PFG-NMR measurement of self-diffusion coefficients of long-chain α-olefins and their mixtures in semi-crystalline polyethylene

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ABSTRACT: The self-diffusion coefficients of C6–C16 long-chain α-olefins and their mixtures in semi-crystalline polyethylene were measured through the pulsed field gradient nuclear magnetic resonance (PFG-NMR). The effects of chain length, polyethylene (PE) type, and co-monomer type in PE on the diffusion coefficients were investigated. Moreover, the influence of halohydrocarbon, cyclo-alkanes, and arene solvents on the diffusion coefficients of C12 α-olefin in PE was characterized. The results have demonstrated that the diffusion coefficient of the single-component α-olefin in PE decreases exponentially with the increase of the carbon number of α-olefin, and the crystallinity and crystal morphology of PE play a more important role than the co-monomer type in determining the diffusion coefficients of α-olefins. In addition, the apparent diffusion coefficients were used to represent the diffusion behaviors of the α-olefin mixtures in PE. Owing to the presence of other hydrocarbon solvents, namely trichloromethane, cyclohexane, and benzene, the diffusion coefficients of C12 long-chain α-olefin in PE are significantly enhanced, and such promoting effect of the hydrocarbon solvents in polyolefin elastomer (POE) is much stronger than those in high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE). © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44143.

INTRODUCTION

The characterization of diffusion behaviors of the long-chain α-olefins and their mixtures in polyethylene is of great importance for the development of ethylene polymerization technologies and degassing processes. For instance, better performance of linear low-density polyethylene (LLDPE) can be achieved by introducing long-chain α-olefins into the main polymer chains as copolymers. The physical properties of LLDPE are strongly dependent on the diffusion characteristics of the long-chain α-olefins and their mixtures. More importantly, the long-chain α-olefin copolymers absorbed in PE particles play an important role in determining the performance of the degassing process, in which the unreacted hydrocarbons are purged from the PE products to comply with environmental regulations and ensure the safety of the products.[1,2] Therefore, it is essential to measure the diffusion coefficient data of the long-chain α-olefins and

their mixtures in PE for the monitoring and operation optimization of the degassing process.

Although the diffusion behaviors of single-component solvents in polymer have been extensively studied, limited attention has been paid to the measurement of diffusion coefficients of solvent mixtures (or named the multicomponent solvents). Until now, most work concerning the multicomponent diffusion focused on the solvents, such as gas, benzene, and cyclohexene. For example, Lewis et al.[1] determined the diffusion coefficients and solubility of oxygen, nitrogen, and carbon dioxide in polyethylene terephthalate membrane by using a mass spectrometer, and found that the diffusion coefficient of oxygen increased while its solubility decreased when nitrogen was added into the system. Hong et al.[3] measured the diffusion coefficients of methyl ethyl ketoxime and polyisobutene in polyisobutene through the Fourier Transform Attenuated Total Reflection

Table I. Physical Properties of PE Samples (I)

Name	Sample type	Co-monomer incorporation	Density (g/cm³)	Crystallinity
PE-1	LLDPE	Butene, 4.21 mol %	0.918	0.216
PE-2	LLDPE	Hexene, 2.59 mol %	0.918	0.279
PE-3	LLDPE	Octene, 1.97 mol %	0.918	0.261
PE-4	HDPE	—	—	0.389
PE-5	HDPE	—	—	0.531
PE-6	POE	Octene	—	0.110

Infrared Spectroscopy (FTIR-ATR), concluding that the diffusion coefficient of the solvent with a higher diffusion speed was affected by the concentration of the solvent with a lower diffusion speed. Dobbyn et al.[4] characterized the diffusion behaviors of haloalkanes such as trichloroethane, tribromethane, and bromodichloromethane in polypropylene membrane through the FTIR-ATR, with the Fick's diffusion model adopted for the fitness of the diffusion coefficients of haloalkanes and their mixtures. Davis et al.[5] employed the capillary column inverse gas chromatography to characterize the diffusion behaviors of a solvent–solvent–polymer ternary system. Grinsted et al.[6] measured the diffusion coefficients of acetone and methanol in polycarbonate by using the proton NMR imaging technique. However, the diffusion characteristics of long chain α-olefins and their mixtures in polymer are still far from understanding.

PFG-NMR is an effective tool to detect the molecular mobility in the intermediate regime and can yield self-diffusion coefficients from a macroscopic scale to a lower limit of 10^{-14} m²/s.[7] Since developed by Stejskal and Tanner[8] in 1965, this method has been widely employed for the measurement of self-diffusion coefficients of solvents and their mixtures,[9–13] owing to its non-destructivity, quick response, and easy operation. For the characterization of the diffusion behaviors of alkanes in polyethylene, Fleischer[10] determined the self-diffusion coefficients of butane, pentane, n-hexane, and cyclohexane through PFG-NMR, concluding that the self-diffusion coefficients were larger under the equilibrium state than those under the non-equilibrium state. The self-diffusion coefficients of hexane in semi-crystalline LLDPE and HDPE were measured by Harding et al.[11] through PFG-¹H NMR. It was shown that the swell effect of hexane was less significant while the self-diffusion coefficient of hexane was larger in semi-crystalline LLDPE than that in HDPE. In this study, the diffusion coefficients of C6–C16 long-chain α-olefins and their mixtures in semi-crystalline polyethylene were measured through PFG-NMR, and the effects of solvent type and concentration, crystallinity and crystal morphology of PE, and co-monomer type on the diffusion coefficients were studied.

EXPERIMENTAL

Materials
In the experiments, 1-hexene, 1-octene, 1-dodecene, 1-hexadecylene, chloroform-d, benzene-d6 and cyclohexane-d12 were used as the long-chain α-olefins under test. All samples were purchased by Sigma-Aldrich, Taufkirchen, Germany, and were used without further purification. The PE samples supplied by a

branch company of SINOPEC were nascent particles obtained from the polymerization reactor. The physical properties of the PE samples are listed in Tables I and II. The density was measured using the standard method in GB/T 1033-86, and the crystallinity (ω_c) of PE was determined through the standard DSC scans on a TA-DSC (Perkin-Elmer 7, USA) under nitrogen atmosphere. The samples were cooled from the melt 180 °C to 25 °C at 10 °C/min, holding there for 5 min, and then heated to 180 °C at 10 °C/min. The crystallinity of PE was calculated from the following equation[14,15]:

$$\omega_c = \frac{\Delta H_m}{\Delta H_{m,100\%}}, \ \Delta H_{m,100\%} = 290 \ \text{J/g} \quad (1)$$

where ΔH_m is the melting enthalpy of the PE sample under test and $\Delta H_{m,100\%}$ the melting enthalpy of PE with the crystallinity of 1. Although this calculated crystallinity may not be exactly the same as the actual crystallinity of PE samples immersed in the solvent in the following article, the variation tendency of crystallinity with the PE type is the same for both the PE samples under the DSC condition and immersed in the solvent. The co-monomer incorporation was determined through the high-temperature ¹³C NMR spectra with deuterated o-dichlorobenzene (o-DCB) as solvent. The polymer solutions (10 wt %) were scanned at 125 °C using a Bruker AC 400 pulsed NMR spectrometer with a spectral width of 8000 Hz, pulse delay time of 8 s, acquisition time of 1.3 s, and pulse angle of 90°. At least 5000 scans were required for a good signal to noise ratio. The ASTM D5017-96 method was employed for the carbon assignments and composition calculation.[16] In addition, the high-temperature gel permeation chromatography (PL-GPC 220 system) was used to determine the molecular weights (M_n and M_w) and polydispersity index (PDI) of the LLDPE samples. The measurement was conducted at 150 °C, using 1, 2, 4-trichlorobenzene as the solvent flowing at a rate of 1.0 mL/min. Universal calibration was performed on the monodisperse polystyrene (PS) standards. The Mark-Houwink constants of PS are $K = 5.91 \times 10^{-4}$ and $a = 0.69$, and those of PE are $K = 1.21 \times$

Table II. Physical Properties of PE Samples (II)

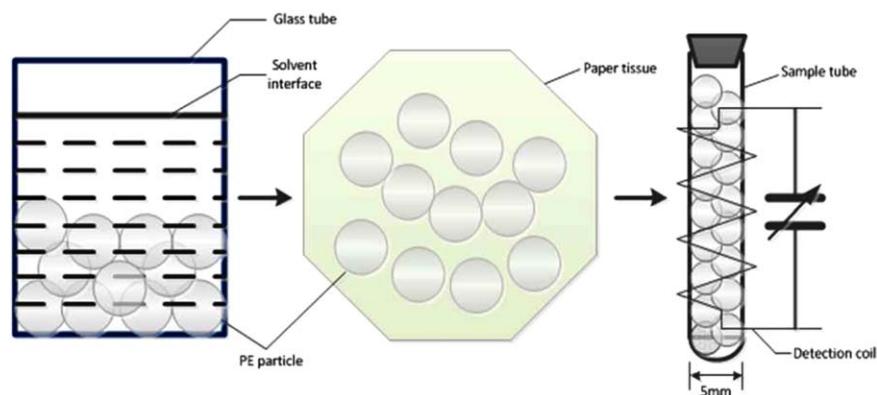| Name	M_w (g/mol)	M_n (g/mol)	PDI
PE-1	86,465	16,832	5.14
PE-2	85,843	16,735	5.13
PE-3	81,419	16,292	5.00

Figure 1. Schematic diagram of the NMR measurement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

10^{-4} and $a = 0.707$. The measurement results are listed in Table II.

Experimental Setup

The experiments were conducted in a Bruker Avance III NMR spectrometer with a proton resonance frequency of 300 MHz. The experimental temperature was kept 300 ± 0.1 K by a temperature-control system equipped in the spectrometer. Prior to the measurement, the PE particles were firstly treated at the room temperature for at least 24 h and then cut into pieces as samples with the equivalent diameter of about 1.5 mm. These samples were degassed in a vacuum environment at 373 K for over 24 h to eliminate the existing unreacted hydrocarbons that might interfere with the measurement results. After that the samples were immersed in the solvent or solvent mixture under test at $0\,°C$ in a fridge for more than 72 h to achieve saturated status. The surface of the samples was then wiped clean to eliminate the residual liquid. In the measurement, the PE samples were transferred into a sealed NMR tube as soon as possible to reduce solvent evaporation, as shown in Figure 1. After the instrument being debugged, the NMR tube was placed on the NMR platform to measure the self-diffusion coefficients by using the pulsed gradient stimulated echo sequence.

MEASUREMENT PRINCIPLE OF PFG-NMR

The measurement of self-diffusion coefficients of molecules in polymer through PFG-NMR is based on the echo amplitude attenuation of an atom between two pulse time intervals in a magnetic field. As the spin–lattice relaxation time T_1 (also regarded as the longitudinal relaxation time) is remarkably longer than the spin–spin relaxation time T_2 (also named the transverse relaxation time), the stimulated spin echo pulse sequence method is employed. Figure 2 shows the pulse sequence adopted in this article, which contains three 90° pulses. τ_1 and τ_2 represent the time interval between the first and the second pulse as well as that between the second and the third pulse, respectively. δ is the duration of a pulsed gradient field and Δ is the initial time interval between two pulsed gradient fields.

In the pulsed gradient field in the axial direction (Z direction), the scattered angle of the signal is expressed as[17,18]

$$\phi(z) = \gamma g z \Delta \qquad (2)$$

where γ is the gyromagnetic ratio of the nucleus, g the gradient field intensity, z the position in Z direction, Δ the initial time interval. After Δ, the molecule position and scattered angle are changed due to the molecule diffusion. Therefore, the signal cannot be reunited after the second pulsed gradient field exerted. With the increase of the gradient field intensity, the detected position change of the molecule in the Z direction is reduced, leading to less signal reunited. The attenuation curve of the molecular signal with the increase of gradient field intensity is then described by[17,18]

$$\ln \frac{I(x)}{I(0)} = -\gamma^2 D \left[\frac{2 g_0^2 \tau^3}{3} + g \cdot g_0 \delta \left(\frac{3}{2} \tau^2 - \frac{\delta^2}{6} \right) + g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right] - \frac{2\tau}{T_2}$$

$$(3)$$

where $I(x)$ and $I(0)$ are the stimulated echo intensities with and without the gradient field, respectively, D the self-diffusion coefficient, γ the gyromagnetic ratio of the nucleus, g the gradient field intensity, g_0 the background gradient intensity, δ the duration of the gradient field, Δ the initial time interval and also referring to an approximation of the "diffusion time", 2τ the spin echo time, and T_2 the longitudinal relaxation time.

When $g_0^2 \tau^3 \ll g^2 \delta^2 \Delta$, eq. (3) is simplified as[17,18]

$$\frac{I(x)}{I(0)} = \exp \left(-\gamma^2 D g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) - \frac{2\tau}{T_2} \right)$$

$$\approx \exp \left(-\gamma^2 D g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right) \qquad (4)$$

The signal attenuation in the solid is dominated by spin diffusion which is in the order of 10^{-15} m²/s or even smaller. However, the lower limit of the diffusion coefficients measured by
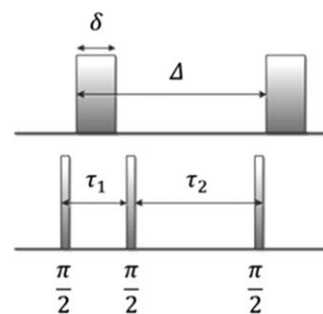

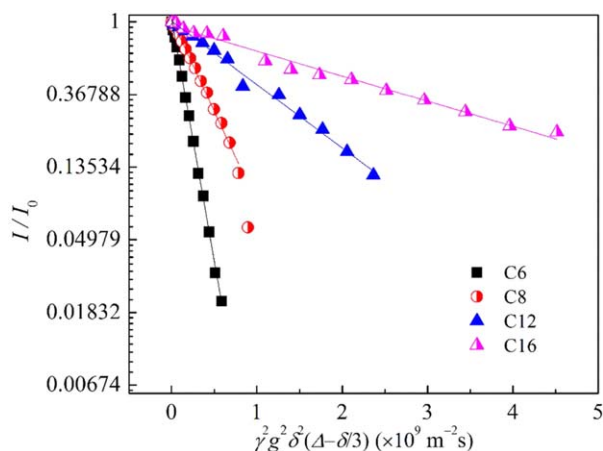Figure 2. Stimulated spin echo pulse sequence.

Figure 3. Decay curves of the NMR signal intensity of different long-chain α-olefins in the bulk solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Decay curves of the NMR signal intensity of different long-chain α-olefins in PE-1 sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

NMR is in an order of magnitude of 10^{-14} m^2/s,[19] which means the signal detected by NMR is solely generated by the diffusion of solvent molecules. In combination with eq. (4), the self-diffusion coefficient D of solvent molecules in solid samples is acquired. If the signal induced by different groups overlaps each other, the normalized echo decay can be expressed in a multi-exponential form as

$$I(x) = A_1 \exp(-D_1 x) + A_2 \exp(-D_2 x) + \dots \qquad (5)$$

where A_1, A_2…are the percentages of different components and D_1, D_2…the corresponding diffusion coefficients.

RESULTS AND DISCUSSION

Self-Diffusion Coefficients of Long-Chain α-Olefins in Bulk Solvents

The self-diffusion coefficient of water at 300 ± 0.1 K was firstly determined for the method verification. The average self-diffusion coefficient measured was 1.03×10^{-9} m^2/s, consistent well with the literature data of 1.10×10^{-9} m^2/s.[20] The reliability of the measurement technique employed in this article was thus verified. A series of measurement was then carried out on the bulk solvents of C6, C8, C12, and C16 α-olefins. Figure 3 shows the decay curves of the NMR signal intensity of different long-chain α-olefins in the bulk solvents. Based on eq. (4), the self-diffusion coefficients of C6, C8, C12, and C16 α-olefins were determined, as listed in Table III. With the increase of carbon number, the self-diffusion coefficient significantly decreases, since the motion of olefin molecules is restricted by the increased molecular chain length.

Self-Diffusion Coefficients of Long-Chain α-Olefins in PE

Influence of Chain Length. The decay curves of the NMR signal intensity of different long-chain α-olefins in PE-1 sample are shown in Figure 4. According to eq. (4), the self-diffusion
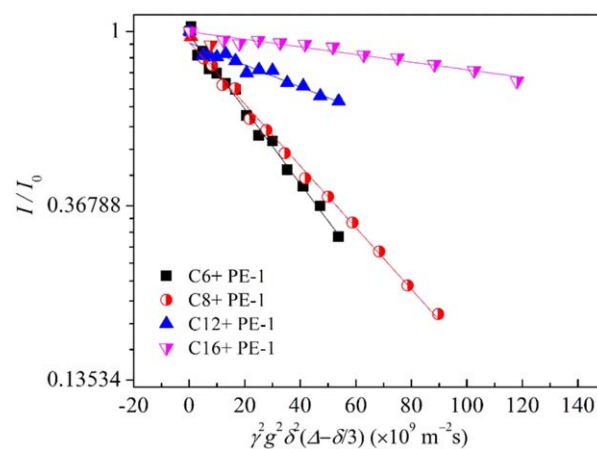
coefficients of C6, C8, C12, and C16 α-olefins were obtained and displayed in Figure 5. It is indicated that the self-diffusion coefficients in PE-1 sample are two orders of magnitude smaller than the corresponding coefficients in the bulk solvents (or regarded as the bulk self-diffusion coefficients), because of the space restriction effects of the PE chains on the motion of α-olefin molecules. In addition, the self-diffusion coefficient is reduced with the increase of chain length, agreeing with the variation tendency in the bulk solvents.

Influence of PE Type. The influence of PE type on the self-diffusion coefficients of C6 and C12 α-olefins is shown in Figure 6, with w_α representing the mass percentage of the amorphous phase. The self-diffusion coefficients of both C6 and C12 α-olefins increase with the decrease of PE crystallinity. On one hand, the diffusion of the α-olefin solvent molecules occurs in the amorphous phase and is inhibited by the existence of crystalline phase.[11] On the other hand, the amorphous phase of PE is swollen by the α-olefin solvents, resulting in larger space for the free movement of solvent molecules. However, such swelling effect is weakened by the crystalline phase, leading to the inhibition of solvent molecular motion.[21] The higher the crystallinity is, the weaker the swelling effect will be. Moreover, the self-diffusion coefficients in HDPE and LLDPE are close and increase linearly with the increase of amorphous-phase mass fraction, while those in POE are much larger. This is because the structures and physical properties of HDPE and LLDPE are similar, indicating similar inhibition effects of the crystalline phase on the solvent molecular motion. Yet POE used in this article is the very low-density (crystallinity) homogeneous ethylene/octene copolymer (the mass fraction of octene over 20–30%), which has a fringed micelle crystal morphology and exhibits a very different deformation behavior as compared to

Table III. Self-Diffusion Coefficients of Long-Chain α-Olefins in Bulk Solvents

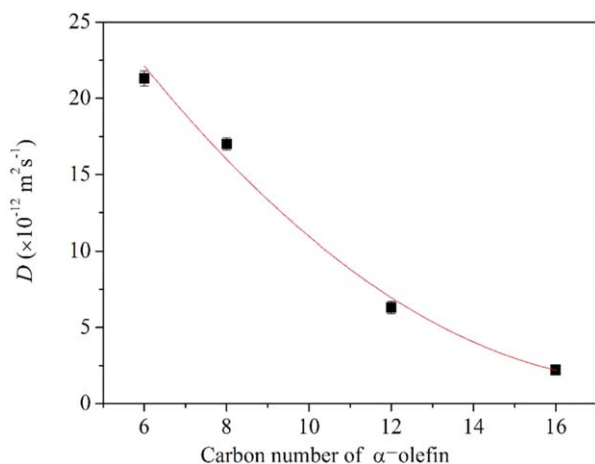| Solvent	1-Hexene (C6)	1-Octene (C8)	1-Dodecene (C12)	1-Hexadecene (C16)
D (10^{-9} m^2/s)	6.80 ± 0.07	2.54 ± 0.05	0.87 ± 0.02	0.35 ± 0.01

Figure 5. Self-diffusion coefficients of long-chain α-olefins in PE-1 sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. Decay curves of the NMR signal intensity of different C6–C12 mixtures in PE-1 sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the higher density copolymers with lamella crystal structures.[22,23] The small fringed micelle crystals dispersed in the soft, amorphous matrix act as tie-points to anchor the amorphous chains during deformation, leading to an elastic recovery upon release of stress.[23] Compared to HDPE and LLDPE, the dramatically enhanced self-diffusion of the C6 and C12 α-olefins in POE is owing to the crystalline structure differences between these polymers. HDPE and LLDPE crystallizes normally into lamellae and lamellar stacks which significantly inhibit the direct "diffusion" of α-olefin molecules through the crystal and crystal stacks. In contrast, POE crystallizes into fringed micelle crystals without the extended lamellae and lamellar stacks, leading to the minimal restriction to the diffusion of α-olefin molecules. In terms of the different LLDPE samples, the self-diffusion coefficient of C12 α-olefin in PE-3 is larger than that in PE-1, probably owing to the lower percentage of chain branches (co-monomer incorporation, as shown in Table I) in PE-3 and the corresponding weaker inhibition effects on the solvent diffusion.
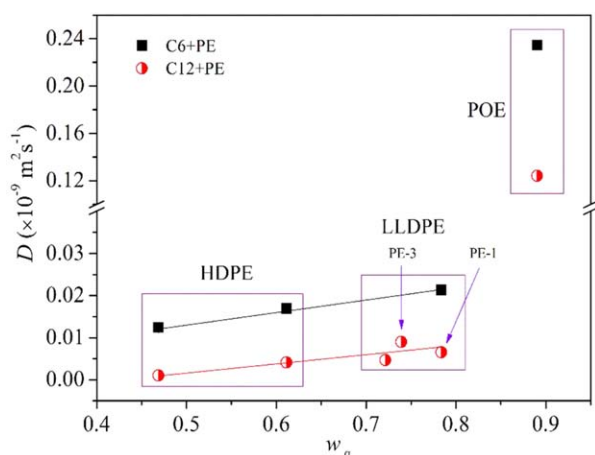
Self-Diffusion Coefficients of Long-Chain α-Olefin Mixtures in PE

Influence of α-Olefin Concentration. The bi-component solvent mixtures adopted in this article were composed of C6 and C12 α-olefins with large difference in self-diffusion coefficients. The mole ratio of the two α-olefins (C6:C12) in three mixtures under test was 1:4, 1:1, and 4:1, respectively. Figure 7 shows the decay curves of the NMR signal intensity of the three mixtures in PE-1 sample. Due to the complete miscibility of the C6 and C12 components and the complete overlap of the signals generated by their characteristic groups, only one self-diffusion coefficient is exhibited for each bi-component solvent sample, even if eq. (5) was used for the curve fitting. Such self-diffusion coefficients are regarded as the apparent diffusion coefficients of the bi-component solvent mixtures, as displayed in Figure 8. Because of the interaction between the two components, the diffusion of the C12 molecules was promoted while that of the C6 molecules was slowed down. A compromised balance state was finally achieved and the resulted apparent diffusion coefficient was between the self-diffusion coefficients of the two components. With the increase of the C6 or C12 α-olefin

Figure 6. Influence of PE type on the self-diffusion coefficients of C6 and C12 α-olefins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
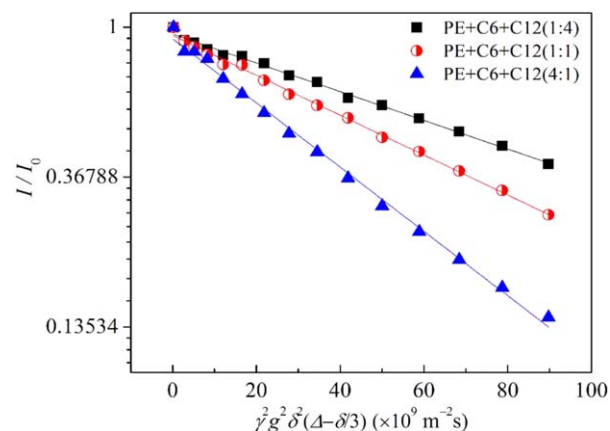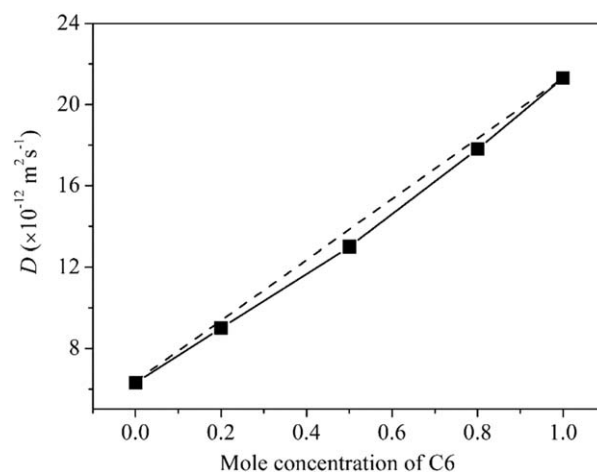

Figure 8. Variation of the apparent diffusion coefficient with the C6 α-olefin concentration.
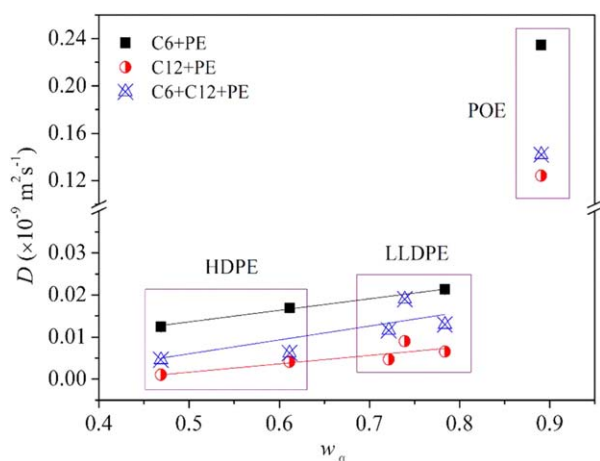
Figure 9. Influence of PE type on the apparent diffusion coefficient of the C6–C12 bi-component mixture. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentration, the apparent diffusion coefficient became closer to the self-diffusion coefficient of the C6 or C12 α-olefin. In addition, the apparent diffusion coefficient was slightly smaller than the weighted average of the self-diffusion coefficients of the two components due to the nonideality of the mixed solvent. A concave variation curve of the apparent diffusion coefficient with the increase of the C6 α-olefin concentration was thus obtained, consistent with the measurement results in literature.[24,25]

Influence of PE Type. The influence of PE type on the apparent diffusion coefficient of the bi-component solvent mixture in PE samples is shown in Figure 9, with w_α representing the mass percentage of the amorphous phase. The mole ratio of the two components (C6:C12) was 1:1. Based on the inhibition effects of the crystalline phase, the apparent diffusion coefficients in the HDPE, LLDPE, and POE samples increase with the decrease of crystallinity, similar to the variation tendencies of the single-component α-olefins in PE samples (Influence of PE Type Section). Since POE crystallizes into fringed micelle crystals without the extended lamellae and lamellar stacks as those in HDPE and LLDPE, the restriction to the diffusion of α-olefin molecules is minimized and the apparent diffusion coefficients in

POE are significantly larger than those in HDPE and LLDPE. In addition, the apparent diffusion coefficients in all the PE samples are between the corresponding self-diffusion coefficients of the C6 and C12 α-olefins.

Influence of PE co-Monomer. The co-monomer type and its corresponding content play an important role in determining the diffusion characteristics of the bi-component solvent mixtures in PE. Table IV gives the apparent diffusion coefficients in three LLDPE samples produced with different co-monomers. Although the crystallinity of PE-3 copolymerized with octene is higher than that of PE-1 copolymerized with butene, the fewer branches in PE-3 give rise to weaker inhibition effects on the diffusion of C12 α-olefin molecules and larger apparent diffusion coefficients in PE-3. Besides, the apparent diffusion coefficients of the C16 + C12 solvent mixture in different LLDPE samples are basically the same, indicating that when the solvent molecular size is large, the diffusion characteristics of the solvent mixture are weakly dependent on the crystallinity of PE due to the limited space for the solvent molecular motion.

Self-Diffusion Coefficients of C12 α-Olefin in A/B/PE Ternary Systems

In the presence of a second solvent, the diffusion behaviors of α-olefin solvent in PE can be affected. In this section, the self-diffusion coefficients of C12 α-olefin molecules in PE were determined with the coexistence of halohydrocarbon, alkane, and arene as the second solvents. Such solvent mixtures are regarded as the A/B/PE ternary systems, in which A represents the α-olefin solvent and B the second solvent.

Influence of the Type and Concentration of Solvent B. Table V shows the measured self-diffusion coefficients of C12 α-olefin (A) in different A/B and A/B/PE systems. Trichloromethane (CDCl$_3$), cyclohexane (C$_6$D$_{12}$), and benzene (C$_6$D$_6$) were adopted as the Solvent B, and PE-3 was used as a representative of the PE samples. It is shown that the self-diffusion coefficients of C12 α-olefin in both the A/B and A/B/PE systems are larger than those in the absence of the Solvent B, and the influence level of Solvent B follows the order of C$_6$D$_6$ > CDCl$_3$ > C$_6$D$_{12}$. Based on the estimated average molecular size of C12 α-olefin of 2.3 nm using the Materials Studio software,[26] it is indicated that the diffusion of C12 α-olefin is promoted when the

Table IV. Apparent Diffusion Coefficients of Different Bi-Component Solvent Mixtures in LLDPE Samples

PE sample	Co-monomer	Density (g/cm^3)	Crystallinity	Components	Diffusion Coefficient (10^{-12} m^2/s)
				C6+C12 (1:1)	13.0 ± 0.2
PE-1	Butene	0.918	0.216	C8+C12 (1:1)	10.3 ± 0.2
				C16+C12 (1:1)	3.6 ± 0.2
				C6+C12 (1:1)	11.6 ± 0.2
PE-2	Hexene	0.918	0.279	C8+C12 (1:1)	8.0 ± 0.3
				C16+C12 (1:1)	3.7 ± 0.2
				C6+C12 (1:1)	19.0 ± 0.4
PE-3	Octene	0.918	0.261	C8+C12 (1:1)	13.6 ± 0.2
				C16+C12 (1:1)	3.8 ± 0.1

Table V. Self-Diffusion Coefficients of C12 α-Olefin (A) in Different A/B and A/B/PE Systems

Solvent B	$CDCl_3$	C_6D_6	C_6D_{12}	None
Molecule size (nm)	0.65	0.68	0.69	—
Polarity	polar	nonpolar	nonpolar	—
Self-diffusion coefficient in the A/B system (10^{-9} m^2/s)	0.965	1.021	0.894	0.87
Self-diffusion coefficient in the A/B/PE system (10^{-9} m^2/s)	0.0089 (A/B=4:1) 0.0125 (A/B=1:1) 0.0216 (A/B=1:4)	0.0132 (A/B=1:1)	0.0118 (A/B=1:1)	0.0063 (A/B=1:1)

molecular size of Solvent B is smaller than that of C12 α-olefin. In addition, although the molecular size of C_6D_6 was larger than that of $CDCl_3$, the polarity of C_6D_6 was closer to that of the C12 α-olefin, leading to stronger influence of C_6D_6 on the diffusion behaviors of C12 α-olefin molecules. Therefore, both the molecular size and polarity of the second solvent play an important role in determining the self-diffusion coefficients of C12 α-olefin in the binary and ternary systems. Moreover, the influence of $CDCl_3$ concentration on the self-diffusion coefficient of C12 α-olefin in the A/B/PE system is exhibited in Table V, with the mole ratio of A and B is 4:1, 1:1, and 1:4, respectively. It can be concluded that when the molecular size of Solvent B is smaller than that of C12 α-olefin, the promoting effect of Solvent B is enhanced with the increase of the concentration of Solvent B.

Influence of PE Type. The influence of PE type on the self-diffusion coefficient of C12 α-olefin in the A/B/PE system is shown in Figure 10, which is also compared to that without the Solvent B of $CDCl_3$. It is found that the promoting effect of Solvent B on the self-diffusion coefficients of C12 α-olefin is significantly enhanced in POE, owing to the existence of fringed micelle crystals without the lamellae and lamellar stacks in POE, as stated above.
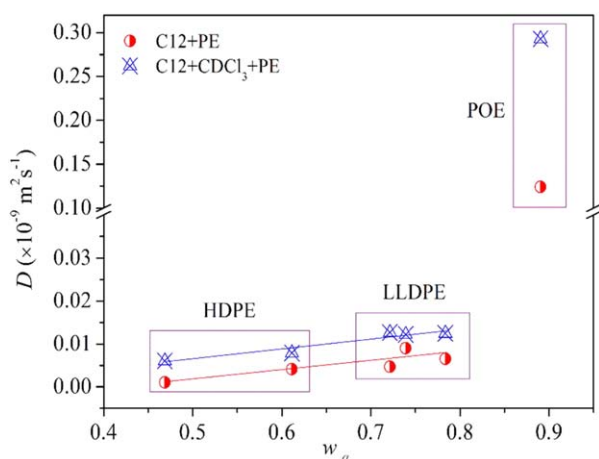
CONCLUSIONS

In this article, the diffusion behaviors of long-chain α-olefins and their mixtures in the semi-crystalline polyethylene were characterized by the PFG-NMR. The self-diffusion coefficients of long-chain α-olefin in PE decreased with the increase of chain length, and the self-diffusion coefficients in POE were much larger than those in HDPE and LLDPE. For the diffusion of a bi-component solvent mixture, only one apparent diffusion coefficient was obtained due to the complete miscibility of the C6 and C12 components and the complete overlap of the signals generated by their characteristic groups. The increase of the concertation of C6 α-olefin and the decrease of PE crystallinity increased the apparent diffusion coefficient. In addition, both the polarity and molecular size of the second solvent played an important role in determining the self-diffusion coefficients of C12 α-olefin in the binary and ternary systems. When the molecular size of the second solvent was smaller than that of the C12 α-olefin, the diffusion of the C12 α-olefin molecules was promoted. The closer the polarity of the second solvent and C12 α-olefin was, the stronger the promoting effect of the second solvent would be. Moreover, the promoting effect of the second solvent on the self-diffusion coefficient of C12 α-olefin was significantly enhanced in POE, owing to the existence of fringed micelle crystals without the lamellae and lamellar stacks in POE.

Figure 10. Influence of PE type on the self-diffusion coefficient of C12 α-olefin in the A/B/PE system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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