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Solid-state high-resolution ^{13}C NMR study on the interphase in lamellar semi-crystalline polymers

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Abstract

The ^{13}C spin-lattice relaxation time T_{1c}, the spin–spin relaxation time T_{2c}, the chemical shift values as well as mass fractions of the interphase of PE samples crystallized under various conditions were reported mainly in this work. The existence of the interphase is identified by the method of solid-state high-resolution ^{13}C NMR and the thickness of interfacial region has been obtained. Also, a model of chain folding in the interphase region is proposed and compared with Flory's calculations; consequently, the applicable extent of the theory is examined.

Keywords: Crystalline PE; Phase structure; Interphase; ^{13}C NMR; Folded-chain lamellae

1. Introduction

In a semi-crystalline aggregate of flexible chain polymers, a large amount of the adjacent regular-folded tiny lamellae coexists with the amorphous phase whose chains have only random spatial arrangement. This "crystalline–non-crystalline two-phase model" has been widely accepted and used to describe the structure and properties in condensed state. The crystalline morphology of PE prepared by various methods have been studied, and it is found that all have micro-crystallites in the structure of folded-chain lamellae with the thickness varying from 10 to 100 nm, the molecular chain axes are normal to the lamellar surface [1–3]. Nevertheless, a transition or interfacial region should exist between the crystalline and the amorphous region. The morphology and chain arrangement in the interphase would resemble neither that in the crystalline or that in the amorphous phase. In this aspect, a three-phase model is required to describe the properties of the semi-crystalline polymers.

Flory et al. [4] proposed the existence of the interphase based on the lattice model by which the lattice layers are parallel to the lamellar faces (see Fig. 1). According to this model, the thickness of the interphase varies from 1.5 to 2.0 nm depending on the geometry of the crystal lattice during crystallization. Due to the experimental difficulties, this three-phase model has not been fully explored, thus lacking of sufficient experimental evidence.

This work reports mainly the ^{13}C spin-lattice relaxation time T_{1c}, the spin–spin relaxation time T_{2c}, the chemical shift values as well as mass fractions of the interphase of PE samples crystallized under various conditions. By using the method of solid-state high-resolution ^{13}C NMR, the existence of the interphase is identified and the thickness of interfacial region has been obtained (these results are usually ascribed to the amorphous phase). A model of chain folding in the interphase region is proposed and compared with Flory's calculations; consequently, the applicable extent of the theory is examined.

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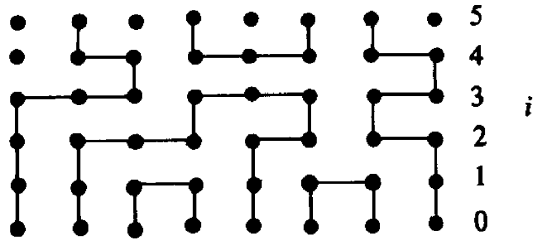

Fig. 1. Schematic cross-sectional view of the interphase in a lamellar semi-crystalline polymer [4].

2. Experimental

2.1. Sample preparation

The melt-grown samples were prepared by melting fractionated PE [5] (original sample HDPE AZ3442, supplied by Showadenko Company, Japan) with different molecular weight and then crystallized at 130°C. The dilute-solution-grown samples (BP Rigidex 9) were prepared by crystallizing the 0.08% PE in toluene at 85°C [6]. The quasi-dilute-solution-grown samples were prepared by quenching a 0.4% UHMWPE (supplied by Mitsui Petrochemical Company, Japan)/decalin solution [7], and the high-pressure-grown samples were prepared following the method used in Ref. [3].

2.2. Solid-state high-resolution ^{13}C NMR spectroscopy

The experiments were performed on a FX-200 spectrometer equipped with a solid CP/DD/MAS detector. The magic field intensity was 4.7 T, the resonant frequency of ^{13}C and ^{1}H ($\gamma B_1/2\pi$) was 69.4 MHz, which becomes 59.5 MHz under the condition of DD without CP, and the MAS rate was 3.4 kHz. The adjustment of MAS angle and MAS rate was carried out by the side band of ^{79}Br of KBr filled in the samples [8]. The chemical shifts relative to $Si(CH_3)_4$ were determined from the CH line ($\delta = 29.50$) of solid adamantane ($C_{10}H_{16}$). The mass fractions of the crystallite, interphase and amorphous phase were determined by the least-square fitting of the Lorentz-like spectral lines.

3. Results and discussion

Fig. 2 shows the DD/MAS spectra of the melt-grown samples. The chemical shift of peak I at the low field intensity end is 33.1, which is close to the average of the chemical shift tensor's principal value 1/3 ($\sigma_{11} + \sigma_{22} + \sigma_{33}$) of the [–$CH_2$–] chain in a *trans*-configuration. This peak is attributed to an orthorhombic crystal. At the high field end, the δ of peak II is 31, close to that of the

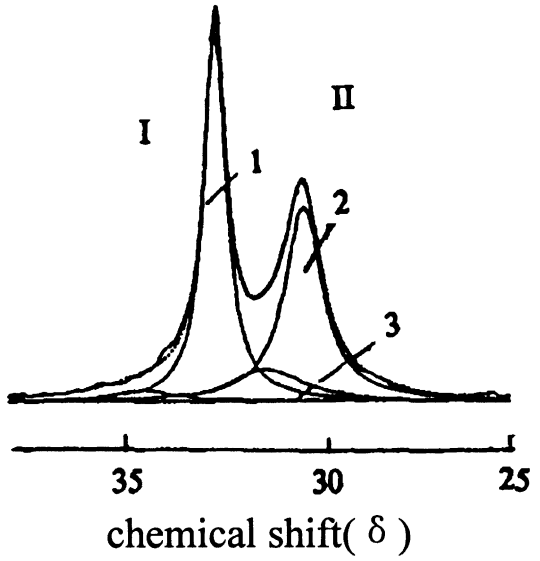

Fig. 2. Solid-state high-resolution ^{13}C NMR DD/MAS spectroscopy of UHMWPE by quasi-dilute-solution gelling and annealing (145°C): (1) crystalline phase; (2) interphase; (3) amorphous rubber.

melted PE [9], which is assigned to the contribution of the amorphous phase.

From determining T_{1c}, it is found that peak I consists of three relaxation times 10^3, 10^2, 10^0 s so that there exist three different modes of oscillation of the spinning nuclei ^{13}C in the crystallites [7]. On the other hand, the partial relaxation spectrum obtained from the inversion recovery method (π–τ–$\pi/2$–FID–10 s) shows only one longitudinal relaxation time T_{1c} ($\sim$0.4 s) in peak II.

Nucleus spinning relaxation occurs due to the Fourier component perturbation of the energy difference between two spinning states. In the system of ^{13}C and ^{1}H, it is regarded as the result of the ^{13}C–^{1}H dipole–dipole interaction changing with time. The longitudinal (T_{1c}) and transverse (T_{2c}) relaxation times of a dual-spin system can be expressed as follows:

$$1/NT_1 = \Upsilon_C^2\Upsilon_H^2h^2/16r^6[J_0(\omega_H - \omega_C) + 18J_1(\omega_C) + 9J_2(\omega_H + \omega_C)] \quad (1)$$

$$1/NT_2 = \Upsilon_C^2\Upsilon_H^2h^2/32r^6[4J_0(0) + J_0(\omega_H - \omega_C) + 18J_1(\omega_C) + 36J_1(\omega_H) + 9J_2(\omega_H + \omega_C)] \quad (2)$$

where J is the spectral density; N is the number ^{1}H directly bonded to ^{13}C.

Eqs. (1) and (2) relate T_{1c} and T_{2c} to the high frequency (10^8 Hz) and low frequency oscillations of ^{13}C correspondingly. In the amorphous peak, only T_{1c} has been observed, which indicates that the indistinguishable

Table 1
T_{1c}, T_{2c} values, interphase and amorphous phase thickness in PE sample crystallized under different conditions

Crystallization condition	$\overline{M}_v$	T_{1c} [s($\times 10^{-1}$)]		T_{2c} (ms)		Layer thickness (nm)		
		Inter-phase	Amorphous phase	Inter-phase	Amorphous phase	Crystal	Interfacial	Rubber
Dilute-solution crystallization	1.0×10^5	4.6	4.6	–	–	15	2.2	0
Quasi-dilute-solution gelling	3.4×10^6	4.6	4.6	2.3×10^{-2}	–	8.4	2.1	0
Heat treatment (145°C/4 min)	3.4×10^6	4.5	4.5	5.4×10^{-2}	5.5	15.2	2.1	12.3
Isothermal crystallization after melting	3.0×10^6	3.7	3.7	4.4×10^{-2}	2.4	60	8.2	14.5
Crystallization under high pressure	2.8×10^4	4.5	4.5	4.9×10^{-2}	–	625	–	14.5
	2.3×10^5	4.0	4.0	10×10^{-2}	2.2	280	8.6	16.7
	1.1×10^6	3.6	3.6	20×10^{-2}	2.0	380	16	22
Oriented crystallization	3.8×10^5	4.0	4.0	–	–	32.0	9.9	12.2

oscillation mode in this phase is a fast and short-range motion. Therefore, the slow but long-range oscillation motion of the chains was investigated, the transverse relaxation (T_{2c}) was measured and the results are tabulated in Table 1.

Most of the crystalline samples listed in Table 1 show a low frequency correlated time τ_l which corresponds to the motions related to T_{2c}; in other words, the τ of interphase is longer than the related time of amorphous chain motions, its long-range motion is constrained. According to Flory's lattice model, its motion is limited by the ordered adjacent crystal lattices. The motion-related time τ_l is similar neither to that of the chains in the crystalline region (where τ_l is extremely large due to its oscillation being confined in its equilibrium position) nor to that of the chains in amorphous region (where τ_l is relatively short due to the highly viscous liquid-like phase). However, from the observed short-range motion-related time τ_s, it is found that the interphase and the amorphous phase have the same value. This special chain motion of the interphase is coincident with Flory's definition of the interphase.

In order to obtain the mass fraction of the interphase and its chemical shift quantitatively, the whole spectrum of the portion shown in Fig. 2 was analyzed. A spectral line with half width of ~130 Hz and chemical shift of 31.3 was determined. It is clearly different from the crystalline region of highly ordered chain arrangement (which has the specific chemical shift tensor of the molecular axes in all directions) and the highly disordered amorphous region (with isotropic characteristics). It shows a certain degree of order in interphase with various chain conformations. Finally, the mass fractions of individual phase were obtained from the corresponding spectral peak area, which can be converted to the interphase thickness (L_i) by the following equation:

$$L_i = 1/2 L_c X_i / X_c$$

where, L_c is the mean thickness of the lamellae which can be obtained by TEM or by the nitrate acid etching/GPC method. The values of L_i are listed in Table 1.

The curves plotted in Fig. 3 show the correlation of $2L_i$ of melt-grown PE and its molecular weight ($\overline{M}_v$). From the curves, it can be seen that for $\overline{M}_v < 3 \times 10^4$ only the interphase appears in between the lamellae; as $\overline{M}_v$ increases, the amorphous emerges at $\overline{M}_v = 1.1 \times 10^5$, but the thickness of the interphase remains at 1.7 nm consistently. Flory [4] predicted that as the thickness of the non-crystalline phase is greater than 4.0 nm, the amorphous region emerge, which is consistent with the occurrence of the amorphous phase shown in Fig. 3

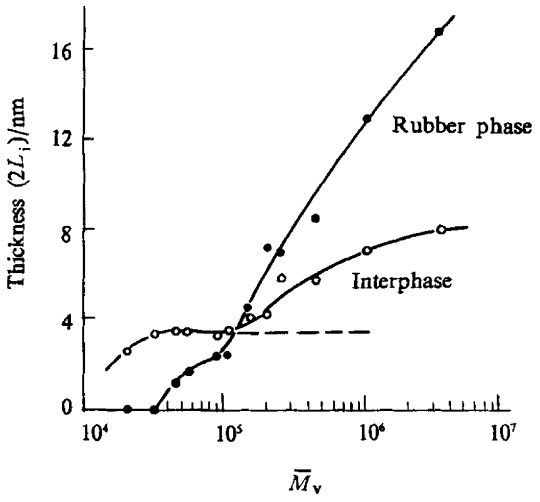

Fig. 3. Relationship curve between interfacial and amorphous rubber layer thickness in melting crystallization.

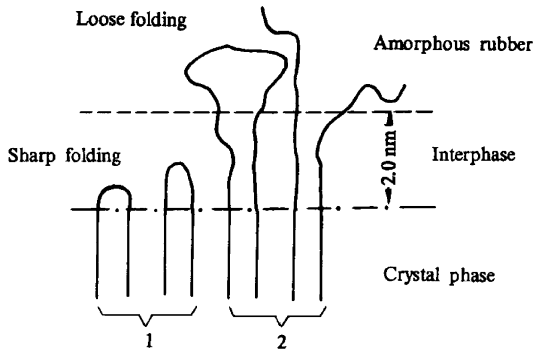

Fig. 4. Schematic view of molecular chain folding model in crystalline–non-crystalline interphase.

while $2L_i$ is greater than 3.4 nm. As $\overline{M}_v$ increases further ($>1.1 \times 10^5$), both the interphase and amorphous phase increase clearly. Therefore, in order to elucidate this observation, the chain lengths of the polymers crystallized under various conditions should be considered; they should follow the folding mechanism as shown in Fig. 4.

For the lower molecular weight PE, it would match the sharp folding as shown in Fig. 4; as the molecular weight increases to a certain value, the main mode becomes loose folding. For those solution-grown crystals (in dilute or quasi-dilute solution), although the molecular weight reaches 10^6, the interphase thickness remains the same as that predicted by Flory ($\sim$2.0 nm). Thus, the samples crystallized under this condition almost all exhibits sharp folding. Besides, from the results shown in Table 1, samples crystallized under various conditions, such as high pressure, drawing orientation, and annealing, have the interphase thickness many times greater than 2.0 nm, which proves that the originate forces of forming the folded-chain lamellae are not merely the Van der Waals force.

4. Conclusion

Flory's model is based on the chains parallel to the surfaces of the lattice, assuming that the molecular chains have lattice length in unit of 3.5-mer of CH_2 groups (about 0.45 nm) and are at equidistance to the lattice face. Thus predicting that there will be 4–5 layers of such interphase lattices which could not form an amorphous region due to the influence of the crystal lattice region. In this experiment, those observed thickness greater than 1.7 nm were obtained from the solution-grown and the melt-grown samples, implying that a longer lattice length (>0.45 nm) as a result of the different crystallization conditions is required to explain the increased thickness of the interphase. Therefore, an assumption from which the thickness of the interphase is deduced should be made for the crystallization conditions to reflect the realistic situation.

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