Evaluation for most probable distance between adjacent amorphous molecular chains taking preferred orientation with respect to a spinning fiber

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ABSTRACT

Most probable distance between adjacent molecular chains was evaluated as the first trial for oriented amorphous polymers, using the two-dimensional radial distribution function formulated by a series expansion of Bessel and Legendre functions of coherent X-ray intensity curves. Poly(phthalazinone ether ketone) (PPEK) was selected as the test specimen, since PPEK dissolved in some solvents was one of typical amorphous polymers with high impact strength and high-temperature resistance and PPEK could produce fine fibers by dry spinning in spite of amorphous polymer. Non-crystallization of PPEK chains were analyzed in comparison with chain structure of undrawn amorphous poly(ethylene terephthalate) triggering oriented crystallization. Additionally, the strain between adjacent PPEK chains under external stress along the fiber axis was measured by a homemade instrument in relation to the chain orientation degree. These results indicated that the amorphous chains were connected with strong intermolecular force between adjacent PPEK chains, and the force could achieve fiber spinning.

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1. Introduction

This paper deals with evaluation for the most probable distance between adjacent amorphous main chains in an oriented amorphous polymeric material with rigid chains. Amorphous polymeric materials are generally uniform and tough against external impact in comparison with crystalline polymers, since no existence of the grain boundary region between crystal and amorphous phases which associated with steep density fluctuation [1,2], suppresses the generation of cracks against the external impact. The fiber formation by perfect amorphous polymers has never been reported except few papers for polyvinyl chloride (PVC) with ca. 20% crystallinity [3]. The difficulty in producing amorphous polymer fibers is probably thought to be attributed to weak intermolecular force between adjacent amorphous chains.

Recently, the successful method of dry spinning concerning a perfect amorphous polymer was confirmed for poly(phthalazinone ether keton) (PPEK) without transformation from amorphous phase to crystal phase by drawing of mono-filaments at around 325 °C. This paper refers to the successful reason from three viewpoints; 1) the distance between adjacent amorphous chains, 2) the amorphous chain orientation, and 3) the modulus between adjacent main chains perpendicular to their chain axes. Among the three, the most difficult evaluation is to calculate the most probable distance between adjacent oriented amorphous main chains, since the distance is dependent upon the orientation degree of the chains in the fiber. As a well-known fact, the lattice constants of crystal units for most of crystallite polymers provide their intrinsic values independent of orientation of crystallites in the elongation material under no external stress at room temperature. Hence orientation modes of crystallites by uniaxial or simultaneous biaxial stretching can be evaluated according to the intrinsic distance between established crystal planes relating to the different shapes of crystal unit such as orthorhombic [4–10], monoclinic [11–13], triclinic [14,15] etc. and the different distance between the adjacent chains in the crystal unit, is independent of the crystallite orientation in the sample after stress relaxation. On the other hand, the

amorphous chains with different orientation directions in bulk, which are due to compression and expansion modes, provide different distances between their adjacent chains. Because of such complicated behavior of amorphous chains, there is no report for the detailed evaluation concerning the distance between adjacent chains in oriented amorphous materials, although there are many reports for liquids, metals and polymers with amorphous structure by normal (one-dimensional) radial distribution function [16—18]. However, the one-dimensional evaluation cannot be applied to the oriented system. Accordingly, this paper focuses on the experimental and theoretical evaluations for obtaining correlation function of electron density distribution calculated by coherent X-ray intensity, which has been termed as radial distribution function for one-dimensional analysis.

PPEK is one of the amorphous polymers containing a novel bisphenol-like monomer, 4-(4′-hydroxyphenyl)-2,3-phthalazin-1-one (DHPZ), synthesized originally through simple reactions from phenol and phthalic anhydride, which was developed by Jian et al. to improve the poor solubility of polyarylether resins which are well-known polymers as special engineering plastic with excellent heat-resistance, fatigue resistance, radiation resistance, and chemically stable property [19].

Following Jian et al. [20—27], PPEK could dissolve in common solvents such as chloroform, *N*-methyl pyrrolidone (NMP) and trichloroethylene (TCE) in spite of the rigid chemical chains. Such property is required to carry out wet and/or dry spinning and molding and to realize oriented system of PPEK chains, since it was found to be impossible to elongate PPEK fiber or film uniformly in hot oven setting at temperatures beyond the glass transition temperature of 263 °C. The detailed information is described in Supporting Information I.

Molecular structure of PPEK is slightly similar to poly(ethylene terephthalate) (PET). Different from PET which would have orientation-induced crystallization [28—31], however, the dry spinning PPEK fibers maintain amorphous structure in spite of the molecular orientation.

Judging from the extended chain structures of PPEK and PET in Fig. 1, it may be postulated that PET with high symmetry is essentially crystalline polymer during drawing or spinning [28,32—34]. The extended molecular structure of PET chains promotes the chain arrangement on a zigzag plane ensuring high crystallinity and rapid crystallization, since adjacent amorphous chains come near together by elongation and heat treatment [35,36].

On the other hand, extended PPEK chains do not crystallize in spite of any trials, since PPEK chains consist of non-coplanar and twisted structure for combination of benzene and naphthalene rings which hamper to form regular helix structure or the arrangement on a zigzag plane.

In this paper, detailed analyses are proposed as to the reason why PPEK chains can produce amorphous fiber by dry spinning. The main point is carried out by using the two-dimensional radial distribution function (most existing probability of electrons) about the oriented system. As described already [16—18], such an evaluation is the first trial.

The radial distribution function is formulated by series expansion of Bessel and Legendre functions for coherent X-ray intensity curves. In the oriented system of PPEK chains, the radial distribution function in PPEK fibers is represented as most probable distance between adjacent main chains oriented at polar angle with respect to the fiber axis. The experimental method is developed by the horizontal scanning of one-dimensional scintillation counter (detector). Namely, the proposed method can evaluate exactly rather than two-dimensional position sensitive proportional counter (PSPC) and Weissenberg photograph (image).

Furthermore, the inner strain between adjacent oriented amorphous PPEK chains was investigated by using a homemade machine as a function of tilting angle of PPEK chains with respect to the applied external stress along the fiber axis. This measurement is important to justify that the amorphous chains are connected with enough intermolecular force between adjacent PPEK chains ensuring fiber spinning.

The present work shall shed light on evaluation techniques to study characteristics of oriented amorphous polymer films and fibers in terms of experimental and theoretical aspects.

2. Experimental

2.1. Materials

PPEK with chemical structure (see Fig. 1(a)) of $M_w = 144,900$ and $M_n = 75,800$ ($M_w/M_n = 1.91$), was purchased from Dalian Polymer New Material Co. LTD. The powder was purified before use by dissolving it in chloroform and filtering out the insoluble impurities. The purified powder was separated out in ethanol and dried in a vacuum oven for 24 h.

PET was furnished from Toyobo Industries, Inc., of which M_n was 15,000 and the polydispersity index termed as M_w/M_n was 3.47. The density of the PET film is ca. 1.335 g/cm^3, indicating amorphous PET [37].

2.2. Dry spinning of PPEK solutions

Process of dry spinning was carried out by using a homemade monofilament extrusion. The schematic diagram is shown in
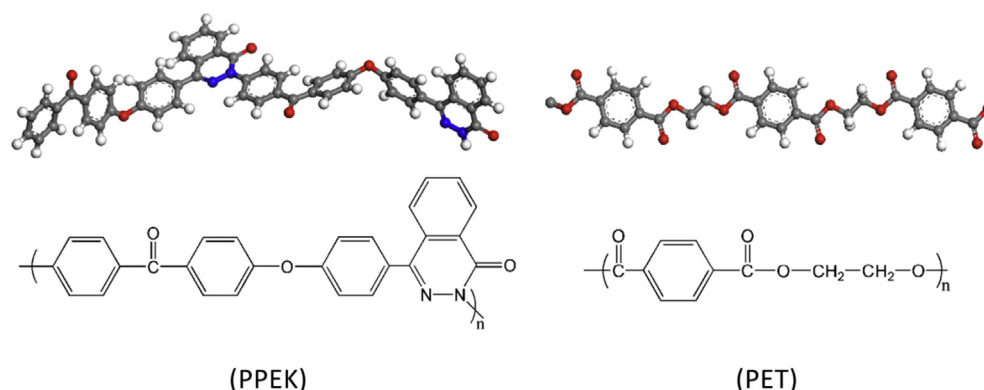

Fig. 1. Extended chain structures of PPEK and PET.