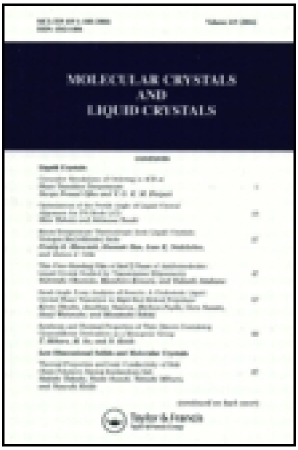

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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NMR of Stiff Macromolecules with Flexible Side Chains

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NMR OF STIFF MACROMOLECULES WITH FLEXIBLE SIDE CHAINS

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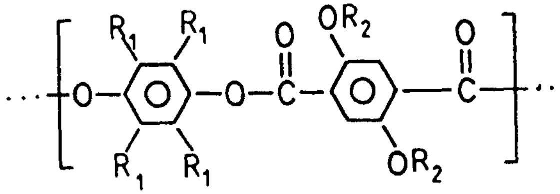
Abstract A rigid rod polymer with flexible alkyl side chains (poly-(1,4-phenylene-2,5-dihexadecyloxyterephthalate)), selectively deuterated in the aromatic rigid chain part and in the flexible alkyl chain, was studied by ^{2}H-NMR. The temperature dependent motional behaviour of the polymer chain and of the alkoxy side chain is discussed as well as the molecular order of the system generated by the magnetic field.

INTRODUCTION

Rigid rod polymers are materials of increasing interest for applications such as high modulus fibers. Due to the high melting points and insolubility in almost all solvents, however, the technical processing of such systems is difficult. By modifying the stiff backbone with flexible side chains the transition temperature can be decreased dramatically[1]. Based on this concept systems are obtained, which form nematic phases, if the side chains are short, and which have smectic-like layered structures for longer alkyl side chains[2,3]. The modified polymers can be ordered by both mechanical and magnetic forces.

We have recently started ^{2}H-NMR investigations on typical representatives of this class of macromolecules, poly-(1,4-phenylene-2,5-dialkoxyterephthalate)s[4] (Figure 1). For alkoxy side chains containing more than ten carbon atoms these polyesters form layered structures[2,3]. Information on the mobility of different parts of the macromolecules is obtained from ^{2}H-NMR of specifically deuterium labelled systems. The molecular order of the system is also studied by ^{2}H-NMR[5].

In this preliminary report we present the first results of our investigation on a specifically deuterated polyester with hexadecyloxy side chains:



I: $R_1 = {}^{2}H$ $R_2 = (CH_2)_{15}\text{-}CH_3$

II: $R_1 = H$ $R_2 = (CH_2)_6\text{-}C^{2}H_2\text{-}(CH_2)_8\text{-}CH_3$

FIGURE 1. Specifically deuterium labelled (I or II) poly(1,4-phenylene-2,5-dihexadecyloxy-terephthalate).

EXPERIMENTAL PART

Synthesis

The specifically chain deuterated polyesters II are prepared by the following route: Decylacid ethylester was reduced with $LiAlD_4$ to the 1,1-d_2-decanol which was transformed with HBr to 1-decylbromide. The respective Grignard reagent was condensed with 1,6-dibromohexane to 7,7-d_2-1-bromohexadecane[6]. The 1-bromohexadecane was reacted with diethyl-2,5-dihydroxyterephthalate using the method of Claisen[7]. After saponification with aqueous potassium hydroxide the resulting acid was converted with thionyl chloride into 2,5-di-(7,7-d_2-hexadecyloxy) terephthalic acid chloride. The polyester was prepared by solution or melt polycondensation of this acidchloride and hydrochinone[4].

Phenylring deuterated polyesters I are prepared by the same method using 1-bromohexadecane and deuterated hydrochinone[8].

Characterization of the polymers

These polyesters exhibit two different phases A and B[3], which could be identified by differential scanning calorimetry (Perkin Elmer DSC-7, calibrated with indium) and wide-angle X-ray scattering (Ni filtered Cu K_α radiation in reflection mode)[2,3]. Some characteristic data of the polyesters I and II are given in Table 1.

TABLE 1 Solid/solid transition temperatures T_s, melting temperature T_m, isotropic transition temperatures T_i, intrinsic viscosities and layer spacings at room temperature from poly(1,4-phenylene-2,5-dihexadecyloxyterephthalte)s I and II

Sample	T_s/K	T_m/K	T_i/K	$[\eta]/\frac{dl}{g}$	d/Å
I	337/372 1)	400	460	0.49	18/26 1)
	335 2)				26 2)
II	334/370 1)	402	450	0.52	18/26 1)
	335 2)				26 2)

1) from powder, 2) from melt

The solid/solid transition is due to an order/disorder transition in the alkyl part[9], whereas the layer spacings do not change. The lower transition temperature T_S

in Table 1 was found in phase A, where the alkyl chains are parallel to the layer normal, the higher one in phase B, where the alkyl chains are tilted with respect to the layer normal[3]. The spacings were determined by X-ray scattering to be 26 Å in phase A and 18 Å in phase B measured at room temperature. The coexistence of phase A and B was only found in the sample as received from solution, from the melt only pure phase A was obtained. Pure phase B could be produced by treating the powder with dioxane[10].

NMR measurements

NMR spectra were only taken of pure phase A. The samples were sealed in evacuated glass tubes after heating into the melt and subsequent quenching to room temperature. The measurements were performed on a Bruker CXP-300 spectrometer at a magnetic field of 7 Tesla.

In order to determine the type of motion, NMR spectra of both samples were obtained at different temperatures. Information on the macroscopic order was obtained from spectra at different angles of the director with respect to the magnetic field.

The temperature dependent spectra were first measured by rising the temperature from 230K in steps of 5K up to the melting point T_m and then in steps of 10K up to 20K above T_i. Spectra were also taken by cooling down the samples to the same temperatures. The angular dependent spectra were measured after the sample was quenched from the mesophase to room temperature in the magnetic field.

RESULTS AND DISCUSSION

Molecular Dynamics

Temperature dependent ^{2}H-NMR measurements of sample I (phenyl deuterated) showed at the lowest temperature of 230K only a Pake spektrum corresponding to the rigid powder[11] (Figure 2). On rising the temperature the motional averaged spectrum due to a 180^0 phenyl flip[11] appeared and became stronger while the rigid spectrum became weaker. At about 340K a sharp line corresponding to isotropic motion could be observed, which grew with increasing temperature, till it was the only signal above 465K. The same behaviour was observed during cooling. Samples with heigher and lower averaged molecular weight exhibited the same spectra.

The spectra of the hydrochinone part of the polymer below the solid/solid transition give evidence of a 180^0 jump motion of the phenyl ring augmented by oscillations of the phenyl by angles around 40 to 60 degrees[12]. In the high temperature phase the coexistence of an isotropic motion and the phenyl flip indicates a broad two phase region in this system, which is also typical for semiflexible main chain polymers[13]. At the melting point, as measured by DSC, no remarkable change of the spectrum is observed, similar to observations in semiflexible main chain polymers[14]. The temperature dependent ^{2}H-NMR spectra obtained from sample II (deuterated in the side chain) did not show the rigid Pake spektrum (Figure 3), not even at 230K, indicating residual chain motion. With increasing temperature the lineshape of the spectra changed to a rectangle and then to a triangle corresponding to a kink motion[11] of the side chain. Above 330K the sharp line indicating isotropic motion was observed. No difference was observed for samples of different averaged molecular weights.

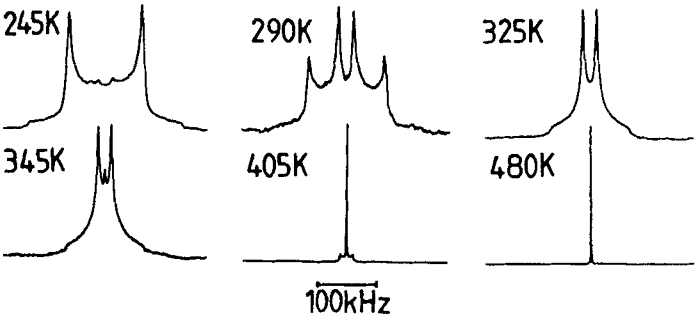


FIGURE 2. Temperature dependent ^{2}H-NMR spectra of sample I.

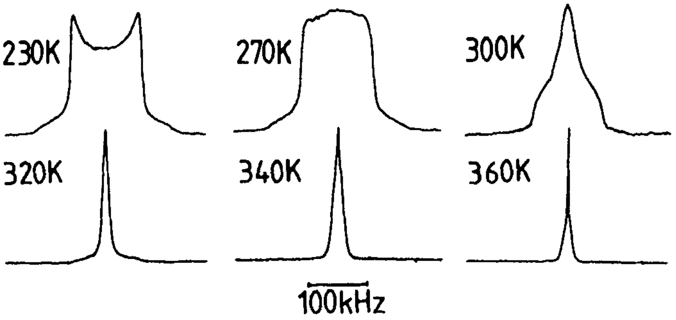


FIGURE 3. Temperature dependent ^{2}H-NMR spectra of sample II.

T_2 measurements of samples I and II (cf. Figure 4) showed a T_2 minimum at about 330K for sample I and a discontinuity of T_2 at about 295K for sample II. The changes in T_2 can be related to the solid/solid transition, as indicated by the shaded areas in Figure 4.

These results show considerable dynamics even in the solid state. The local motion in the 7-position of the alkoxy side chain below T_s increases gradually with temperature and at T_s there are additional degrees of motional freedom (shorter correlation times) as obtained from the

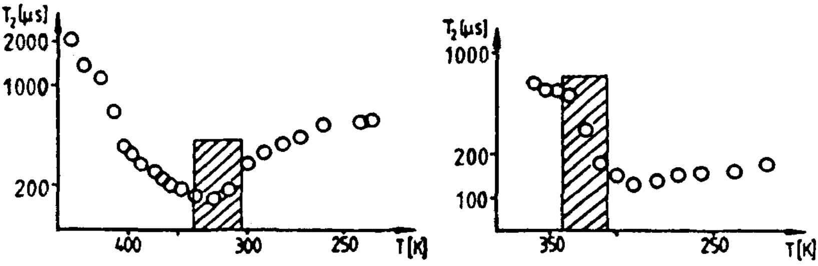


FIGURE 4. Temperature dependent T_2 of sample I (a) and sample II (b), the shaded areas indicate the width of the solid/solid phase transition as measured by DSC.

T_2 measurements for the 7-position of the alkyl chain. Similar motional behaviour is observed at solid/solid transitions in the flexible spacer of semiflexible main chain polymers[14] and in perovskites[15].

Molecular order

^{2}H-NMR spectra of the polyester I (phenyl deuterated) oriented in the magnetic field are shown in Figure 5 as a function of the angle of the director with respect to the magnetic field. The sample was kept in the magnetic field at 430K for thirty hours and subsequently quenched to room temperature, since the sample crystallizes during slowly cooling. The lineshapes consist in superpositions of spectra corresponding to an isotropic and an oriented

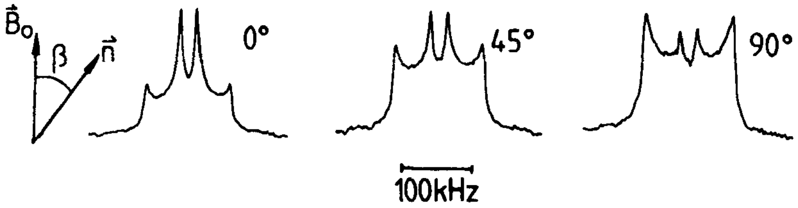


FIGURE 5. Angular dependent spectra of sample I at 295K.

part of the sample, as expected from the biphasic behaviour in the high temperature phase. The amount of oriented polymer is estimated to be about 20% in this case. The macroscopic order, introduced by aligning the sample in the magnetic field, as well as the kinetics of the alignment depend on the degree of polymerization. This behaviour is a strong argument for the existence of a mesophase, although our NMR data do not allow to specify its nature in detail.

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