NOTE

Effect of the blend ratio of cyclic and linear polyethylene blends on isothermal crystallization in the quiescent state

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Abstract

The role of entanglements that form between cyclic and linear polymers in crystallization is of particular interest, but it is not fully understood. We investigated the crystallization behaviors of blends of cyclic polyethylene (C-PE) and linear polyethylene (L-PE) in a quiescent state to elucidate the role of this novel entanglement in crystallization. The samples were prepared by mixing the prepared C-PE and L-PE specimens at L-PE weight fraction ($\Phi_{L\text{-}PE}$) values of 0–100 wt%, with the weight average molecular weights of C-PE and L-PE being 175×10^3 and 154×10^3, respectively. The isothermal crystallization behaviors were analyzed through polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The morphology observed through POM was similar to that of $\Phi_{L\text{-}PE}$. From the time evolution of the heat flow measured via DSC, we obtained the half-crystallization time ($t_{1/2}$) values as functions of $\Phi_{L\text{-}PE}$ at different degrees of supercooling (ΔT). The $1/t_{1/2}$ values of the C-PE and L-PE homopolymers were approximately the same at $\Delta T = 25.5$ and 26.5 K. At a larger ΔT value, the $1/t_{1/2}$ value of C-PE was significantly larger than that of L-PE. In contrast, $1/t_{1/2}$ reached a minimum value at $\Phi_{L\text{-}PE} = 30$–40 wt%, irrespective of ΔT. As the entanglement density increased with increasing $\Phi_{L\text{-}PE}$, the crystallization rate was expected to decrease monotonically. By considering the experimental relationship between $1/t_{1/2}$ and $\Phi_{L\text{-}PE}$, we speculated that the suppression of crystallization in the blended system was caused by a novel entanglement formed by the penetration of the L-PE chain into the C-PE chain.

Introduction

The crystallization mechanisms of linear polymers in quiescent states have been studied for several decades. Numerous studies have been devoted to clarifying the effect of molecular weight on crystallization, such as studies on the crystallization characteristics of polyolefins and polyesters from isotropic melts; these investigations are conducted because it is known that the topological nature of chain molecules is explicitly dependent on their molecular weight. For example, Hoffman et al. [1] conducted a series of studies on the crystal growth of polyethylene. Okui et al. [2] reported the primary nucleation and crystal growth attributes of several polymers in the melt. The role of chain entanglements in polymer crystallization is one of the most challenging problems of this process. Psarski et al. [3] and Hikosaka et al. [4] independently reported that entanglements suppress the nucleation and growth of polymers. However, it remains unclear which type of entanglement (knots, twists, or threads) most strongly affects polymer crystallization.

Cyclic polymers have long been of interest because, unlike linear polymers, they have the unique topological feature of no chain ends. Many studies on the viscoelastic properties of cyclic polymers have been conducted. These results indicate that cyclic polymers have fewer entanglements than linear polymers because of their lack of knot entanglements [5]. In the last few decades, the number of studies on the crystallization of cyclic polymers has markedly increased [6–10]. The reported results are controversial, and discussions are still ongoing [10]. Therefore, with this study, we do not intend to reach a universal conclusion about whether cyclic or linear polymers crystallize faster than the other.

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Recently, López et al. [11] and Ruiz et al. [12] analyzed the crystallization characteristics of blends of cyclic and linear polyesters. In these cases, it is expected that the novel entanglements formed between the cyclic and linear polymers, known as the threading effect [11, 12], are important. Scholars have noted several times that the influences of linear contaminants are apparent in the rheological behaviors of tested specimens. For example, Kapnistos et al. found that the entanglements formed by blending cyclic and linear polystyrene are more difficult to disentangle than those formed with cyclic polystyrene through stress relaxation only [13].

In this work, we investigate the crystallization behaviors of blended cyclic polyethylene (C-PE) and linear polyethylene (L-PE) samples in a quiescent state. The M_w values of C-PE and L-PE are fixed for all specimens, and the blend ratios of C-PE and L-PE are changed. The half-crystallization time ($t_{1/2}$) is measured for a fixed degree of supercooling (ΔT), not for a fixed crystallization temperature (T_c). The effects of the entanglement species formed by C-PE and L-PE and their blends on crystallization are discussed.

Experimental procedures

Sample preparation

C-PE and L-PE were prepared using previously reported procedures [14]. Cyclic and linear polyoctenamers, which are PE precursors, were synthesized by the ring-opening metathesis polymerization of *cis*-cyclooctene after catalysis by a cyclic Ru-alkylidene complex and a second-generation Grubbs catalyst, respectively. Both PE precursors were hydrogenated with *p*-toluenesulfonyl hydrazide and converted to the corresponding PE. The chemical structures of the samples were confirmed through FT-IR spectroscopy (JASCO FT/IR-410 spectrometer) and ^{1}H- and ^{13}C-NMR spectroscopy (JEOL AL300 SC-NMR). The weight average molecular weights, M_w, of C-PE and L-PE were determined by measuring the intrinsic viscosities [η] of the PE precursors in tetrahydrofuran at 30 °C [14]. The M_w values of the C-PE and L-PE precursors were converted to those of C-PE and L-PE, respectively, by assuming 100% hydrogenation. The M_w values of C-PE and L-PE were 175×10^3 and 154×10^3 g/mol, respectively. The equilibrium melting temperatures (T_m^0) of C-PE and L-PE [15, 16] were calculated by assuming that the T_m^0 of C-PE was equal to that of the perfect extended chain crystals of an L-PE specimen with half the M_w of the C-PE specimen. The T_m^0 values of C-PE and L-PE were 140.9 and 146.1 °C, respectively. For the T_m^0 of blended samples (T_m^0(C/L)), we assumed an additive property

given by the following equation:

$$T_m^0(C/L) = \left(1 - \frac{\phi_{L\text{-PE}}}{100}\right) \times T_m^0(C\text{-PE}) + \frac{\phi_{L\text{-PE}}}{100} \times T_m^0(L\text{-PE}) \tag{1}$$

where T_m^0(C-PE) and T_m^0(L-PE) are the T_m^0 values of the C-PE and L-PE homopolymers, respectively. Since the blend of C-PE and L-PE could be regarded as a perfectly miscible system, this treatment was accepted as a first-order approximation.

A blend of C-PE and L-PE was prepared as follows: C-PE and L-PE homopolymers were mixed with hot *o*-xylene. The solution was poured into excess methanol, and the precipitate was recovered. The powder blended samples were dried in vacuo. The weight fraction of L-PE ($\Phi_{L\text{-PE}}$) in the blended samples was varied from 0 to 100 wt%.

Instruments and measurements

The isothermal crystallization behavior in the quiescent state was observed through polarizing optical microscopy (POM; Olympus, BX-53) using a hot stage (Linkam 10002L) and differential scanning calorimetry (DSC; PerkinElmer, DSC 8000) in a nitrogen stream (20 mL/min) to avoid sample degradation. The samples were sandwiched between two cover glasses for POM analysis and placed in an Al pan for DSC analysis. Each sample was heated at a rate of 30 °C/min and annealed at a temperature above T_m^0 (melt annealing temperature $T_{max} = 160$ °C) for 1 min to erase the previous thermal history. The samples were then cooled to T_c at a rate of 30 °C/min. The range of ΔT was 25.5–28.5 K. The isothermal crystallization behavior was recorded through POM using a video camera (Victor KY-F1030). During isothermal crystallization, we measured the heat flow as a function of crystallization time t using DSC. The experimental conditions of isothermal crystallization are summarized in Table 1.

Table 1 T_m^0, T_c, and ΔT values used in this study

$\Phi_{L\text{-PE}}$/wt%	T_m^0/°C	T_c/°C			
0	140.9	115.5	114.5	113.5	112.5
10	141.4	116.0	115.0	114.0	113.0
30	142.5	117.0	116.0	115.0	114.0
50	143.5	118.0	117.0	116.0	115.0
70	144.5	119.0	118.0	117.0	116.0
90	145.6	120.0	119.0	118.0	117.0
100	146.1	120.5	119.5	118.5	117.5
	ΔT/K	25.5 ± 0.1	26.5 ± 0.1	27.5 ± 0.1	28.5 ± 0.1

Kinetic analysis with the Avrami equation

In this study, the isothermal crystallization kinetics of the C-PE and L-PE blends were analyzed using the classical Avrami equation [17, 18]. The Avrami equation could be expressed as follows:

$$1 - X_t = \exp(-kt^n) \tag{2}$$

where X_t is the relative degree of crystallinity at time t, k is the overall crystallization rate constant, and n is the Avrami index. X_t could be defined as follows:

$$X_t = \frac{\Delta H_t}{\Delta H_\infty} \tag{3}$$

where ΔH_t is the heat generated at t and ΔH_∞ is the total heat generated until the end of crystallization. Equation (2) could be transformed into a double logarithmic form as follows:

$$\log[-\ln(1 - X_t)] = n \log t + \log k \tag{4}$$

The Avrami index n could be determined from the slope of the $\log[-\ln(1 - X_t)]$ vs. $\log t$ curve. Fitting between experimental data and Eq. (4) was performed with the data under the condition of $X_t < 0.2$, as recommended by Lorenzo et al. [18]. The fitting parameters are summarized in Supplementary Table S1. The Avrami index n is related to the nucleation and geometry types of the growing crystal, and its value usually ranges from 0.5 to 4 [17]. By substituting $X_t = 0.5$ into Eq. (4), we could obtain $t_{1/2}$; that is, we could obtain the time necessary for the completion of 50% crystallization as follows:

$$t_{1/2} = (\ln2/k)^{1/n} \tag{5}$$

In this study, we calculated the $t_{1/2}$ values using the n and k values determined from the Avrami plot based on Eq. (4). Notably, the half-crystallization time included the contributions of both primary nucleation and crystal growth. In this study, we did not intend to prove the validity of the Avrami analysis, and we only used it for the quantitative estimation of $t_{1/2}$. For reference, the $t_{1/2}$ values obtained from the curve of the relative degree of crystallinity ($t_{1/2 \, exp}$) and calculated by Eq. (5) using k and n values determined from the Avrami plot ($t_{1/2 \, fit}$) are summarized in Supplementary Table S2.

## Results and discussion

Morphologies of the blends of C-PE and L-PE observed by POM

Figure 1 shows typical examples of POM images of the crystals formed in the blends of C-PE and L-PE at (a) $\Phi_{L-PE} = 0$ wt%, (b) $\Phi_{L-PE} = 50$ wt%, and (c) $\Phi_{L-PE} = 100$ wt%. ΔT and t are fixed at 25.5 K and 210 s, respectively. This crystallization period observed by POM corresponds to the early stages of crystallization, which is mainly the nucleation stage. Nucleation at $\Phi_{L-PE} = 0$ wt%, that is, the C-PE homopolymer, occurs with the highest density, although each nucleus remains small. The nucleation density at $\Phi_{L-PE} = 100$ wt%, that is, the L-PE homopolymer, is slightly more diluted than that of the C-PE homopolymer; however, each nucleus grows to a relatively large size. Eventually, the nucleation at $\Phi_{L-PE} = 50$ wt% becomes the slowest among the samples. The overall crystallization rate includes the contributions of both the primary nucleation rate and the crystal growth rate. Because the M_w values of C-PE and L-PE are different, it is difficult to conclude which homopolymer has a faster crystallization rate. The morphology of the formed crystal does not seem to be significantly different according to the blend ratio, as reported for the cyclic and linear blends of poly(ε-caprolactone) [11] and poly(L-lactide) [12].

Crystallization kinetics of the blends of C-PE and L-PE

Figure 2a shows a typical example of the time evolution of heat flow for the blends of C-PE and L-PE at $\Delta T = 27.5$ K. All samples show uniform exothermic peaks, although the half-widths of the peaks differ depending on the blend ratio. The peak positions of the C-PE and L-PE homopolymers,

Fig. 1 Typical examples of POM images of the formed crystals of the blends of C-PE and L-PE at **a** $\Phi_{L-PE} = 0$ wt%, **b** $\Phi_{L-PE} = 50$ wt%, and **c** $\Phi_{L-PE} = 100$ wt%. The ΔT and t values were fixed at 25.5 K and 210 s, respectively. The scale bar represents 50 μm

(a) $\Phi_{L-PE} = 0$ wt%

(b) $\Phi_{L-PE} = 50$ wt%

(c) $\Phi_{L-PE} = 100$ wt%
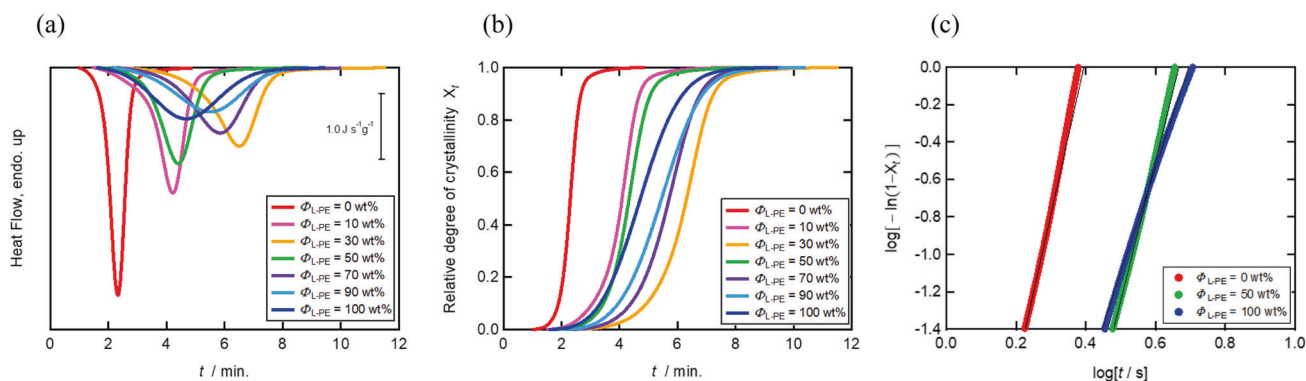
(a)

(b)

(c)
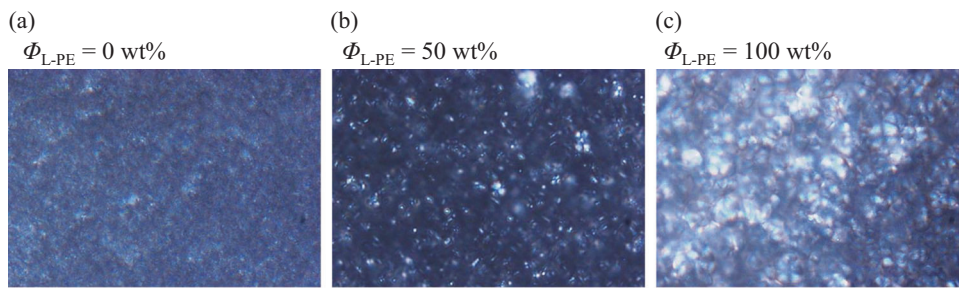
Fig. 2 Typical examples of the time evolution of **a** heat flows of the blends of C-PE and L-PE at $\Delta T = 27.5$ K and **b** relative degrees of crystallinity X_t of the blends of C-PE and L-PE at $\Delta T = 27.5$ K.

c Typical examples of the Avrami plots of the blends of C-PE and L-PE when $\Phi_{\text{L-PE}} = 0$, 50, and 100 wt% at $\Delta T = 27.5$ K
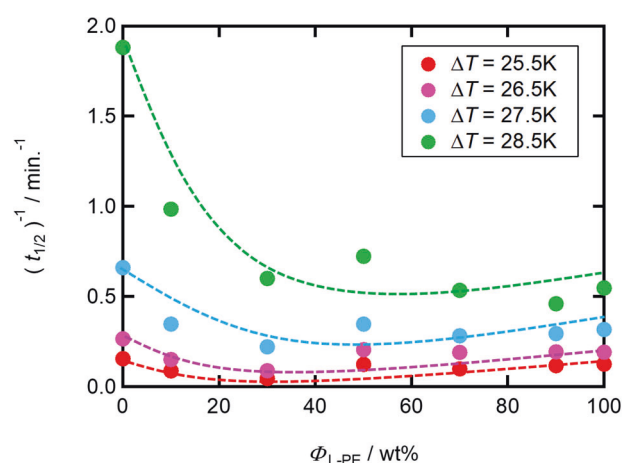

Fig. 3 Plots of $1/t_{1/2}$ against $\Phi_{\text{L-PE}}$ for different ΔT values

that is, $\Phi_{\text{L-PE}} = 0$ and 100 wt%, are significantly different. The peak position for $\Phi_{\text{L-PE}} = 30$ wt% shifts to the slowest crystallization time. According to Eq. (3), the time evolution of the heat flow is converted to that of the relative degree of crystallinity. Figure 2b shows a typical example of the time evolution of the relative degrees of crystallinity X_t of the blends of C-PE and L-PE at $\Delta T = 27.5$ K. All samples show single sigmoidal curves irrespective of $\Phi_{\text{L-PE}}$. By comparing the data for $\Phi_{\text{L-PE}} = 0$ and 100 wt%, we find that the completion of crystallization for the former sample is faster than that for the latter sample. The onset and completion of crystallization at $\Phi_{\text{L-PE}} = 30$ wt% are the slowest among all samples. Figure 2c shows typical examples of the Avrami plots for the blends of C-PE and L-PE when $\Phi_{\text{L-PE}} = 0$, 50, and 100 wt% at $\Delta T = 27.5$ K. From the initial slope of the Avrami plots, the Avrami index n can be obtained. The experimental points are still in good agreement with the straight line beyond the fitting range ($X_t < 0.2$). The obtained index n ranges from 3.0 to 4.1 and does not show clear ΔT or $\Phi_{\text{L-PE}}$ dependences. Slightly

smaller n values have been reported by Krumme et al. for high-density polyethylene with high and low M_w values [19], and similar n values have been reported by Ergoz et al. for polyethylene with low M_w and low T_c values [20]. As the ΔT values used in this study are relatively large, it is natural to consider that general polyethylene crystallizes via three-dimensional spherulitic growth. In this situation, the Avrami index n is expected to be close to 3 for heterogeneous nucleation and 4 for homogeneous nucleation. The morphology observed in Fig. 1 resembles a two-dimensional distorted shape but not a three-dimensional one. This phenomenon may be caused by the sample prepared by the hydrogenation of polyoctenamers, which have certain imperfect chemical structures with spectroscopically undetectable levels. Figure 3 shows plots of the inverse of the half-crystallization time ($1/t_{1/2}$) against $\Phi_{\text{L-PE}}$ for different ΔT values. The $1/t_{1/2}$ for C-PE is approximately the same as that for L-PE at $\Delta T = 25.5$ and 26.5 K. At a larger ΔT, the former is significantly larger than the latter. As mentioned before, $t_{1/2}$ involves contributions from both primary nucleation and crystal growth. It is well known that the primary nucleation density easily fluctuates depending on the density of heterogeneity within the system [4]. According to the data obtained at a large ΔT value where the contribution of nucleation is relatively low, C-PE seemingly crystallizes faster than L-PE. Conversely, the $\Phi_{\text{L-PE}}$ dependence of $1/t_{1/2}$ roughly shows a downward convex curve, and a minimum of $1/t_{1/2}$ is observed at approximately $\Phi_{\text{L-PE}} = 30\text{–}40$ wt%, irrespective of ΔT. López et al. [11] and Ruiz et al. [12] reported the plots of the inverse of the half-crystallization ($1/t_{1/2}$) against the weight fraction Φ of the cyclic polymer at a fixed T_c. The scholars have demonstrated a complicated dependence of $1/t_{1/2}$ on Φ. The difference between their results and this study may arise from the difference between plotting against T_c or ΔT. Since crystallization is suppressed by the entanglements, the suppression effect of crystallization by the entanglements is

Fig. 4 Schematic illustration of the role of the entanglement species in the crystallization of C-PE and L-PE and their blends
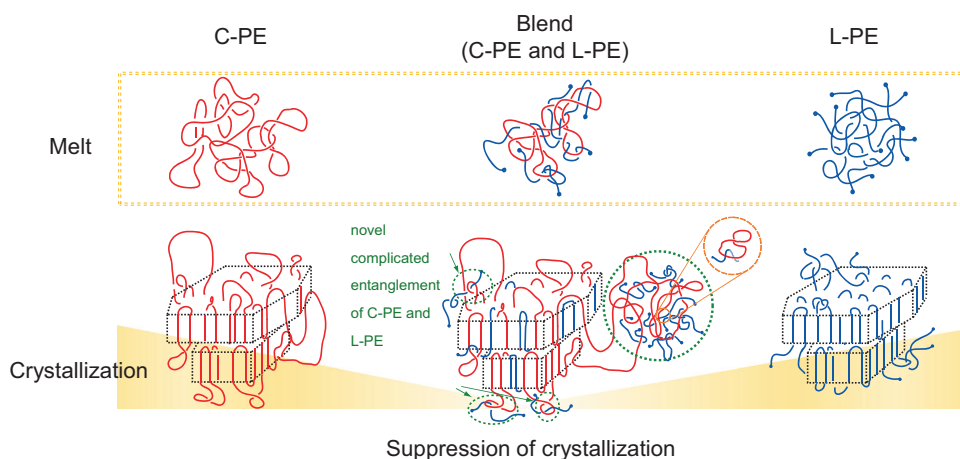
maximized at $\Phi_{L\text{-PE}} = 30\text{–}40$ wt%. The suppression effect should consider the contributions of both the entanglement quantity and disentangling ability. As reported by Roovers [5], the entanglement quantity, i.e., the number density of the entanglement (ν_e), of linear polymers is much larger than that of cyclic polymers with the same M_w. In this study, L-PE is expected to have a larger ν_e than C-PE because of the small differences in their M_w values. However, cyclic polymers have entanglements that are easy to disentangle due to the lack of chain ends. The entanglements of linear polymers are more complicated and difficult to disentangle than those of cyclic polymers. The effects of relatively low ν_e values and the disentangling ability on the crystallization of C-PE are of significance at a large ΔT. In the blend of C-PE and L-PE, in addition to the entanglements formed by single polymers, the formation of a novel entanglement is expected so that the L-PE chain penetrates the C-PE ring. It is speculated that this type of entanglement is difficult to disentangle, as discussed by Ruiz et al. [12]. Notably, the curves shown in Fig. 3 exhibit somewhat wavy patterns. Depending on the perspective, the curve may appear to have a local maximum at $\Phi_{L\text{-PE}} = 50$ wt%. An example of such composition dependence is typically seen in the Gibbs free energy of mixing for polymer blends. However, it is unlikely that the relationship between $1/t_{1/2}$ and $\Phi_{L\text{-PE}}$ follows a similar functional form as shown in this example, making it unreasonable to consider the presence of a local maximum. One possible reason for the wavy curve is the assumption of the additive property of $T_m{}^0$. In this study, we assume a linear additive property, resulting in $T_m{}^0$ values increasing linearly with $\Phi_{L\text{-PE}}$. If the $T_m{}^0$ values exhibit a sigmoidal change with $\Phi_{L\text{-PE}}$, different ΔT values from those used in this study will arise. Consequently, the wavy change may disappear from the $\Phi_{L\text{-PE}}$ dependence of $1/t_{1/2}$. To clarify this issue, it is necessary to verify the validity of the $T_m{}^0$ estimation method. Figure 4 shows a schematic illustration of the role of entanglement species in the crystallization of

C-PE, L-PE, and their blends. Because the L-PE chains in the molten state are complexly entangled with each other, disentangling and chain diffusion become slower. Therefore, crystallization from such melts slows. Conversely, since C-PE chains can disentangle easily, crystallization from such melts accelerates. In the blends of C-PE and L-PE, due to the novel complicated entanglement, the chains in the melt are difficult to disentangle. Consequently, the crystallization of the blends is slower than that of the C-PE and L-PE homopolymers. We speculate that this effect will be maximized at $\Phi_{L\text{-PE}} = 30\text{–}40$ wt% when the M_w values of C-PE and L-PE in the blends are slightly different.

Conclusion

To clarify the effects of entanglement species on crystallization in a quiescent state, we studied the $t_{1/2}$ values of blends of C-PE and L-PE from the melt as functions of $\Phi_{L\text{-PE}}$ and ΔT through POM and DSC. We prepared C-PE and L-PE specimens with M_w values of 175×10^3 and 154×10^3, respectively. The $1/t_{1/2}$ values of the C-PE and L-PE homopolymers were approximately the same at $\Delta T = 25.5$ and 26.5 K. In contrast, the $1/t_{1/2}$ values of the blends of C-PE and L-PE were significantly lower than those of the C-PE and L-PE homopolymers, and a minimum value of $1/t_{1/2}$ was observed at $\Phi_{L\text{-PE}} \approx 30\text{–}40$ wt%. This finding suggested that the suppression of crystallization in the blended system was caused by the novel entanglement formed by the penetration of the L-PE chain into the C-PE chain.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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References

1. Hoffman JD, Lauritzen JI. Crystallization of bulk polymers with chain folding: theory of growth of lamellar spherulites. J Res Natl Bur Stand A. 1961;65A:297–336.
2. Umemoto S, Okui N. Power law and scaling for molecular weight dependence of crystal growth rate in polymeric materials. Polymer. 2005;46:8790–5.
3. Psarski M, Piorkowska E, Galeski A. Crystallization of polyethylene from melt with lowered chain entanglements. Macromolecules. 2000;33:916–32.
4. Hikosaka M, Watanabe K, Okada K, Yamazaki S. Topological mechanism of polymer nucleation and growth – the role of chain sliding diffusion and entanglement. Adv Polym Sci. 2005;191:137–86.
5. Roovers J. Viscoelastic properties of polybutadiene rings. Macromolecules. 1988;21:1517–21.
6. Su HH, Chen HL, Díaz A, Casas MT, Puiggalí J, Hoskins JN, et al. New insights on the crystallization and melting of cyclic PCL chains on the basis of a modified Thomson-Gibbs equation. Polymer. 2013;54:846–59.
7. Tezuka Y, Ohtsuka T, Adachi K, Komiya R, Ohno N, Okui N. A defect-free ring polymer: size-controlled cyclic poly(tetrahydrofuran) consisting exclusively of the monomer unit. Macromol Rapid Commun. 2008;29:1237–41.
8. Takeshita H, Poovarodom M, Kiya T, Arai F, Takenaka K, Miya M, et al. Crystallization behavior and chain folding manner of cyclic, star and linear poly(tetrahydrofuran)s. Polymer. 2012;53:5375–84.
9. Ono R, Atarashi H, Yamazaki S, Kimura K. Molecular weight dependence of the growth rate of spherulite of cyclic poly(ε-caprolactone) polymerized by ring expansion reaction. Polymer. 2020;194:122403.
10. Pérez RA, Córdova ME, López JV, Hoskins JN, Zhang B, Grayson SM, et al. Nucleation, crystallization, self-nucleation and thermal fractionation of cyclic and linear poly(ε-caprolactone)s. React Funct Polym. 2014;80:71–82.
11. López JV, Pérez-Camargo RA, Zhang B, Grayson SM, Müller AJ. The influence of small amounts of linear polycaprolactone chains on the crystallization of cyclic analogue molecules. RSC Adv. 2016;6:48049–63.
12. Ruiz MB, Pérez-Camargo RA, López JV, Penott-Chang E, Múgica A, Coulembier O, et al. Accelerating the crystallization kinetics of linear polylactides by adding cyclic poly (L-lactide): nucleation, plasticization and topological effects. Int J Biol Macromol. 2021;186:255–67.
13. Kapnistos M, Lang M, Vlassopoulos D, Pyckhout-Hintzen W, Richter D, Cho D, et al. Unexpected power-law stress relaxation of entangled ring polymers. Nat Mater. 2008;7:997–1002.
14. Bielawski CW, Benitez D, Grubbs RH. An "endless" route to cyclic polymers. Science. 2002;297:2041–4.
15. Wunderlich B, Czornyj G. A study of equilibrium melting of polyethylene. Macromolecules. 1977;10:906–13.
16. Broadhurst MG. The melting temperatures of the n-paraffins and the convergence temperature for polyethylene. J Res Natl Bur Stand A. 1966;70:481–6.
17. Mandelkern L. Crystallization of polymers. 2nd ed. Vol. 2. Cambridge: Cambridge University Press; 2004.
18. Lorenzo AT, Arnal ML, Albuerne J, Müller AJ. DSC isothermal polymer crystallization kinetics measurements and the use of the Avrami equation to fit the data: guidelines to avoid common problems. Polym Test. 2007;26:222–31.
19. Krumme A, Lehtinen A, Viikna A. Crystallisation behaviour of high density polyethylene blends with bimodal molar mass distribution 1. Basic characteristics and isothermal crystallisation. Eur Polym J. 2004;40:359–69.
20. Ergoz E, Fatou JG, Mandelkern L. Molecular weight dependence of the crystallization kinetics of linear polyethylene. I. Experimental results. Macromolecules. 1972;5:147–57.