Structure and anisotropy in PC*)

II. WAXS, anisotropic heat conduction and birefringence in oriented samples

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Abstract: Birefringence, anisotropic heat conduction, and wide angle X-ray scattering (WAXS) investigations have been performed on one set of uniaxially drawn samples of polycarbonate (PC). The orientation parameters from heat conduction and from WAXS are well correlated. The intrinsic birefringence is determined to \( \Delta n_0 = 0.106 \) in agreement with the monomer polarizability calculated on the basis of model structures. The short range order as evidenced by WAXS does not depend on the degree of orientation in PC. Over small regions (≤ 1.5 nm) the molecular arrangement is similar to that in the crystalline state.

Key words: Polycarbonate, anisotropic heat conduction, intrinsic birefringence, wide angle X-ray scattering (WAXS), local structure.

Introduction

It is of interest to know the orientation of chain molecules within an anisotropic samples for many purposes. Knowledge of the second moments of the orientation distribution in the form of the generalized Legendre polynomials [1] is sufficient for all properties which are described by second rank material tensors. Fourth rank tensor properties such as the elastic tensor necessitate in addition the knowledge of the fourth moments. Wide angle X-ray scattering (WAXS) allows the determination of these moments if information on the short range structure is available. The preceding paper [17] by Schubach and Heise shows how the WAXS measurements can be evaluated. In contrast to X-ray analysis which requires a large amount of computer time, birefringence measurements are extremely rapid and simple. However, the orientation of the chains can only be determined if the intrinsic (i.e. monomer or segmental) birefringence \( \Delta n_0 \) is known.

Unfortunately reliable values of \( \Delta n_0 \) are difficult to obtain. Recently, Biangardi [2] has reported a value of \( \Delta n_0 = 0.236 \) for the monomer unit of PC. This value has been evaluated from X-ray measurements which will be discussed subsequently.

Anisotropy of heat conduction [3], though seldom measured, allows the determination of the upper and lower bounds of the chain orientation on the basis of very general assumptions [4].

In this paper we present measurements of the anisotropy of heat conduction obtained by an improved DeSénarmont method [5]. The orientation parameters deduced from the measurements are compared with those determined by WAXS. They allow only a small range of values of the intrinsic birefringence. The intrinsic birefringence is also calculated using polarizability data of the PC-monomer analogues published by Erman et al. [6] and structure models of the PC chain.

1. Experimental

Sample preparation

Sheets of polycarbonate with the trade name Makrolon 3200 (kindly supplied by Bayer AG, Leverkusen) were oriented above...
the glass transition temperature \( T_g = 149^\circ C \) at \( T = 160^\circ C \) with a nominal strain rate of \( \dot{e} = 0.03 \sec^{-1} \). After drawing, the samples were rapidly cooled to room temperature in a stream of cold air whilst keeping their position in the clamps fixed. For comparison, two samples were oriented below the glass transition temperature at \( T = 25^\circ C \) and \( 129^\circ C \), respectively with a nominal strain rate of \( \dot{e} = 6 \times 10^{-4} \sec^{-1} \).

At \( 25^\circ C \) PC deforms by necking, at \( 129^\circ C \) by formation of diffuse shear zones.

The birefringence of each sample was determined at a wavelength of 545 nm with a polarizing microscope, equipped with an Ehringhaus compensator. The measurements were carried out by compensating large retardations with a wedge-shaped piece of PC and small ones with the Ehringhaus compensator.

**Anisotropic heat conduction**

The anisotropy of heat conduction is closely related to the orientation of chain segments. If one is only interested in the orientation of chain segments the measurements of absolute values are dispensable. In this case the anisotropy ratio \( A = k' / k_\perp \) where \( k' \) and \( k_\perp \) denote the thermal conductivities in stretching direction and perpendicular to it, contains the information needed [3]. This ratio can be determined directly with the so-called DeSénarmont method [3, 5] which is a transient point source method. This method and the equipment used are described in [5]. The measurements have been carried out at \( 30^\circ C \). The results are plotted in figure 1 against the birefringence. The magnitude of the anisotropy compares well to values derived from measurements of Hennig [7] \( (A \approx 1.8, A \approx 1.8) \). PC exhibits the highest anisotropy of all amorphous polymers investigated hitherto.

2. Orientation and anisotropic heat conduction

In amorphous polymers the heat conduction mechanism is essentially that of a polymeric liquid even in the glassy state. In the normal liquids the contribution from convective heat transport is negligible (less than 1%) [8]. Thus only the collisional part is operative, yielding a constant mean free path \( l \) in the kinetic equation [9]

\[
k = (1/3) C v l.
\]

The temperature dependence of the conductivity \( k \) is given by that of the specific heat \( C \) from \( T_g \) down to \(-25 \) K since the “sound velocity” \( v \) is only slightly temperature dependent. The small deflection observed when passing through \( T_g \) to higher temperatures [10] is mainly due to the step in the thermal expansion coefficient [11] \( (C \) is the specific heat per volume at constant pressure) and to the step in the sound velocity gradient.

In this picture the anisotropy in thermal conductivity must be attributed to the anisotropy in the collision process which results from the presence of van der Waals and covalent bonds. The collisions due to the van der Waals forces result in the intrinsic perpendicular contribution \( k_\perp \) and the collisions due to the primary bonds result in the intrinsic parallel contribution \( k_\parallel \). If these contributions are averaged like the macroscopic ones, i.e. like second rank tensors, then the conductivity (parallel) and the resistivity (series) averaging pose the limits of the macroscopic conductivities. Because of the small mean free path (\(-0.15 \) nm [9]) it is assumed that the conductivity averaging will be the most suitable for the collisional model. The magnitude of the intrinsic anisotropy of thermal conductivity has been estimated from the conductivities of ordinary liquids (van der Waals bonds) and of glasses (covalent bonds) to be in the range [12]

\[
5 \leq A_o \leq 25
\]

with the most probable value \( A_o \sim 10 \).

The macroscopic anisotropy of thermal conductivity is a function of orientation and intrinsic anisotropy and is given by

\[
A = \frac{1 + 2 q_c P_2}{1 - q_c P_2}; \quad q_c = \frac{A_o - 1}{A_o + 2}.
\]

From this equation the orientation parameter \( P_2 \) obtained after conductivity averaging can be determined via

\[
P_2^2 = \frac{A - 1}{A + 2} \cdot \frac{A_o + 2}{A_o - 1}
\]

provided the intrinsic anisotropy is known. All the amorphous polymers we have measured so far [4] exhibit values of \( A_o \sim 10 \). In view of the high anisotropies measured we assume \( 10 \leq A_o \leq 16 \) for the PC chain. The upper limit has been estimated roughly from the van der Waals type description of real networks [13a] applied to the glassy state [13b]. An

![Fig. 1. Heat conduction anisotropy \( A \) versus birefringence \( \Delta n \) at \( T = 22^\circ C \). ○ sample stretched at \( T_s = 160^\circ C \); □ sample stretched at \( T_s = 25^\circ C \); ● sample stretched at \( T_s = 129^\circ C \); — calculated with \( \Delta n_o = 0.106 \) and \( A_o = 10 \).](image)