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A tin-containing liquid crystalline polymer with two glass temperatures

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A tin-containing liquid crystalline side group polymer was synthesized and characterized. Two glass transitions were detected by calorimetric investigations. The X-ray pattern corresponds to a smectic C order of the side groups and a disordered isotropic main chain. Dielectric measurements show two relaxation ranges which are influenced by the glass transitions and a fast local process. The low frequency mechanism can be related to the reorientation of the side groups and the higher glass transition temperature. The second is connected with the α-relaxation of the main chain and freezes in at lower temperatures.

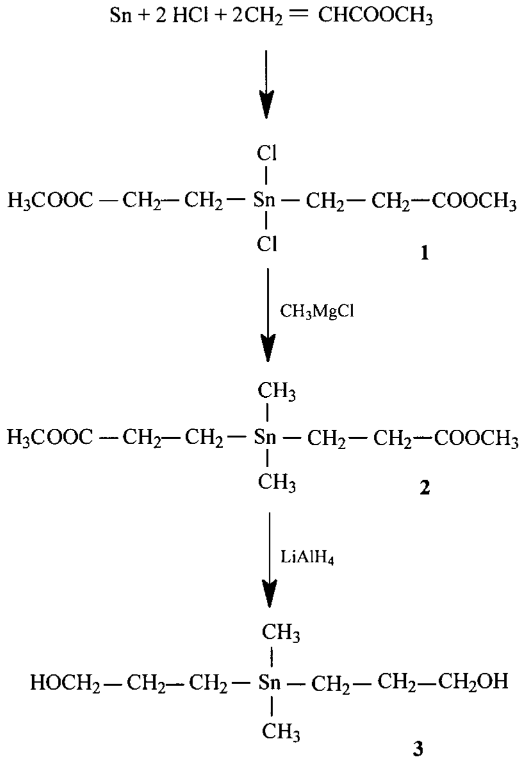
1. Introduction

The partial substitution of carbon atoms by tin in a homopolymer results in an increasing electron density of the tin–organic unit. Just this part will give a higher contribution to the X-ray scattering, and furthermore, a tendency towards phase separation on a nanometer scale can take place [1, 2]. In order to study these effects, a side group polymer was synthesized which contains the tin–organic unit in the main chain and has a strongly polar liquid crystalline side group. Therefore, we can expect to obtain information from X-ray scattering about the order of the main chain and side group, and also from dielectric investigations about the dynamics of both parts [3].

2. Synthesis, analytical and calorimetric results

The synthesis of the tin–organic liquid crystalline side group polyester is outlined in the following reaction scheme 1.

Bis(3-hydroxypropyl)dimethylstannane (**3**) was prepared in three steps. First bis[2-(methoxycarbonyl)-ethyl]dichlorostannane (**1**) was obtained by treatment of a mixture of metallic tin and methyl acrylate in dry diethyl ether with gaseous hydrogen chloride. Reaction of compound **1** with methylmagnesium chloride gave bis[2-(methoxycarbonyl)ethyl]dimethylstannane (**2**). Bis(3-hydroxypropyl)dimethylstannane (**3**) was then prepared by reduction of compound **2** by lithium aluminium hydride.



Scheme 1.

The liquid crystalline diethyl malonate **5** was synthesized according to scheme 2. Monoetherification of 4,4′-dihydroxybiphenyl with 4-nitrobenzyl bromide was carried out in dry 2-butanone with anhydrous potassium

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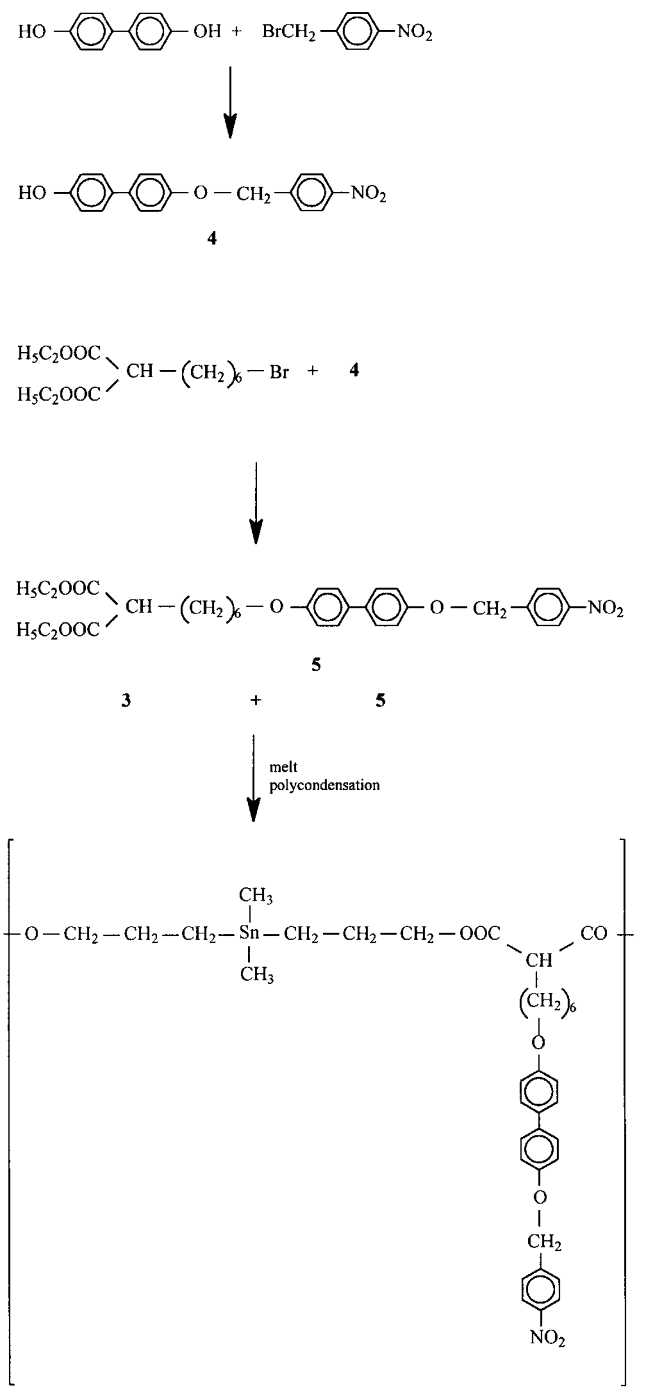
carbonate as base. To yield compound **5**, the benzyl ether **4** was further etherified with diethyl 6-bromohexylmalonate in the same manner. Melt polycondensation of the tin–organic diol **3** with compound **5** gave the polyester **6**.



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Scheme 2.

2.1. *Bis[2-(methoxycarbonyl)ethyl]dichlorostannane (1)*

This compound was prepared by the method of Burley *et al.* [4], but anhydrous diethyl ether was used as solvent. Recrystallization from methanol gave compound **1** in 48% yield; m.p. 134°C ([4] 132°C).

2.2. *Bis[2-(methoxycarbonyl)ethyl]dimethylstannane (2)*

To compound **1** (120.7 g; 0.33 mol) in 500 ml of anhydrous diethyl ether, methylmagnesium chloride (50.4 g; 0.665 mol) dissolved in tetrahydrofuran was slowly added with stirring and cooling (0°C). The mixture was stirred for 60 min at 0°C and then heated under reflux for 6 h. After cooling, dilute hydrochloric acid was added. The mixture was filtered and the ether layer separated and dried over sodium sulphate. After removal of ether and tetrahydrofuran, the residue was fractionated *in vacuo* yielding 89.2 g (84%) of compound **2**, b.p. (20 mbar) 141–144°C.

2.3. *Bis(3-hydroxypropyl)dimethylstannane (3)*

Compound **3** was obtained as described by Jurkschat *et al.* [5]. The product was distilled and then purified by column chromatography on silica gel (Kieselgel 0.063–0.200 mm, 'Baker Analyzed' zur Analyse, Netherlands) using chloroform/ethanol (vol. ratio 10/1) as eluting solvent. Yield 57%; b.p. (0.033 mbar) 111–115°C (lit [2], 0.066 mbar, 120–125°C). ^1H NMR ($CDCl_3$): $\delta = -0.037$ (s; 6H, $-Sn-CH_3$), 0.7 (t; 4H, $-Sn-CH_2-$), 1.65 (q; 4H, $-CH_2-CH_2-CH_2-$), 3.446 (t; 4H, $-CH_2-OH$), 3.092 (s; 2H, $-CH_2-OH$).

2.4. *Diethyl 6-[4-(4-nitrobenzyloxy)biphenyl-4′-oxy]-hexylmalonate (5)*

Compound **5** was prepared as described recently [6].

Polyester (6)

The preparation and purification of the polyester was carried out as described previously [7]. Additionally the sample was dissolved in toluene and washed with water/methanol (1/1). After evaporation of the solvent in vacuum the sample was dried at 323 K *in vacuo*. This procedure was necessary to obtain the low electrical conductivity necessary for the separation of the low frequency dielectric relaxation.

The polyester was characterized by elemental analysis and ^1H NMR spectroscopy and gel permeation chromatography. The results given below are in agreement with the proposed structure.

M_n [g mol^{-1}]: 6800 (by gel permeation chromatography (Fa. Knauer, FRG) after calibration with polystyrene standards in chloroform).

Elemental analysis of $(SnC_{36}H_{45}NO_8)_n$, $M = (738.45)_n$: calc, C 58.55, H 6.14, N 1.90; found, C 58.51, H 6.26, N 1.83%.

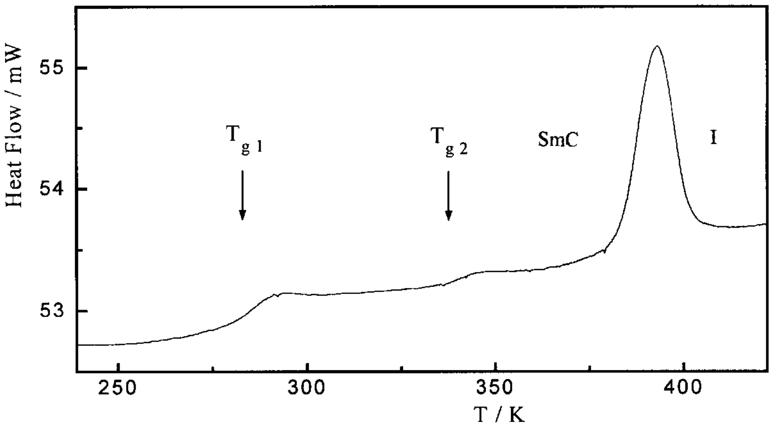

Figure 1. DSC trace of a sample of the polyester on a first heating run (10 K min^{-1}).

^{1}H NMR ($CDCl_3$): $\delta = -0.01$ (s; 6H, $-\mathrm{Sn}-\mathrm{C}H_3$), 0.70–0.78 (t; 4H $-\mathrm{Sn}-\mathrm{C}H_2-$), 1.20–1.90 (m; 14H, $-\mathrm{C}H_2-$), 3.27–3.35 (t, 1H, $-\mathrm{C}H=$), 3.89–4.06 (m; 6H, $-\mathrm{O}-\mathrm{C}H_2-\mathrm{CH}_2-$), 5.16 (s; 2H, $-\mathrm{O}-\mathrm{C}H_2-$), 6.87–6.98 (m; 4H, H_{arom}); 7.39–7.46 (m, 4H, H_{arom}), 7.56–7.60 (d; 2H, H_{arom}), 8.19–8.23 (d; 2H, H_{arom}).

It has to be pointed out that the product of the polycondensation shows a distribution of molecular mass as normally observed. For compound **6**, the phase sequence SmC 393 K I has been found by polarizing microscopy. Due to the distribution of molecular mass, a clearing interval of about 10 K was observed.

The results of calorimetric investigation (DSC7, heating rate 10 K min^{-1}) are shown in figure 1. Surprisingly, two glass transitions with onset temperatures of about 286 and 341 K could be detected. The broad peak at 390 K indicates the clearing interval.

3. X-ray and dielectric investigations

The X-ray studies were performed using the Guinier method (film camera or a goniometer, Huber Diffraction Technic, FRG) for non oriented samples and a flat film camera for oriented samples. It was difficult to optimize the sample thickness for an appropriate overall scattering diagram. Therefore we divided the measurement into the low angle part and the wide angle part, as shown in figure 2. The remarkable feature of the powder-like pattern is, that, besides the layer reflection in the small angle region ($q = 1.18\,\mathrm{nm}^{-1}$; $d = 5.34\,\mathrm{nm}$), two outer scattering maxima appear; these have not been observed in the corresponding homologue without Sn and are maintained up to room temperature.

The diffuse scattering was fitted by two Gaussians (figure 3), which led to scattering vectors at the maxima $q_1 = 1.157\,\mathrm{nm}^{-1}$ and $q_2 = 1.435\,\mathrm{nm}^{-1}$. The second corresponds with the well known lateral distances between mesogenic groups in a SmC layer, whereas the first is caused by the Sn-containing main chain. It was possible to study an oriented sample as a very thin fibre. Unfortunately however, the extremely low intensity on a high background does not allow reproduction of the pattern. A schematic representation is given in figure 4. The layer spots were recorded perpendicular to the fibre axis (equal to the equator), whereas the second diffuse scattering is split off and observed out of the equator. This is explained by a tilt angle of the side groups of about 32° with respect to the layer normal. The first diffuse scattering, however, forms a closed diffuse ring, indicating statistically distributed scattering units; this means a randomly oriented main chain. These different orders in a homogeneous phase demand a structural model in which the main chains are separated from the side groups and that the smectic layer consists of two sub-groups with different structures. Using the experimental data (tilt angle and layer thickness) a structural model shown in figure 5 can be constructed.

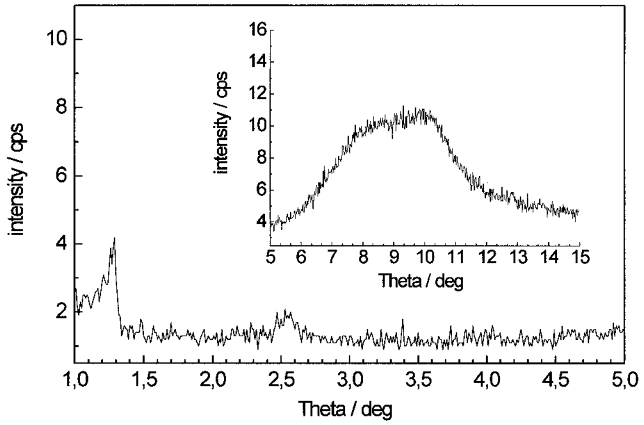

Figure 2. Small and wide angle scattering diagrams at $T = 90°\mathrm{C}$. The two parts were measured with different counting times.

Both the glass transitions shown in figure 1 should be connected with a freezing-in process of different molecular motions. The nature of these particular motions can be detected by dielectric methods if the respective molecular

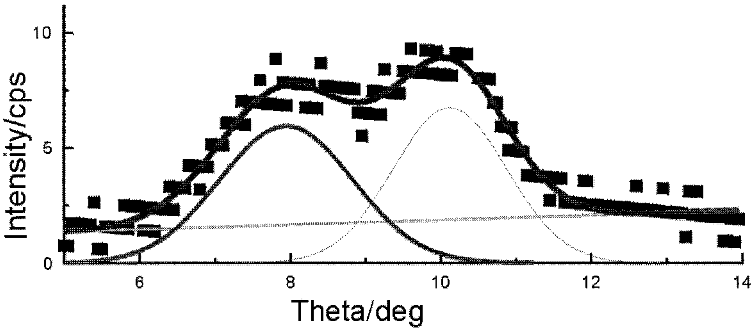

Figure 3. Measured and fitted X-ray intensities of the outer scattering at 303 K (glassy state).

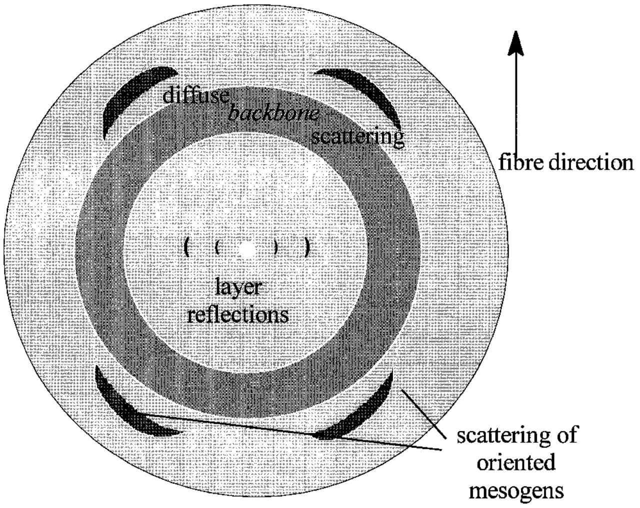

Figure 4. Schematic representation of the scattering from a drawn fibre at room temperature.

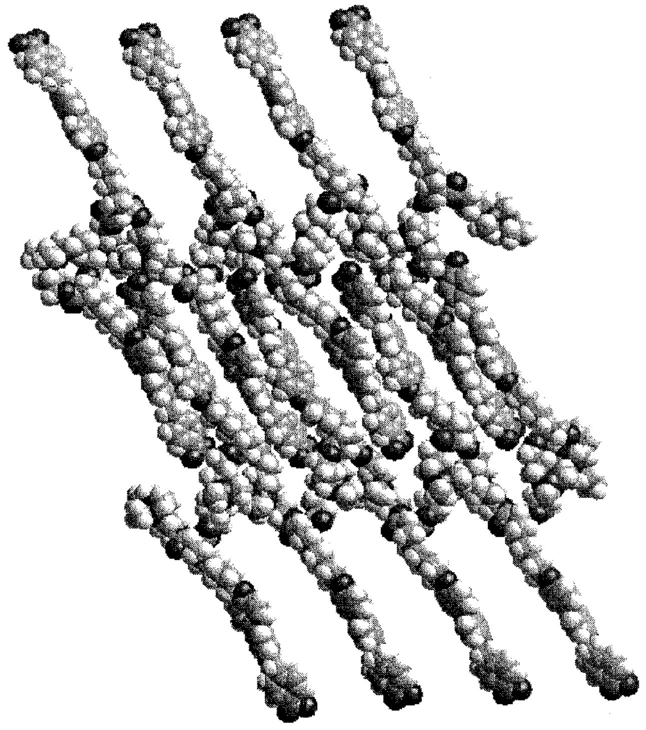

Figure 5. CPK model of the smectic C phase.

units contain dipole moments. Therefore, dielectric investigations were carried out using a plate capacitor. The gold electrodes were separated at 0.05 mm by spacers. All attempts to orient the sample by a bias voltage or a magnetic field failed. Capacity and loss were measured in the frequency range between 10^{-3} Hz and 10 MHz by a Solartron-Schlumberger device in combination with a Chelsea interface. Experimental data are presented in figure 6. Generally, there exist three absorption ranges from which only two are observed at a given temperature due to the limitations of the frequency range.

Therefore, it was possible to fit the data to two Cole–Cole equations:

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (\mathrm{i}\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (\mathrm{i}\omega\tau_2)^{1-\alpha_2}} + \frac{\mathrm{i}A}{f} \qquad (1)$$

with ε^* = complex dielectric constant, ε_0 = static dielectric constant, ε_1 = high frequency limit after the first relaxation process and so on, $\omega = 2\pi f$ (f = frequency), α = distribution parameter and τ = relaxation time. The term $\mathrm{i}A/f$ with $A = \sigma(2\pi\varepsilon^0)^{-1}$ (σ = specific conductivity, ε^0 = absolute dielectric constant) concerns the conductivity. Equation (1) was partially extended by the term B/f^n in order to

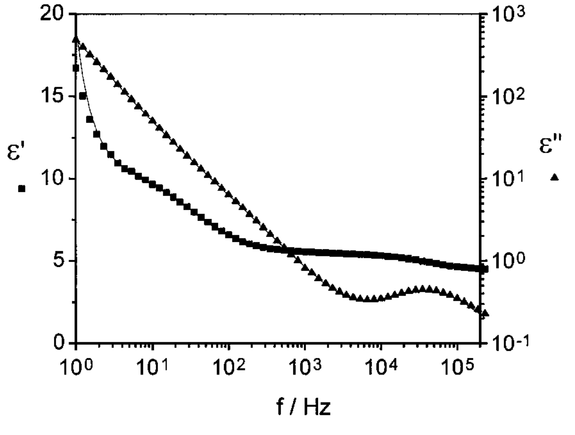

Figure 6. Dielectric absorption and dispersion together with the fitted curves at 381 K.

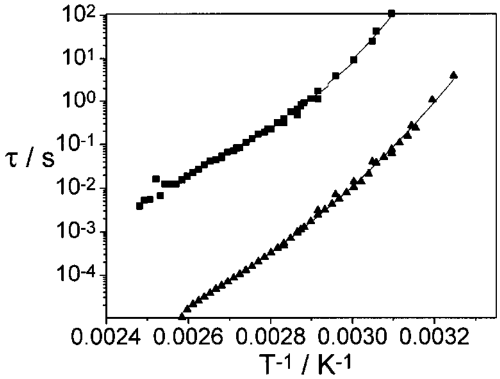

Figure 7. Relaxation times as functions of the reciprocal temperature.

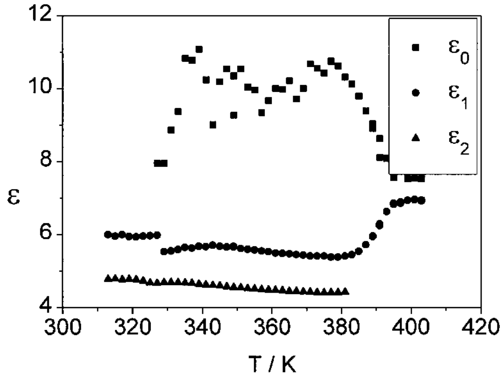

Figure 8. Static and quasistatic dielectric constants of the sample.

describe the capacity of the double layer. In this way the relaxation times of the two low frequency processes and the respective dielectric increments were calculated. The relaxation times are presented in figure 7. For the description of the two low frequency processes, the Vogel–Fulcher equation $\tau = \tau_\infty \exp[A/(T - T_0)]$ was applied. The parameters $\tau_\infty(1) = 6.24 \times 10^{-12}$ s, $A(1) = 2557$ K, $T_0(1) = 213.2$ K; $\tau_\infty(2) = 1.14 \times 10^{-5}$ s, $A(2) = 890$ K, $T_0(2) = 268$ K confirm the existence of two glass transitions. The difference in the Vogel temperatures of about 55 K agrees well (within the experimental error) with that of the glass temperatures shown in figure 1. In order to relate the glass temperatures to particular molecular motions, the calculated dielectric constants are given in figure 8. The dielectric increment $\Delta_1 = \varepsilon_0 - \varepsilon_1$ of about 5 (at lower frequencies) should be related to the reorientation of the strongly polar side groups [8]. $\Delta_2 = \varepsilon_1 - \varepsilon_2$ of about 1 for the second relaxation range must be caused by the dynamics of the main chains (α-relaxation). So, our experimental results support the concept of different freezing-in processes for different parts of the polymer molecule: the dynamics of the side groups is freezing in at a higher temperature than that of the main chain. Such a behaviour has not been observed in liquid crystals before.

The third process, not shown in figure 8 and observed only at lower temperatures, is related to local motions. Typical data are: $\varepsilon_2 - \varepsilon_3 = 2$, $\tau_3 = 3 \times 10^{-6}$ s, $\alpha_3 = 0.4$ at $T = 311$ K. Due to the high distribution parameter and the influence of resonance effects at high frequencies it was difficult to calculate activation parameters.

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