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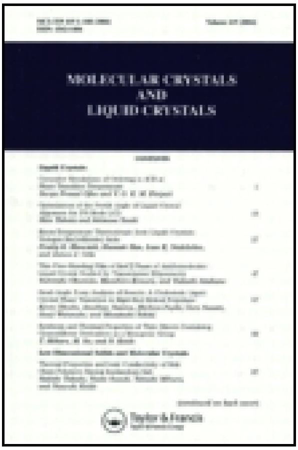

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Partially Deuterated Side-Chain Liquid Crystalline Monomers and Polymers: Characterization and Order by ^{2}H NMR

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Two partially deuterated liquid crystalline monomers **1, 2** and side-chain polymers **3, 4** therefrom were synthesized. The principal order parameter and biaxiality of the monomers were determined from their ^{1}H and ^{2}H NMR spectra. The ^{2}H orientational order of the polymers was also evaluated, which showed the coexistence of different phases over certain ranges of temperature.

Keywords: deuterated liquid crystal; ^{2}H NMR; order parameter; biaxiality

INTRODUCTION

There is a growing interest in the properties of chiral side-chain liquid crystalline polymers, because of their potential applications in electrooptical devices[1]. For the elucidation of their structure, order and dynamics NMR spectroscopy has proved to be very valuable[2], including ^{2}H NMR of perdeuterated or selectively deuterated liquid crystals[3].

In this work we prepared two new monomers **1, 2** and the corresponding polysiloxanes **3, 4** in which the aromatic mesogenic core comprised a partially

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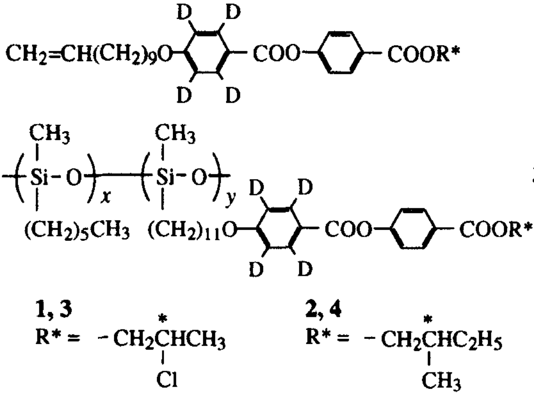
deuterated bis(oxybenzoate) unit and a chiral group R* of different nature. Their structure and orientational order were investigated by ^1H and ^2H NMR.



1, 2

3, 4

EXPERIMENTAL PART

Synthesis

Side-chain monomers **1** and **2** and corresponding polymers **3** and **4** were prepared following a similar procedure, which is described here for **1** and **3** as typical examples.

4-Hydroxybenzoic acid-d_4 (6): 10 g of 4-hydroxybenzoic acid (**5**) were dissolved in 30 ml of D_2O in the presence of 4 g of KOH and 1 g of 10% Pt/C and refluxed for one week. The catalyst was filtered off, the heavy water evaporated and the procedure was repeated twice. Finally, after three weeks the catalyst was filtered off, the solution acidified and the resulting precipitate filtered off. The mother liquors were extracted with diethyl ether and the organic phase was evaporated to dryness. The solids were combined giving 7.1 g of **6**. For establishing the deuteration rate, xylose was used as a reference material in equimolar amount.

^1H-NMR (D_2O) δ (ppm): 6.9 (d, 0.20H, H3+H5), 7.9 (d, 1.56H, H2+H6).

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4-(10-Undecenyloxy)benzoic acid-d_4 (7): 1.3 g (31.8 mmol) of potassium were dissolved with cooling in 3 ml (31.8 mmol) of heavy water and 11 ml of ethanol-d_1. 3.7 g (15.8 mmol) of 11-undecenyl bromide, 2.0 g (14.4 mmol) of **6** and a catalytic amount of KI were then added and the mixture was refluxed for 16 h. During the reaction a white precipitate formed, which was dissolved by addition of 30 ml of D_2O. 20% DCl was used for adjusting the pH = 3, and the mixture was refluxed for an additional 1h. After cooling the precipitate was filtered off, and washed with water. The solid residue was suspended in n-hexane and then recrystallized from methanol giving 2.9 g (71% yield) of **7**: Cr 84 °C SmC 124 °C N 138 °C I

4-(Ethoxycarbonyloxy)benzoic acid (8): 35.8 g (0.26 mol) of **5** were dissolved in 800 ml of water containing 30.0 g (0.75 mol) of NaOH. 43.4 g (0.4 mol) of ethyl chloroformate were then added dropwise at 5 °C and the mixture was let to react for an additional 4 h. The solution was acidified to pH = 5 by 20% HCl and the precipitate formed was filtered, dried and crystallized from benzene, giving 49.1 g (90% yield) of **8**: m.p. 156-157 °C.

(-)-(R)-2-Chloropropanol (9) ($[\alpha]^{25}_D$ = -20.6 (neat)) was synthesized from (-)-(*S*)-ethyl lactate according to a previous procedure[4].

(R)-2-Chloropropyl 4-(ethoxycarbonyloxy)benzoate (11): 7.0 g (33.3 mmol) of **8** were reacted at reflux with 20 ml of oxalyl chloride for 4 h. After cooling, the excess oxalyl chloride was removed by vacuum distillation, and the resulting acid chloride was used without further purification. 25.5 g (0.12 mol) of the acid chloride were added with 24.8 g (0.18 mol) of potassium carbonate to a solution of 11.3 g (0.12 mol) of **9** in 300 ml of dry diethyl ether. After refluxing for 5 h, the reaction mixture was cooled and the solid was filtered off. The solution was evaporated to dryness and the residue was purified by flash chromatography on silica using ethyl acetate as eluent, giving 25.0 g (73% yield) of **11**: R_f = 0.66; b.p. 96-100 °C/0.1 mmHg.

(R)-2-Chloropropyl 4-hydroxybenzoate (13): 15.0 g (52.3 mmol) of **11** were dissolved in 100 ml of ethanol and 110 ml of 25% NH_4OH were added at 5 °C. After 10 min, the pH = 5 was adjusted by 5% HCl. The cold reaction mixture was extracted with 200 ml of cold ethyl acetate. The organic layer was quickly washed with brine, dried over $MgSO_4$ and evaporated to dryness. The

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solid was crystallized from ethanol and finally from benzene, giving 7.8 g (70% yield) of **13**: m.p. 124-125 °C; $[\alpha]^{20}_D$ = -14.6 (ethanol).

(R)-4-[(2-Chloropropyl)oxycarbonyl]phenyl 4-(10-undecenyloxy)benzoate-d_4 (1): 1.0 g (3.4 mmol) of **7** and 0.7 g (3.4 mmol) of **13** were dissolved in 30 ml dry dichloromethane in the presence of a catalytic amount of p-dimethylamino pyridine. A solution of 0.7 g (3.4 mmol) of dicyclohexyl carbodiimide in 10 ml dichloromethane was added dropwise. After stirring overnight at room temperature, the precipitate was filtered off and the solution was evaporated to dryness. The residue was suspended in ethyl acetate, and the resulting solution was extracted with 5% DCl/D_2O, water, dried over Na_2CO_3, and evaporated to dryness. The solid was purified by column chromatography on silica gel using n-hexane:ethyl acetate 4:1 by vol. as eluent, giving 0.6 g (37% yield) of **1**: R_f = 0.56; $[\alpha]^{25}_D$ = -10.2 ($CHCl_3$).

^1H NMR ($CDCl_3$) δ (ppm): 1.60 (d, 3H, J = 6.8 Hz, CH_3), 1.25-2.10 (m, 16H, 8 CH_2), 4.05 (t, 2H, OCH_2), 4.32 (m, 1H, CH), 4.42 (d, 2H, J = 5.2 Hz, $COOCH_2$), 4.93 (m, 1H, J_{cis} = 10.2 Hz, CH_2=), 4.99 (m, 1H, J_{trans} = 17.2 Hz, CH_2=), 5.82 (m, 1H, CH=), 6.97 (m, 0.35H, H3+H5), 7.31 (m, 2H, H3'+H5'), 8.14 (m, 2H, H2'+H6'), 8.15 (m, 1.52H, H2+H6).

IR (KBr) $\bar{\nu}$ (cm^{-1}): 3079 ($\nu_{as}CH_2$=), 1722 (νC=O), 1642 ($\nu CH=CH_2$).

Polysiloxane 3: 0.40 g (0.8 mmol) of **1** and 0.05 g (0.7 mmol r.u.) of poly(hydrogenmethyl siloxane) (**16**) were dissolved in 40 ml of dry toluene under nitrogen atmosphere. 0.02 ml of a 2% xylene solution of platinum divinyltetramethyl disiloxane were added and the solution was stirred at 50 °C for 96 h. 1.0 ml (16.0 mmol) of 1-hexene (**15**) was then added and the mixture was let to react for an additional 12 h at room temperature. The solution was poured into a large excess of methanol and the coagulated polymer was purified by repeated precipitations from diethyl ether solution into n-hexane, giving 0.35 g (70% yield) of **3**: $[\alpha]^{25}_D$ = -8.2 ($CHCl_3$).

^1H NMR ($CDCl_3$) δ (ppm): 0.5 and 0.1 (2m, 9H, $SiCH_2$ + $SiCH_3$), 0.9-1.9 (m, 37H, aliphatic), 4.0-4.2 (2m, 5H, OCH_2, $COOCH_2$, CHCl), 6.9 (m, 0.35H, H3+H5), 7.2 (m, 2H, H3'+H5'), 8.1 (m, 3.5H, H2+H6 and H2'+H6').

IR (film) $\bar{\nu}$ (cm^{-1}): 1728 (νC=O), 1410 (δ_{as}Si-C), 1160 (νSi-O).

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Characterization

The structure of the compounds was confirmed by elemental analysis, IR (Nicolet Magna 750 FT-IR spectrophotometer) and ^{1}H NMR (Varian VXR 400 spectrometer).

The transition temperatures were determined by a Mettler TA4000 differential scanning calorimeter (scanning rate 10 °C/min) on samples that had been annealed by cooling from the isotropic liquid. They were also verified by visual observation of the birefringent textures by a Reichert Polyvar polarizing optical microscope.

The ^{2}H and ^{1}H NMR measurements in the mesophases were performed at 46.07 and 300 MHz, respectively, on a Varian VXR 300 spectrometer equipped with a variable temperature control. ^{2}H spectra were also recorded under proton decoupling conditions at each temperature.

RESULTS AND DISCUSSION

Side-chain monomers **1** and **2** and the corresponding copolysiloxanes **3** and **4** were synthesized by the reaction procedure illustrated in Fig.1.

TABLE I Transition temperatures of monomers **1** and **2**.

sample	R*	T_m (°C)		$T_{S\text{-}S}$ (°C)		T_i (°C)
1	2-chloropropyl	48	SmA*	--	--	64
2	2-methylbutyl	44	(SmC*	34.5)	SmA*	56

TABLE II Transition temperatures of copolysiloxanes **3** and **4**.

sample	x	y	M_n (g/mol)	M_w/M_n	T_g (°C)		T_i (°C)
3	21	14	18,000	2.6	-10	Sm*	163
4	4	31	27,000	2.4	-17	Sm*	113

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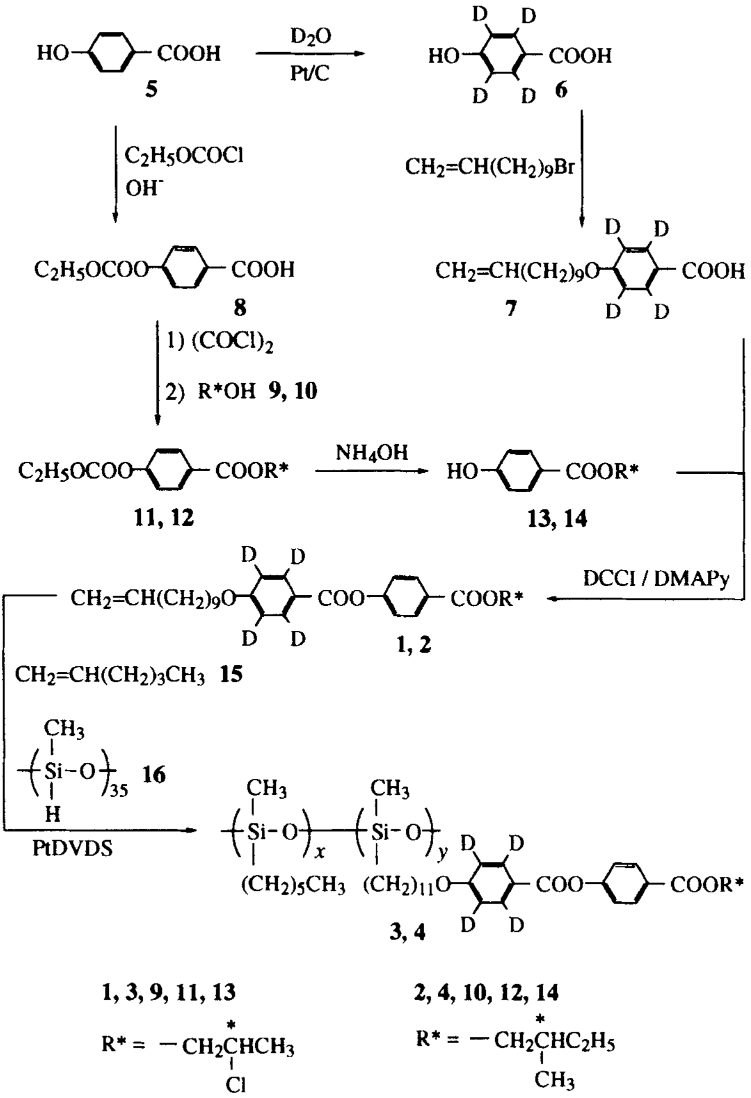

FIGURE 1. Reaction scheme for the synthesis of monomers **1** and **2** and corresponding polymers **3** and **4**.

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Copolysiloxanes of varying composition (x and y) were prepared by a conventional Pt-catalyzed hydrosilylation reaction by sequential grafting of either monomer **1** or **2** and 1-hexene (**15**) in the order onto a preformed poly(hydrogenmethyl siloxane) ($DP_n = 35$) (**16**) (Fig.1). Incorporation of even substantial contents of non-mesogenic side chains from **15** (60% mol in **3**) did not prevent the formation of a mesophase. On the other hand, this resulted in a rather low glass transition temperature ($T_g \leq -17$ °C), and consequently both **3** and **4** exhibited a chiral smectic (Sm*) mesophase directly at room temperature. We emphasize that the clearing temperature and the range of existence of the smectic mesophase for the copolysiloxanes were much greater than those of the corresponding monomers, for example $T_i = 163$ °C and $T_i - T_g = 173$ °C for **3** as compared to $T_i = 64$ °C and $T_i - T_m = 16$ °C for **1** (Tables I and II).

All the ^{2}H and ^{1}H NMR spectra were recorded by decreasing the temperature from the isotropic phase and allowing for temperature equilibration with a suitable pre-acquisition delay. As an example, the ^{2}H spectra of the SmA* phase of **1**, either with or without proton decoupling, at different temperatures are given in Fig.2. The very narrow-range SmC* phase of **2** appeared just above the crystallization, as was evidenced by both an increase in the line broadening and a small decrease of the splittings.

The two smectic monomers were partially deuterated. From their ^{2}H and ^{2}H proton decoupled spectra it was straightforward to extract the ^{2}H quadrupolar splittings and the D-H dipolar couplings. The quadrupolar splittings can be expressed in terms of local order parameters by Eq.1:

$$\Delta\nu_q = \frac{3}{2}q[S_{aa} + \frac{\eta}{3}(S_{cc} - S_{bb})] \qquad (1)$$

where q, the quadrupolar coupling constant is 185 kHz and η, the asymmetry parameter, is 0.04[5]. The a axis of the local reference frame, where the electric field gradient tensor is diagonal, coincides with the C-D bond direction, and the b axis is perpendicular to the aromatic ring plane. The dipolar splittings are related to the order parameters relative to the internuclear

D-H direction by Eq.2:

$$\Delta D_{DH} = -2K_{DH}\frac{S_{DH}}{r_{DH}^3} \tag{2}$$

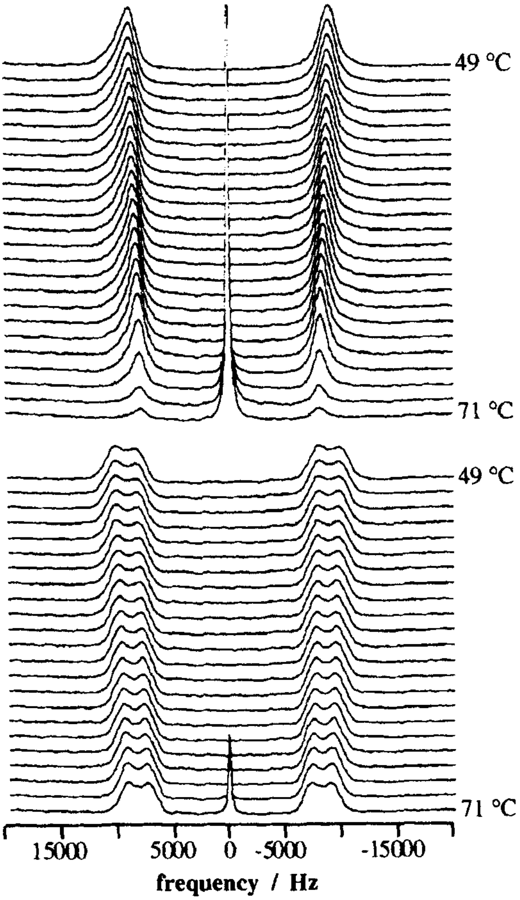

FIGURE 2. ^{2}H NMR spectra of monomer **1** with (top) or without (bottom) proton decoupling at different temperatures.

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where $K_{DH} = \frac{\gamma_D \gamma_H h}{4\pi^2}$ and r_{DH} is the internuclear distance. From Eqs.1 and 2, by combining the C-D and H-D order parameters it was possible to obtain the order parameter $(S_{zz})_D$ and the biaxiality $(S_{xx} - S_{yy})_D$ relative to a local frame fixed in the deuterated phenyl ring.

On the other hand, the ^{1}H spectra are informative for the orientational order of the *para* axis of the non-deuterated ring: the AA'BB' subspectrum of the non-deuterated phenyl ring appeared isolated from the other peaks and was dominated by the *ortho* H-H dipolar coupling from which the order parameter $(S_{zz})_H$ of the second ring could be evaluated with reasonable precision. By relating $(S_{zz})_D$ and $(S_{zz})_H$, an angle of 11-12 ° between the *para* axes of the two phenyl rings was evaluated for each monomer, consistent with previous determinations on the phenyl benzoate unit[6]. The temperature dependence of the order parameters determined is displayed in Fig.3.

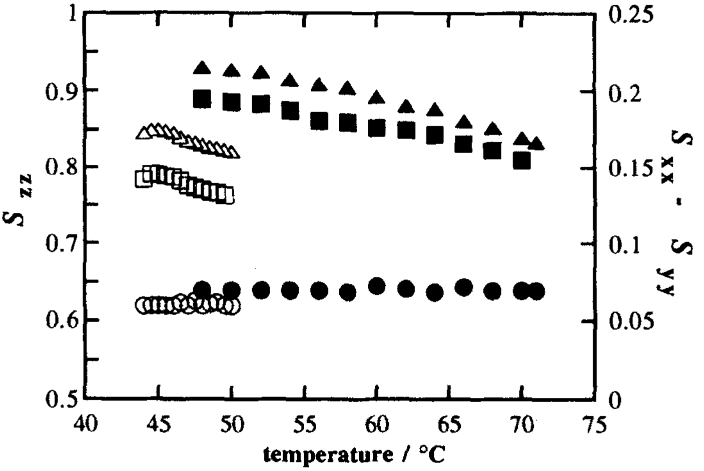

FIGURE 3. Temperature dependence of the principal order parameters $(S_{zz})_D$ (■, □) and $(S_{zz})_H$ (▲, △) and the biaxiality $(S_{xx} - S_{yy})_D$ (●, ○) for monomers **1** (filled symbols) and **2** (open symbols).

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The deuterium spectra of polymers **3** and **4** depended on their thermal histories but were completely reproducible after repeated annealing cycles by cooling from the isotropic liquid.

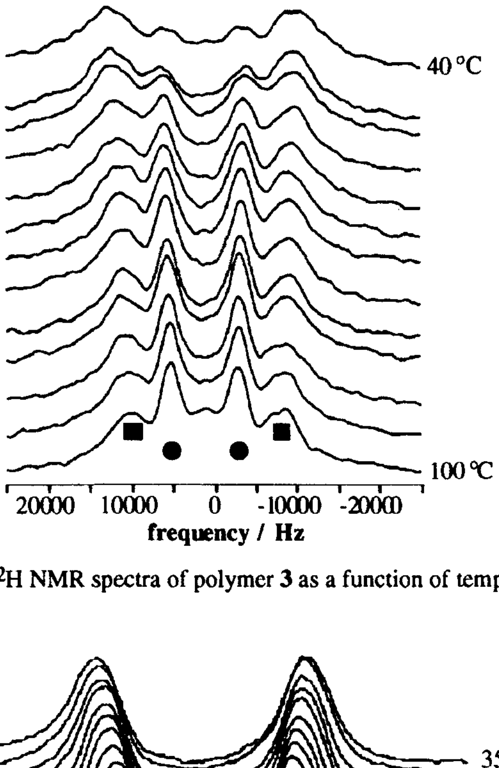

FIGURE 4. ^{2}H NMR spectra of polymer **3** as a function of temperature.

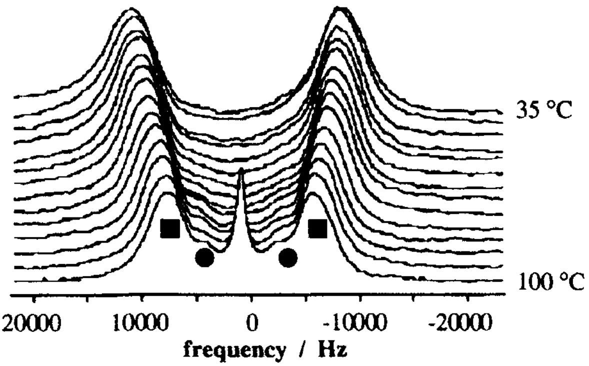

FIGURE 5. ^{2}H NMR spectra of polymer **4** as a function of temperature.

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The spectra revealed that two phases differing in their orientational order coexisted, the relative amount of which changed with temperature. For **3** the more oriented phase and that less oriented phase were in approximately 1:1 ratio at 100 °C. On cooling, this ratio progressively increased and became 4:1 at 40 °C (Fig.4). For **4** there was a small amount of a less oriented phase which disappeared on cooling below 80 °C (Fig.5).

The orientational order of the lateral mesogenic units was evaluated from the quadrupolar splittings (the linewidth was of the order of 4 KHz and therefore the dipolar splittings could not be extracted) and by assuming the same molecular structure and the same biaxiality as for the monomers. Its temperature dependence is shown in Figs.6 and 7.

In conclusion, in the monomers the fully protonated ring was slightly more oriented than the partially deuterated one, the two rings forming an angle of 11-12 °; for the deuterated ring the biaxiality was also computed. The structural data of the monomers allowed the evaluation of the ^{2}H orientational order of the polymers, in which two phases coexisted over defined ranges of temperature. This was probably due to a dilution effect of the non-mesogenic units. Further investigations are in progress to elucidate this aspect.

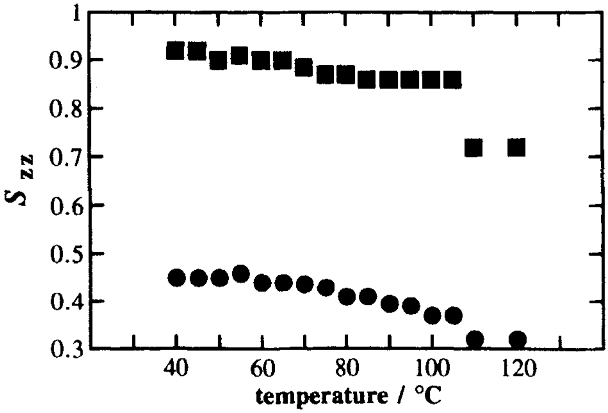

FIGURE 6. Temperature dependence of the orientational order parameter (S_{ZZ}) for the more oriented (■) and less oriented (●) phase of polymer **3**.

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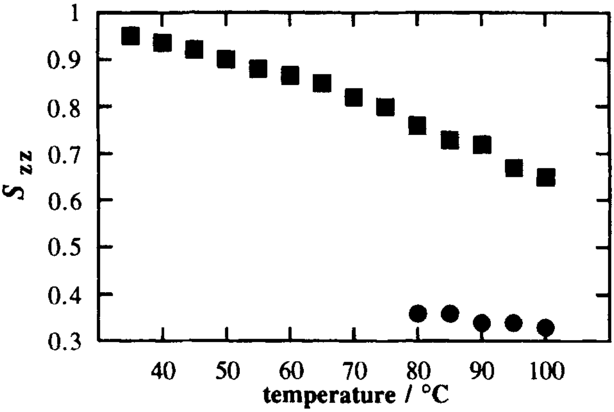

FIGURE 7. Temperature dependence of the orientational order parameter (S_{ZZ}) for the more oriented (■) and less oriented (●) phase of polymer **4**.

Acknowledgments

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