Conformational Behavior of the Spacer in a Liquid Crystalline Main-Chain Polymer in Its Nematic and Glassy States

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ABSTRACT: NMR investigations of a liquid crystalline main-chain polyether are presented. This glass-forming polymer consists of the aromatic mesogen 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB) linked through a perdeuterated decylene spacer. At higher temperatures in the nematic mesophase the conformational behavior of the alkyl group is consistent with the alternate trans model, predicted by calculations of Yoon. At lower temperatures in the glassy state the hydrocarbon chain is found to be an extended chain containing an increased amount of trans conformers. This change in the conformational statistics is accompanied by reduced conformational mobility in the glassy state. Evidence for two glass transitions is presented, one being associated with the freezing of the mesogens and the other, at the lower temperature, being due to freezing of the spacer mobility.

1. Introduction

Liquid crystalline main-chain polymers have generated substantial technical interest as polymers of the "rigid-rod"-type.[1–3] However, they can also be used as model compounds for the study of particular aspects of polymer chain conformation and dynamics. In this respect polymers consisting of mesogens which are connected to each other by hydrocarbon spacers are of special interest.[4–6] This special polymer structure fixes the spacer at both ends. The end to end vector of the spacer group is virtually held constant so that the number of possible conformers is reduced and the dynamic behavior is expected to be simpler as compared to that of a free polymer chain. Hence, the study of such a model system should allow a deeper insight into the behavior of free polymer chains.

Semiflexible liquid crystalline main-chain polymers have been previously studied to a large extent.[6–9] Rotational isomeric state (RIS)[10] calculations of Yoon for main-chain polymers with an even number of methylene groups in the alkyl chain linked via ether groups to the mesogens gave rise to the "alternate trans model"[6–8] (Figure 1a). In this model every second bond between methylene groups is found to be in a trans conformation, while for the other carbon–carbon bonds exchange between trans and gauche conformations is allowed. For a decylene spacer 243 conformers of similar energies are expected. On the basis of these conformational calculations, ^{2}H NMR spectra of the alkyl spacer could be simulated in the nematic mesophase for several systems.[6–8,13] In general, a good agreement with the alternate trans model was found in the nematic phase. In this model the long axes of the mesogens are aligned along the orientation of the elongated polymer chains and all C–H bonds of a given alkyl chain are located on a cone with an apex angle of 70.5° with respect to the mesogenic segmental axis. For the different conformers with an alternate trans chain, a *mean* cone angle α (cf. Figure 1) of the alkyl chain axis with respect to the mesogenic segmental axis and therewith to the director $\vec{n}$ of ±10° was estimated. As a consequence, the mesogenic units build up an almost elongated polymer chain with probably few hairpins as proposed by the neutron scattering investigations.[11]

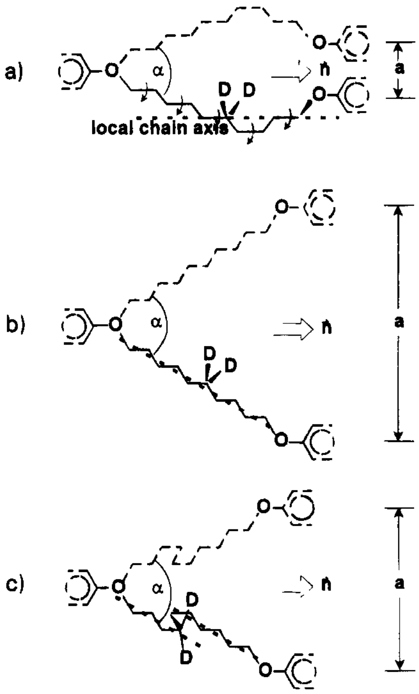

Figure 1. Conformations of an alkyl chain with a high degree of elongation: (a) alternate trans chain; (b) all-trans chain; (c) trans chain with gauche defect. The local chain axis is indicated by the dotted lines. Also indicated is the cone angle α of the alkyl chain axis with respect to the mesogenic segmental axis and the resulting distance *a* between the mesogenic units on such a cone. Please note the extreme case for an all-trans chain as compared to other possible conformations.

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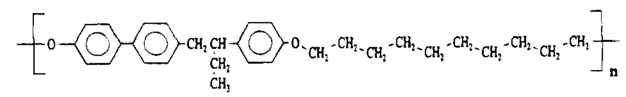

Figure 2. Scheme of the chemical repeat unit of TPB-10.

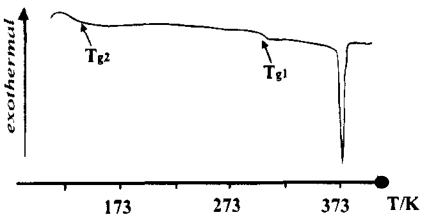

Figure 3. Differential scanning calorimetric measurement of TPB-10. The data were recorded using a heating rate of 5 K/min to achieve a high sensitivity.

In the solid state the alternate trans model could not be confirmed by NMR investigations of liquid crystalline main-chain polymers, contrary to the situation for the nematic mesophase.[9,12] It should be noted that the systems investigated so far showed a high tendency to crystallize, forming semicrystalline polymers in the solid state. Here, evidence of a high content of trans conformers (Figure 1b,c) in connection with a high degree of orientational order[9] was found. For such an all-trans chain the extreme case with a maximum cone angle α of the chain axis with respect to the mesogenic segmental axis amounts to ±30° (Figure 1b). In this case the mesogenic units are inclined with respect to the polymer chain axis which is in good agreement to the occurrence of the cybotactic nematic phase as found from SANS and X-ray studies;[11] see below. This extreme situation is reduced with a small number of gauche defects (cf. Figure 1c). The discrepancy with the model of Yoon can be related to the tendency of these systems to crystallize at low temperatures.

In this paper, ^{2}H NMR results are presented on a semiflexible liquid crystalline main-chain polymer which does not crystallize, i.e. the system poly-[1,10-decylene-1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane][13] (Figure 2), named TPB-10 according to ref 14. Due to the carefully chosen branched structure of the mesogen and the presence of two constitutional stereoisomers, the crystallization of the polymer is suppressed. In the DSC trace of TPB-10 three thermal transitions are observed (Figure 3). At 375 K a transition from the isotropic phase to a nematic phase is found, at 304 K (T_{g1}) the nematic phase is frozen in, while at 130 K (T_{g2}), near the glass transition T_γ of polyethylene (140 K),[15] a second glass transition is observed. In addition, at about 343 K a transition from a cybotactic nematic to a nematic phase is observed only by X-ray and SANS experiments.[11] Molecular order and dynamics was investigated by solid-state ^{2}H NMR methods in the nematic mesophase and in the glass with the aim of checking the model considerations on the alkyl chain conformation in an amorphous semiflexible liquid crystalline main-chain polymer.

NMR Background. A powerful method for the study of molecular order and dynamics is ^{2}H solid-state NMR spectroscopy.[16] For the case of an axially symmetric electrical field gradient tensor at the deuteron, as found in aliphatic C−^{2}H bonds, the frequency ω of an NMR transition is given by:

$$\omega = \omega_0 \pm \frac{\delta}{2}(3\cos^2\theta - 1) \quad (1)$$

where ω_0 is the Larmor frequency, δ is the quadrupolar coupling constant (128 kHz), and θ denotes the angle between the magnetic field $\mathbf{B}_0$ and the C−^{2}H bond. Hence, through the angular dependence of eq 1 it is possible to measure orientations by changes of the line shape as a result of motional averaging between different orientations. It is also possible to obtain information about the geometry of such motions (e.g., jump type or diffusive motions).

Very detailed information about the geometry of motion occurring on the time scale of milliseconds to seconds can be obtained by two-dimensional (2D) NMR.[17-19] Here two frequencies are detected at two different times separated by the so-called mixing time. This mixing time is the characteristic time window for the experiment. Slow motions during this time will lead to off-diagonal intensity in the plane of a 2D spectrum. The line shape of such an exchange pattern allows one to extract detailed information about the geometry of molecular motions.[18,19] In particular, for discrete jump type motions elliptical exchange patterns are observed.

2. Experimental Section

All NMR experiments were performed on a Bruker CXP-300 spectrometer. For one-dimensional NMR experiments the solid-echo pulse sequence[20] was used. Details for the recording of two-dimensional spectra are given in ref 18.

The synthesis of the TPB-10 was performed using 0.1 mmol of 1-bromopentene, 0.9 mmol of perdeuterated 1,10-dibromodecane, and 1.0 mmol of TBP; for details of the procedure, see ref 14. The use of the perdeuterated analogue of 1,10-dibromodecane led to a polymer with a fully deuterated spacer, hence, its order and dynamics could be monitored selectively. The molecular weight of the polymer was checked by GPC using polystyrene standards, resulting in M_n = 16 000 and M_w/M_n = 1.76.

Spectra were recorded on powder samples as well as on oriented samples. The samples could easily be oriented by slowly cooling them from the isotropic phase into the mesophase in the presence of the 7.0 T magnetic field of the NMR magnet. At lower temperatures a goniometer probe was used, where the oriented sample could be rotated to different angles β with respect to the magnetic field. In order to measure powder spectra at this temperature, the sample was quenched from the isotropic state to the desired temperature and spectra were recorded using the minimum amount of time, so that orientational effects during the data acquisition can be neglected.

3. Chain Dynamics in the Nematic and in the Glassy State

The chain order and dynamics in the *nematic mesophase* have recently been studied in detail by Sherwood et al.[13] Therefore, only the main conclusions are reported here. The ^{2}H NMR spectrum of an unoriented sample in the nematic phase (T = 348 K, Figure 4a) exhibits a Pake pattern reduced in width by a factor of 3 compared with a rigid solid (T = 180 K; Figure 4c). This is consistent with the alternate trans model mentioned above, where an exchange between three sites leads to the observed reduction factor. Further support of this model can be obtained by the observation of a single quadrupolar splitting for the fully deuterated decylene spacer in the ordered sample (Figure 4d), corresponding to an order parameter S = 0.88 (corresponding to a Gaussian distribution with ±12° full width at half-height) at this temperature.

Below the *glass transition* temperature T_{g1} = 304 K, however, the ^{2}H NMR spectrum of the unoriented sample is remarkably different (T = 300 K; Figure 4b); the chain motion is not frozen in, but its geometry is

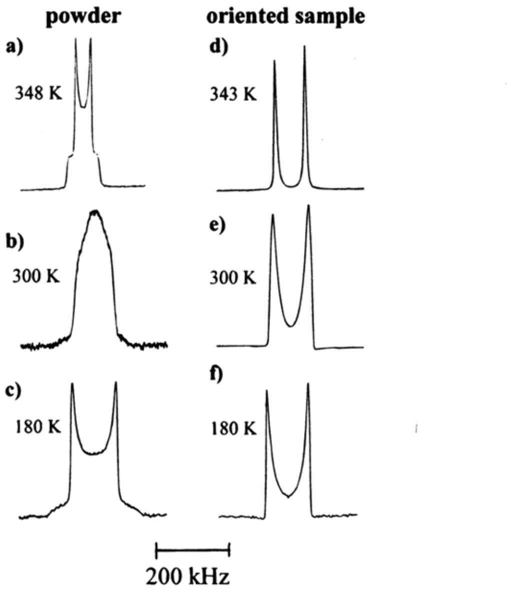

Figure 4. Solid-echo spectra of TPB-10 at different temperatures: (a–c) spectra of the unoriented sample in the glassy state and the nematic phase; (d–f) spectra of the oriented sample at the same temperatures as in a–c, with the director parallel to the magnetic field $\mathbf{B}_0$ ($\beta = 0$).

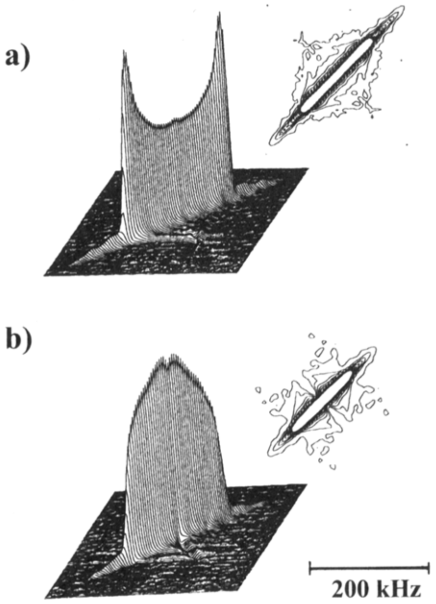

Figure 5. 2D exchange spectra of TPB-10 recorded at temperatures above the glass transition T_{g2} at different temperatures and mixing times: (a) $T = 220$ K, $t_m = 1$ ms; (b) $T = 292$ K, $t_m = 1$ ms.

changed considerably. The line shape of Figure 4b is commonly observed in amorphous polymers, liquid crystals, and model membranes and referred to as a “kink spectrum”.[16] It results from conformational exchanges of alkyl chains between two nonequally populated sites involving reorientations of individual C–H bonds by angles around the tetrahedral angle.[21,22] Thus, whereas in the nematic phase a given C–^{2}H bond exchanges between three different positions on a cone due to transitions within the alternate trans conformation, only two different conformations (C–^{2}H orientations) are accessible for each unit below T_{g1} on a time scale below 1 μs. Since the chain motion is not frozen in at T_{g1}, this glass process is ascribed to a freezing in of the mesogens. The spacer still fluctuates, but it is fixed at its ends through the immobile mesogens. In fact, an essentially identical behavior has previously been observed in amorphous ionene polyelectrolytes,[23] where the glass transition was shown to be due to the melting of the ionic structure and the alkyl chains between the ionic centers exhibit restricted mobility in the glassy state.

At lower temperatures conformational exchange becomes slow on the time scale of a 1D experiment, so that the typical Pake pattern is observed at these temperatures (Figure 4c); however, motions on the time scale of milliseconds to seconds still can be detected by 2D exchange NMR.[19] Such 2D ^{2}H spectra of powder samples are displayed for different temperatures in Figure 5. It is immediately obvious that no elliptical exchange patterns are observed. Such patterns give strong evidence of discrete jump angles; therefore, the occurrence of such discrete jumps can be directly excluded. On the other hand, the exchange pattern extends over a large spectral region of the 2D spectrum, which indicates that large-angle motions must be involved. Again, the same behavior has previously been observed in the glassy ionenes.[23]

The 2D spectra of Figure 5 are representative of a series of 2D spectra at different temperatures between 200 and 290 K and at different mixing times. For all spectra, very similar exchange patterns are observed. The low ratio of exchange intensity versus diagonal intensity in the 2D spectrum, corresponding to nonmobile components, changes only slightly during this temperature interval. This almost temperature-independent behavior can only be explained by the assumption of motions with a relatively low energy of activation and a broad distribution of correlation times. A low activation energy indicates that this motion must be highly local and not hindered by packing effects. Indeed, conformational exchanges between trans and gauche conformers in free hydrocarbon chains have an energy of activation of only about 12 kJ/mol.[24]

At lower temperatures, a second glass transition at $T_{g2} = 130$ K is observed. Therefore, it is interesting to relate the restricted chain motion to this glass transition. Around 80 K above T_{g2}, the motions of some of the hydrocarbon chains become so slow that they fall outside the time window covered by ^{2}H 1D experiments. Contrary to that for typical glass-forming polymers such as amorphous polystyrene, this slowing down is observed only 40 K above T_g.[25] Therefore, TPB-10 is not following a typical WLF behavior.[26] However, due its proximity to the T_γ of polyethylene, it is still likely that the glass transition T_{g2} is associated with the freezing in of the hydrocarbon chain motions.

4. Molecular Order in the Glassy State

The proposed change in conformational freedom of the alkyl spacer observed at T_{g1} poses the question of whether or not the chain order in the *glassy* state also deviates from that of the *nematic* mesophase.

First, we note that the sample clearly remains macroscopically ordered in the *glass*, as can be seen from the differences between the 1D line shapes of the powder sample (Figure 4a,b) and the oriented sample (Figure 4d,e). For this oriented sample the director $\vec{n}$ is aligned parallel to the magnetic field $\mathbf{B}_0$. However, for a better determination of the orientational distribution, spectra at different angles β between $\vec{n}$ and $\mathbf{B}_0$ are required.[27] In Figure 6 experimental spectra of the oriented sample (Figure 6a) for different β are displayed together with simulations (Figure 6b–c). The experiments were

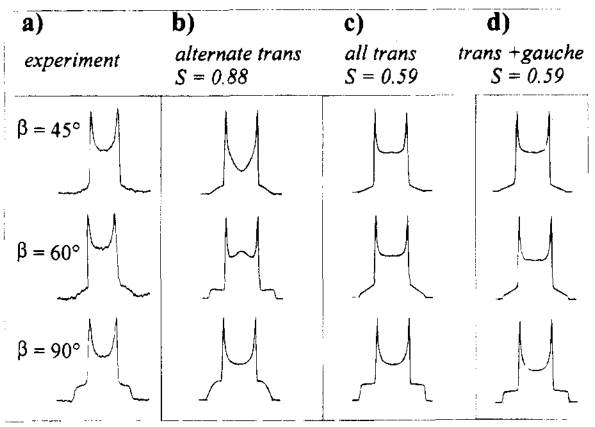

Figure 6. Solid-echo spectra of the oriented sample recorded at $T = 180$ K. The sample was rotated around an angle β with respect to the aligning magnetic field $\mathbf{B}_0$: (a) experimental spectra; (b) calculated line shapes for the assumption of the alternate trans model as observed in the nematic mesophase; (c) calculated line shapes for the assumption of an all-trans chain; (d) calculated line shapes for the assumption of an all-trans chain containing 30% of gauche defects.

recorded at a temperature of $T = 180$ K considerably below the glass transition T_{g1}, where the line shape of a corresponding powder spectrum at this temperature shows a Pake pattern with a quadrupolar splitting of $\Delta\nu_q = 120$ kHz. Hence, for the simulations of the oriented samples, molecular motions need not to be taken into account.

As pointed out above, the orientation dependence of the resonance frequency (cf eq 1) allows the determination of the orientational distribution function in ordered systems. Since the EFG tensor of the deuteron generally lies along the C$-^2$H bond, its orientational distribution is reflected in the spectral line shape. Therefore, a C$-^2$H order parameter S_D can be extracted from a series of spectra taken at different angles between the order axis and the magnetic field.[27] From this value the molecular order parameter can be deduced if the orientation between the C$-^2$H bond and the molecular order axis is known.[28] In the case of the decylene chain in the semiflexible liquid crystalline main-chain polymer, the angle between the C$-^2$H bond and the order axis is 70.5° and 90° for the alternate trans chain and the all-trans chain, respectively. Thus, in the nematic phase the order parameter S_D, as measured in ^{2}H NMR, can be interpreted as:

$$S_D = S_{\text{mol}}^{\text{nem}}\frac{1}{2}(3\cos^2 70.5° - 1) = 0.88(-1/3) = -0.29 \tag{2}$$

In Figure 6b simulations of spectra are shown, which would be expected if the order of the nematic phase could be frozen in, i.e., the alternate trans model is retained with all deuterons located on a cone with the angle $\alpha = 70.5°$ with respect to the order axis. The same order parameter of $S_{\text{nem}}^{\text{mol}} = 0.88$ as determined in the mesophase has been assumed corresponding to a Gaussian distribution around the cone angle of ±12°, but no fast rotations on this cone were allowed. It is immediately obvious that the simulations for this model do not match with the experiment. In particular, the line-shape differences calculated for $\beta = 60°$ and $\beta = 90°$ in Figure 6b are opposite to the experimental ones (Figure 6a). In order to fit the data, the different conformational statistics in the glassy state due to energetic reasons has to be taken into account. For an extended trans chain the C$-^2$H bond is perpendicular to the order axis.[27] This corresponds to a reduction of the molecular order parameter by a factor of $(3\cos^2 70.5 - 1)/(3\cos^2 90 - 1) = {}^2/_3$, resulting in a value of $S = 0.59$. Simulations of line shapes based on this assumption (Figure 6c) result in a highly satisfactory fit to the experiment. It should be noted that the order parameter for the C$-^2$H bonds of the alkyl chains does *not* change when freezing into the glassy state, where now for the extended trans regions of the chain:

$$S_D = S_{\text{mol}}^{\text{glass}}\frac{1}{2}(3\cos^2 90° - 1) = 0.59(-1/2) = -0.30 \tag{3}$$

Thus, the reduction of $S_{\text{mol}}^{\text{glass}}$ with respect to $S_{\text{mol}}^{\text{nem}}$ nearly reflects the fact that an extended trans chain segment will typically not be aligned along the director but rather inclined to it (cf. Figure 1). Note that, due to the cylindrical symmetry of the nematic glass, positive and negative inclination angles will be equally probable. This is reflected in the X-ray and SANS experiments which indicate a cybotactic nematic phase at low temperatures with inclination angles of ±30°.[11]

In a more realistic treatment, gauche defects were included. In the gauche conformers the deuterons are situated on a cone with $\alpha = 35°$. The comparison between parts c and d of Figure 6 reveals that up to 30% of gauche components can be assumed, without deteriorating the fit.

5. Discussion

Our study of chain dynamics and order clearly shows that the chain conformation in the glassy state differs from that in the nematic mesophase. Whereas in the latter the ^{2}H NMR spectra are consistent with the alternate trans model, in the former extended trans conformations with a reduced gauche content are present. At T_{g1} a rather abrupt change between the two conformational states is observed.

The extended trans and the alternate trans chains assume different orientations of the chain axis relative to the director, so that a change from alternate trans to extended trans must be accompanied with a change of the polymer chain orientation. In fact, the reorientation of the hydrocarbon chain deduced here from NMR results is corroborated by the observation of the reorientation of the mesogens by small-angle neutron scattering (SANS) and X-ray diffraction experiments,[11] which indicate a transition from a cybotactic nematic to a nematic phase.

It is interesting to note that, whereas ^{2}H NMR confirms the alternate trans model for the decylene spacer at higher temperatures in the nematic mesophase, ^{13}C NMR investigations on a similar polymer with nonylene spacers have confirmed a conformational model, where only every third C$-$C bond is found in the trans conformation, while for the other bonds fast exchanges between trans and gauche take place.[29] This behavior can be explained by the fact that the alternate trans model is expected for hydrocarbon chains with $2n$ carbons only. Then, due to symmetry the carbons $1 + k$ and $2n - k$ $(0 \le k \le n)$ are equivalent. Therefore, an "even−odd" effect concerning the dynamic and conformational behavior of hydrocarbon chains is expected.

As mentioned above, similar motional behavior of hydrocarbon chains has also been found in polyionenes,[23] which contain hydrocarbon chains of equal length with fixed ends in the glassy state. In fact, two glass transitions have been found for ionenes as well.[30] Therefore, it seems that the motional behavior observed here is typical for polymer chains between anchoring points. For such systems, two separate glass transitions are expected. At the glass transition temperature T_{g2}, which is close to the temperature referred to as T_γ of polyethylene, the onset of restricted motion of the hydrocarbon chains occurs. At considerably higher temperatures (T_{g1}) the anchoring points themselves become mobile and therefore lead to new degrees of freedom in polymer chains.

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