NOTE

A New Method for Obtaining Local Ordering in Amorphous Polymers from X-Ray Scattering Intensity

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The radial distribution function (RDF) analysis of polymers in the amorphous state can be used to indicate local order and molecular chain packing. The chain conformation is characterized by unconditional probabilities, P_t for *trans* and P_g for *gauche*, and/or higher-order probabilities, for instance, P_{tt} and P_{tgg} , which are defined by a set of rotational angles about the skeletal bonds.

Since polyethylene (PE) is one of the simplest molecules in polymers, a number of RDF studies on its amorphous structure have been reported in the last few years.^{1–5} Nevertheless, the local conformation of the PE chain in the amorphous state has not been quantitatively evaluated by these RDF studies. Recently, we made a very careful RDF analysis of amorphotized PE and ethylene-propylene random copolymer in order to obtain the *trans* fraction in the chains.⁶

On the other hand, Windle and his coworkers⁷ proposed a method for evaluating the *trans* fraction by comparing the experimental scattering curve with those calculated for various structure models and showed that any significant degree of long sequences of regular conformation cannot be found in molten PE.

We have shown that the experimental RDF of amorphous PE can be modelled for the interchain damped oscillation in terms of a set of simple functions.⁸ In this paper, we propose a new method for obtaining information on the *trans* fraction and the interchain packing in amorphous PE by a comparison of the experimental scattering curve and the Fourier transform of the RDF modelled for the

intrachain and interchain orders.

METHOD

Figure 1a shows the s -weighted normalized intensity, $si(s)$, of the amorphotized PE reported by Yoda *et al.*⁴ where $s = 4\pi \sin \theta / \lambda$. Cu- $K\alpha_1$ rays were monochromatized by α -quartz on the incident side, and X-ray diffraction measurement was carried out at room temperature. PE was amorphotized by γ -ray irradiation of 4000 Mrad (4000 Mrad PE).

The experimental RDF, $G_e(r)$, is derived from the inverse Fourier transform of $si(s) \cdot \exp(-\gamma s^2)$ as,

$$G_e(r) = 2r/\pi \int_{s_{\min}}^{s_{\max}} si(s) \cdot \exp(-\gamma s^2) \sin(rs) ds \quad (1)$$

where, $\exp(-\gamma s^2)$ is a damping factor to minimize the termination errors due to the finite range of s from $s_{\min}$ ($=0.1 \text{ \AA}^{-1}$) to $s_{\max}$ ($=7.7 \text{ \AA}^{-1}$). Figure 1b shows $si(s) \cdot \exp(-\gamma s^2)$, in which $\exp(-\gamma s^2)$ takes a value of 0.2 at $s_{\max} = 7.7 \text{ \AA}^{-1}$. The dotted line in Figure 2 indicates $G_e(r)$ above 4Å of the radial distance, which is obtained from $si(s) \cdot \exp(-\gamma s^2)$ shown in Figure 1b. The sharp peaks are smeared out in $G_e(r)$ because of the finite s range and the damping factor.⁴

The modelled RDF, $G_m(r)$, in the range of r smaller than 4Å is formed as follows: (1) We chose r_1 at which $G_m(r_1)$ takes a minimum value. For $0 < r < r_1$, we have,

$$G_m^{(1)}(r) = -4\pi r^2 \bar{\rho} + G_p^{(1)}(r) \quad (2)$$

Figure 1. Experimental $si(s) \cdot \exp(-\gamma s^2)$ for PE amorphotized by γ -ray irradiation of 4000 Mrad. Damping factor $\exp(-\gamma s^2)$ equals 1.0 for (a) and takes a value of 0.2 at $s_{\max} = 7.7 \text{ \AA}^{-1}$ for (b).

where $\bar{\rho} (= 0.041 \text{ \AA}^{-3})$ is the average number of C atoms per unit volume corresponding to the macroscopic density ($= 0.95 \text{ g cm}^{-3}$) of the 4000 Mrad PE and $G_p^{(1)}(r)$ expresses the intrachain peaks within r_1 . (2) We took r_2 near 4 Å in which $G_e(r) = 0$.

For $r_1 < r < r_2$, we have,

$$G_m^{(2)}(r) = Q \cdot r(r_2 - r) + G_p^{(2)}(r) \quad (3)$$

where $G_p^{(2)}(r)$ expresses intrachain peaks between r_1 and r_2 and Q is a parameter. The value of Q is determined from the condition which must be satisfied by $G_m(r)$ ⁹:

$$\int_0^\infty G_m(r) dr = -\{Z_C^2 + (2-x)Z_H^2\} / \{Z_C + (2-x)Z_H\}^2 \quad (4)$$

where Z_C and Z_H are the atomic numbers of the C and H atoms, and $2-x$ is the composition ratio of the H atoms to the C atoms, that is, the H/C ratio, where x denotes the fraction of H atoms liberated by γ -ray irradiation. Elementary analysis showed $2-x = 1.79$ for 4000 Mrad PE. The resultant function, $G_p(r)$ ($= G_p^{(1)}(r) + G_p^{(2)}(r)$) for the intrachain C-C and C-H peaks within r_2 is expressed by the following form¹⁰:

$$G_p(r) = 2r/\pi \int_0^\infty \{f_C + (2-x)f_H\}^{-2} \sin(rs) \times ds \left[f_C^2 X^{CC} \left\{ \sum_{i=1}^2 \sin(r_i^{CC}s)/r_i^{CC} \right\} \right.$$

$$+ \sum_{n=1}^2 P_n \sin(r_{3n}^{CC}s)/r_{3n}^{CC} \left. \right\} + f_C f_H \left\{ \sum_{i=1}^2 X_i^{CH} \sin(r_i^{CH}s)/r_i^{CH} + \sum_{n=1}^3 X_3^{CH} P_n \sin(r_{3n}^{CH}s)/r_{3n}^{CH} \right\} \quad (5)$$

Here, f_C and f_H are the atomic scattering factors for C and H atoms, r_i^{CC} (or r_i^{CH}) is the C···C (or C···H) distance separated by i bonds, and X_i^{CC} (or X_i^{CH}) the number of equivalent pairs. r_{3n}^{CC} and r_{3n}^{CH} are the C···C and C···H distances for $i=3$, where $n=1$ denotes *trans* and $n=2$ and 3 *gauche*, and P_n , the fraction of the n -state. These distances are shown in Table I. The r_i^{CC} and r_i^{CH} distances for $i=1$ and 2 are independent of the chain conformation.

On the other hand, for the long distance $r > r_2$ where the interchain contribution is dominant, a modelled RDF is determined that will fit the experimental RDF, $G_e(r)$, shown by the dotted line in Figure 2.

For $r > r_2$, we have,

Table I. Intrachain distances between atoms separated by i bonds

i	n	$r^{CC}(\text{\AA})$	$r^{CH}(\text{\AA})$
1		1.54	1.09
2		2.54	2.16
	1 (<i>trans</i>)	3.9	2.77
3	2 (<i>gauche</i>)	3.0	2.77
	3 (<i>gauche</i>)		3.48

Figure 2. Modelled RDF $G_m(r)$ (solid line) and experimental RDF $G_e(r)$ (dotted line) for PE amorphotized

$$G_m^{(3)}(r) = A \cdot r \cdot \sin w(r-r_2) \cdot \exp \{-(r-r_2)/a\} \\ + B \cdot r \cdot \sin 2w(r-r_2) \cdot \exp \{-(r-r_2)/b\} \quad (A > B) \quad (6)$$

where the second term in the $G_m^{(3)}(r)$ expresses the asymmetry of the damped oscillation appearing in $G_e(r)$ for $r > r_2$. A , B , w , a and b are adjustable parameters determined so that $G_m^{(3)}(r)$ fits $G_e(r)$ and $A=0.72$, $B=0.22$, $w=1.43$, $a=5$ and $b=3$ were chosen. Although intrachain contributions are included in $G_m^{(3)}(r)$, they are less dominant in the region of $r > r_2$ than interchain contributions.

RESULTS AND DISCUSSION

The solid line in Figure 2 shows the modelled RDF, $G_m(r)$ ($=G_m^{(1)}(r)+G_m^{(2)}(r)+G_m^{(3)}(r)$), in which the intrachain peaks, $G_p(r)$, are omitted. There is good agreement between $G_m^{(3)}(r)$ and $G_e(r)$ over 4Å. $si(s)$ can be derived analytically from the Fourier transform of $G_m(r)$ through eq 2–6 without numerical calculation. It is interesting to examine how the Fourier transforms of each part of the modelled RDF, $G_m(r)$, contribute to $si(s)$. Figures 3a, b and c show the respective Fourier transforms ($si^{(k)}(s)$ ($k=1$ to 3)) of $G_m^{(1)}(r)+G_m^{(2)}(r)-G_p(r)$, the first and second terms in $G_m^{(3)}(r)$. Figure 3a shows that the average number of C atoms per unit volume, $\bar{\rho}$ and the distances of r_1 and r_2 (parameters for the closest approach of atoms in the neighbouring chains) affect significantly $si^{(1)}(s)$ up to

Figure 3. Fourier transforms ($si^{(k)}(s)$ ($k=1$ to 3)) of (a) $G_m^{(1)}(r)+G_m^{(2)}(r)-G_p(r)$, (b) the first term and (c) the second term in $G_m^{(3)}(r)$. ($G_m(r)=G_m^{(1)}(r)+G_m^{(2)}(r)+G_m^{(3)}(r)$).

$s=4\text{Å}^{-1}$. The highest peak at $s=1.5\text{Å}^{-1}$ in the $si^{(2)}(s)$ curve shown in Figure 3b is due to the damped oscillation in $G_m^{(3)}(r)$ over r_2 . On the other hand, the highest peak at $s=3\text{Å}^{-1}$ shown in Figure 3c indicates that the second peak of the $si(s)$ curve in Figure 1a strongly reflects the asymmetry in the radial distribution of interchain packing. Figures 4a, b, c, and d show the Fourier transforms of $G_p(r)$ ($si^{(4)}(s)$) for the *trans* fractions (P_t) of 1.0, 0.75, 0.6, and 0.45, respectively. These curves show that the $si(s)$ curve in the region of $s > 4\text{Å}^{-1}$ is determined for the most part only by the intrachain C–C and the C–H peaks of distances separated by i bonds ($i=1,2$ and 3).

Figure 4. Fourier transform ($si^{(4)}(s)$) of intrachain peaks $G_p(r)$ for *trans* fractions of (a) 1.0, (b) 0.75, (c) 0.6, and (d) 0.45.

Figure 5. $si(s)$ curves calculated from $G_m(r)$ for *trans* fractions of (a) 1.0, (b) 0.75, (c) 0.6 and (d) 0.45.

Figure 5 shows the $si(s)$ curves synthesized from Figures 3 and 4. It is noteworthy that the intensity of the shoulder appearing at $s \approx 3.5 \text{ \AA}^{-1}$ is highest when $P_t = 1.0$ and decreases as P_t decreases. The area of the shoulder at $s \approx 3.5 \text{ \AA}^{-1}$ separated by the dashed line in the experimental $si(s)$ in Figure 1a is compared with those in the calculated $si(s)$ as shown in Figure 5b and c. The experimental area showed the best agreement with the calculated area for $P_t = 0.65$. On the other hand, the *trans* fraction for PE γ -ray irradiated for 5000 Mrad (5000 Mrad PE) was determined as 0.6 from our RDF study.⁶ The *trans* fraction of 0.65 for the 4000 Mrad PE is a little higher than 0.6 for the 5000 Mrad PE. This suggests that regularity in the chain conformation was reduced with an increase in γ -ray irradiation from 4000 to 5000 Mrad, even though both the PE's were amorphotized. This may be related to the RDF result in which the regularity of interchain packing for 4000 Mrad PE is better than that for the 5000 Mrad.⁴

The present method is very effective for studying the local ordering in polymers, provided a scattering intensity measured exactly within $5 \text{ \AA}^{-1}$ of s can be used. We are going to apply this method to the scattering curves for the 5000 Mrad PE and ethylene-propylene random copolymer, and their temperature dependence. Comparison between their chain conformations analyzed by this method and by the RDF method will be reported in the near future.

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