **2b**, the dimer **3b** and the polymer **4b**, all deuteriated in the 1-position of the heptyloxy side groups, a series of orientation dependent spectra ($\beta_0 = 0°$ and $\beta_0 = 90°$) was found, analogous to the series for the undoped compounds **2a, 3a, 4a** reported elsewhere [16]. In figure 5, left hand column, the spectra for a planar distribution perpendicular to $\mathbf{B}_0$ ($\beta_0 = 0°$) are shown. The significantly different spectra indicate different mobilities for the monomer **2b**, the dimer **3b** and polymer **4b**. For the monomer **2b** free rotation of the discs around the column axis results in averaging the electric field gradient of the C–^{2}H bonds to an axially symmetric tensor with the unique direction parallel to the column director. Consequently the averaged electric field tensors mirror the planar distribution of the column directors. This results in a spectrum of only two single lines when the magnetic field $\mathbf{B}_0$ is perpendicular to the director distribution ($\beta_0 = 0°$). After 90° rotation of this planar distribution around the sample axis a state is observed, where $\mathbf{B}_0$ lies in the plane of the planar distribution ($\beta_0 = 90°$), all angles from 0° to 90° between the unique axes of the averaged tensors occur, resulting in a broad spectrum with four singularities [8, 16, 20–22]. In the charge transfer complexes of the dimer **3b** and the polymer **4b** this free rotation of the triphenylene cores around the column axis is quenched due to the interlinking of the columns by the spacer (**3b**) or the polymer chain (**4b**). These results are analogous to the motional behaviour of the undoped compounds.

3.5. *Motion of the TNF molecules*

In figure 6 spectra of the aligned monomer **2a** and the corresponding monomer **2b** doped with perdeuteriated TNF are shown. Here the two singularities for the $\beta_0 = 0°$ position and the broad spectrum of a planar distribution with four singularities for the $\beta_0 = 90°$ rotation position are observed, indicating free rotation of the TNF

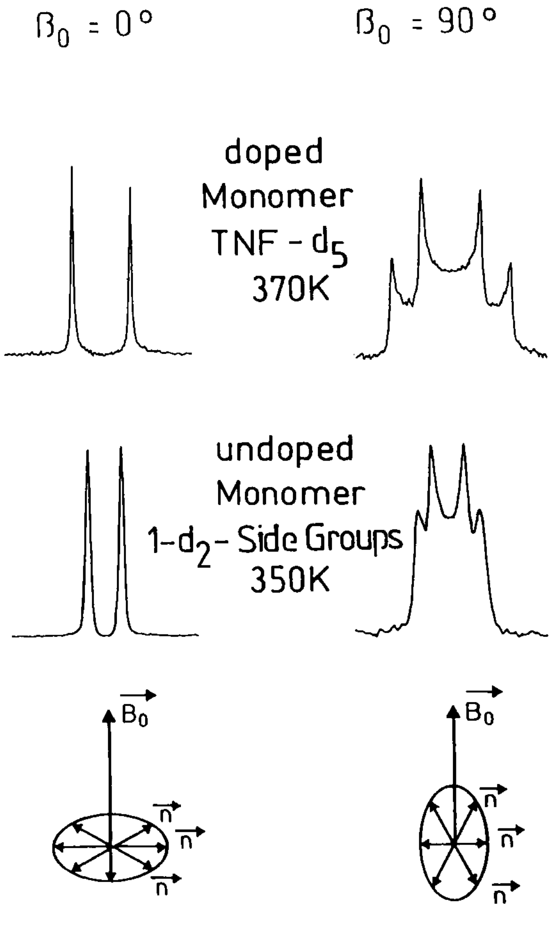
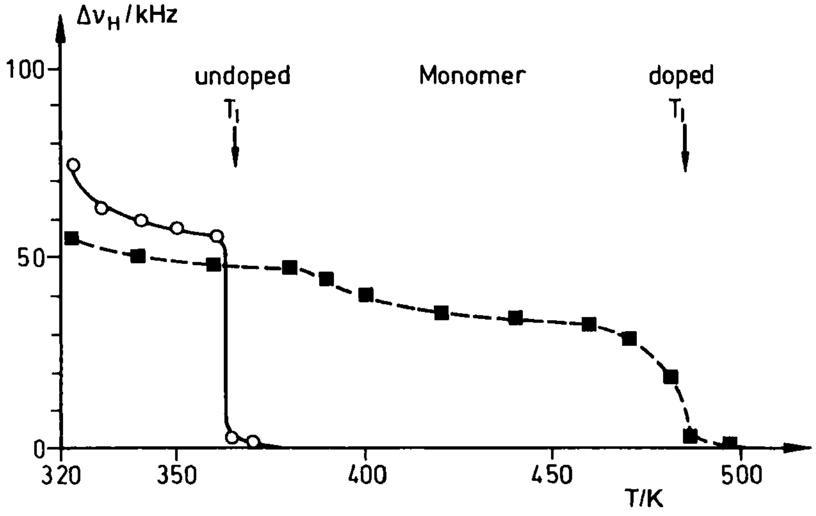


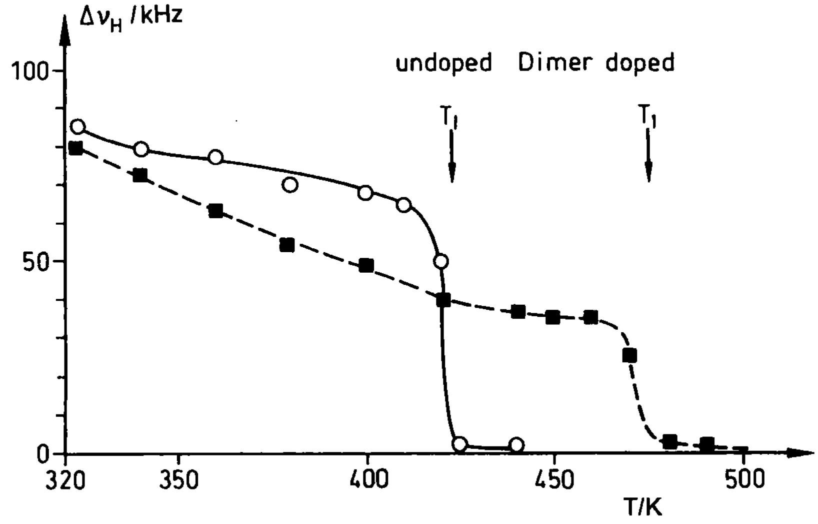
Figure 6. ^{2}H NMR spectra of the aligned doped monomer **2b** (upper row), with perdeuteriated TNF, and the aligned undoped monomer **2a**, deuteriated in the 1-position of the heptyloxy side groups (down row). Left: planar alignment of the columns perpendicular to the magnetic field $\mathbf{B}_0$. Right: planar alignment with the magnetic field $\mathbf{B}_0$ in plane, β_0 denotes the angle between the macroscopic order axis and $\mathbf{B}_0$.

molecule around the column axis. This proves beyond any doubt that the TNF molecules are incorporated into the columns. The same spectra are obtained for the corresponding samples of the dimer **3b** and the polymer **4b** (see figure 4, right hand column). Free rotation of the TNF molecules takes place even in the dimer and the polymer, where neighbouring columns are interlinked, preventing free rotation of the triphenylene discs [15, 16].

In contrast to that in a mixture of the monomer **2a** and the polymer **4a** free rotation of the monomer disc is quenched, caused by steric effects of the side group/spacer system of the main chain polymer [16]. Apparently the TNF molecule centred in the ring system of neighbouring triphenylene discs in the columns is small enough to avoid steric interference with the side groups or the spacer of the triphenylene dimer or polymer. Also the charge transfer interaction between the triphenylene core and



(*a*)



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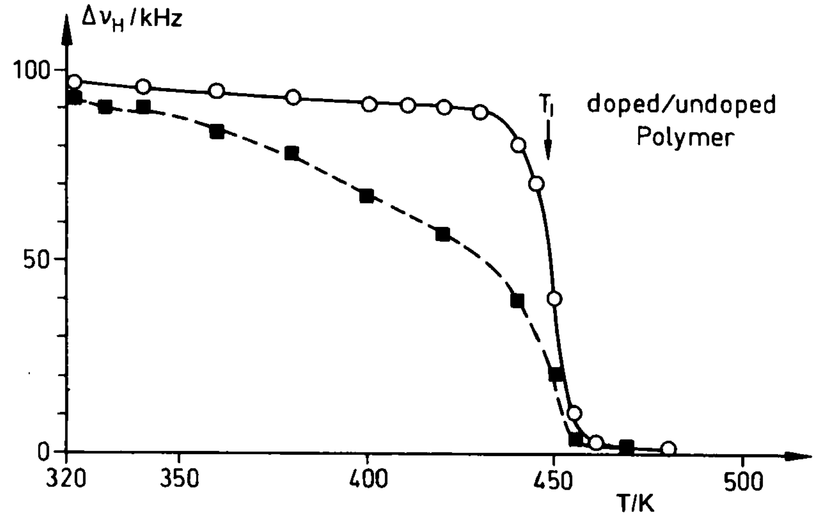


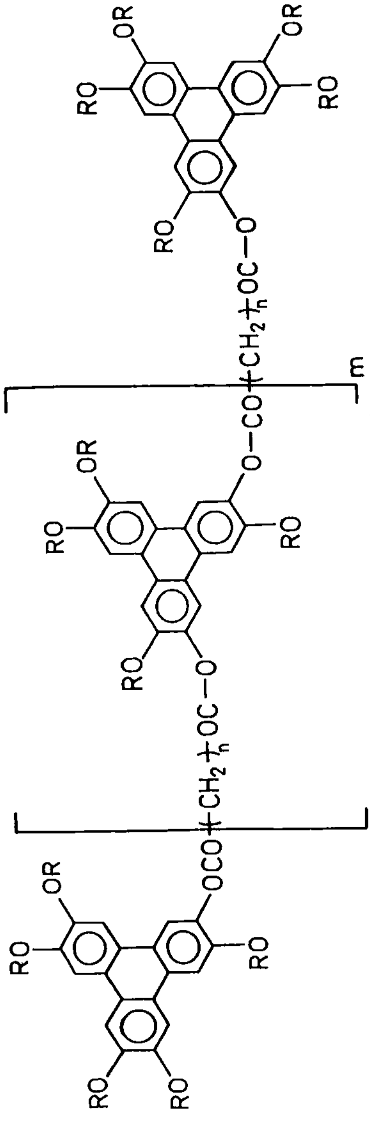
(*c*)

Figure 7. Plots of the ^{2}H NMR spectral width at half height as a function of temperature: (*a*) for the triphenylene monomer **2a** and the doped monomer **2b**, (*b*) for the triphenylene dimer **3a** and the doped dimer **3b**, (*c*) for the polymer **4a** and the doped polymer **4b**. (○) indicate the behaviour for the pure triphenylene compounds, (■) indicate the behaviour of the doped materials. The clearing temperatures T_l for the doped and undoped systems are indicated by arrows.

TNF is not strong enough to couple disc-motion and TNF-motion to such an extent that rotation of the TNF molecule around the column axis is prevented. A finite hindrance of the TNF motion due to restricted mobility of the discotic matrix does, however, exist. It is illustrated by the different temperatures, where the rotation freezes in on the timescale defined by ^{2}H NMR lineshapes observed for the monomer **2b**, dimer **3b** and polymer **4b**. Free rotation of the TNF molecule in sample **2b** freezes in at temperatures as low as 240 K. In the doped dimer **3b** and polymer **4b**, however, at much higher temperatures: 320 K and 360 K, respectively. Moreover the rotation of the discotic monomer in the charge transfer complex freezes in at 240 K, also 80 K lower than in the undoped system. This indicates increased motional freedom of the discs in the doped systems.

3.6. *Side group mobility*

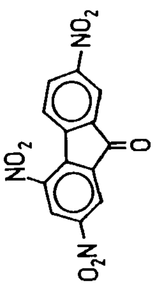
Increased motional freedom in the charge transfer complexes is also detected in the side groups of the discotics. The temperature at which local motions in the side groups are activated at a given frequency depends on the position of the methylene group. For the triphenylene compounds **2a**, **3a**, **4a** the onset of motional narrowing in the 1-position of the side groups takes place at 250 K. As expected, motional processes in the 3-position are activated already at a lower temperature (200 K) [16, 17]. The incorporation of the TNF molecules into the columns results in wider spacings between triphenylene discs within the columns [13, 14]. This should increase the free volume of the side groups, resulting in a higher side group mobility. In order to obtain a quantitative measure of the different mobilities for the doped and the undoped systems figure 7 shows the ^{2}H NMR spectra width at half height in the mesophase as



3a,4a

$R = -(CH_2)_6-CH_3$

$n = 14$



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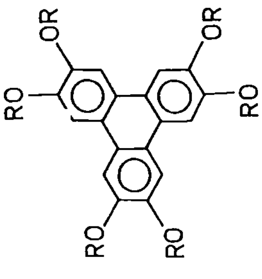

2a

a function of temperature. All samples were deuteriated in the 1-position of the heptyloxy side groups. The width at half height, first of all, drops to essentially zero at the phase transition from the discotic phase to the isotropic phase. This transition temperature (T_1) is substantially higher for the doped dimer and the doped dimer compared with the undoped systems (see the table). Figure 7 (*a*) shows the curves for the hexaheptyloxy triphenylene monomer **2a** and the doped monomer **2b**. In figure 7 (*b*) the curves for the corresponding dimer samples **3a**, **3b** and in figure 7 (*c*) for the polymer samples **4a**, **4b** are given. In the discotic mesophase the spectral width in the doped systems is significantly reduced, compared with that of the undoped samples.

Analogous behaviour is found by comparing the width at half height of compounds having heptyloxy side groups deuteriated in the 3-position. Again the width at half height is reduced in the doped materials, proving that the enlarged disc-to-disc distance in the doped materials results indeed in a higher side group mobility. The analysis of the ^{2}H NMR spectral width at half height of a doped monomer **2b**, and an undoped monomer **2a**, both deuteriated in the ring position of the triphenylene discs shows, however, that for the triphenylene cores in the columns no additional spectral narrowing is observed by adding TNF.

For possible applications more studies on these doped triphenylene materials, in terms of the molecular packing and the degree of order than can be generated by alignment in the magnetic field and by additional mechanical forces, are currently underway.

We would like to thank H. Zimmermann, MPI für Medizinische Forschung, Heidelberg, for his help in the deuteriation of TNF. This work was supported by Deutsche Forschungsgemeinschaft (SFB 262), which is gratefully acknowledged.

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