^{2}H NMR Studies of Molecular Motions and Alignment Processes of Discotic Liquid Crystalline Compounds Based on Substituted Triphenylenes

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ABSTRACT: ^{2}H NMR measurements on discotic compounds based on heptyloxy-substituted triphenylenes are reported. Monomers, model dimers, polycondensates, and a cross-linked polycondensate were studied. Macroscopic alignment in a 7-T magnetic field proves that all of them exhibit discotic liquid crystalline mesophases. Their phase behavior is characterized by an analysis of the spectroscopic data as a function of temperature. While for the monomer the phase transition from the mesophase to the isotropic phase is well defined, for the dimer and the polymer biphasic behavior over a broad temperature interval is observed. ^{2}H NMR measurements on aligned samples allow the separation of side-group motions and motions of the rigid core. In the monomers full axial rotation of the core around the column axis occurs in the mesophase, while this rotation is quenched in the dimer and the polymer. Combination of magnetic and mechanical forces allow the generation of monodomains, where the columns are aligned parallel to each other. The kinetics of this alignment process is monitored by ^{2}H NMR spectroscopy.

1. Introduction

Disklike molecules consisting of a flat rigid core with laterally bound aliphatic side groups exhibit mesophases, where the disks stack together into columns.[1-3] 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 show discotic liquid crystalline behavior.[4-6] These polymers are of particular interest because they show special properties. They can be ordered macroscopically, either by magnetic fields[7,8] or by mechanical forces.[9,10] Cooling below the glass transition temperature results in highly ordered anisotropic glasses.[8-10]

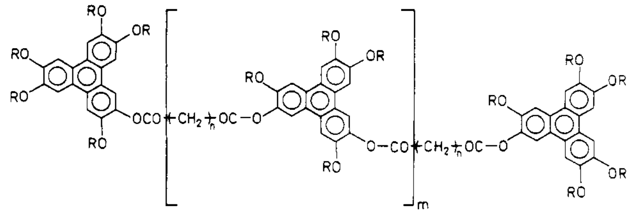
In a previous paper[11] we presented studies concerning the phase behavior of main-chain polymers and oligomers having alkylated triphenylene derivatives as mesogenic units. These compounds exhibit mesophases of the D_h type, where the columns pack into a hexagonal lattice. By variation of the length of the alkyl side groups the phase transition temperatures as well as the dynamic behavior can be strongly influenced. Recently, Ringsdorf et al. showed that discotic liquid crystalline systems based on substituted triphenylenes can be doped to form charge-transfer complexes. In fact, it is even possible to induce liquid crystalline behavior by doping amorphous discotic polymers with electron acceptors.[12]

^{2}H NMR spectroscopy offers unique possibilities to study liquid crystalline phases and the glassy state in terms of the dynamic properties and the degree of order.[13-15] Here we present our ^{2}H NMR studies on the molecular dynamics of the mesogenic units and their macroscopic alignment in the magnetic field. Moreover, we show that monodomain samples, where all the discotic columns are aligned parallel to each other, can be generated for main-chain polymers by combining magnetic and mechanical forces, whereas magnetic force alone forms planar distributions of column axes only. ^{2}H NMR studies of the phase behavior and molecular motions in *doped* discotic liquid crystalline systems are reported elsewhere.[16]

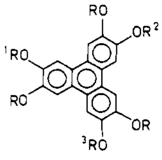
2. Experimental Section

Materials. The compounds studied are listed in Table I. Their syntheses (compounds 1-5) are described in refs 5 and 11. The cross-linked polycondensate 6 was prepared in analogy to the polycondensate 5 by acid-catalyzed melt polycondensation of a 2:1 mixture of the diacetate 2 and the triacetate 3. This highly cross-linked polycondensate is insoluble.

Table I
Molecular Structures of the Synthesized Compounds 1-5[a]



4,5



1 - 3

compd	R	R^1	R^2	R^3	*n*	*m*	M_n
1	Y	Y	Y	$COCH_3$			
2	Y	Y	$COCH_3$	$COCH_3$			
3	Y	$COCH_3$	$COCH_3$	$COCH_3$			
4	Y				14	0	
5	Y				14	19	1700
6	Y				14	cross-linked	

[a] Y stands for $CH_3(CH_2)_6$. The structures of 2 and 3 are not unambiguous; synthesis results in a mixture of isomers.[5]

For ^{2}H NMR measurements selectively deuterated compounds ((heptyl-*1,1-d*$_2$)oxy groups or (heptyl-*3,3-d*$_2$)oxy groups) were prepared.[17,18]

Characterization. All compounds were characterized by optical microscopy, DSC, ^{1}H NMR, and elemental analysis. DSC measurements were carried out with a Mettler DSC 30.

The molecular weight estimations of the polycondensates are based on GPC with polystyrene as a reference and on ^{1}H NMR end-group determination. Both techniques gave similar results.

The ^{2}H NMR spectra were recorded via the solid echo technique on a Bruker CXP 300 spectrometer equipped with a home-built goniometer as described elsewhere.[8,13] The goniometer is operated by a step motor that can be synchronized to the spectrometer. The delay between the two pulses in the solid echo sequence was 30 μs. Typically 1000 scans were accumulated. The solid echo sequence was also used to measure the transversal

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Table II
Caloric Data of Compounds 1, 2, and 4–6

compd	phase transition temp, K	specific transition enthalpies, J/g
1	k 323 D_{ho} 390i	k 17 D_{ho} 8.0i
2	k 324 D_{ho} 391i	k 11 D_{ho} 8.0i
4	D_h 420i	D_h 9.0i
5	g 323 D_h 455i	D_h 9.0i
6	g 330 D 450i	D 8.0i

relaxation time T_2 via the echo intensities. X-ray measurements were performed with a rotating anode and a two-dimensional detector.

3. Results and Discussion

Phase Transitions. The caloric data of the compounds studied are presented in Table II for reader convenience. The phase transition from the discotic liquid crystalline phase to the liquid isotropic phase at T_i show a pronounced dependence on the molecular weight.[11] T_i increases from 391 K for monomer **2** to 420 K for dimer **4** and reaches a plateau value of ca. 455 K for polymer **5**. The melting temperature of monomer **2** and the glass transition of polymer **5**, both a 323 K, correspond to the onset of the mesophase. It is remarkable that for dimer **4** no glass transition was detected by DSC, because the transition is very weak. An analysis of ^{2}H NMR spectroscopic data shows the formation of the mesophase to begin at 325 K.[11] The caloric data for cross-linked polycondensate **6** indicate discotic liquid crystalline behavior. It shows a glass transition at 330 K, and its specific transition enthalpy ΔH_i is comparable to that of polymer **5** (Table II). Also its optical properties are similar to those of polymer **5**: Under a polarizing microscope textures with extremely small blurred contours are observed. Above T_i it shows, different from polymer **5**, elastic behavior.

^{2}H NMR Measurements on Isotropic Samples. In Figure 1 transverse relaxation times T_2 and ^{2}H NMR line shapes are plotted as a function of temperature. The samples are monomer **2** (Figure 1a), dimer **4** (Figure 1b), and polymer **5** (Figure 1c), all deuterated in the 1-position of the heptyloxy side groups. The mobilities of the labeled methylene groups and the triphenylene core in the columns increase with increasing temperature. This leads to motional narrowing of the NMR line shapes (see also Figure 2). The dependence of T_2 on temperature, however, is more complicated. Increasing mobility can lengthen or shorten T_2, depending on the nature and the time scale of the molecular motion.[13,14]

Let us discuss monomer **2** first. At temperatures below 300 K in the crystalline phase line shape 1 resembles the Pake diagram of a solid. Correlated to this a T_2 plateau value of 300 μs is observed, indicating the absence of restricted motions. At ca. 310 K motional narrowing of the line shapes takes place (spectrum 2). Parallel to this T_2 reaches a minimum of very low vaues (30 μs). This is due to the activation of the rotation of the disks around the column axis (see also Figure 3).[11,17] With increasing temperature further spectral narrowing takes place while T_2 increases, indicating that the rotational motion becomes faster. Reaching the mesophase at 323 K, no further spectral narrowing occurs, but the ^{2}H NMR spectrum 3 is a motionally narrowed Pake diagram reflecting the axial motion of the disks. Moreover, T_2 becomes temperature independent, because molecular motions are fast now on the NMR time scale (correlation times $\tau_c \ll 1$ μs). On reaching T_i, further spectral narrowing is observed, until isotopic motion completely averages the quadrupolar interaction (spectrum 4). T_2 reaches a plateau value of 1000 μs.

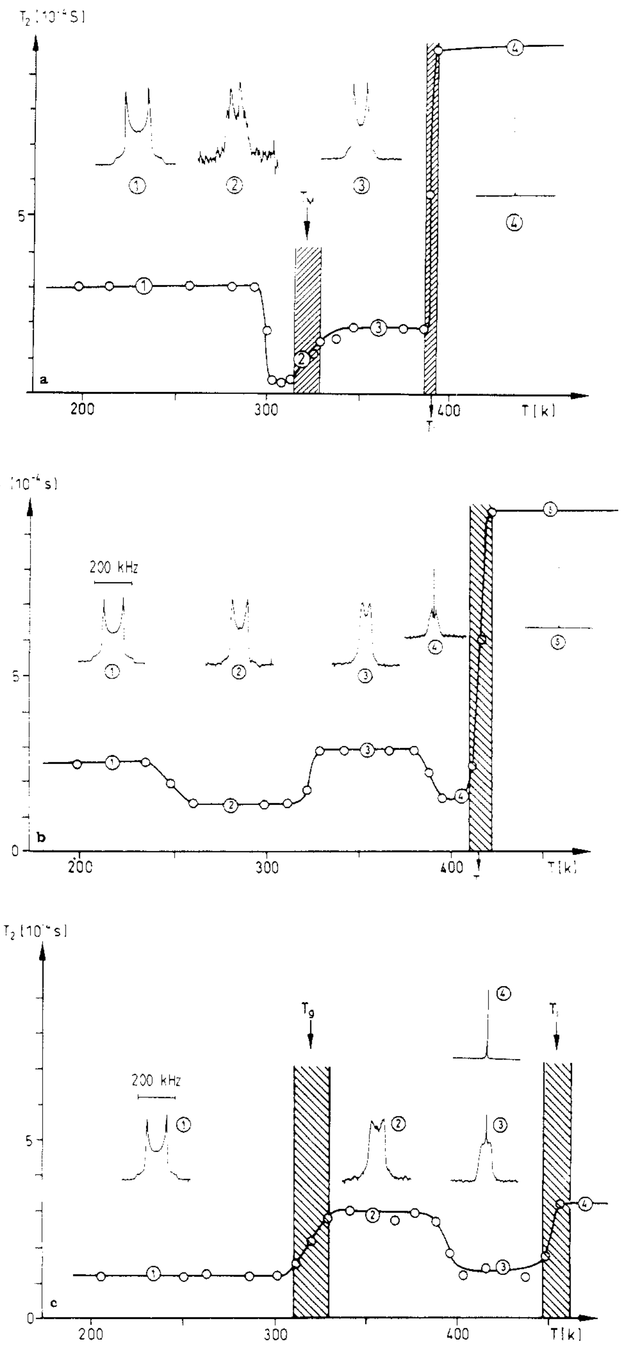

Figure 1. Dependence of transverse relaxation time T_2 and ^{2}H NMR line shapes on temperature for monomer **2** (a), dimer **4** (b), and polymer **5** (c). All compounds are deuterated in the 1-position of the heptyloxy side groups. Phase transitions as detected by DSC are also indicated.

The behavior of dimer **4** (Figure 1b) is somewhat different from that of monomer **2**. For temperatures below 250 K spectrum 1 again is the Pake diagram of a solid. Above 260 K the low T_2 value accompanied by a slight spectral narrowing (spectrum 2) indicates restricted mobility. On approaching the mesophase at 325 K, further spectral narrowing takes place, parallel to increasing T_2 values. As shown later, this corresponds to the activation of motions of the disks around the column axis about ill-defined angles.[11,17-20] In the mesophase line shapes (spectrum 3) and T_2 values are almost temperature independent. On approaching T_i, a minimum of T_2 values is observed.

The behavior of polymer **5** (Figure 1c) is rather similar to that of dimer **4**. Yet there are two characteristic differences. At temperatures below 250 K the value for

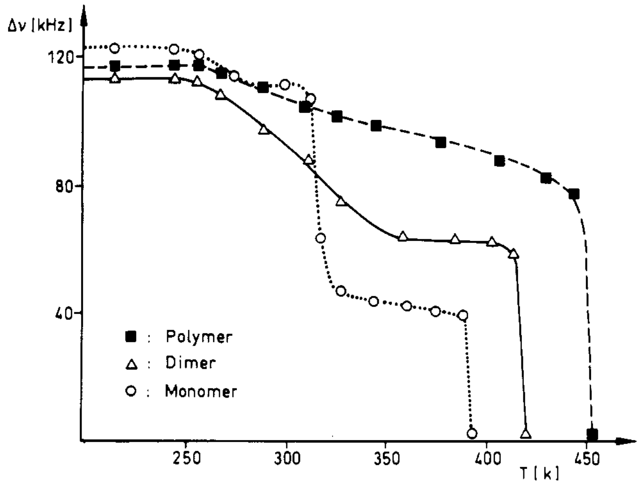

Figure 2. Width at half-height of ^2H NMR spectra as a function of temperature for monomer **2**, dimer **4**, and polymer **5**, deuterated in the 1-position of the heptyloxy side groups.

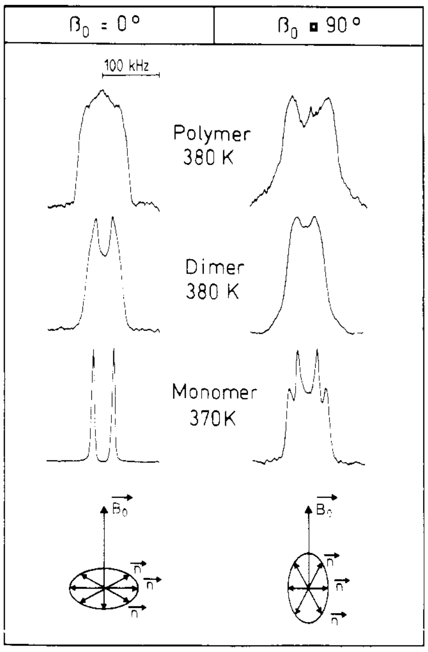

Figure 3. ^2H NMR spectra of aligned samples of monomer **2**, dimer **4**, and polymer **5**, deuterated in the 1-position of the side groups: left column, planar alignment of the columns perpendicular to the magnetic field $\mathbf{B}_0$, right column, planar alignment with the magnetic field $\mathbf{B}_0$ in plane. β_0 denotes the angle between the macroscopic order axis and $\mathbf{B}_0$.

T_2 is very low (120 μs) compared to that of dimer **4** (230 μs). This means the restricted alkyl and alkylene chain conformational motions are not frozen in at temperatures below 250 K as they are for dimer **4**. The second point is the minimum of T_2 on approaching T_i, which is for polymer **5** much broader in temperature than that of dimer **4**.

A similar minimum is not observed for monomer **2**. The phase transition process at T_i is somewhat different from that for dimer **4** and polymer **5**. In fact, our ^2H NMR data clearly show that the transition from the discotic mesophase to the isotropic phase is not well defined but occurs within a considerable temperature range, where these two phases coexist for dimer **4** and polymer **5**. This is demonstrated by spectrum 4 in Figure 1b and spectrum 3 in Figure 1c, respectively, which are superpositions of broad and narrow components. When approaching T_i, as detected by DSC, the isotropic part increases continuously in intensity. The biphasic range is <5 K for monomer **2**, ~15 K for dimer **4**, and ~80 K for polymer **5**. We therefore attribute it to the interlinking of columns by the spacer.

To get a quantitative measure of the different mobilities of monomer **2**, dimer **4**, and polymer **5** in the discotic liquid crystalline phase in Figure 2, we plot the width at half-height of the ^2H NMR spectra of these compounds, all deuterated in the 1-position of the heptyloxy side groups, as a function of temperature.

As mentioned above, increasing mobilities of the labeled methylene groups as well as increasing mobility of the triphenylene core results in spectral narrowing. For temperatures below 310 K the general mobility of monomer **2** is lower than the mobilities of dimer **4** and polymer **5**, reflecting the fact that the monomer is crystalline, whereas dimer **4** and polymer **5** are amorphous. This changes in the mesophase. Here the mobility of monomer **2** is much higher. This is due to the rotation of the disks around the column axis of monomer **2** and its lower viscosity in the mesophase. For dimer **4** and polymer **5** the motional processes are similar, even though the viscosity of dimer **4** is lower, but different from that of monomer **2**: Only ill-defined angle motions of the disks around the column axis are possible. The substantially stronger motional narrowing in dimer **4**, however, shows that the amplitude of the angular excursion must be larger in dimer **4** compared with polymer **5**.

The spectral narrowing, in fact, starts at temperatures as low as 250 K for all compounds (Figure 2). This is due to the onset of motions in the labeled methylene groups. Compounds deuterated in the 3-position of the heptyloxy side groups show spectral narrowing already at temperatures of 200 K, and at 280 K 80% of the maximum spectral narrowing is already achieved indicating high side-group mobility.[17]

Separation of the Side-Group Motion from the Motion of the Disks. As mentioned above, two major motional processes can be envisaged: planar motion around the column axis and side-group mobilities. In a previous paper[11] we discussed the planar motional behavior of monomers, oligomers, and polymers using ring d_6 deuterated triphenylene derivatives having pentyloxy side groups. Here we will show that this motional behavior can be monitored also by the compounds with heptyloxy side groups deuterated in the 1-position. To get this information we take advantage of the fact that discotic liquid crystalline phases can be macroscopically aligned by magnetic fields. To achieve this, the samples are heated 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.[8,15–18] This alignment can be generated in monomer **2** as well as in dimer **4** and polymer **5**. In the mesophase itself the alignment of the columns is no longer affected by the 7-T magnetic field of the NMR spectrometer. Therefore by a goniometer within the NMR probe we can subsequently rotate the sample about an axis perpendicular to the magnetic field $\mathbf{B}_0$, such that $\mathbf{B}_0$ can form any angle with the normal to the planar distribution. In Figure 3 mesophase spectra of the aligned samples **2**, **4**, and **5** are shown. The left column presents spectra for samples with $\mathbf{B}_0$ perpendicular to the planar distribution, and the right column spectra for samples with $\mathbf{B}_0$ in the plane of the director distribution.

Let us first discuss monomer **2**. The fast rotation of the disks around the column axis results in averaging the electric field gradient of the C–^{2}H bonds to an axially symmetric tensor with a unique direction parallel to the

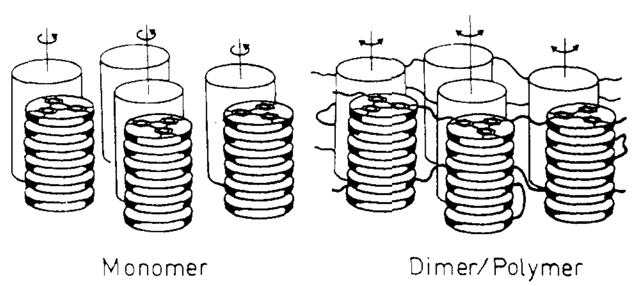

Figure 4. Sketch of the mesophase for monomer **2** and polymer **5**, with full axial rotation of monomer **2** and ill-defined angle motion of polymer **5** around the column axis.

column axis.[11,19] Consequently, for a planar distribution of the column directors perpendicular to the magnetic field, the resulting averaged electric field gradient tensors also exhibit a planar distribution perpendicular to the magnetic field. This results in a spectrum of only two single lines (left column of Figure 3). After 90° rotation of this planar distribution around the sample axis, the magnetic field $\mathbf{B}_0$ lies in the plane of this distribution. For this state of order all angles from 0° to 90° between the unique axes of the averaged tensors and the magnetic field result, giving a NMR spectrum of a planar distribution, as for monomer **2** in the right column of Figure 3. As mentioned above, motional narrowing for dimer **4** and polymer **5** in the mesophase is less pronounced. The spectra for the aligned dimer **4** and the aligned polymer **5** (Figure 3) differ significantly from those of the aligned monomer **2**. Neither the single quadrupole splitting for the planar distribution perpendicular to $\mathbf{B}_0$ nor the broad spectrum with four singularities for a planar distribution with $\mathbf{B}_0$ in that the plane is observed. From X-ray measurements described below, on the other hand, we know that the macroscopic alignment is alike in monomer **2**, dimer **4**, and polymer **5**.[9,10,20] We therefore conclude that even for dimer **4** the rotation around the column axis is quenched. This must be an effect of the spacer. It interlinks disks located in different neighboring columns, thus preventing a full rotation. Only ill-defined angle motions around the column axis take place. The different motional behavior of monomer **2**, on the one hand, and dimer **4**/polymer **5**, on the other hand, is shown schematically in Figure 4. A quantitative line-shape analysis is currently underway.

It is remarkable that the activation of the disks rotation in monomer **2** at ca. 320 K is not responsible for the transition enthalpy detected by DSC at the same temperature. While the rotation immediately freezes in by cooling below 310 K, the transition enthalpy is only detected in the first heating run or after annealing the sample for at least 48 h below 310 K and therefore corresponds to crystallization effects.

In a mixture of four parts disk of polymer **5** and one part disk of monomer **2** which was deuterated in the 1-position of the heptyloxy side groups, the rotation even for the monomer is quenched, resulting in spectral line shapes similar to those of dimer **4** and polymer **5**. It is likely that the rotation of the monomer is prevented by steric effects of the side group/spacer system of the polymer.

As shown in a forthcoming publication[20] on related main-chain and side-group polymers, the quenching of the motion of the disk units also manifests itself in the mechanical behavior.

Side-Group Motions. The temperatures at which local motions in the side groups are activated at a given frequency depend on the position of the methylene group under study. The onset of motional narrowing of the spectra of compounds deuterated in the 1-position takes place around 250 K (first decrease of width at half-height; see Figure 2) and is closely related to the mobility of the disk itself.[20] As expected for the 3-position, motional processes are activated already at lower temperatures (200 K), and at 280 K for this position 80% of the maximum motional narrowing is achieved,[16] indicating high mobility of the C–^{2}H bonds.

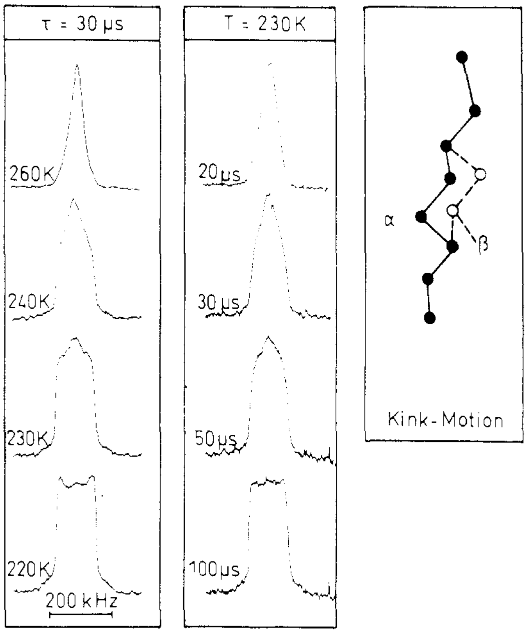

Figure 5. ^{2}H NMR spectra of dimer **4**, deuterated in the 3-position of the heptyloxy side groups. In the left column the temperature is varied with constant delay time τ of the solid echo pulse sequence; in the right column τ is varied at constant temperature.

Figure 5 shows spectra of dimer **4** deuterated in the 3-position of the heptyloxy side groups. In the left column temperature-dependent spectra with a constant delay time $\tau = 30$ μs between the first pulse and the second refocusing pulse of the ^{2}H NMR solid echo pulse sequence are plotted. The right column shows spectra obtained at a constant temperature of 230 K with varying delay times τ. They indicate conformational motions in the side groups as shown by comparison with spectra calculated for such processes in alkyl chains.[21-23] At temperatures above 220 K and below 260 K the correlation times τ_c of these motions are between 1 and 100 μs, while for temperatures above 260 K the motion is fast, $\tau_c < 1$ μs.

Macroscopic Alignment by Magnetic and Mechanical Forces. As noted above, substituted triphenylenes as well as oligomers and polymers can be oriented in the magnetic field[7,8] or by mechanical forces.[9,10] For main-chain discotic liquid crystalline polymers uniaxial stretching results in a planar distribution of column axes perpendicular to the stretching direction only.[9,10,20] A magnetic field alone likewise generates such a planar distribution only.[7,8] This is caused by their liquid crystallinity and the anisotropy of the diamagnetic susceptibility of the triphenylene core, resulting in 90° angles between the static magnetic field $\mathbf{B}_0$ and the director system of the columns (see Figure 3). Even the cross-linked polycondensate **6** can be aligned in the magnetic field, resulting also in a planar director distribution perpendicular to the magnetic field $\mathbf{B}_0$. This alignment was detected by X-ray diffractograms in the glassy state as well as in the discotic mesophase. At a temperature of 425 K, 25 K below T_i, however, a significant reduction in the order was observed. The residual order is lost at T_i = 450 K only. This effect may be attributed to a coupling

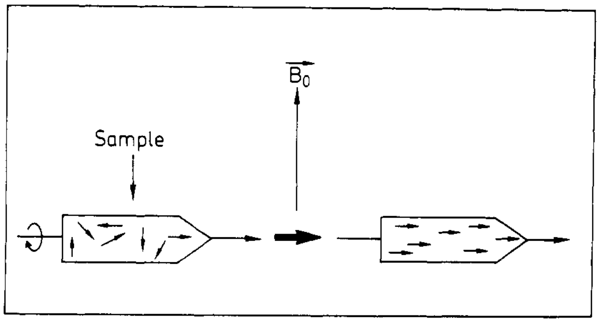

Figure 6. Sample cylinder, macroscopic rotation axis, and magnetic field $\mathbf{B}_0$ in the rotation experiments for generating monodomains.

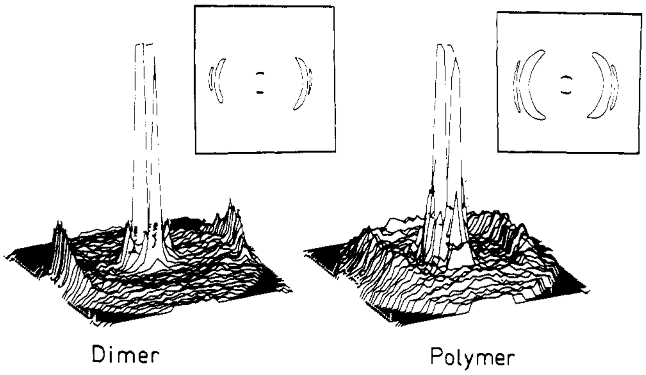

Figure 7. Two-dimensional X-ray diffractograms of the monodomain samples of dimer **4** (left) and polymer **5** (right). Stack as well as contour plots of the scattered intensity are shown.

between the discotic mesophase order and the polymer network, where the latter apparently relaxes at temperatures below T_i.

For possible applications of discotic liquid crystalline polymers it is highly desirable, however, to align all columns parallel to each other. As discussed by Luz et al.[7] on monomeric discotics such monodomain samples can be generated by additional mechanical forces. The usual way to ge these aligned samples is to heat above T_i, followed by slow cooling below T_i, while simultaneous rotating around the sample axis (see Figure 6).

With this procedure we succeeded in getting monodomains not only for monomer **2** but also for dimer **4** and the main-chain polymer **5** as determined by X-ray diffractograms (Figure 7). The X-ray beam is perpendicular to the director axes of the column system. Two sharp reflections in the small-angle region correspond to the distance between neighboring columns, proving their alignment along the sample axis, being similar for dimer **4** and polymer **5**. Perpendicular to this, two broad reflections in the wide-angle region correspond to the side-group packing and the distance between the disks in the columns.[9,10,20] For dimer **4** these wide-angle reflections are sharper than for polymer **5**, indicating a higher degree of order for the packing of the disks in the columns for dimer **4**.

The same procedure applied to cross-linked polycondensate **6**, however, did not lead to a monodomain sample. Apparently the network prevents an alignment of the columns along the rotation axis.

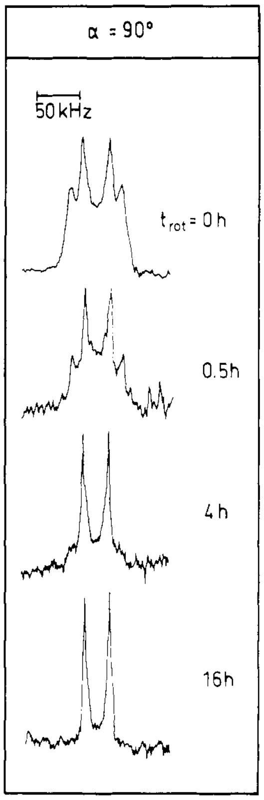

Figure 8. Time-dependent formation of the monodomain of monomer **2**, labeled in the 1-position of the side groups, monitored via ^{2}H NMR spectra taken before the start of rotation, after 30 min, and after 4 and 16 h in the α = 90° rotation position.

Kinetics of Monodomain Generation in the Monomer. ^{2}H NMR even offers a means for studying the kinetics of monodomain formation. As discussed above (cf. Figure 3), the spectrum of the planar distribution is a doublet for $\beta_0 = 0°$ but displays four singularities for $\beta_0 = 90°$, where β_0 denotes the angle between the macroscopic order axis and $\mathbf{B}_0$. If subsequently a monodomain with director axis parallel to the rotation axis is formed, the spectra of $\beta_0 = 0°$ and $\beta_0 = 90°$ are identical doublets. To follow the kinetics we heated monomer **2** above T_i and then slowly it to 10 K below T_i in the magnetic field without sample rotation, resulting in an aligned sample with a planar director distribution, perpendicular to the magnetic field (Figure 3, left column). This aligned sample was rotated around the axis of the sample tube, i.e., perpendicular to $\mathbf{B}_0$, via a synchronized goniometer motor at this temperature (380 K) with a rotation frequency of $\nu = 360°/\text{min}$. The rotation angle is denoted α. Whenever, the sample reached the α = 90° rotation angle position, 200 scans were accumulated to give the spectra shown in Figure 8. As a function of time the outer singularities as well as the central part vanish. The sample experiment applied to either dimer **4** or polymer **5** did not succeed; see also below. Thus even in this respect triphenylene dimers behave similarly to the main-chain polymers and can serve as model compounds for the corresponding polymer, as concluded earlier based on similarities of molecular mobilities.[11]

To quantify the time dependence of the alignment process for the monomeric compound **2**, an empirical order parameter $R = 1 - ah_1/h_2$ was defined (see Figure 9a). Here, h_1 and h_2 are the spectral intensities of the singularities and the central region, respectively. The parameter a is adjusted such that $R = 0$ for a planar distribution. For complete alignment R approaches 1. In Figure 9a the dependence of R on time is plotted for the monodomain formation of monomer **2** in the mesophase (at 380 K) with a rotation frequency of $\nu = 360°/\text{min}$. The influence of the time on R is very pronounced in the beginning; for longer experimental times R slowly reaches a plateau value close to 1. A semilogarithmic plot shows that the time dependence of R cannot be described by an exponential.

As noted above, monodomains for monomers, dimers, and polymers can be generated by slow cooling below T_i,

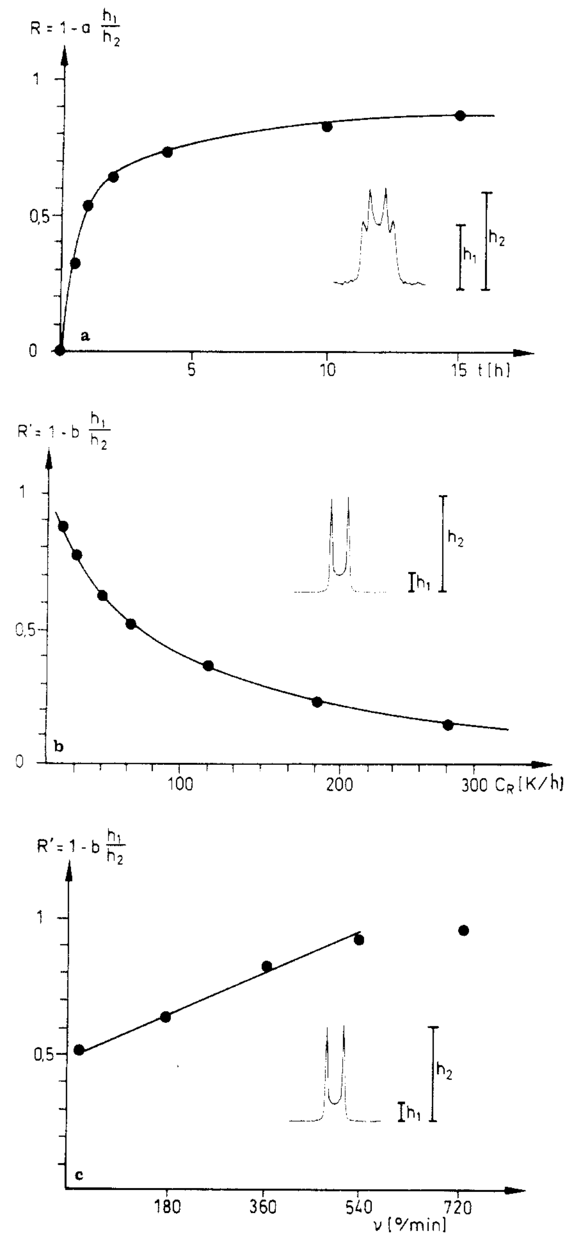

Figure 9. Kinetics of monodomain formation for monomer **2**, deuterated in the 1-position of the hepytloxy side groups. (a) Time-dependent process of monodomain formation in the mesophase (380 K). The parameter a is adjusted such that $R = 0$ for a planar distribution. (b) Dependence of monodomain formation on the cooling rate. (c) Dependence of monodomain formation on the rotation frequency ν. The parameter b in (b) and (c) is adjusted such that $R' = 0$ for an isotropic distribution.

while rotating around an axis perpendicular to the magnetic field. The degree of alignment that is generated, however, depends on the cooling rate as well as on the rotation frequency ν. This is demonstrated for monomer **2** in Figure 9b,c. Again an order parameter $R' = 1 - bh_1/h_2$ was defined, where the parameter b is adjusted such that $R' = 0$ for an isotropic distribution.

To study the influence of the *cooling rate*, we kept the temperature interval of cooling constant at 20 K from $T_i + 10$ K to $T_i - 10$ K. The rotation frequency was kept constant at $\nu = 360°$/min (cf. Figure 9b). For small cooling rates a high degree of order is produced, while for increasing cooling rates the order parameter R decreases significantly, approaching $R' = 0$.

To study the influence of the *rotation frequency*, we kept the cooling rate constant at 0.33 K/min and varied ν between 720 and 36°/min. For low rotation frequencies a linear dependence of R' on ν was found (cf. Figure 9c).

For comparison the monodomains for dimer **4** and polymer **5**, described above, were obtained at a cooling rate of 0.083 K/min (5 K/h) and a rotation frequency $\nu = 360°$/min.

Alignment Processes in Monomer, Dimer, and Polymer. As discussed above, cooling of discotic liquid crystals in the presence of a magnetic field results in the formation of oriented samples with a planar director distribution perpendicular to the magnetic field direction. By rotating the sample within the magnetic field, all domains except those parallel to the rotation axis experience alternating magnetic torques that tend to align them parallel to the rotation axis. To our knowledge no theoretical description has been provided so far for the alignment kinetics of columnar mesophases. We hope that the experimental data presented here may help to stimulate the interst of theoreticans. As described above, monodomains are formed in this fashion for the monomer but not for dimer and polymer. Since in the latter samples the columns are interlinked by the spacers, a breakdown of the ordered structure would be necessary in order to result in the new arrangement of a monodomain.

The alignment process achieved by cooling from the isotropic phase while simultaneously rotating the samle is somewhat different from that in the mesophase. In this case it can be imagined that nucleation of domains aligned preferentially along the axis of rotation is responsible for the macroscopic alignment of the entire sample. In the nucleation process the interlinkage of columns apparently is less critical for the formation of monodomains. Consequently, with this slightly different alignment procedure monodomains are obtained not only for the monomer but also for dimer and polymer.

Summarizing these alignment experiments, we showed that oligomers as well as polymers are able to build monodomain samples by combining magnetic and mechanical forces. For the monomer the viscosity in the mesophase (10 K below T_i) is low enough to allow the formation of monodomains from planar distributions. For the polymer and even for the dimer the viscosities are too high to allow alignment processes in the mesophase. By proper choice of rotation frequency and cooling rate, monodomains with high order parameters can be generated by cooling below the isotropic phase.

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Mean-Square Radius of Gyration of Oligo- and Poly(methyl methacrylate)s in Dilute Solutions

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ABSTRACT: The mean-square radius of gyration $\langle S^2 \rangle$ was determined by small-angle X-ray scattering and light scattering for 20 samples of atactic oligo- and poly(methyl methacrylate)s (a-PMMA), each with the fraction of racemic diads $f_r = 0.79$, in the range of weight-average molecular weight M_w from 4.02×10^2 to 2.83×10^6 in acetonitrile at 44.0 °C (Θ). The ratio $\langle S^2 \rangle / x_w$ as a function of the weight-average degree of polymerization, x_w, exhibits unusual behavior; it passes through a maximum at $x_w \simeq 50$ before reaching its asymptotic value for large x_w. First, a comparison is made of the experimental data with the theoretical values on the basis of three types of the rotational isomeric state model, and it is shown that none of them can explain the observed maximum. Then, it is shown that the helical wormlike (HW) chain theory may well explain the data with the parameter values $\lambda^{-1}\kappa_0 = 4.0$, $\lambda^{-1}\tau_0 = 1.1$, $\lambda^{-1} = 57.9$ Å, and $M_L = 36.3$ Å^{-1}, where κ_0 and τ_0 are the curvature and torsion, respectively, of the characteristic helix taken at the minimum of energy, λ^{-1} is the stiffness parameter, and M_L is the shift factor. The present a-PMMA chain has a larger λ^{-1} (stiffness) but smaller Kuhn segment length (average chain dimension for large x_w) than an atactic polystyrene chain ($f_r = 0.59$), on which a similar study was previously made. In order to illustrate the situation, a picture is given of representative instantaneous contours of HW Monte Carlo chains for the two polymers.

Introduction

In this series of experimental work on dilute solutions of oligomers and polymers, we have already determined the mean-square optical anisotropy $\langle \Gamma^2 \rangle$, intrinsic viscosity $[\eta]$, and mean-square radius of gyration $\langle S^2 \rangle$ for atactic polystyrene (a-PS), using well-characterized samples of narrow molecular weight distribution and fixed stereochemical composition (the fraction of racemic diads $f_r = 0.59$),[1–4] and analyzed the data at the Θ temperature on the basis of the helical wormlike (HW) chain model.[5–9] As a next step, in the present and forthcoming papers, we proceed to make a study on atactic poly(methyl methacrylate) (a-PMMA) in the same spirit, using well-characterized samples over a wide range of molecular weight M, including the oligomer region, and with $f_r = 0.79 \pm 0.01$.[10] The present paper deals with only $\langle S^2 \rangle$.

Now, there have already been a number of both experimental and theoretical investigations[11–19] on dilute solutions of a-PMMA or syndiotactic poly(methyl methacrylate) (s-PMMA). Among these, the most remarkable experiment is due to Kirste and Wunderlich,[14,15] who showed that the so-called Kratky plot of the scattering function, $P(\theta)$, determined from small-angle X-ray scattering (SAXS) exhibits damped oscillation around an asymptotic straight line for the rodlike polymer. On the theoretical side, Yoon and Flory[19] showed on the basis of the rotational isomeric state (RIS) model that, for PMMA chains with an f_r greater than a certain value, the characteristic ratio C_n first increases with increasing chain length, then passes through a maximum, and finally goes down to its asymptotic value C_∞. These results are inconsistent with the theoretical predictions based on the Gaussian chain and even on the Kratky–Porod (KP) wormlike chain,[20] and indeed this led us to the introduction of the HW chain model.[5–7]

We have already made an analysis of some of the literature data for $[\eta]$ and $\langle S^2 \rangle$ as functions of M for a- (or s-)PMMA on the basis of the HW model[9,21] and preliminarily concluded, from a comparison with the results for the a-PS,[2–4] that there is a remarkable difference between chain conformations of these two polymers.[3,4] However, the existent data for a-PMMA scatter considerably and are not good enough to permit an accurate determination of the HW model parameters for a quantitative discussion of its chain conformations in dilute

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