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Molecular dynamics of discotic charge-transfer complexes, dielectric spectroscopy and ^2H NMR studies

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Using a combination of solid state ^2H NMR spectroscopy on selectively deuteriated samples and dielectric spectroscopy, the molecular dynamics of discotic charge-transfer (CT) complexes were investigated. These complexes show particular thermodynamic and flow properties. Considered were mixtures of low molar mass donors and acceptors, low molar mass donors with main chain acceptor polymers and covalently linked donor–acceptor twins with different lengths of the spacer. A main result is that correlated rotational motions of discotic molecules or groups about the columnar axis are observed in all systems except for the twin with the short spacer. This type of motion seems to be a general feature of columnar phases. The non-discotic acceptor which is incorporated in the columns participates in this motion. The twin possessing a long spacer displays at high temperatures an additional process: it performs a diffusion process between the columns. A further result is that broad biphasic regions exist in CT mixtures at the transition from the discotic to the isotropic state.

1. Introduction

The molecular dynamics of columnar mesophases are expected to display some unique features due to the generally high intercolumnar and intracolumnar order. It is for this reason that we have performed detailed investigations of the dynamics of such systems. Our aim in particular was the study of charge-transfer systems; they are characterized by particular structural and thermodynamical properties discussed below.

The materials under investigation consist of discotic molecules based on triphenylene with several laterally fixed, flexible alkoxy side chains. Mixtures of electron-rich donor molecules, like derivatives of triphenylene, with electron acceptor molecules, such as for example 2,4,7-trinitro-9-fluorenone (TNF), give rise to charge-transfer (CT) interactions. It was shown earlier that this interaction often leads

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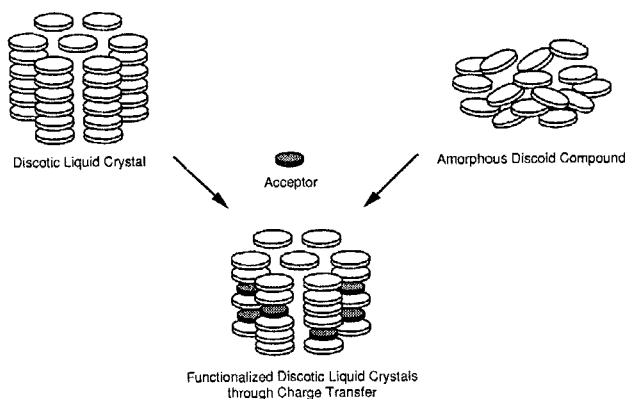


Figure 1. Structure formation on doping with an electron acceptor (schematic drawing).

to a broadening of the columnar phase range exhibited and that it may induce columnar phases in previously nematic discotic systems or even in amorphous systems comprised of disc-like molecules [1–3]. Previous X-ray and solid state NMR studies showed that the non-discotic electron acceptor molecules are mostly incorporated into the columns—see figure 1. Whereas the strong CT-stabilization effect on the columnar phase has been well established, the origins of particular properties such as reduced viscosity combined with elevated clearing temperature still remain unknown. In fact, as will be shown in this contribution, many of these properties can be tracked back to the molecular dynamics of such systems.

Dielectric spectroscopy is one of the techniques employed for investigations of the molecular dynamics of liquid crystals [4–10]. Often the dynamical process can only be investigated indirectly by comparative studies of various compounds or by a detailed analysis of oriented samples [10].

We would like to present an approach whereby molecular reorientational processes are also probed by solid state ^2H NMR spectroscopy on selectively deuteriated samples. As has been shown before, this method allows a detailed description of the motional geometry by NMR techniques coupled with the complementary detailed frequency information given by dielectric spectroscopy [1, 4, 5, 11].

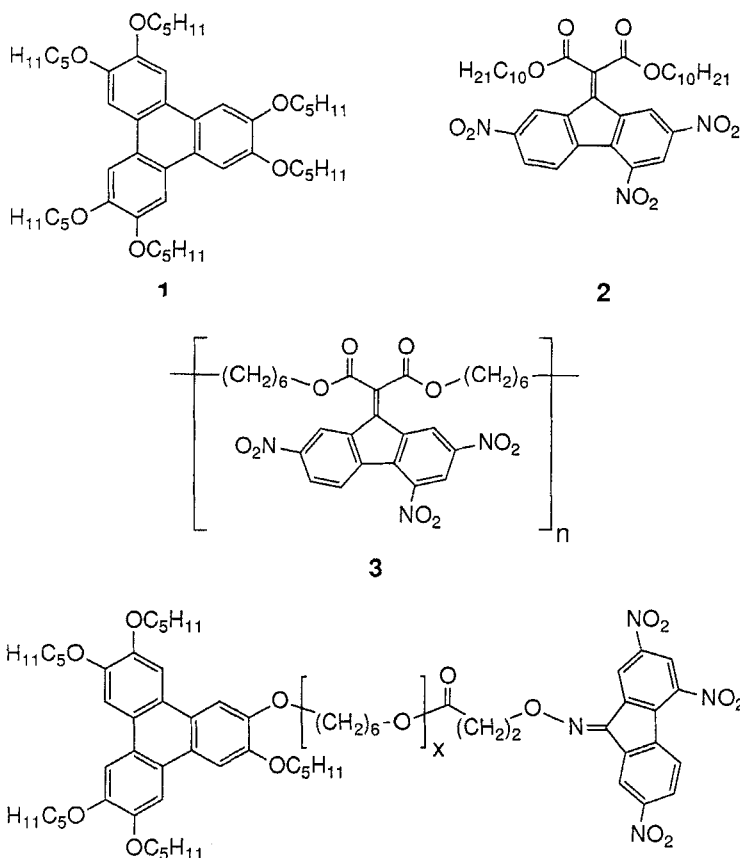
In this paper the results of studies on a mixture of low molar mass hexakis(pentoxo)triphenylene **1** [12] and a TNF-derivative with long aliphatic chains **2** [13], on a mixture of hexakis(pentoxo)triphenylene and an acceptor main chain polymer **3** [3] and on two covalently linked donor–acceptor–twin molecules **4**, **5** with different lengths to the coupling spacer [14] are presented.

For ^2H NMR investigations, all systems were selectively deuteriated in the aromatic position either of the donor or the acceptor.

2. Experimental

2.1. Synthesis

The compounds investigated (see scheme) were synthesized as described in the literature: 2,3,6,7,10,11-hexakis(pentoxo)triphenylene **1** [12], 2-(2,4,7-trinitrofluoren-9-ylidene)malonic acid didecyl-ester **2** [13], acceptor main-chain polymer **3** (GPC(CHCl_3 , polystyrene) $M_n = 4000 \text{ g mol}^{-1}$, $M_w = 8750 \text{ g mol}^{-1}$) [3], 3-(2,4,7-trinitrofluoren-9-ylideneamino-oxy)propanoic acid (3,6,7,10,11-pentakis(pentoxo)oxy-



4 $x = 1$
5 $x = 0$

Scheme

triphenylene-2-yloxyhexyl ester) **4** [14] and 3,(2,4,7-trinitrofluorene-9-ylidene-aminoxy)propanoic acid (3,6,7,10,11-pentakis(pentyloxy)triphenylene-2-yl hexyl ester **5** [14].

The deuteriated starting materials were obtained by known procedures [15]. Triphenylene moieties were deuteriated by recrystallization from deuteriated trifluoroacetic acid (Aldrich 99 per cent). The precursor for all deuteriated acceptor derivatives was deuteriated fluorene which can be obtained by treatment with dilute $\text{DC1/D}_2\text{O}$ under high pressure (tantalum vessel) and at high temperature (-200°C). Deuteriated trinitrofluorenone and its derivatives were synthesized according to [15].

The mixtures of **1** with **2** and **3**, respectively in the molar ratio 2:1 (donor: acceptor) were made by combining two solutions of each compound in tetrahydrofuran. After evaporating the solvent, the brown solids were dried in vacuum at 60°C .

2.2. Physical measurements

The optical textures were analysed with a Leitz Orthoplan polarizing microscope equipped with a Mettler FP82 hot stage. Investigations of the phase behaviour were performed with a Perkin-Elmer DSC 4. The usual heating rate was 20 K min^{-1} . A

computer controlled Hewlett–Packard impedance analyser HP 4192A was used for dielectric investigations in the frequency range from 1 kHz to 1 MHz. The impedance analyser has a resolution in $\tan \delta (= \epsilon''/\epsilon')$ of 10^{-3} . The experiments were performed in the temperature range 100 K to 450 K with a stability of ± 0.5 K. The samples were mounted between two aluminium plates with an area of 240 mm^2 , and a separation of $50 \mu\text{m}$ was maintained by a Capton foil.

NMR investigations were performed using a Bruker CXP 300 spectrometer with a 7 T superconducting magnet and a deuteron Larmor frequency of 46.07 MHz. The home-built probe could be temperature controlled over the range 190 K–460 K with an accuracy of ± 1 K. Measurements at higher temperatures were performed using a water-coolable probe designed by G. Scheeler [16]. The quadrupolar echo sequence was used for the recording of spectra with a typical 90° -pulse length of 2.7 ms. Pulse train repetition lengths were between 0.2 and 4 s, and 400 up to 8000 spectra were accumulated depending on the filling factor.

3. Results and discussion

First the phase behaviour of the mixtures and compounds investigated is discussed. Transition temperatures of components 1–5 are summarized in the table. All systems form a columnar discotic liquid crystalline phase. In mixtures 1/2 and 1/3 broad biphasic regions were observed. Up to now, this behaviour at the transition from the discotic to the isotropic phase has only been mentioned once for mixtures of TNF with discotic dimers and polymers [1]. However it seems to be a general feature for mixtures of discotic donors with acceptor molecules and can be observed by optical polarizing microscopy as well as in DSC studies where broad transition peaks occur. Further evidence for the existence of biphasic regions will be presented later in the discussion of the ^2H NMR experiments. In contrast to the mixture, the donor–acceptor twins 4 and 5 have very high clearing temperatures; without any biphasic regions. However, the studies at very high temperatures were limited because of the onset of partial thermal degradation around 470 K [14].

3.1. Mixture of low molar mass donor 1 and acceptor 2 with long alkyl chains

For the mixture 1/2, which exhibits a hexagonal ordered columnar mesophase, two relaxational processes were observed in the dielectric studies (see figure 2). The results of the dielectric studies are summarized in figure 3. The low temperature process shows Arrhenius behaviour with an activation energy $E_a = 26 \pm 2 \text{ kJ mol}^{-1}$. This process is attributed to side chain librations, as observed in a neat sample of 1 [17]. The high temperature process, the so called α -process, shows non-Arrhenius behaviour. This process is related to the dynamic glass transition process and the temperature

Thermodynamic data for the compounds studied.

Compound	Transitional temperatures/K
1	C 344 D _{ho} 394 I
3	g 301 i
4	LC† 538 I
5	g 287 LC† 515 I

† Orthorhombic structure see [14].

dependence of the relaxation time was thus analysed by the empirical Williams-Landel-Ferry function (WLF) [18]

$$\log \frac{\tau}{\tau_0} = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \quad (1)$$

Here C_1 and C_2 are constants and τ_0 corresponds to the correlation time at T_g . The parameters have the values $C_1 = 11$; $C_2 = 98$ K; $\log \tau_0 = 0.5$. These values are not very

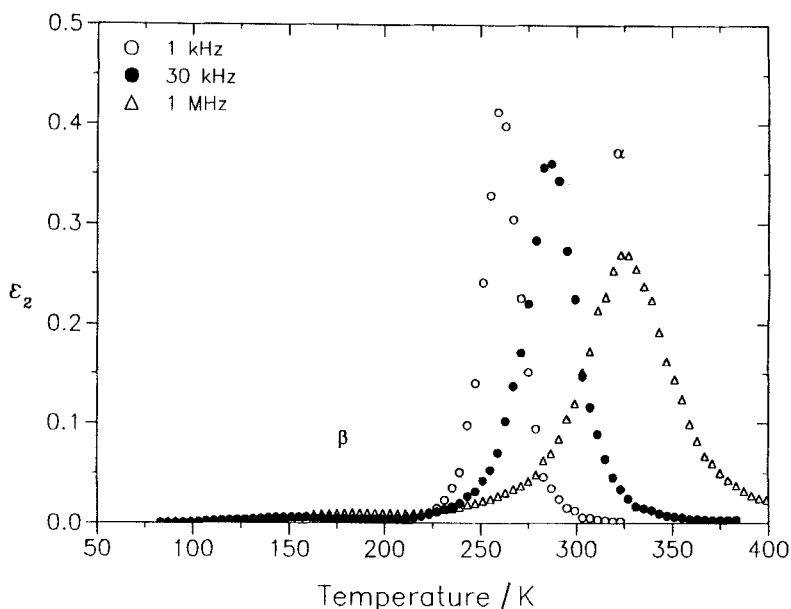


Figure 2. Dielectric results (ϵ_2) obtained for the mixture 1/2 at different frequencies.

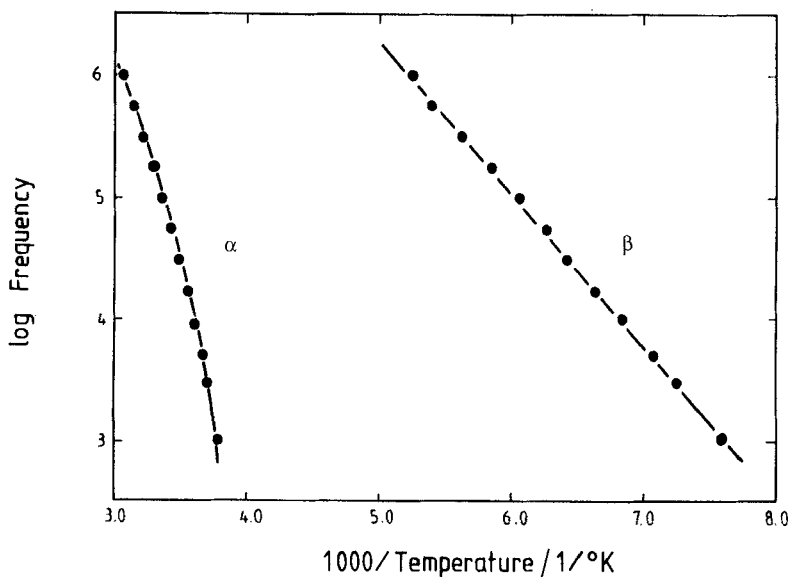


Figure 3. Activation diagram obtained for the mixture 1/2.

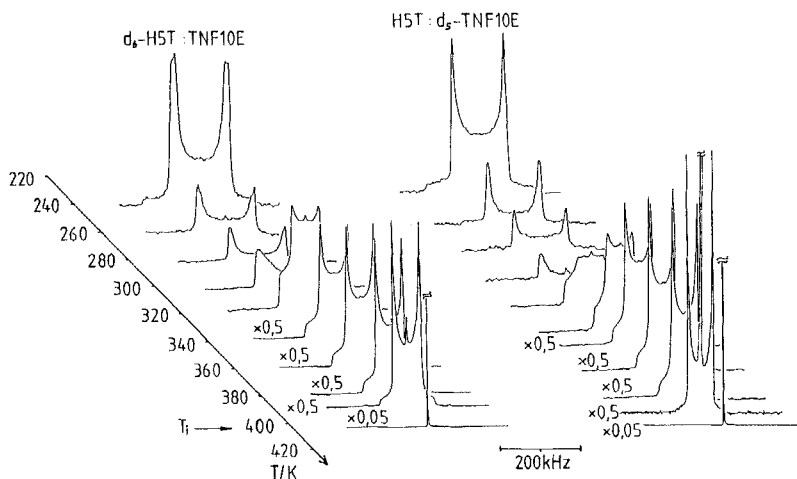


Figure 4. Solid state ^2H NMR spectra of the mixture **1/2** (donor or acceptor deuteriated in the aromatic core).

precise, as the result of instrumental limitations to low frequencies. In a heat discotic liquid crystal which exhibits a D_{h0} phase with a glass transition temperature of 228 K and a clearing temperature of 455 K, the WLF parameters have the values $C_1 = 9.7$, $C_2 = 61$ K and $\log \tau_0 = 1.0$ —values which are quite comparable except for C_2 [4]. The value of $1/C_1C_2$ is related to the thermal expansion factor of the free volume according to the theory of Vogel, Fulcher and Tamam [19]. The higher C_2 reflects the stabilization effect by the CT interaction. On the other hand, the resonance frequencies of the high temperature process in the CT mixture at equal temperatures are considerably higher than in the neat columnar phase—by a factor 3 to 5 [4, 5]. In addition, the activation energy of the β -process in the CT mixture is significantly diminished compared to that for the neat columnar phase, for which it amounts to 33 ± 2 kJ mol $^{-1}$ [17]. These two findings coincide directly with the observation that CT mixtures in general have lower flow viscosities than the neat discotic compounds. This property allows, for example, flow orientation by shearing [2, 14, 20]. In addition, the higher motional mobility of the flexible side chains close to the aromatic cores has been noted before in solid-state ^2H NMR experiments of CT mixtures where the discotic side chains were selectively deuteriated [1].

All these experimental results can be qualitatively explained by a general packing scheme for columnar phases and the anticipated packing problems leading to the frustration phenomena discussed by de Gennes [21]. The different packing densities of the aliphatic and aromatic regions of discotic molecules lead to packing problems: the aromatic moieties can pack closer than the aliphatic side chains. This frustration can be solved either by a tilt of the aromatic moieties or by a density modulation of the aromatic core packing along the column. The latter has indeed been observed recently by 2D exchange NMR on rufigallol mesogens [22]. In the case when the aromatic moieties are intercalated by acceptor molecules, the packing problem is solved or even inverted, because the central aromatic columnar region is expanded. Now the aliphatic side chains near the aromatic cores pack less densely, resulting in a higher mobility and lower activation energy, and ultimately in a lower flow viscosity.

The solid state ^2H NMR spectra of the mixtures **1/2** where either the donor or the

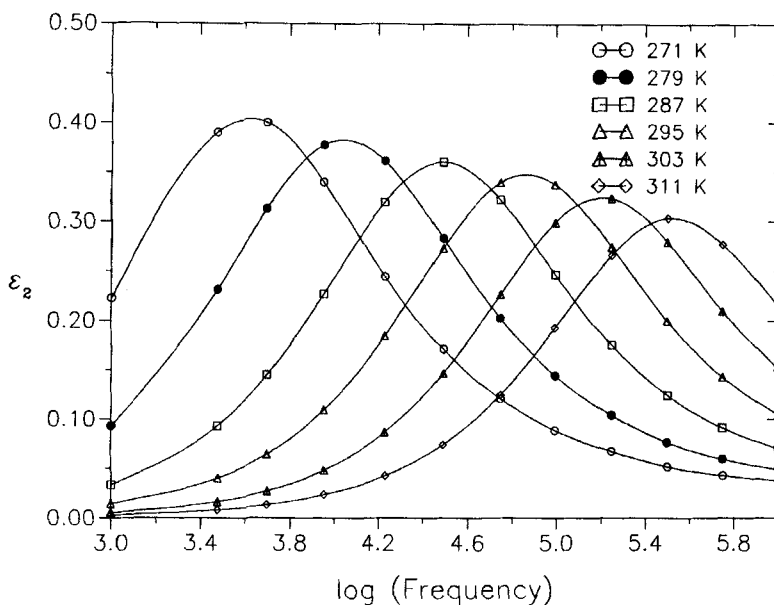


Figure 5. Fit of the dielectric data (ϵ_2) to the Havriliak–Negami function for the mixture 1/2.

acceptor was deuteriated in the aromatic core are displayed in figure 4. At a first glance, it is evident that the two components show nearly identical motional behaviour. This proves that the acceptor molecules are well-inserted into the columns and that the molecular motions of the donor and acceptor are strongly coupled. The spectra at higher temperatures in the mesophase are motionally narrowed by a factor of 2 which arises from the uniaxial motion of the molecules around the columnar axis [23]. From the time–temperature dependence of the spectral shapes, the correlation time of this rotational motion can be deduced by comparison with calculated spectra which were simulated on the basis of a simple three-fold jump model, as has been shown before [24]. This analysis proves the direct relation between the rotational motion and the high-temperature process found in the dielectric measurements. We can hence conclude that the strongly coupled donor and acceptor rotations in the columns converge into one process directly linked to the dynamic glass transition.

The relaxation time-spectra of the high temperature process were analysed with the Havriliak–Negami function [25], which describes the frequency dependence of the complex dielectric function (see figure 5)

$$\epsilon^* = \epsilon(\infty) + \frac{(\epsilon(0) - \epsilon(\infty))}{(1 + (i\omega\tau_0)^{1-\alpha})^\beta} \quad (2)$$

The values of the real part of ϵ^* at the low frequency and at the high frequency side of the relaxation are $\epsilon(0)$ and $\epsilon(\infty)$. τ_0 is the mean relaxation time. α and β are fitting parameters characterizing the symmetrical and the asymmetrical broadening of the process. Typical fitting parameters for the high temperature process are $\alpha = 0.05$; $\beta = 0.5$. Their temperature dependence is negligible. For a neat columnar phase, comparable values of $\alpha = 0.2$; $\beta = 0.6$ are found [5]. Therefore the relaxation time distribution is not significantly modified by the CT interactions.

At elevated temperatures, differences in the ^2H NMR spectra of donor and acceptor occur (see figure 6). Isotropic spectral components occur which have different

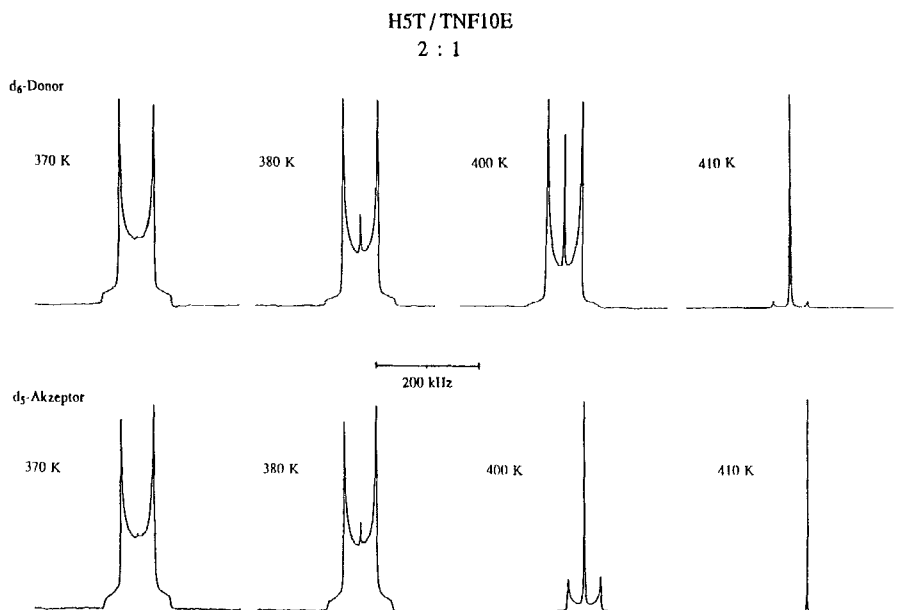


Figure 6. Temperature dependence of the ^2H NMR spectra for the donor and the acceptor.

intensities for the two components. We have already stated our observations of biphasic regions in which the columnar and the isotropic phases coexist which allow us to attribute the isotropic spectral lines to the coexisting isotropic phase. In a previous publication, the isotropic components were attributed to acceptor molecules being in the columnar phase, but not inserted in the columns; that is, they are located in the intercolumnar aliphatic region [1]. In this case, however, some residual quadrupolar splitting should be observable even in the 'isotropic' component due to the location in the anisotropic medium. We have never found this anisotropic contribution, which further corroborates our previous statement of the existence of a really biphasic regime. Furthermore, the isotropic contribution of the acceptor-deuteriated sample is greater at equal temperatures than that of the donor-deuteriated one. It follows that at the beginning of isotropization, the isotropic phase is enriched with acceptor molecules, and the greater part of the discotic donor component performs the transition into the isotropic phase only at higher temperatures in the biphasic region. No indication of a stable mixing ratio was found in this case. It follows that no dystecticum or any other kind of azeotropic feature exists in this investigated mixture and none was reported before for other similar systems. Why then are highly elevated clearing points observed for CT mixtures using pure TNF? For an explanation, the strong CT interaction which acts normal to the aromatic rings and so stabilizes the columnar structure has to be considered. We are dealing with a strongly interacting mixture where anisotropic aggregations are favoured. Since the highest clearing points are observed at mixing ratios 2:1 (donor:acceptor), a sandwich complex, with a TNF molecule intercalated between two triphenylenes, seems to be a particularly stable feature [26]. This biphasicity is certainly the origin of the easy orientability of the mixtures by either mechanical or magnetic forces. It probably contributes also to the observed low viscosities when compared with neat discotic compounds exhibiting columnar phases.

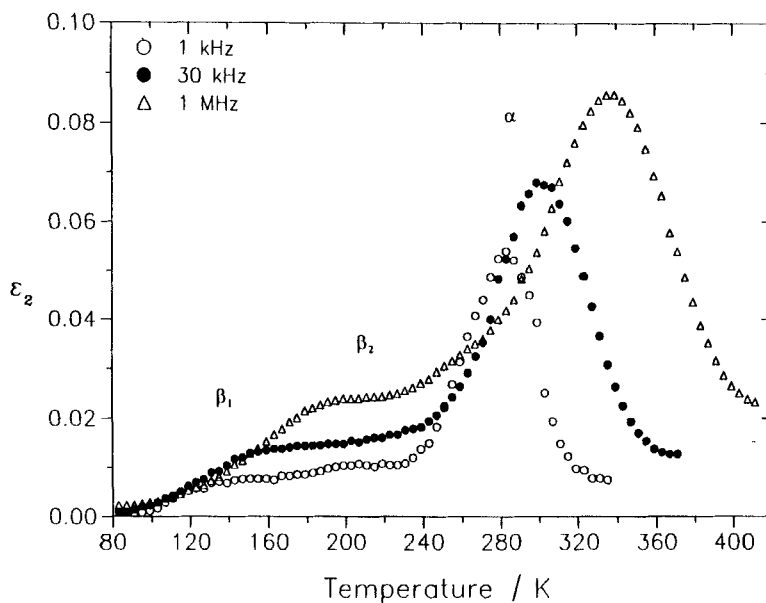


Figure 7. Dielectric relaxation (ϵ_2) data obtained for the mixture 1/3.

3.2. Mixture of low molar mass donor **1** and main chain acceptor polymer **3**

The mixture 1/3 consists of the discotic donor compound **1** and an amorphous polymer containing acceptor moieties of the TNF type **3**. Even in this combination, which is in contrast to many mixtures already investigated in which the acceptor always was a monomer, we find an apparent high miscibility and one homogeneous columnar mesophase [27].

In figure 7 a plot of the imaginary part of the complex dielectric function versus temperature is displayed. One high temperature process only occurs above the glass transition established by DSC. In analogy to other discotic systems—here including also the mixture 1/2—it is ascribed to the dynamic glass transition process. Two further relaxation processes are found which must be of local nature and are probably related to the side chain motion and a local polymer main chain motion, respectively.

In contrast to mixture 1/2, free rotation of the acceptor molecules must be strongly hindered due to the polymer attachment. The high temperature process (see figure 8) can be fitted by the WLF function (equation (1)) with the following parameters: $C_1 = 19$; $C_2 = 110$ K; $\log \tau_0 = 1.5$. These values—especially C_1 —are significantly higher than those for monomeric compounds, hinting at a modified reorientational mechanism. A clearer picture arises on investigating the spin-echo spectra of the deuteriated acceptor and donor components at identical temperatures. As depicted in figure 9 the spectra differ significantly from each other. Whereas the donor component can rotate freely in the columns as proven by the motionally reduced spectral width by a factor of 2, the acceptor moieties cannot rotate freely. Nevertheless they exhibit substantial mobility, as deduced from the ^2H NMR spectra which are similar to those found before for dimers and polymers where discoid units rotate around the columnar axis with angles up to 60° [28]. So the intrinsically amorphous polymer exhibits the same kind of reorientation process as a discotic polymer when it is mixed with discotic donor molecules. In contrast to low molar weight mixtures (for example, 1/2), the motion is

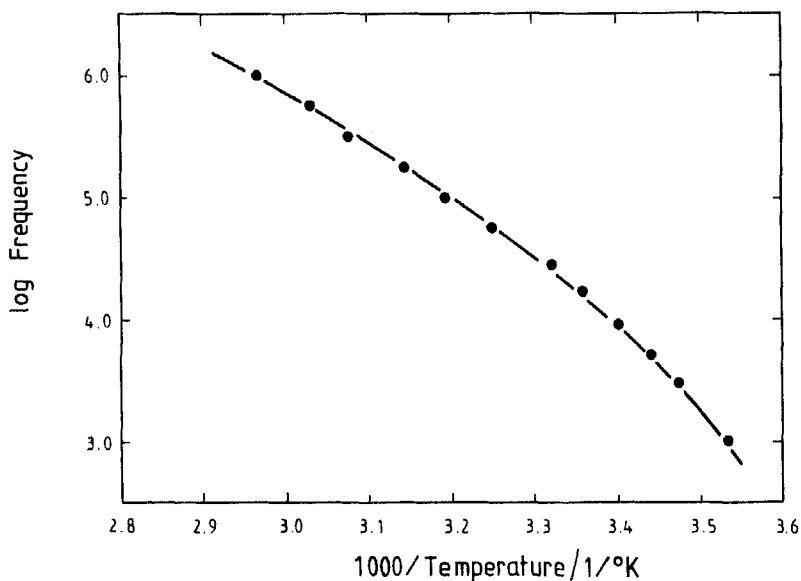


Figure 8. WLF diagram of the high temperature dielectric relaxation of the mixture 1/2.

less coupled and this could explain the appearance of an additional decoupled low temperature process.

The less favourable interaction also leads to greatly increased biphasic regions. Very broad biphasic regions of about 30°–50° seem to be a general feature of CT mixtures involving polymer components [1, 29].

The mixture 1/3 can be well-oriented by slow cooling (0.1 K min⁻¹) from the isotropic to the columnar phase in a strong magnetic field (7 T), resulting in a planar

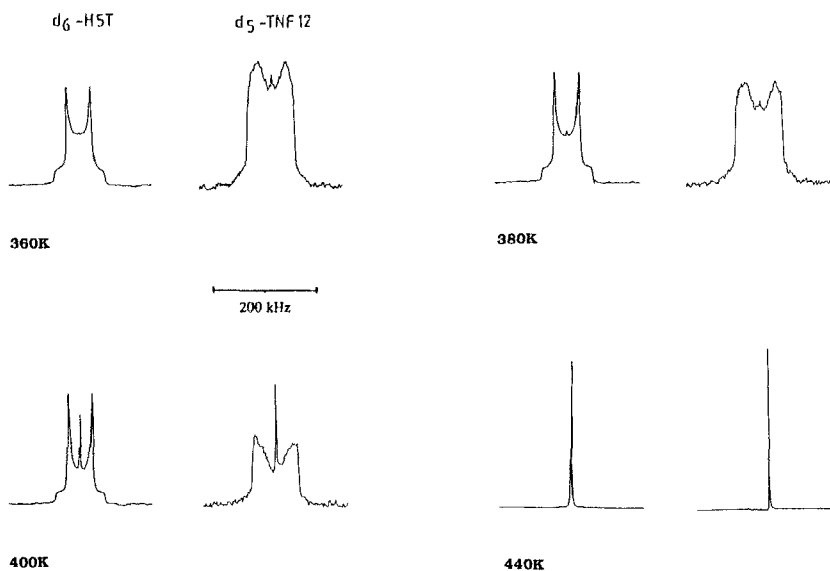


Figure 9. Spin-echo spectra of the deuterated acceptor and donor components of the mixture 1/2.

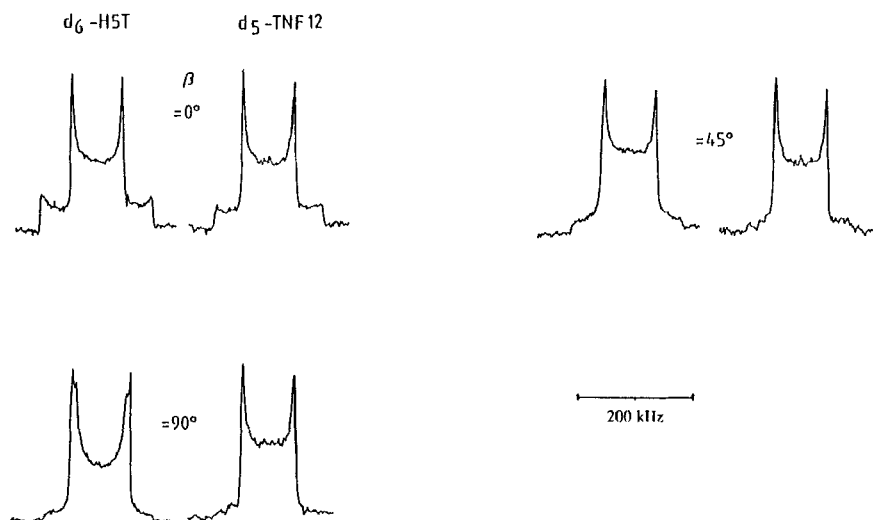


Figure 10. NMR data on the orientation of the donor and acceptor components in the mixture **1/3**.

distribution of columnar domains as described elsewhere [29]. As can be seen from figure 10 both components are equally oriented. A close inspection reveals differences in the degree of orientation of donor and acceptor components. The degree of orientation of the donor component can be described by an order parameter $S = -0.40$, whereas the acceptor component can be described by a superposition of two contributions: an oriented fraction with an equal order parameter $S = -0.40$ and 30 per cent of an isotropic component. This finding hints at a non-perfect mixing of donor and acceptor components and is probably an important cause of the large biphasic region observed.

3.3. Donor-acceptor twin with long spacer **4**

The system consisting of one donor and one acceptor unit CT dimer, coupled chemically via a flexible spacer exhibits a hexagonal ordered phase with very high stability. In fact, at the very high clearing temperature of 515 K, decomposition has already started.

By dielectric spectroscopy three motional processes can be detected (see figure 11). As in the mixtures **1/3** and **1/2**, the high temperature process can be attributed to the dynamic glass transition process. This can be concluded from a WLF-fit (equation (1)), where the relationship between the caloric and the dynamic glass transition is established, the parameters being; $C_1 = 9$; $C_2 = 96$ K; $\log \tau_0 = 1.1$. These are very similar to the corresponding parameters for the mixture **1/2**. Additionally, as in mixture **1/3**, two broad low temperature processes, so called β_1 and β_2 , are observed and must be of local nature.

A first analysis of the spin-echo spectra (see figure 12) of both components at different temperatures reveals a nearly identical dynamical behaviour of the two molecular moieties. The motion of the donor and acceptor are strongly coupled. In the temperature regime between 300 K and 320 K, spectra with low intensities are observed. This T_2 minimum coincides with the dielectrically observed dynamical glass transition at about 100 kHz. An increase in temperature, however, does not directly lead to spectra which are reduced in their spectral width by a factor 2, thus indicating a fast rotation

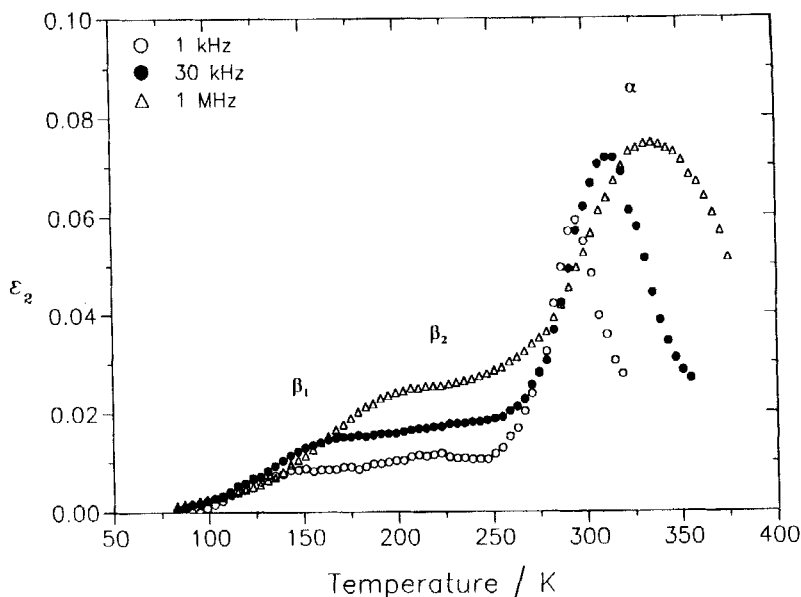


Figure 11. Dielectric relaxation data obtained for the CT dimer **4**.

of the molecules around the columnar axis. Instead, at 340 K, spectra which resemble those of polymers, where only large angular librations around the columnar axis occur, are found [28]—see also figure 9. This finding strongly supports the assumption that the donor and acceptor parts of a twin are located in different columns. Furthermore, a backfolding of the spacer so that both donor and acceptor are inserted in the same column can be neglected.

At even higher temperatures, 380–420 K, yet another regime with diminished

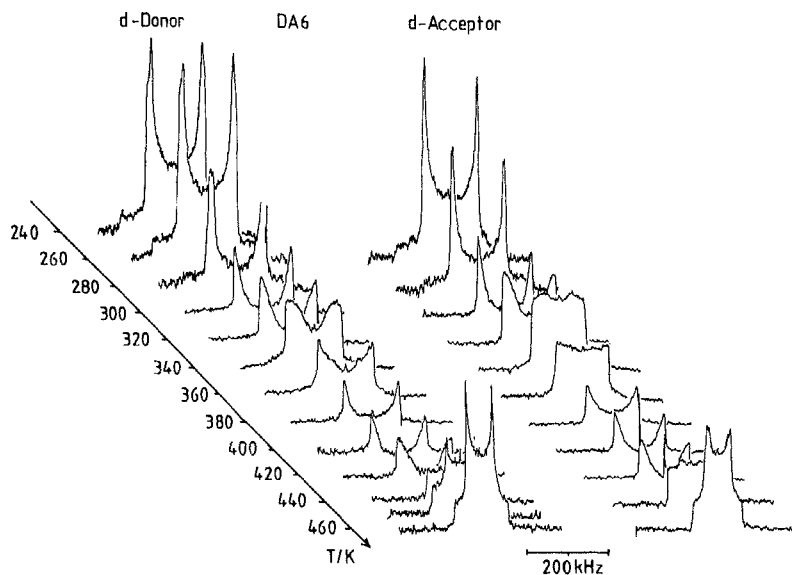


Figure 12. Spin-echo spectra of both components, of the CT dimer **4** at various temperatures.

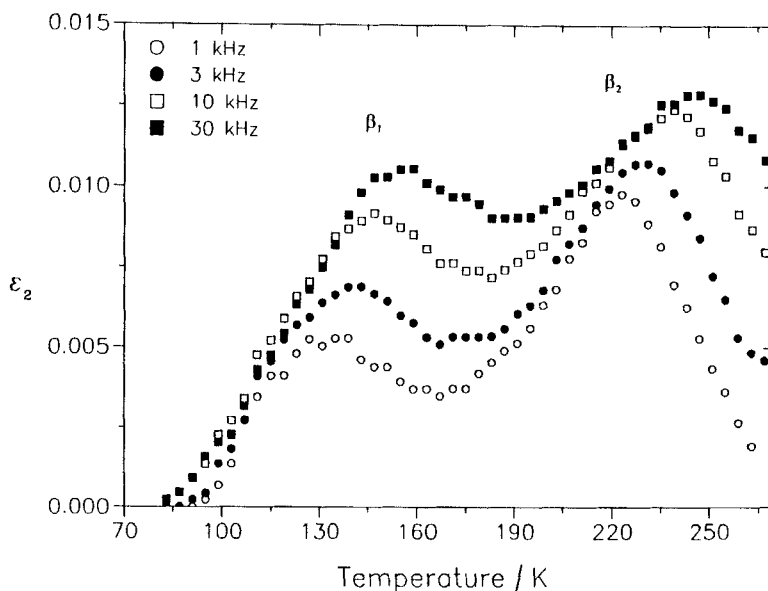


Figure 13. Dielectric relaxation data obtained for the CT dimer **5** at various frequencies.

spectral intensities is found. No corresponding dielectric process could be found due to the very high temperatures and the onset of electrical conductivity. The spectra obtained above this temperature regime are those typical for the fast rotational process in columnar mesophases. This process at very high temperatures therefore allows complete rotations of donor and acceptor moieties and this can only occur if a fast diffusion between columns takes place. Hence, for the first time we were able to observe directly the molecular exchange process between adjacent columns. From an approximate analysis of the spin-echo spectra, an activation energy $E_a = 59 \text{ kJ mol}^{-1}$ can be estimated.

3.4. Donor-acceptor twin with short spacer **5**

The CT dimer **5** with its short spacer forms no classical hexagonal ordered columnar phase. Instead, it has a complicated columnar phase with a superimposed layered structure [14].

Figure 13 shows the results of dielectric studies on the twin compound **5**. Only two low temperature processes of local nature are observed, which exhibit Arrhenius behaviour with an activation energy $E_a = 25 \text{ kJ mol}^{-1}$ (β_1) and $E_a = 70 \text{ kJ mol}^{-1}$ (β_2). In comparison with mixture **1/2**, the process β_1 can be attributed to side-chain librations. The second process probably arises from a local spacer motion. No high temperature motional process as in the other systems was observed. This is in agreement with the fact that no glass transition could be detected by DSC [30]. The NMR spectra, up to very high temperatures of 450 K, of both moieties are of the Pake type, thus demonstrating that neither columnar rotation nor any other large angular motion takes place. The lack of a glass transition in compound **5** can be anticipated from the complex phase structure, which is more closely related to a crystal structure—although strongly disordered—than to that of an ordinary mesophase [14].

4. Conclusions

The correlated rotational motion of discotic molecules or groups about the columnar axis seems to be a general feature of columnar phases. This motion occurs similarly in pure discotic low molar mass systems, in mixtures of discotic donors and non-discotic acceptors, in dimers where the acceptor and donor are coupled by flexible groups and occurs even if the units are part of a polymer main chain, the only effect of such a chemical modification being the restriction of the free rotation type to motion of a librational type. The acceptor participates in the type of motion in all cases. In the particular case of the CT dimer with the long spacer, a relaxation mode is observed which reflects a diffusion of the molecular moieties between the columns. The rotational motion is suppressed only in the particular case where the donor and acceptor moieties are strongly coupled by a short spacer. Finally, it has become apparent that broad biphasic regions exist for CT mixtures at the transition from the discotic to the isotropic state.

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