



Isotope effect on the structural evolution process in the isothermal crystallization phenomenon of polyoxymethylene



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ABSTRACT

Isotope effect on the structural evolution process in the melt-isothermal crystallization phenomenon of polyoxymethylene (POM) has been studied on the basis of the time-resolved simultaneous measurements of FTIR spectra, small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) for a series of copolymers with the different D/H contents. The quantitative analysis of FTIR band intensities for a series of POM D/H random copolymers revealed the critical sequence lengths or the minimal helical segmental lengths necessary for the detection of the IR band intensity. The quantitative analysis of the time-resolved SAXS and WAXD data revealed the formation of the domains of higher density in the melt, the increasing correlation between these domains and the growth of the crystalline lamellae. The time-resolved FTIR data gave the generation and growth of the helical segments in parallel. By combining all the data collected simultaneously, the following observations have been deduced about the structural evolution process from the melt: (1) immediately after the temperature jump, some portions of random coils in the melt regularize into the domains consisting of the aggregation of the short helical segments of 3–5 turns, (2) these domains approach each other to have stronger correlation, (3) and they form the crystalline lamellae. These lamellae grow furthermore by adding the helical segments on the surface. (4) When the degree of supercooling (the difference between the equilibrium melting point and the crystallization temperature) is high, the insertion of new lamellae into the originally-generated lamellae occurs. These structural evolution processes were found to be common to all the isotopic species including a normal POM (POM-H), a fully-deuterated POM (POM-D) and the random copolymer of deuterated (CD₂O) and hydrogenous (CH₂O) monomeric units. However, these processes were found to occur at the different rate depending sensitively on the D/H content: the slowest POM-D \ll D/H-random copolymer \ll the fastest POM-H. These different structural evolutions were found to be scaled systematically by shifting along the time axis over a wide range of the degree of supercooling.

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1. Introduction

Polyoxymethylene (POM, $-(\text{CH}_2\text{O})_n-$), one of the most important engineering plastics, crystallizes fast [1]. It is needed to study the crystallization behavior in detail from the various points of view. The utilization of isotopic species such as deuterated POM (POM-D, $-(\text{CD}_2\text{O})_n-$) and its blends with POM-H and a series of random copolymers between CD₂O and CH₂O monomeric units may be useful for the study of crystallization since the crystal structure is essentially the same among them but the chemical potential is different

because of the difference in atomic mass between H and D. In the previous papers [2,3] we have discussed the isotope effect on the melting and crystallization behaviors of POM on the basis of the thermal data collected for a series of D/H random copolymers and POM-D/POM-H blend species. The kinetic study of isothermal crystallization was made by measuring the thermal energy change as a function of time in the temperature jump process from the melt to the predetermined crystallization temperature. The isothermal crystallization rate from the melt was found to decrease with an increment of D content when compared at the same degree of supercooling [2,3]. In the DSC (differential scanning calorimetry) measurement about the isothermal crystallization phenomenon, we notice the existence of the so-called induction time before the appearance of the thermal energy due to the crystallization [4,5].

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What occurs in the induction period when viewed from the molecular level? What is the microscopic structural image of a nucleus necessary for the induction of the growth of crystallites? In most of the papers concerning POM, the optical microscopic observation was mainly made in the crystallization process, but the structural information was difficult to obtain for the induction period [6–34]. For answering the above-mentioned questions correctly, we need to trace the structural evolution in the process of induction, nucleation and growth of crystallites from the various hierarchical levels.

The information of structural evolution process in the isothermal crystallization was limited in the long history of the structural study of POM. Hama et al. performed the time-resolved measurements of wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) data in the process of isothermal crystallization of POM, and combined these data with the FTIR spectral data, which were collected separately but in almost the same isothermal crystallization condition [35–38]. The generation of stacked lamellae and the insertion of new lamellae into the originally-existed lamellae were revealed from the quantitative SAXS data analysis. The IR data analysis gave the information of the formation of folded and/or extended chain crystallites [39–43]. From these data, they proposed that the finally obtained sample consists of the originally-generated mother lamellae and the daughter lamellae inserted between these mother lamellae and that some chains pass through the stacked lamellae to give the tie chains with the extended-chain-crystal-like structure. The experiment and data analysis reported by Hama et al. might be the first try to trace the structural evolution process in the isothermal crystallization phenomenon of POM. Unfortunately, however, they did not measure the early stage of crystallization before the appearance of the stacked lamellae, *i.e.*, the formation process of the regular helices in the melt which may gather together to form a nucleus necessary for the growth of lamellae. For the purpose to trace the conformational regularization of the random coils the FTIR method will give us the most concrete information as exemplified by the various cases of *isotactic* polypropylene [44–46], 1,4-*trans*-polyisoprene [47], nylon [45,48], *syndiotactic* polystyrene [49–54] *etc.*

The thus-obtained IR data must be combined together with the X-ray scattering data. But the combination of the various data collected separately using the different sample species may be a little dangerous in such a sense that the samples used in there might not be in the exactly same conditions. The simultaneous measurement of these data should be the most ideal in the treatment of the soft materials which may change their higher-order structures sensitively depending on the environmental conditions. The recent development of a rapidly-operated and highly-sensitive detector has made it possible to measure the SAXS and WAXD data at the faster rate than before [55–64]. The FTIR technique has been also developed remarkably [65]. Therefore it is now possible to measure both the IR spectra and X-ray scattering data at the same time during the isothermal crystallization of one sample species. Such a so-called simultaneous measurement of the various techniques was reported in many papers [45–48,55–64]. Among them, the simultaneous measurements of the Raman spectra and WAXD/SAXS data were relatively easily carried out in the several papers because the laser incidence can be made for any shape of the sample [55–60,62,63]. Recently, we have developed the simultaneous measurement system of SAXS/WAXD and transmission-type FTIR spectra [47,48,62,64]. This system allows us to perform the study of the structural evolution in the isothermal crystallization of POM.

As mentioned above, the IR spectral information of POM is useful for the study of the regularization process of the helical

chains in the early stage of crystallization phenomenon. For this purpose, the evaluation of the so-called critical sequence length m^* of the helical chain is needed, which is a *minimal* number of monomeric units included in a helix necessary for the detection of the infrared band [49,50,66–70]. When the infrared band with a short m^* value appears in an earlier timing than the band of a long m^* value, it may be said that the regular helical segment grows the length during this time gap. In this way, the m^* values are useful for tracing the growth of the regular helices concretely [49–54]. The estimation of m^* was hard and quite limited to only the several kinds of polymers: *syndiotactic* polystyrene (the study of solvent-induced crystallization) [45,49–54], *isotactic* polypropylene (the study of isothermal crystallization from the melt) [44–46], and vinylidene fluoride-trifluoroethylene copolymers (the study of the ferroelectric phase transition) [71,72]. The quantitative evaluation of m^* value can be made based on the so-called isotope dilution method using a series of D/H random copolymers [49,50,66–70].

In the present paper, we will describe the structural evolution process in the isothermal crystallization of the various isotopes of POM, *i.e.*, the POM-H, fully-deuterated POM-D and the D/H random copolymers by performing the simultaneous SAXS/WAXD/FTIR measurements and also by estimating the m^* values using these D/H copolymers. The present paper is also important in such a point that the crystallization behavior is compared among the various types of POM isotopes. The isotope effect on the equilibrium melting temperature and the crystallization rate was already clarified for a series of POM D/H copolymers on the basis of the thermal analytical method [2,3]. These macroscopically-detected isotope effects will be revealed more concretely from the viewpoint of the hierarchical structure covering the molecular chain, crystal lattice and stacked lamellar structure. The systematic study of crystallization using a series of D/H copolymers cannot be found in the literature. We believe the present research may be the first case study.

2. Experimental section

2.1. Samples

The samples used here are listed in Table 1. Delrin 500[®] is a homopolymer of POM-H. The fully-deuterated POM-D and the random copolymer of D48/H52 molar ratio were synthesized by ourselves as already reported in the previous paper [2]. The molecular weights of these samples are not necessarily in the same order. In the previous papers [2,3] we compared the crystallization rate among the POM-H samples with the different molecular weight, *i.e.*, Delrin 100[®] (M_w 198000 g/mol), Delrin 500[®] (108000 g/mol) and H100 (52400, home-made). The rate constant k was as follows: $\log(k/\text{sec}) = -1.9, -1.8$ and -1.8 at the degree of supercooling $\Delta T = 38$ °C, respectively. Here ΔT is defined as $\Delta T = T_m^0 - T_c$ (T_m^0 is an equilibrium melting temperature [4,5] and T_c is a crystallization temperature). On the other hand, the $\log(k)$ is -2.9 for D48/H52 copolymer (65400 g/mol, $\Delta T = 38$ °C) and about -8.0 for POM-D (172000 g/mol, the value extrapolated to

Table 1
Characterization of POM samples used in the present experiment.

Sample	M _w	M _n	M _w /M _n	T _m ⁰ /K ^a
POM-H (Delrin 500 [®])	108000	39200	2.8	463.5
D29/H71 copolymer	60400	26400	2.3	464.2
D48/H52 copolymer	65400	27600	2.4	469.8
D69/H31 copolymer	75300	29800	2.5	472.8
POM-D	172000	64800	2.7	481.5

^a T_m⁰: an equilibrium melting temperature [2].

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