Microscopically-viewed relationship between the chain conformation and ultimate Young's modulus of a series of arylate polyesters with long methylene segments

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ABSTRACT

Relationship between the chain conformation in the crystal lattice and the ultimate Young's modulus has been discussed on the basis of the crystal structural information revealed by the X-ray diffraction analysis for a series of arylate polyesters with long methylene segments ($-[-COC_6H_4CO-O(CH_2)_mO-]_n-$). The X-ray structural analysis revealed that the molecular chains take the all-*trans*-zigzag conformations for all of the even-numbered polyesters and their model compounds as well as the odd-numbered polyesters with the methylene segmental length longer than $(CH_2)_{14}$. These chain conformations have been correlated well to the ultimate Young's modulus along the chain axis or the crystallite modulus E_c, which has been estimated experimentally by the X-ray diffraction method under a constant stress and also predicted theoretically using the X-ray-analyzed crystal structures on the basis of the molecular mechanics method. The E_c was found to show the minimum at around $m = 4-6$ and increased gradually with an increment of m and approached the crystallite modulus of polyethylene, 235 GPa (X-ray value) $\sim$ 316 GPa (calculate) at an infinite m value. This behavior of E_c as a function of the number of methylene segmental units m was reasonably interpreted by developing the theoretical equation of E_c for a simplified zigzag chain model composed of a repetition of two linear rods representing the benzene–ester and methylene segmental parts respectively. These findings may promise that the mechanical property of arylate polyester can be controlled by adjusting the methylene segmental length m.

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1. Introduction

Among the various types of polyesters, a series of arylate polyesters with the methylene segments of various lengths ($-[-COC_6H_4CO-O(CH_2)_mO-]_n-$) are being attractive both scientifically and industrially [1,2]. They are called here mGT, among which 2GT (PET), 3GT and 4GT are industrially utilized in a wide application field. The many basic knowledge of these polyesters was accumulated as seen in many literature [1–3]. For the members of $m = 5-9$ the crystallization behaviors including the spherulite formation were mostly studied [4–11]. Still much less information is known about the polyester members with longer methylene segments, although the synthesis of the members of m up to 20 was reported in a literature [12,13]. When the m value is increased infinitely, the polyester approaches polyethylene $-[-CH_2CH_2-]_n-$. However, the presence of rigid benzene–ester parts might disturb the regular and compact packing of the long methylene segments, and a sensitive balance between the flexible methylene segments and the hard benzene–ester parts might give us a chance to realize an unexpectedly interesting property.

We focus our attention here on relationship between the chain conformation and crystal structure and ultimate mechanical property of these mGTs with long methylene segments, which will be quite useful for the future development of novel polyester compounds with more excellent mechanical (and thermal)

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property. However, the detailed information about the crystal structure and the ultimate Young's modulus, which are necessary for this discussion, had been limited at all. In the literature, the unit cell parameters and/or crystal structures were reported for 2GT [14,15], 3GT [16–18], 4GT [19–22], 5GT [23,24], 6GT [25–27], 8GT [28] and 10GT [12]. We have synthesized here the mGT with $m = 9–20$.

The present paper consists of two parts. In the first half part, we will describe a systematic variation of the chain conformation on the basis of X-ray crystal structure analysis. In the second half part, the ultimate Young's modulus along the chain axis (E_c) or the crystallite modulus was estimated experimentally and theoretically for these polyesters, which was related reasonably to the X-ray-analyzed molecular chain conformation. As will be mentioned in a later section, the change of methylene segmental length has been found to give the systematic change of E_c, giving us a possibility of the control of the mechanical property of polyesters by the variation of methylene segmental length. This information is quite important as a guiding principle to choose the polyester with the mechanical property adjustable to our request.

2. Experimental

2.1. Samples

Arylate polyesters with $m = 9–20$ were synthesized by the condensation polymerization reaction of terephthalic dichloride with *n*-alkane diol $HO(CH_2)_mOH$. The *n*-alkane diols were purchased commercially from Tokyo Chemical Industry Co., Japan. The *n*-alkane diols with $m = 15$ and 20 were obtained by the reduction of the corresponding α,ω-dicarboxylic acid $HOOC(CH_2)_{m-2}COOH$. The uniaxially-oriented mGT samples were prepared by stretching the melt-quenched (0 °C) samples by about 4 times the original length at about 100 °C followed by the heat treatment under tension for 2 h at a temperature 20 °C below the melting point, which is listed up in Table 1. The model compounds $CH_3(CH_2)_{m-1}OCOC_6H_4COO(CH_2)_{m-1}CH_3$ were synthesized by the condensation reaction of terephthalic dichloride and *n*-alkyl alcohol $HO(CH_2)_{m-1}CH_3$. The single crystals of these model compounds were prepared by a solvent evaporation method from the solutions at room temperature, where toluene, petroleum ether, acetone *etc.* were used as solvents.

2.2. X-ray diffraction measurements

The X-ray diffraction diagrams of the oriented samples were measured at room temperature using a Rigaku R-axis Rapid-2 X-ray diffractometer with a cylindrical camera of 12.74 cm radius equipped with an imaging plate detector. The graphite-monochromatized Mo-Kα line was used as an incident X-ray beam ($\lambda = 0.71073$ Å).

For the X-ray crystal structure analysis of the low-molecular-weight model compounds, about 6000 X-ray diffraction spots were collected by on oscillation method (oscillation angle $\Delta\omega = 1–3°$ in the full range $\omega = 0–120°$) using a Rigaku R-axis Rapid-2 X-ray diffractometer where the Mo-Kα line was incident on the sample. The crystal structure analysis was performed with a software "Crystal Structure" based on the direct method (SIR92) [29] for getting an initial structure model and the full-matrix least squares method for the structure refinement.

2.3. Crystallite modulus

The crystallite modulus along the chain axis E_c was estimated by measuring the shift of X-ray diffraction peak corresponding to the crystal lattice planes with the normal vector parallel to the chain axis under a constant tensile stress [30–32]. As shown in Fig. 1, the sample was vertically hung down with a weight W. The transmission mode was employed for the X-ray diffraction measurement, where a Rigaku RINT TTR-III X-ray diffractometer was used to obtain the diffraction profile. By changing the weight W, the peak position was shifted by $\Delta(2\theta)$, from which the strain (ε_c) of the crystal lattice along the chain axis was calculated using the following equation. From the Bragg's equation ($2d\sin\theta = \lambda$),

$$\varepsilon_c = \frac{\Delta d}{d} = -\frac{\cot\theta}{2}\Delta(2\theta)$$

where d is the lattice spacing, λ is the X-ray wavelength and $\Delta(2\theta)$ is the shift of Bragg angle 2θ. By assuming a homogeneous stress distribution in the bulk sample, i.e., the bulk stress (σ_b) equal to the crystalline stress (σ_c), the (apparent) crystallite modulus E_c was estimated from the slope of the stress–strain curve ($\sigma_c = E_c\varepsilon_c$). The bulk stress σ_b was assumed as $\sigma_b = W/A$, where A was the averaged cross-sectional area of the sample and estimated by measuring the sample length and the sample density with a hydrometer. Copper powder was pasted on the sample surfaces for the correction of the diffraction angle. When the sample was tensioned by applying a load, the sample was more or less shifted due to it, affecting the accurate evaluation of the 2θ shift induced by a tensile stress. Since the diffraction peak coming from the copper powder should be constant, the correction of the diffraction angle could be made by referring to the drift of the peak position of copper powder.

On the basis of X-ray-analyzed crystal structure of a series of polyesters, the theoretical crystallite moduli were calculated by utilizing a commercial software Cerius² (version 4.10, Accelrys Inc.) based on the second derivatives method [33] as well as by the lattice dynamical method [34–36]. The COMPASS (condensed-phase optimized molecular potentials for atomic simulation studies) force field was used as the potential functional parameters in the calculation using Cerius², which is said now to be one of the

Table 1
Melting points of mGT samples measured at 5 °C/min.

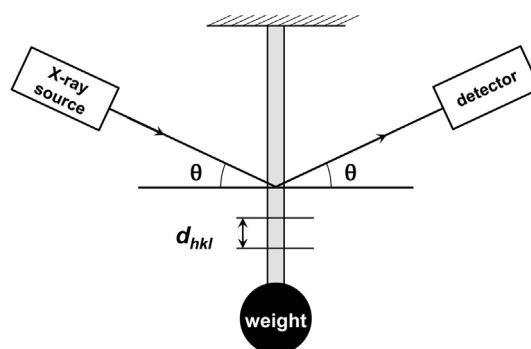| m	Melting point/°C
9	92.8
10	125.5
11	96.5
12	122.7
15	101.9
16	115.2
20	117.1

Fig. 1. A schematic illustration of the measurement system of crystallite modulus by X-ray diffraction method.