



Phenomenological study of the isotope effect on the equilibrium melting point of polymer crystal



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ABSTRACT

The equilibrium melting point (T_m^0) or the ultimate melting point of a polymer crystal is different between the hydrogenous (H) and deuterated (D) species, as exemplified for the various cases of polyethylene, isotactic polypropylene, polyoxymethylene and so on. The present study has focused on the specific case of the blend samples of hydrogenous and deuterated polyoxymethylenes (POM-H $[-(\text{CH}_2\text{O})_n-]$ and POM-D $[-(\text{CD}_2\text{O})_n-]$) and the random copolymers between the CH_2O and CD_2O monomeric units. As the POM-H samples, the homopolymers composed of H-trioxane monomeric units and the copolymer containing a small amount of ethylene oxide (EO-POM copolymer) were used since these two samples were different in the melting point. The T_m^0 of the blend samples was found to change continuously depending on the D/H content, although the content dependence was different between the blend samples of POM-D with POM-H homopolymer and those of POM-D with EO-POM copolymer. The T_m^0 of the D/H random copolymers was found to change also remarkably. Such an isotopic effect on T_m^0 has been interpreted reasonably on the basis of the thermodynamic equations derived with the statistical probabilities of the D and H component distributions taken into account. The agreement between the experimentally-evaluated values and the theoretically-estimated values is good for the T_m^0 in both the cases of D/H blends and D/H random copolymers.

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1. Introduction

Polymer isotopes are sometimes utilized in the study of crystallization, phase separation *etc* [1]. For example, a small amount of deuterated *atactic* polystyrene [D-PS, $-(\text{CD}_2\text{CD}(\text{C}_6\text{D}_6))_n-$] was mixed with the hydrogenous polystyrene [H-PS, $-(\text{CH}_2\text{CH}(\text{C}_6\text{H}_6))_n-$] or *vice versa* [2,3]. The thus-prepared D/H PS blend samples were quite useful for the evaluation of the spatial dimension of a single chain in the amorphous phase by the measurement of small-angle neutron scattering (SANS), since the high contrast is obtained between the D and H chains due to their remarkably different neutron scattering cross sections [4]. As for the crystalline polymers, similarly, the SANS experiment was performed in the crystallization process from the melt to reveal the dimensional change from the random coil in the melt to the folded chain form in the crystalline lamella [1]. Typical case was reported for the blend samples of deuterated high-density polyethylene

[DHDPE $-(\text{CD}_2\text{CD}_2)_n-$] and hydrogenous high-density polyethylene [HDPE $-(\text{CH}_2\text{CH}_2)_n-$] [3,5–7]. However, the blend between DHDPE and HDPE was not necessarily suitable for this purpose since the mixture of the D and H species shows a partial phase separation when slowly cooled from the melt [3,5–7]. In other words, the perfect cocrystallization cannot be attained for this pair, making the discussion ambiguous more or less. Almost perfect cocrystallization was found for a pair of DHDPE and linear-low-density polyethylene (LLDPE) with small amount of short branches (for example, 17 ethyl branches per 1000 skeletal carbon atoms) even when cooled slowly from the melt [8–14]. In fact, using a series of the various blend samples of DHDPE and LLDPE, the experimental data of infrared spectra and SANS revealed successfully the spatial distribution of chains in the crystallization process from the melt [14]. The molecular chain does not change the dimension very much during the crystallization, and the D-PE and H-PE stems are randomly arrayed in the lamella, so the molecular chain is folded randomly on the lamellar surface, supporting the concept of random reentry mechanism of chains. Another point to be noticed is the difference in the melting point and melt-crystallization rate between the D and H species. In the case of

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above-mentioned DHDPPD/LLDPE blends, the melting point was detected as a single peak and the peak position shifted continuously depending on the D/H content. The similar phenomenon was observed for *isotactic* polypropylene [*it*-PP, $-(\text{CH}_2\text{CH}(\text{CH}_3))_n-$] [15–17]. The melting point between the D and H species is different: 153 °C for D-species and 156 °C for H-species. The crystallization rate was also found different remarkably between these two species. The D- and H-species of *it*-PP were found to cocrystallize when cooled slowly from the melt. The infrared spectra of the D/H blend samples were utilized to clarify the intermolecular interactions and the packing mode of the polymer chain stems [14–18].

In this way, the isotopically-different polymer species is quite useful for the structural study from the various points of view. It is important to notice that the melting point is remarkably different between the D and H polymer species by a detectable amount. For example, the melting point of DHDPE is 127 °C and that of HDPE is 136 °C [5–7]: the difference of melting point (mp) between the D and H species ($\text{mp}(\text{H}) - \text{mp}(\text{D})$) is about 9 °C. In the case of *it*-PP, the mp difference is about 3 °C, as already mentioned above. These large isotopic effects of melting point of polymer is highly contrast to the case of small molecules such as benzene, which shows very small difference in melting point between the D and H species (~ 1 °C) [19]. The covalently-bonded array of D monomeric units along the polymer chain is considered to cause the cooperative effect or the so-called *polymer effect* on the melting point by accumulating the small difference of chemical potential between the D and H monomeric units several thousand times. The evaluation of an ultimate melting point or the equilibrium melting point (T_m^0) is needed for understanding the remarkable isotope effect on the thermodynamic property of the polymer [20].

In the present paper we focus on polyoxymethylene (POM). The remarkable difference in the melting point was found between the D and H species: 165 °C for POM-H [$-(\text{CH}_2\text{O})_n-$] and 178.5 °C for POM-D [$-(\text{CD}_2\text{O})_n-$] [21,22]. In our previous paper [22], a phenomenological treatment was performed to interpret such an isotope effect on T_m^0 with the probability of spatial arrangement between the D and H stems in the common lattice taken into account. Quite recently, we have succeeded to synthesize the random copolymers between D-trioxane and H-trioxane with the various D/H contents. The thus-polymerized samples are not the random copolymers between D- and H-trioxanes but the random copolymers between CH_2O and CD_2O units. The melting point and the crystallization rate were found to sensitively change depending on the D/H content. It may be a good chance to investigate the isotope effect on the melting point in more detail since both the D/H blend samples and the D/H random copolymers have been obtained for POM.

In the present study, the isotope effect on T_m^0 of POM is interpreted phenomenologically for a series of POM-D and POM-H blend samples as well as the D/H random copolymers. The detailed study of the thermodynamic property of isotopically different POMs is needed as a basic information in the research of the chain aggregation in the melt and the spatial array of individual chains in the crystalline lamella by performing the SANS and FTIR spectral measurements. The utilization of D and H blend samples of POM might be useful for the confirmation of our previous studies which reported the generation of taut tie chains passing through the neighboring lamellae [23–25], that is to say, we might expect that the D-tie chains might be distinguished from the matrix of H-chains. The isotopic effect on the crystallization rate of POM will be reported in a separate paper.

Before the description of the experimental data and their theoretical interpretation, it is needed to point out that the commercially-available POM-H samples must be distinguished

strictly between the homopolymer (Delrin, for example) and the copolymer including some amount of comonomer (Duracon, for example). In our previous paper the POM-H with ethylene oxide (EO) 2.2 mol% was utilized in the study of isotropic effect on the melting point of POM-D and POM-H samples. However, the D/H random copolymers to be treated here do not contain any such third comonomer component as EO in the samples. The melting point between the homopolymer and EO-copolymer is about 5 °C different from each other. Therefore, in the present paper, we have to investigate the isotopic effects on the melting behaviors for the following 3 sets of the POM samples:

- (i) a series of D/H copolymers without any EO comonomer units,
- (ii) a series of blend samples between POM-D and POM-H (Delrin-type homopolymer) and
- (iii) a series of blend samples between POM-D and POM-H with small amount of EO comonomer units (EO-POM-copolymer).

2. Experimental section

2.1. Samples

The samples utilized in the present paper are listed in Table 1. The POM-H samples were Delrin 100 and 500, both of which were homopolymers of trioxane, and Duracon (M90), a copolymer containing EO unit of 2.2 mol%. The POM-H homopolymer sample (H100), which was synthesized by ourselves using the similar technique to that of D/H random copolymers described below, was also included in this table. The D/H random copolymers (and the POM-H sample) were synthesized in the present study. The D/H molar ratios were 100/0, 69/31, 48/52, 29/71 and 0/100. The details of the synthesis were described in a literature [26]. Briefly speaking about the process, the copolymers were synthesized by the cationic polymerization reaction for a mixture of H-trioxane and D-trioxane in the dried cyclohexane solution, where small amounts of boron trifluoride butyl ether and butyl ether were added as a catalyst [26]. The end OH units were capped by acetic acid to stabilize the sample from the thermal degradation in the melting process. The randomness of CH_2O and CD_2O units in the chain was confirmed on the basis of high-resolution ^{13}C NMR (nuclear magnetic resonance) spectral data measured for the deuterated hexafluoroisopropanol solutions. The ^{13}C NMR spectra were measured for a series of D/H copolymers. As shown in Fig. 1, the peaks of $^{13}\text{CD}_2$ unit split into 5 peaks due to the spin–spin couplings between ^{13}C and D magnetic spins. Besides, the 5 peaks were noticed to consist of fine peaks individually. That is to say, the positions of the original 5 peaks were shifted toward the lower magnetic field side corresponding to the various sequences (*triad*) of $\text{CD}_2\text{O}-\text{CD}_2\text{O}-\text{CD}_2\text{O}$ (DDD), $\text{CD}_2\text{O}-\text{CD}_2\text{O}-\text{CH}_2\text{O}$ (DDH) and $\text{CH}_2\text{O}-\text{CD}_2\text{O}-\text{CH}_2\text{O}$ (HDH), as illustrated in Fig. 1 (b). The integrated intensities of these finely-split peak components gave the fractions of *diad* (DD, DH and HH) and *triad* sequential probabilities of CD_2O and CH_2O units. From these values, the so-called run number R was calculated, which is defined as the number of boundary between the H and D monomer sequences included in the chain of 100 monomer units [27]. For example, $R = 3\%$ in the sequence of $\text{D}_{35}-\text{H}_{30}-\text{D}_{15}-\text{H}_{20}$, and $R = 10\%$ for the sequence $\text{D}_{10}-\text{H}_3-\text{D}_{10}-\text{H}_{20}-\text{D}_5-\text{H}_3-\text{D}_{10}-\text{H}_{20}-\text{D}_4-\text{H}_5-\text{D}_{10}$. The R s of the D/H copolymers were calculated from the *diad* values as listed in Table 1. These R values were compared with those predicted for the various such models as random copolymer of CD_2O and CH_2O units, block copolymer $-(\text{CD}_2\text{O})_n-(\text{CH}_2\text{O})_m-$ and alternating copolymer of $\text{CD}_2\text{OCH}_2\text{O}$ sequence. As seen in Table 1, the R values of the POM

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