Radial Distribution Function Study for Ethylene–Propylene Random Copolymer by X-Ray Diffraction Method

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ABSTRACT: The local chain conformation and packing in the amorphous solid of a polymer were determined for ethylene–propylene random copolymer (EPRC) by the analysis of the radial distribution function (RDF) obtained from X-ray diffraction measurement at room temperature. A new method was devised for removing the contribution of H atoms to the observed RDF in such a polyatomic system consisting of C and H atoms, and the C–C pair RDF for EPRC was derived. From the C–C pair RDF, the number of intrachain and interchain atoms were obtained. From this result, it was found that the amorphous bulk state and the isolated state in θ -solvent are nearly equal in the conformational probabilities for *trans* and *gauche* states in the EPRC chain.

KEY WORDS Radial Distribution Function / Ethylene–Propylene Random Copolymer / Amorphous Solid / C–2H System / C–C Pair RDF / Conformation / Chain Packing /

Radial distribution function (RDF) analysis is a very powerful tool for studying local chain conformation and packing of polymer chains in the amorphous state. The RDF characterizes short range orders in terms of the number of neighboring atoms (the area under the RDF curve) and peak positions. On the other hand, chain conformations are characterized by unconditional probabilities, P_t for *trans* and P_g for *gauche*, and/or higher order probabilities, for instance, P_{tt} and P_{tg} , which are defined by a set of rotational angles about the skeletal bonds.

Polyethylene (PE) is the most suitable polymer for such RDF studies because of the simplicity of its molecular structure. But it is difficult to observe the amorphous intensity exactly at room temperature by X-ray diffraction since PE is a highly crystalline polymer. RDF studies of PE have been made only in the molten or amorphotized states by irradiation,^{1–6} but no quantitative information on the local chain conformation in the amorphous state has yet been obtained from these RDF studies. RDF of such C–2H systems is governed by H atoms as well as C atoms, although the former is not dominant. The intrachain peaks associated with H atoms are almost smeared out in the RDF pattern obtained from X-ray diffraction measurement.⁷ For

such a polyatomic system, it is not easy to obtain exact conformational information from the RDF. It is therefore desirable to derive the number of intrachain atoms only for C–C pairs from the RDF data, by eliminating the contribution from H atoms.

In this paper, a new method is proposed for obtaining a C–C pair RDF from the experimental RDF of a C–2H system obtained by X-ray diffraction measurement. The local chain conformation and interchain packing for an ethylene–propylene random copolymer (EPRC) with a high ethylene fraction, which is a C–2H system, are studied, because EPRC is in the amorphous solid state at room temperature and its chain structure as simple as PE.

EXPERIMENTAL

Sample

A 1 mm thick film of ethylene–propylene copolymer (propylene-unit fraction; 20 mol%) was provided by the Japan EP Rubber Co. The ¹³C NMR data show that the populations of propylene sequences $(-\text{CH}_2\text{CHCH}_3-)_n$ contained are 85% for $n=1$, 15% for $n=2$, and <1% for $n>3$.

From this result, the sample is considered to be a random copolymer,* and is referred to as EPRC. The melting point of the as-received sample is 38°C and the glassy transition temperature, -53°C. By quenching from the molten state at about 100°C to -20°C, a completely amorphotized film having a density of 0.865 g cm⁻³ was made.

X-Ray Measurement

X-Ray measurements were carried out at room temperature, using Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$), which was monochromatized by balanced Zr-Yt Ross filters equipped on the incident side. The scintillation counter and pulse height analyzer were employed as a detecting system. The symmetrical transmission technique with a divergence slit of $1/6^\circ$ was used below 36° of 2θ at angular intervals of 0.2° in $\Delta 2\theta$, while the symmetrical reflection technique with a divergence slit of $1/2^\circ$ was used over 28° of 2θ at angular intervals of 0.4° in $\Delta 2\theta$. Intensity data were collected over an angular range from $2\theta = 2$ to 105° , by point counting in the fixed count mode; the counts per point were 2×10^4 and 8×10^4 for the transmission and reflection techniques, respectively. The intensity curve was made smooth, and then the scattering intensity $I_{\text{obs}}^c(s)$ was corrected for air scattering, absorption, polarization and multiple scattering,⁸ where $s = 4\pi \sin \theta / \lambda$.

EXPERIMENTAL RESULTS

Intensity Curve

Figure 1 shows the observed coherent intensity curve $I(s)$ in electron units obtained by removing the incoherent scattering. In order to transform the intensity in an arbitrary unit to that in electron units, the normalization factor was determined by the following high angle method⁹:

$$\beta = \frac{\int_{s_{\text{high}}}^{s_{\text{max}}} [I_{\text{C}}^{\text{inc}}(s) + 2I_{\text{H}}^{\text{inc}}(s) + f_{\text{C}}^2(s) + 2f_{\text{H}}^2(s)] ds}{\int_{s_{\text{high}}}^{s_{\text{max}}} I_{\text{obs}}^c(s) ds} \quad (1)$$

* A Monte Carlo chain of 500 monomers consisting of ethylene and propylene units (20 mol% of propylene unit) indicated that the populations of propylene sequences were 84% for $n=1$, 16% for $n=2$, and 0% for $n>3$.

where $s_{\text{high}} = 10 \text{ \AA}^{-1}$ and $s_{\text{max}} = 14 \text{ \AA}^{-1}$, $I_{\text{i}}^{\text{inc}}(s)$ and $f_{\text{i}}(s)$ are the incoherent scattering intensity and the scattering factor for the i-type atom ($i = \text{C}$ (carbon) or H (hydrogen)).¹⁰ The normalization factor calculated by the RDF method⁹ showed only a deviation of 0.02% from the value calculated by eq 1. Since EPRC is a random copolymer consisting of ethylene units ($-\text{CH}_2-\text{CH}_2-$) and propylene units ($-\text{CH}_2-\text{CH}(\text{CH}_3)-$), it can be treated as a C-2H system in X-ray scattering. For the C-2H system, the s -weighted normalized intensity $si(s)$ is given by,

$$si(s) = [I(s) - f_{\text{C}}^2(s) - 2f_{\text{H}}^2(s)] / [f_{\text{C}}(s) + 2f_{\text{H}}(s)]^2 \quad (2)$$

The $si(s)$ curve is shown in Figure 2.

Figure 1. Coherent scattering intensity in an electron unit $I(s)$ for ethylene-propylene random copolymer, EPRC (propylene mole fraction=20%) measured at room temperature.

Figure 2. s -weighted normalized intensity $si(s)$ for EPRC, obtained from the coherent scattering intensity at room temperature.

Figure 3. Experimental DRDF $G^e(r)$ for EPRC at room temperature, obtained from $si(s)$; (a) without a damping factor and (b) with a damping factor of $\exp(-0.01 s^2)$.

DRDF and RDF

The experimental differential radial distribution function (DRDF) $G^e(r)$ is obtained from the $si(s)$ data in Figure 2 using the following equation:

$$G^e(r_j) = 2r_j/\pi \sum_{s_k=s_{\min}}^{s_{\max}} s_k i(s_k) \cdot \exp(-\gamma s_k^2) \sin(r_j s_k) \Delta s \quad (3)$$

where

$$s_{\min} = 0.35 \text{ \AA}^{-1}, \Delta s = 0.05 \text{ \AA}^{-1}, \text{ and } \exp(-\gamma s_k^2)$$

is a damping factor to minimize truncation errors. Intervals of r_j in DRDF are 0.05 Å for $r < 6$ Å and 0.1 Å for $r > 6$ Å. Figure 3a shows the $G^e(r)$ obtained from the $si(s)$ curve in Figure 2 with no damping factor, i.e., with $\gamma = 0.0$. There exist

Table I. Intrachain distances of C_0C_j pairs separated by j bonds ($j=1$ to 4) for a linear polyethylene chain

Bond j	C_0C_j distance	Conformation	C_0H_j distance
	Å		Å
1	1.54		1.09
2	2.54		2.16
3	3.01	$g^\pm$	$\left\{ \begin{array}{l} 2.77 \\ 3.48 \end{array} \right.$
	3.91	t	2.77
	3.63	$g^\pm g^\pm$	$\left\{ \begin{array}{l} 2.63 \\ 4.00 \end{array} \right.$
4	4.43	$tg^\pm$	$\left\{ \begin{array}{l} 4.20 \\ 4.69 \end{array} \right.$
	5.08	tt	4.19

Figure 4. Experimental RDF $H^e(r)$ ($=G^e(r) + 4\pi r^2 \bar{\rho}$) for EPRC at room temperature.

many peaks in $G^e(r)$, but most of them are considered to be spurious peaks due to truncation errors. At first sight, many peaks within 6 Å seem to correspond to the intrachain-CC and -CH distances which were assigned by Voigt-Martin *et al.*¹ in the DRDF of molten PE obtained from electron diffraction measurement. Longman *et al.*² made a similar finding from X-ray diffraction measurement, and suggested that such peaks are due to intrachain the CC and CH distances themselves and truncation errors are not serious in the region of $1 < r < 6$ Å. In our previous paper,⁷ however, it was indicated that the intrachain CH peaks should be smeared out

when DRDF was obtained from the X-ray scattering experiment, since the scattering intensity from H atoms decreases rapidly with an increase in s . It was also indicated that the use of a damping factor $\exp(-0.01 s^2)$ almost extinguishes spurious peaks, which are caused by the finite truncation of $s_{\max} = 14 \text{ \AA}^{-1}$, without overdamping true peaks. Figure 3b shows the $G^e(r)$ obtained by applying the damping factor of $\exp(-0.01 s^2)$. Intrachain CC and CH distances calculated for a linear PE chain are shown in Table I. In Figure 3b, intrachain CH peaks have almost disappeared, while intrachain CC peaks appear at $1.55 \text{ \AA}$, $2.55 \text{ \AA}$, and $4.0 \text{ \AA}$. A shoulder appearing at about $3 \text{ \AA}$ corresponds to the *gauche* CC distance given in Table I. Figure 4 shows RDF $H^e(r)$ ($G^e(r) + 4\pi r^2 \bar{\rho}$), where $\bar{\rho}$ is the average number of C atoms per unit volume. The value of $\bar{\rho}$, calculated from the macroscopic sample density, was $0.0371 \text{ \AA}^{-3}$.

DATA ANALYSIS

Scattering Intensity from a C-2H System

The coherent scattering from a C-2H system is given by

$$I(s) = f_C^2(s) + 2f_H^2(s) + f_C^2(s) \int_0^\infty g_{CC}^0(r) \sin(sr)/(sr) dr \\ + 4f_C(s)f_H(s) \int_0^\infty g_{CH}^0(r) \sin(sr)/(sr) dr \\ + 4f_H^2(s) \int_0^\infty g_{HH}^0(r) \sin(sr)/(sr) dr \quad (4)$$

where the i - j pair DRDF $g_{ij}^0(r)$ is defined by $4\pi r^2(\rho_{ij}^0(r) - \bar{\rho})$, with $\rho_{ij}^0(r)$ the number density of j type atoms at a distance r from an i type atom.

DRDF $G(r)$ is obtained by the inverse Fourier transform of $si(s)$,

$$G(r) = 2r/\pi \int_{s_{\min}}^{s_{\max}} si(s) \sin(rs) \cdot \exp(-\gamma s^2) ds \quad (5)$$

where $si(s)$ is defined by eq 2. If $f_H(s)/f_C(s)$ is a constant, the scattering factors can be expressed as $f_C(s) = Z_C f_e(s)$ and $f_H(s) = Z_H f_e(s)$, where $f_e(s) = [f_C(s) + 2f_H(s)]/(Z_C + 2Z_H)$ and Z_i is the atomic number of the i type atom. In this case, $G(r)$ reduces to the weighted sum of the i - j pair DRDF

$g_{ij}(r)^*$, i.e., $G^l(r)$. Thus,

$$G(r) = G^l(r) = [Z_C^2 g_{CC}(r) + 4Z_C Z_H g_{CH}(r) \\ + 4Z_H^2 g_{HH}(r)] / (Z_C + 2Z_H)^2 \quad (6)$$

When $f_H(s)/f_C(s)$ is not a constant, however, it is not easy to derive meaningful information on the pair distribution from $G(r)$. We treat the X-ray scattering in this case as follows. The scattering factors are expressed as $f_C(s) = Z_C f_e(s) + \Delta f_C(s)$ and $f_H(s) = Z_H f_e(s) + \Delta f_H(s)$.

Substituting these $f_C(s)$ and $f_H(s)$ into eq 4, we obtain the following relations:

$$si(s) = si_0(s) + \Delta si(s) \quad (7)$$

$$si_0(s) = \int_0^\infty \{ [Z_C^2 g_{CC}^0(r) + 4Z_C Z_H g_{CH}^0(r) + 4Z_H^2 g_{HH}^0(r)] \\ / [r(Z_C + 2Z_H)^2] \} \sin(sr) dr \quad (8a)$$

and,

$$\Delta si(s) = F_{CC}(s) \int_0^\infty [g_{CC}^0(r)/r] \sin(sr) dr \\ + 4F_{CH}(s) \int_0^\infty [g_{CH}^0(r)/r] \sin(sr) dr \\ + 4F_{HH}(s) \int_0^\infty [g_{HH}^0(r)/r] \sin(sr) dr \quad (8b)$$

where,

$$F_{ij}(s) = \{ f_e(s) [Z_i \Delta f_j(s) + Z_j \Delta f_i(s)] + \Delta f_i(s) \Delta f_j(s) \} / \\ \{ f_C(s) + 2f_H(s) \}^2 \quad (8c)$$

$F_{CC}(s)$ and $F_{CH}(s)$ were calculated numerically from the theoretical values of $f_C(s)$ and $f_H(s)$ ¹⁰; the calculated results are shown by the solid lines in Figure 5. We can approximate $F_{CC}(s)$ and $F_{CH}(s)$ by the simple function,

$$F_{ij}(s) = K_{ij} [1 - \exp(-a_{ij}s^2)] \quad (9)$$

where $K_{CC} = 0.425$, $a_{CC} = 0.025 \text{ \AA}^{-2}$, $K_{CH} = -0.091$, and $a_{CH} = 0.024 \text{ \AA}^{-2}$. The open circles in Figure 5 show such approximations for $F_{CC}(s)$ and $F_{CH}(s)$. Substituting eq 7–8 into eq 5, we derive RDF $H(r)$ ($= G(r) + 4\pi r^2 \bar{\rho}$):

* $g_{ij}(r)$ in eq 6 is different from $g_{ij}^0(r)$. The former is smeared out by the truncation effect, and hereafter is referred to as i - j pair DRDF.

Figure 5. Correction terms for scattering factors, (a) $F_{cc}(s)$ and (b) $F_{ch}(s)$. Solid line are calculated numerically by using the theoretical values of $f_c(s)$ and $f_H(s)$. Open circles show approximations of $F_{ij}(s)$'s expressed by simple functions in eq 9.

$$H(r) = H_{cc}(r) + H_{ch}(r) \quad (10)$$

Here,

$$H_{cc}(r) = [Z_C^2 / (Z_C + 2Z_H)^2] h_{cc}(r) + \Delta H_{cc}(r) \quad (11a)$$

$$H_{ch}(r) = 4[Z_C Z_H / (Z_C + 2Z_H)^2] h_{ch}(r) + 4\Delta H_{ch}(r) \quad (11b)$$

and $H_{HH}(r)$ is neglected, where the i - j pair RDF $h_{ij}(r)$ is defined by $4\pi r^2 \rho_{ij}(r)$. $H_{ij}(r)$ is hereafter referred to as atomic-number-weighted i - j pair RDF. The second terms in eq 11a and b are given by,

$$\Delta H_{ij}(r) = r f_{ij}(r) * [h_{ij}(r)/r] \quad (11c)$$

$$f_{ij}(r) = 1/\pi \int_0^\infty F_{ij}(s) \cos(rs) ds \quad (11d)$$

where * denotes the convolution product.

C-C Pair RDF

In order to make clear local conformation as well as local packing in the amorphous EPRC, the smeared-out CH peaks were removed from the experimental RDF $H^e(r)$ by the following procedures:

- i) The conformational probabilities for the

Table II. Conformational probabilities calculated for an isolated EPRC chain (propylene mole fraction=20%) at room temperature

P_t	0.59
$P_{g^\pm}$	0.41
P_{tt}	0.36
$P_{tg^\pm}$	0.54
$P_{g^\pm g^\pm}$	0.10

EPRC chain (propylene mole fraction=20%) were calculated on the rotational isomeric state model for *trans* (t), *gauche* ($g^\pm$), tt , $tg^\pm$, $g^\pm g^\pm$, as shown in Table II. (The outline of calculation is described in Appendix 1.) The intrachain C-H pair RDF $h_{CH}^{0 \text{ intra}}(r)$ was obtained from the conformational probabilities and the C_0H_j distances separated by j bonds in the chain. If the intrachain C-H pair RDF is obtained from the observed $si(s)$ by eq 5, its distribution must be broadened by a finite $s_{\max}$ and the damping factor. According to Warren,¹¹ such an intrachain C-H pair RDF $h_{CH}^{\text{intra}}(r)$ can be calculated from $h_{CH}^{0 \text{ intra}}(r)$ by the following equation:

$$h_{CH}^{\text{intra}}(r) = r s_{\max} / \pi \int_0^\infty h_{CH}^{0 \text{ intra}}(y) / y \left[\frac{0.588 \sin(r-y)s_{\max}}{(r-y)s_{\max}} + 0.206 \frac{\sin(2.15\gamma + |r-y|s_{\max})}{(2.15\gamma + |r-y|s_{\max})} + 0.206 \frac{\sin(2.15\gamma - |r-y|s_{\max})}{(2.15\gamma - |r-y|s_{\max})} \right] dy \quad (12)$$

where we have used $s_{\max} = 14 \text{ \AA}^{-1}$ and $\gamma = 0.01$ as described in the experimental part (*cf.* eq 3). For the C_0H_j pair distances ($j=1$ to 4), the values for a linear PE chain were used as shown in Table I. Since the CH peaks are smeared out in $H_{CH}^{\text{intra}}(r)$ because $f_H(s)/f_C(s)$ is not constant, the use of these distances for the EPRC chain yields no serious error. $H_{CH}^{\text{intra}}(r)$, calculated from $h_{CH}^{\text{intra}}(r)$, is shown in Figure 6a. Figure 6b indicates the result when $H_{CH}^{\text{intra}}(r)$ is subtracted from $H^e(r)$, or $H^e(r) - H_{CH}^{\text{intra}}(r)$. This is equal to $H_{cc}(r)$ (the atomic-number-weighted C-C pair RDF) in a small r region. However, a tail of the interchain RDF $H^{\text{inter}}(r)$ still extends to the region below $4 \text{ \AA}$.

- ii) In view of van der Waals contacts, the tail part of $H^{\text{inter}}(r)$ is given by the dotted line shown in Figure 6b. The intrachain CC peaks have been

separated from $H^e(r) - H_{CH}^{intra}(r)$ by drawing the dotted line, in such a way that the resultant area of intrachain peaks in the range of 2.2 to 4.3 Å is equal to the theoretical value predicted for the EPRC chain, $4.4 \times Z_C^2 / (Z_C + 2Z_H)^{2*}$. As a result, the dotted line intersects the $H^e(r) - H_{CH}^{intra}(r)$ curve at about 3.4 Å and 3.7 Å of r . The dashed line in Figure 6b shows another separation for avoiding such an intersection, and the area of the intrachain peaks is also taken to be the theoretical value.

In a large r region, CH_x units ($x=1$ to 3) are assumed to be distributed with random orientation since most of CH_x units belong to different chain segments. Moreover, a C-H distance ($r_{CH}=1.09$ Å) in the CH_x unit is much smaller than interchain radial distances of H and/or C atoms. Therefore, it is assumed that C and H atoms belonging to the same CH_x unit are distributed radially in the same form in the large r region. Therefore, interchain i - j pair DRDF $g_{ij}^{0,inter}(r)$ is given by the following relations:

$$g_{CC}^{0,inter}(r) = g_{CH}^{0,inter}(r) = g_{HH}^{0,inter}(r) \quad \text{for } r > r_0 \quad (13a)$$

$$g_{ij}^{0,inter}(r) = 0 \quad \text{for } r < r_0 \quad (13b)$$

and

$$g_{ij}^0(r) = g_{ij}^{0,inter}(r) + g_{ij}^{0,intra}(r) \quad (13c)$$

where r_0 is the nearest distance of interchain atoms. When such relations are taken into consideration in eq 4, the coherent intensity is given by,

$$I(s) = f_C^2(s) + 2f_H^2(s) + [f_C(s) + 2f_H(s)]^2 \int_0^\infty g_{CC}^{0,inter}(r) \sin(sr)/(sr) dr + \sum_{ij} \chi_i \chi_j f_i(s) f_j(s) \int_0^\infty g_{ij}^{0,intra}(r) \sin(sr)/(sr) dr \quad (14)$$

where χ_i is the atomic fraction of the i -type atom. The inverse Fourier transform of $si(s)$, obtained from eq 5, then gives $G^{inter}(r) = g_{CC}^{inter}(r)$ for $r > r_0$, where $G^{inter}(r)$ denotes the interchain part of $G(r)$. $G(r) \simeq G^{inter}(r)$ can be assumed in the large r region. Therefore, $H^e(r) - H_{CH}^{intra}(r)$ above 4.3 Å as well as the dashed or dotted lines below 4.3 Å in Figure 6b can be considered to be the interchain C-C pair

RDF $h_{CC}^{inter}(r)$ in the first approximation.

iii) For the second approximation, the atomic-number-weighted C-H pair RDF for interchain $H_{CH}^{inter}(r)$ must be derived more exactly. If H atoms are distributed with a spherical symmetry about the C atom in the same CH_x unit, interchain C-H pair RDF can be obtained from $h_{CC}^{inter}(r)$, i.e.,

$$h_{CH}^{inter}(r) = \int_0^\infty h_{CH}(r, r_C) h_{CC}^{inter}(r_C) dr_C \quad (15)$$

where $h_{CH}(r, r_C)$ is the RDF of an H atom when the C atom in the same CH_x unit is located at r_C . The derivation of $h_{CH}(r, r_C)$ is described in Appendix 2. $H_{CH}^{inter}(r)$ obtained from $h_{CH}^{inter}(r)$ using eq 11b-d is shown in Figure 6c. Two cases were obtained for $H_{CH}^{inter}(r)$: One is from the dotted line and the other from the dashed line, for $h_{CH}^{inter}(r)$ below 4.3 Å in Figure 6b. However, both $H_{CH}^{inter}(r)$'s were undistinguishably coincident with each other. This may be due to the fact that H atoms are distributed spherically symmetrically about C atom as given by eq 14 and $H_{CH}^{inter}(r)$ is furthermore smeared out because $f_H(s)/f_C(s)$ is not constant. Therefore, inasmuch as the area of $h_{CC}^{inter}(r)$ stays the same, almost the same $H_{CH}^{inter}(r)$ is derived from $h_{CC}^{inter}(r)$. The experimental atomic-number-weighted C-C pair RDF $H_{CC}^e(r)$ was obtained by subtracting the $H_{CH}^{inter}(r)$ from $H^e(r) - H_{CH}^{intra}(r)$; the result is shown in Figure 6d.

iv) The experimental C-C pair RDF $h_{CC}^e(r)$ was obtained using the iterative method as follows. From eq 11b, the relation between $\Delta H_{CC}(r)$ and $h_{CC}^e(r)$ for the n -th iteration is given by,

$$h_{CC}^{e(n)}(r) = [(Z_C + 2Z_H)^2 / Z_C^2] [\Delta H_{CC}^e(r) - \Delta H_{CC}^{(n)}(r)] \quad (16)$$

If $h_{CC}^{e(n-1)}(r)$ is known, $\Delta H_{CC}^{(n)}(r)$ is calculated from the $h_{CC}^{e(n-1)}(r)$ using eq 11c. $[(Z_C + 2Z_H)^2 / Z_C^2] H_{CC}^e(r)$ was used as $h_{CC}^{e(0)}(r)$, and $h_{CC}^{e(n)}(r)$ converged to a certain function after iterations were carried out several times. For $n=11$, $\Delta H_{CC}^{e(n)}(r)$ and $h_{CC}^{e(n)}(r)$ are shown in Figure 6e and f, respectively.

The dotted lines in Figure 6f show the peak separations at about 1.5 Å, 2.5 Å, and 3 Å plus 4 Å. These separations were carried out in such a way that the number of atoms in 1.5 Å, 2.5 Å, and 3 Å plus 4 Å peaks were 2.0, 2.2, and 2.2, respectively, as predicted from the EPRC chain structure (propylene-unit fraction: 20 mol%) presented in the experimental part. Furthermore, each of the 3 Å and 4 Å peaks was separated, as shown by the

* The area of C_0C_2 and/or C_0C_3 pair in the atomic-number-weighted C-C pair RDF $H_{CC}^e(r)$ is given by $2.2 \times Z_C^2 / (Z_C + 2Z_H)^2$.

Figure 6. (a) Atomic-number-weighted C-H pair RDF for intrachain, $H_{CH}^{intra}(r)$, as a function of r . (b) Removal of intrachain H atoms from $H^e(r)$; $H^e(r) - H_{CH}^{intra}(r)$. (c) Atomic-number-weighted C-H pair RDF for interchain, $H_{CH}^{inter}(r)$. (d) Experimental atomic-number-weighted C-C pair RDF, $H_{CC}^e(r)$, that is, $H^e(r) - H_{CH}^{intra}(r) - H_{CH}^{inter}(r)$. (e) Additional term in $H_{CC}^e(r)$; $\Delta H_{CC}(r)$, caused because $f_H(s)/f_C(s)$ is not constant. (f) Experimental C-C pair RDF, $H_{CC}(r)$, at room temperature.

dashed line in Figure 6f. The number of atoms in the 3 Å peak is 0.85, while that of 4 Å peak is 1.35. The ratio of the number of atoms in the 3 Å peak to that in 4 Å peak (*trans-gauche* ratio) is about 0.4/0.6. On the other hand, the *trans-gauche* ratio of an isolated EPRC chain in a θ -solvent was calculated to be 0.41/0.59 at room temperature, as shown in Table II. We see good agreement between the observed and calculated values. It should be noted that the *trans-gauche* ratio in the amorphous bulk is

nearly equal to that in the isolated chain.

Peaks above 4 Å are observed at about 4.5 and 5.3 Å in the C-C pair RDF. The peaks at 4.5 and 5.3 Å correspond to the $tg^\pm$ and tt states of the C_0C_4 pair, respectively. The dashed line about 5.3 Å shows an example of the separation of an intrachain peak from the interchain background, in which separation was performed when the number of atoms in the 5.3 Å peak was equal to the value ($0.8 = 2.2 \times 0.36$) calculated from the EPRC chain

structure and the probability of *tt* conformation (P_{tt}) in Table II. This suggests that the sharp peak appearing at 5.2 Å in the observed $G^*(r)$, shown in Figure 3b, is contributed primarily from the intrachain-*tt*-conformation.

As shown by the dotted line in Figure 6f, the closest possible distance of atoms in the neighboring chains is about 3.6 Å, although some arbitrariness in separation was unavoidable. This value may increase a little if the truncation broadening in the tail part of interchain region of $h_{CC}^*(r)$ is corrected. The number of interchain atoms is also estimated from $h_{CC}^*(r)$. For example, the number of atoms in the interchain region within 4.8 Å is 7.4. Herein, there exist the intrachain peaks of g^+g^+ and tg^+ conformations, as predicted from Table I. If the rotational isomeric state model is adopted, the number of atoms of g^+g^+ and tg^+ conformations are obtained as 0.2 and 1.2 from Table II. By subtracting (0.2+1.2) from the number of atoms in the interchain region within 4.8 Å (=7.4), the number of interchain atoms within 4.8 Å is estimated to be 6.0. We are now applying a similar analysis to PE amorphotized by γ -ray irradiation. The interchain packing in the amorphous solid state of PE-like polymers will be discussed in greater detail in the near future.

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APPENDIX I

Conformational probabilities for an isolated EPRC chain in a θ -solvent can be calculated using the rotational isomeric state model of Flory *et al.*¹² There are three isomeric states in the skelton bonding, which are referred to as *trans* (*t*), *gauche* plus (g^+) and *gauche* minus (g^-). Their conformational probabilities are given by the statistical weight matrices U_i , in which rows are associated with rotational states about the bond $i-1$ and columns with states about the bond i : both rows and columns are indexed in the order *t*, g^+ , g^- . According to Mark,¹³ various combinations of the statistical

weight matrices are used to represent all possible consecutive bond pairs in the EPRC chain (20 mol% of propylene unit).

(I) For bond pairs $\text{CH}_2\text{--CH}_2\text{--CH}_2$: The statistical weight matrix has the form,

$$U_e = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \omega\sigma \\ 1 & \omega\sigma & \sigma \end{bmatrix} \quad (\text{A1})$$

where the parameter σ denotes the statistical weight applicable to a *gauche* state when the proceeding state is either *trans* or *gauche* of the same sign, this statistical weight being relative to the value of unity for the *trans* state. The factor ω takes account of the severe steric overlap of a pair of *gauche* states opposite in sign, (pentane effect).

(II) For a pair of bonds meeting at a CHCH_3 group: The atomic configurations of the group are specified by the *d* and *l* conventions.¹² The statistical weight matrix for the *d* configuration is given by,

$$U_d = \begin{bmatrix} \sigma & \sigma & \tau\sigma \\ \sigma & \sigma & \omega\tau\sigma \\ \sigma & \omega\sigma & \tau\sigma \end{bmatrix} \quad (\text{A2})$$

where τ is the statistical weight of conformation in which CH or CH_2 is syn to both CH_2 and CH_3 . The matrix U_l associated with the *l* configuration is obtained by the simple interchange of both the second and third rows and the second and third columns of U_d .

(III) For pairs of bonds separating two CHCH_3 groups: The statistical weight matrices for the dyads *dd* and *dl* are given by,

$$U_{dd} = \begin{bmatrix} \omega\sigma & \omega\tau\sigma & \sigma \\ \sigma & \omega\tau\sigma & \omega\sigma \\ \omega\sigma & \omega^2\sigma\tau & \omega\sigma \end{bmatrix} \quad (\text{A3})$$

$$U_{dl} = \begin{bmatrix} \sigma & \omega\sigma & \omega\tau\sigma \\ \omega\sigma & \sigma & \omega\tau\sigma \\ \omega\sigma & \omega\sigma & \omega^2\sigma\tau \end{bmatrix} \quad (\text{A4})$$

The matrices U_{ll} and U_{ld} are obtained respectively from U_{dd} and U_{dl} by the interchanges of rows and columns.

(IV) Bond pairs $\text{CHCH}_3\text{--CH}_2\text{--CH}_2$ and $\text{CH}_2\text{--CH}_2\text{--CHCH}_3$: The former are characterized by U_{de} and U_{le} , and the latter by U_{ed} and U_{el} , where,

$$U_{de} = \begin{bmatrix} 1 & \omega\sigma & \sigma \\ 1 & \sigma & \omega\sigma \\ 1 & \omega\sigma & \omega\sigma \end{bmatrix} \quad (A5)$$

$$U_{ed} = \begin{bmatrix} \sigma & \tau\sigma & \sigma \\ \sigma & \omega\tau\sigma & \omega\sigma \\ \omega\sigma & \omega\tau\sigma & \sigma \end{bmatrix} \quad (A6)$$

U_{le} and U_{el} are related to U_{de} and U_{ed} , respectively, by the interchange of rows and columns.

Calculations have been carried out by using the following values^{14,15} for σ , τ , and ω at room temperature; $-RT \ln \sigma = 500$ cal mol⁻¹, $-RT \ln \tau = 450$ cal mol⁻¹, and $-RT \ln \omega = 2000$ cal mol⁻¹. The configuration partition function Z for the EPRC chain of n -bonds can thus be written as,

$$Z = \mathbf{J}^* \left[\prod_{i=2}^{n-1} \mathbf{U}_i \right] \mathbf{J} \quad (A7)$$

where $\mathbf{J}^* = [1 \ 0 \ 0]$ and $\mathbf{J}$ is the transpose of $[1 \ 1 \ 1]$. The probability that the bond i is in state η ($\eta = t, g^+,$ or g^-) is given by,

$$P_{\eta,i} = Z^{-1} \mathbf{J}^* \left[\prod_{h=2}^i \mathbf{U}_h \right] \mathbf{U}'_{\eta,i} \left[\prod_{j=i+1}^{n-1} \mathbf{U}_j \right] \mathbf{J} \quad (A8)$$

where $\mathbf{U}'_{\eta,i}$ is formed from the matrix $\mathbf{U}_i$ by retaining the column η and replacing the elements in other columns by zero. The probability that the bond $i-1$ is in state ξ and the bond i in state η is given by,

$$P_{\xi\eta,i} = Z^{-1} \mathbf{J}^* \left[\prod_{h=2}^{i-1} \mathbf{U}_h \right] \mathbf{U}'_{\xi\eta,i} \left[\prod_{k=i+1}^{n-1} \mathbf{U}_k \right] \mathbf{J} \quad (A9)$$

where $\mathbf{U}'_{\xi\eta,i}$ is formed from the matrix $\mathbf{U}_i$ by replacing all elements with zero except for element $\xi\eta$. The sequences of $\mathbf{U}$'s appearing in eq A7–A9 are specified by the chemical sequences of monomer units along a chain. By the Monte Carlo method, the random sequences of 500 monomers consisting of ethylene and propylene units with 4:1 (20 mo% of propylene unit) are generated in a chain.

$P_{\eta,i}$ and $P_{\xi\eta,i}$ for all bonds except 5 bonds on both ends of the chain are calculated. The averages of $P_{\eta,i}$ and $P_{\xi\eta,i}$ for all bonds are denoted by $(P_t, P_{g^\pm})$ and $(P_{tt}, P_{tg^\pm}, P_{g^\pm g^\pm})$, respectively. Their values are shown in Table II.

APPENDIX 2

Derivation of $h_{CH}(r, r_C)$

We consider the radial distribution function of H atoms belonging to a CH_x unit ($x = 1$ to 3), when H

atoms are distributed in spherical symmetry about the C atom bonding to them. We assume that the number density of an H atom located at a distance r' from the C atom is expressed by a Gaussian function such as,

$$v_H(r') = 1/A \cdot \exp [-(r' - r_{CH})^2/\Delta^2] \quad (A10)$$

and,

$$\begin{aligned} A &= 4\pi \int_0^\infty \exp [-(r - r_{CH})^2/\Delta^2] r^2 dr \\ &= A\sqrt{\pi}^3 (\Delta^2 + 2r_{CH}^2) + 2\pi\Delta^2 r_{CH} \exp (-r_{CH}^2/\Delta^2) \\ &\quad + 2\pi(\Delta^2 + 2r_{CH}^2) \int_0^{r_{CH}} \exp (-z^2/\Delta^2) dz \end{aligned} \quad (A11)$$

where $r_{CH} = 1.09$ Å is a C–H bond length and $\Delta = 0.03$ Å is its amplitude of thermal vibration. When the H and C atoms are placed at $\vec{r}$ and $\vec{r}_C$, r' is given by

$$r' = \sqrt{r^2 + r_C^2 - 2r \cdot r_C \cdot \cos \theta} \quad (A12)$$

where θ is the angle between $\vec{r}$ and $\vec{r}_C$. Following Hosemann *et al.*,¹⁶ the conditional probability, that is, RDF of an H atom, is obtained by integrating eq A10 (when the bonding C atom is located at r_C):

$$\begin{aligned} h_{CH}(r, r_C) &= (2\pi/A) \int_{-1}^1 \exp [-(\sqrt{r^2 + r_C^2 - 2r \cdot r_C \cdot \cos \theta} - r_{CH})^2/\Delta^2] d(\cos \theta) \\ &= (\Delta^2/r \cdot r_C \cdot A) \{ \exp [-(|r - r_C| - r_{CH})^2/\Delta^2] \\ &\quad - \exp [-(r + r_C - r_{CH})^2/\Delta^2] \} \\ &\quad + 2\sqrt{2} r_{CH} \int_{a_1}^{a_2} \exp [-(2r \cdot r_C \cdot z^2/\Delta^2)] dz \end{aligned} \quad (A13)$$

where,

$$a_1 = (|r - r_C| - r_{CH})/\sqrt{2r \cdot r_C}$$

and,

$$a_2 = (r + r_C - r_{CH})/\sqrt{2r \cdot r_C}$$

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