

IMPACT PROPERTIES OF METALLOCENE-CATALYZED ETHYLENE- α -OLEFIN COPOLYMERS*

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Abstract The impact properties of two selected metallocene-catalyzed ethylene-butene copolymers and one conventional copolymer were evaluated using Izod impact test. It is found that the metallocene-catalyzed copolymer shows superior impact properties. This result was explained on the basis of the more homogeneous inter-molecular composition distribution and narrower molecular weight distribution, which leads to more homogeneous morphology with fewer defects. Stepwise crystallization improves the impact properties, especially in the crack propagation process, to a large extent. This is due to the decrease of entanglements by stepwise crystallization, which is advantageous for the chain slip and shear. The polymer with heterogeneous intra-molecular composition distribution exhibits a more evident improvement of impact properties under stepwise crystallization.

Keywords Metallocene-catalyzed ethylene-butene copolymer, Impact properties, Molecular heterogeneities, Thermal treatment

INTRODUCTION

Short chain branched ethylene- α -olefin copolymers are among the most widely applied plastics. The introduction of a small amount of short branches into the polymer chains greatly improves their mechanical properties. However, the influence of various structural factors on the mechanical properties of ethylene copolymer has not been well understood, since too many factors, *e.g.* average molecular weight (MW), molecular weight distribution (MWD), comonomer ratio, comonomer distribution among different polymer chains (inter-molecular composition distribution) and comonomer distribution along the same polymer chains (intra-molecular composition distribution), are involved^[1–5]. The ethylene copolymers produced by conventional heterogeneous Ziegler-Natta catalysts, which usually have plural active sites, exhibit a broad molecular weight distribution and heterogeneous inter- and intra-composition distributions^[6, 7]. The simultaneous effects of these factors cause difficulties in studying the mechanical properties of this type of copolymer.

Copolymerization of ethylene with α -olefins using Kaminsky-type metallocene catalysts, which are generally believed to have “single site”, can yields copolymers with a narrow MWD around 2.0^[8, 9]. The metallocene-catalyzed ethylene- α -olefin copolymers also have relatively more homogeneous (but not absolutely homogeneous) inter- and intra-molecular composition distribution as compared with the conventional copolymers^[10–12]. These structural characteristics will facilitate the study of the relationship between various structural factors and the mechanical properties of ethylene copolymers. It has been reported that the metallocene-catalyzed ethylene copolymers show improved mechanical properties^[2, 13], such as tensile, puncture resistance, impact properties and so on. Nevertheless, the better mechanical properties of the metallocene-

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catalyzed copolymers were usually attributed to their homogeneous inter-molecular composition distribution, while intra-molecular composition distribution was seldom considered.

In our previous work, we characterized the detailed microstructure of some metallocene-catalyzed and conventional ethylene-butene copolymers, including the inter- and intra-molecular composition heterogeneities^[10, 14, 15, 16]. The effect of structural factors on the crystallization of polymer was also studied^[17–19]. In this paper, some selected samples were investigated by impact testing and the effects of ethylene copolymer structure and heat treatments on their impact properties were discussed.

EXPERIMENTAL

Materials

Two ethylene-butene copolymer samples (*m*PE1, *m*PE2) prepared with a metallocene catalyst were supplied by RIPP, SINOPEC. One commercial ethylene-butene copolymer sample ZNPE1, prepared with a conventional Ziegler-Natta catalyst was a commercial product of Qilu Petrochemical Co. China. Some characteristics of these samples are listed in Table 1. The selected samples have close molecular weight (MW).

Table 1. Some characteristics of different samples

Sample	Comonomer	Polymerization process	Comonomer content (mol%)	Density ^a (g/cm ³)	M_w ($\times 10^{-4}$)	M_w/M_n
<i>m</i> PE1	1-Butene	Gas phase	0.38	0.947	11.10	2.28
<i>m</i> PE2	1-Butene	Gas phase	0.87	0.940	15.49	3.80
ZNPE1	1-Butene	Gas phase	0.58	0.949	13.86	6.49

^a Density as received

Characterization

The MW and MWD of ethylene copolymers were measured with a Waters 150 GPC instrument at 135°C using trichlorobenzene as the solvent. The contents of short chain branching were calculated from ¹³C-NMR spectra at 100.7 MHz recorded on a Bruker AMX-400 spectrometer at 97°C. The polymer solutions were prepared by dissolving *ca.* 50 mg polymer at 130°C in 0.5 mL C₆D₄Cl₂. 1% Hexamethyldisiloxane was added as the internal standard. The measurement was conducted with a pulse angle of 90°, a pulse repetition of 10 s, a spectral width of 5000 Hz, and 6000 scans. The densities of ethylene copolymers were determined in a density gradient column consisting of a water-isopropyl alcohol mixture, at a constant temperature of 22°C.

Thermal Treatment of Samples

Specimens of each polymer were prepared by compression molding, followed by a predetermined thermal treatment. About 50 g of copolymer was placed on a 20 × 20 cm, 4.0 mm-thick mold that was positioned between two copper plates. Samples were kept at 170°C for 20 min under the applied pressure of 150 kg/cm², then they were subjected to different crystallization procedures: (I) quickly quenched with ice-water; (II) quickly transferred into a container at 100°C in nitrogen gas atmosphere and kept for 20 h, then quenched with ice-water; (III) quickly transferred into an oil bath at 120°C and the temperature of which was decreased stepwisely. At each temperature step (*i.e.*, 120°C, 115°C, 110°C, 105°C, 100°C, 95°C, 90°C, 85°C, 80°C, respectively), the samples were maintained for 12 h under nitrogen gas atmosphere. Procedures I, II and III are denoted as Q, Y and S, respectively.

Instrumental Impact Test

Samples, treated by different procedures, were machined into Izod impact specimens according to Chinese Standard GB/T 1843-80. The length *L* and *L*₀, width *D*, thickness *B* and notch depth *A* of the specimens are 63.5 mm, 22 mm, 12.7 mm, 4.0 mm and 2.54 mm, respectively.

All samples were tested at 22°C with an impact tester made by Ceast S.P.A., Italy. The force *F* was traced with a force transducer mounted on the top of the pendulum. The energy *E* is integrated with a computer. *F*(*t*) and *E*(*t*) curves are the original results from which further information can be derived. The impact velocity is 3.46 m/s and the mass of the pendulum is 1.25 kg, much larger than that of the specimens.

Dynamic Mechanical Test

Dynamic mechanical properties were tested by Rheometric Science ARES-9A. Test frequency is 1 Hz and test temperature is from -80°C to 100°C .

Optical Microscopy

The samples were cut directly from the molded sheet after treatment and were observed by polarized microscopy (XPR-1, made by JiangNan optical instrument factory, China).

Fracture Surface Morphology (SEM)

Fracture surfaces of the polymer samples were observed by using a scanning electron microscope (SEM, JEOL JEM-T20) after being sputter-coated with gold at a beam voltage of 20 kV.

RESULTS AND DISCUSSION

Impact Test

The $F(t)$ and $E(t)$ curves for all copolymers under different thermal treatments are shown in Fig. 1 and some calculated parameters are listed in Table 2. $F_{\max}$, E_i and E_t are the maximal force, the absorbed energy from the beginning to maximal force and the total absorbed energy during impact process, respectively. $D.I.$ is the ductile index^[20], $D.I. = \frac{E_t - E_i}{E_i}$. Impact strength (G) can be expressed by $G = \frac{E_t}{BD}$, where D and B are the width and the thickness of copolymer samples, respectively.

Table 2. Some characteristic parameters in impact process

Sample	Thermal treatment	Density (g/cm ³)	$F_{\max}$ (N)	E_i (J)	E_t (J)	$E_t - E_i$ (J)	$D.I.$	G (kJ/m ²)
<i>m</i> PE1	Q	0.946	152	0.36	0.81	0.45	1.25	20.1
	Y	0.956	176	0.43	0.67	0.24	0.56	19.0
	S	0.963	188	0.44	0.96	0.52	1.18	27.1
ZNPE1	Q	0.948	134	0.11	0.16	0.05	0.45	4.7
	Y	0.957	158	0.19	0.23	0.04	0.21	6.0
	S	0.964	157	0.16	0.26	0.10	0.63	5.6
<i>m</i> PE2	Q	0.940	147	0.39	0.72	0.33	0.85	19.3
	Y	0.947	166	0.35	0.71	0.36	1.03	19.1
	S	0.952	168	0.42	1.70	1.28	3.05	47.6

$F(t)$ and $E(t)$ stand for the variation of stress and energy with time during impact testing, respectively. The $F(t)$ curves can be divided into two zones based on the variation of $F(t)$ with displacement. In the first zone stress quickly increases with displacement and in the second zone stress rapidly decreases with displacement. Accordingly, these two zones correspond to two processes in impact fracture: crack initiation and crack propagation^[21]. The energy required to initiate the crack (E_i) is the $E(t)$ curve to this point $F_{\max}$. The rest of total energy, $E_t - E_i$, is energy absorbed in the crack propagation.

Effect of Inter-Molecular Heterogeneity

It can be seen from Fig. 1 that the force exerted on the conventional copolymer ZNPE1 decreases very quickly beyond the peak value, irrespective of the thermal treatments. This implies its brittle fracture feature. In contrast, *m*PE1 copolymer with similar MW and density shows ductile fracture. The SEM micrographs of the fracture surfaces for *m*PE1 and ZNPE1 shown in Fig. 2 support this idea. The fracture surface of *m*PE1 is relatively coarse and some trace of shear yield morphology, which is one of the characteristics of ductile fracture. Nevertheless, ZNPE1 has a smooth fracture surface, which is the feature of brittle fracture. More differences were found in the crack propagation zone of the fracture surfaces of *m*PE1 and ZNPE1. The *m*PE1 exhibits obvious shear yield and orientation in the crack propagation zone, while such morphology is not observed in ZNPE1. The data in Table 2 quantitatively illustrate the difference of *m*PE1 and ZNPE1 in impact properties.

The values of $F_{\max}$, E_i and $E_t - E_i$ are much larger for *m*PE1 than those for ZNPE1. All these results show that *m*PE1 has superior impact properties to the ZNPE1. Since these two copolymers have similar densities and there is no large difference in modulus in tensile tests^[14], it seems that the impact fracture of ZNPE1 happens before the expected maximum is reached, indicating the existence of some morphology defects where fracture can easily takes place.

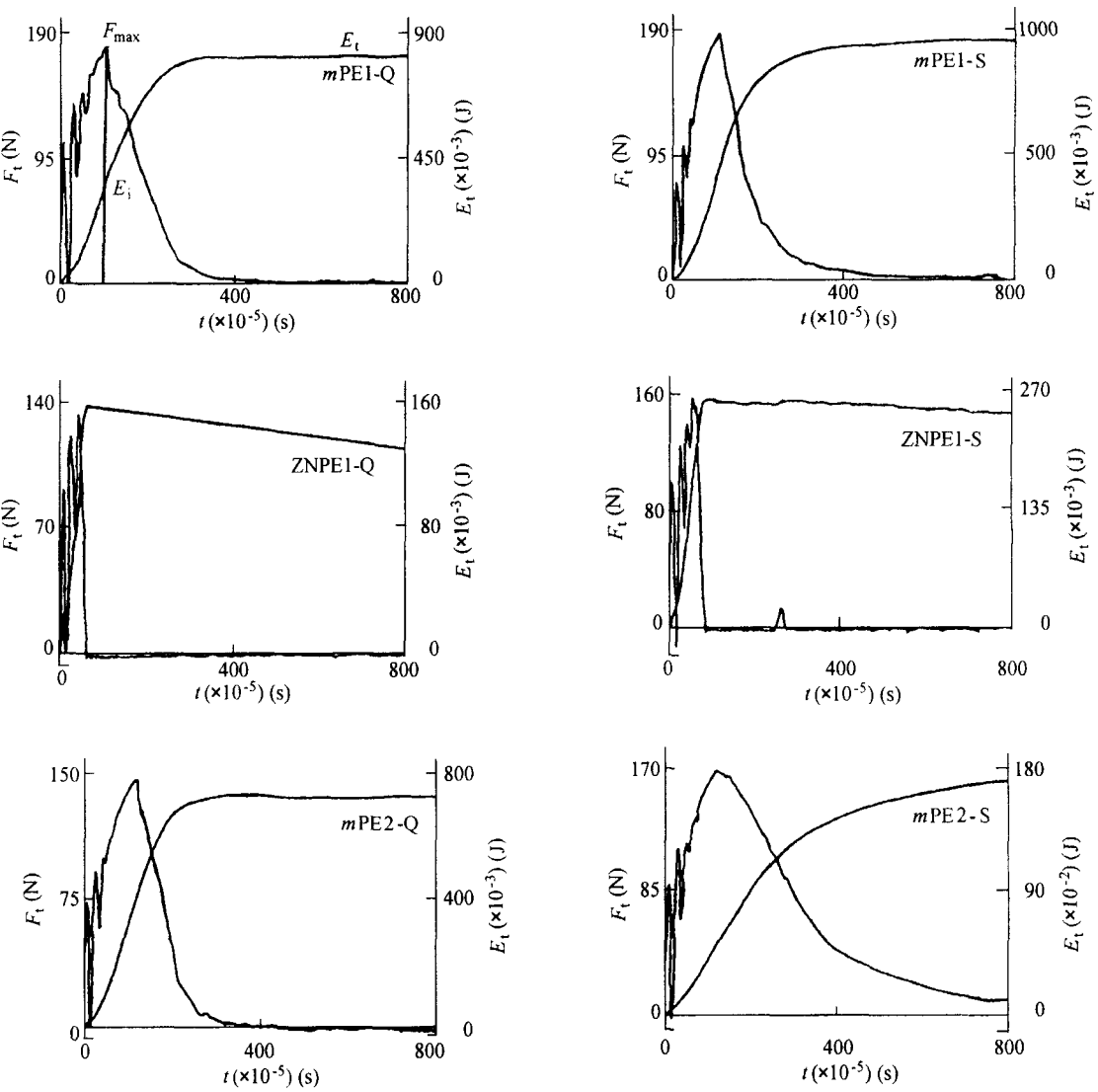
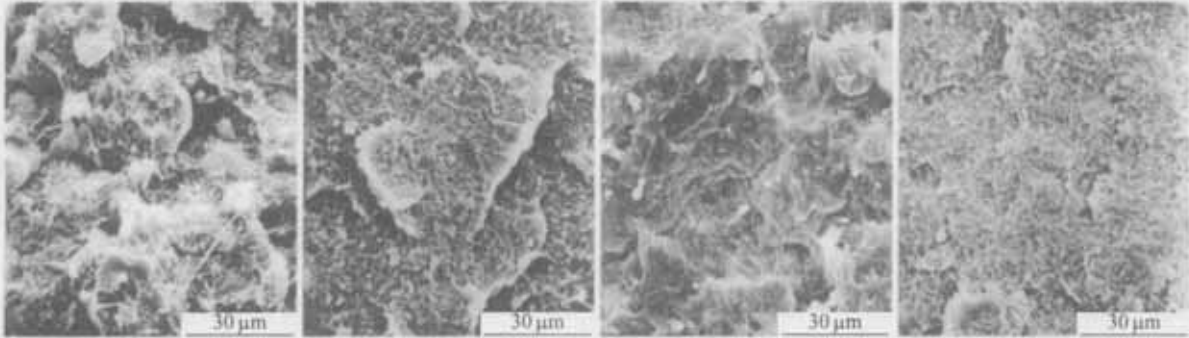


Fig. 1 $F(t)$ and $E(t)$ curves of various copolymer samples

*m*PE1 and ZNPE1 contain few branches yet their densities are relatively high. In such a case, the distance between two branches is much larger than the lamellar thickness of the crystals, thus intra-molecular composition heterogeneity plays a minor role in crystallization and has less influence on other polymer properties^[15]. On the other hand, these two copolymers show a marked difference in inter-molecular composition distribution. Three peaks were observed in the DSC melting trace of stepwise-crystallized ZNPE1, but there is only one melting peak for *m*PE1 which has been subjected to the same thermal treatment^[14]. This means that in ZNPE1, some molecules are densely branched while others are less branched. The difference in inter-molecular composition distribution may have an influence on the crystallization and morphology^[17-19]. Moreover, *m*PE1 and ZNPE1 also have

different MWD. The tie molecules, which connect different lamellar crystals, are related to the molecular weight of polymer. Especially for a polymer containing few branches and having large lamellar thickness, MW becomes an important factor determining the number of tie molecules. The higher the MW, the larger is the number of tie molecules^[22]. Since ZNPE1 has a broader MWD, the molecules with a lower MW may form crystals containing less tie molecules. This is another origin of the brittle fracture of ZNPE1. The above analysis shows that the different impact fracture behavior of *m*PE1 and ZNPE1 mainly arises from the inter-molecular heterogeneity, *i.e.* intermolecular composition distribution and MWD.

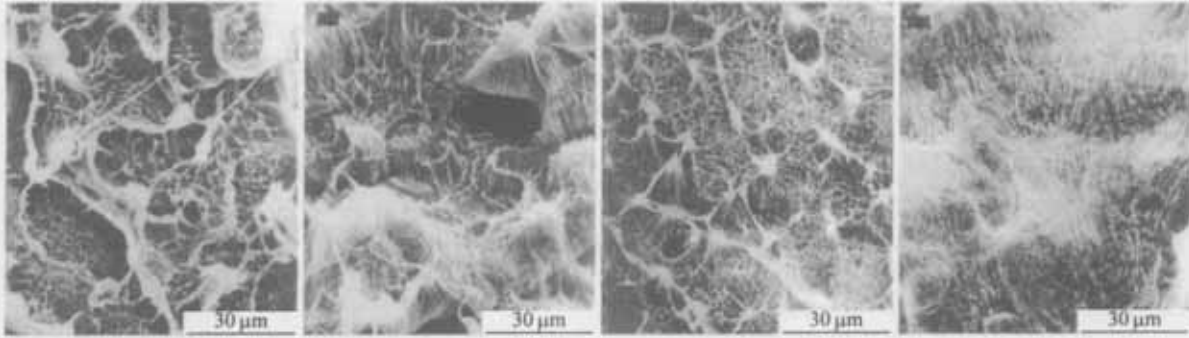


(a) *m*PE1-S (a) ZNPE1-S (b) *m*PE1-S (b) ZNPE1-S

Fig. 2 SEM micrographs of fracture surface for stepwise crystallized *m*PE1 and ZNPE1
a) Crack initiation zone; b) Crack propagation zone

Effects of Thermal Treatment and Intra-Molecular Composition Heterogeneity

Comparing the $F(t)$ curves of *m*PE2 which has been subjected to different thermal treatments, one can see that their major difference lies in the zone beyond F_{max} , *i.e.* the crack propagation zone. The data in Table 2 show that the value of E_i of the stepwise-crystallized *m*PE2 is only slightly larger than that of the quenched sample. Taking the change of density under different thermal treatments into consideration, this difference is reasonable. However, the value of $E_t - E_i$ of the stepwise-crystallized *m*PE2 is much higher than that of quenched *m*PE2, leading to the large difference in the values of the ductile index ($D.I.$). Generally, it is believed that the value of $E_t - E_i$ stands for the energy absorbed during crack propagation, which is related to the lamellar shear and yield. Figure 3 shows the SEM micrographs of fracture surfaces. More obvious shear band and fibrils drawn out of the crystals are observed in the crack propagation zone of the stepwise-crystallized *m*PE2 than in quenched *m*PE2.



(a) *m*PE2-Q (a) *m*PE2-S (b) *m*PE2-Q (b) *m*PE2-S

Fig. 3 SEM micrographs of fracture surface for *m*PE2 copolymers
a) Crack initiation zone; b) Crack propagation zone

All these results reveal that the impact properties of *m*PE2 become better after stepwise crystallization, though the density also increases when compared to the quenched sample. This phenomenon is quite unusual, since the impact properties of semicrystalline polymer become worse as the density increases. Such an anomalous phenomenon was also reported by Kitao *et al.* for the high- and medium-density ethylene copolymers^[23, 24]. They found that the impact properties of PE were improved after annealing. A crack shielding effect was proposed to explain this experimental result. An increase in the size of spherulite as well as the molecular entanglement loss due to enhanced crystallization by annealing was believed to promote the shield effect^[23]. With fewer entanglements, the slip between crystals and shear can take place more easily, thus more energy is absorbed and the mechanical properties are improved. We have two items evidence to support the reduction of entanglement after stepwise crystallization. First, the fraction of interfacial phase, which mainly originated from non-adjacent re-entries in folding^[25], is lower for the stepwise-crystallized samples^[14]. The second one is the change of β transition temperature. Figure 4 shows the loss modulus curves of *m*PE2 under different thermal treatments. It is found that after stepwise crystallization, α transition temperature increases but β transition temperature decreases. The α transition is attributed to chain segment movement in the crystal. The more perfect the crystals are, the lower the mobility of the chain segments will be. The increase in α transition temperature is in accordance with the perfection of crystals after stepwise crystallization. Though there still remain some controversies on the assignment of β transition, it is usually attributed to the movement of polymer chains located in interfacial phase^[26–29]. The decrease in β transition temperature indicates the increase in chain mobility and reduction in entanglements.

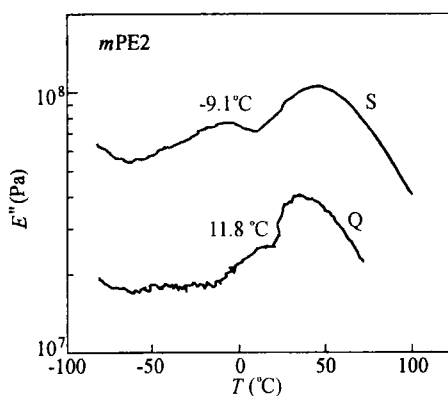
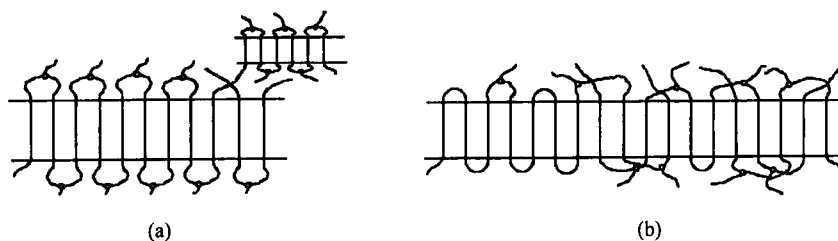


Fig. 4 Loss modulus versus temperature curves of *m*PE2

Comparing *m*PE1 and *m*PE2, we can find that the effect of thermal treatment on these two samples is different. The improvement of impact properties is more evident for *m*PE2 after stepwise crystallization. This is because the number of formed entanglements is not only related to crystallization condition, but also dependent on the chain structure. The sample *m*PE2 has a highly homogeneous inter-molecular composition distribution, since there is only one strong peak besides two very weak peaks in the DSC melting trace of stepwise-crystallized *m*PE2^[14]. On the other hand, multiple melting peaks were still reserved in its stepwise-crystallized fractions, which were obtained by preparative temperature rising elution fractionation (TREF) and eluted in a narrow temperature range^[15]. This indicates that intra-molecular composition heterogeneity exists in this sample and it is responsible for the multiple melting peaks.

For the copolymer *m*PE2 having intra-molecular composition heterogeneity, the ethylene segments with different lengths are accommodated into the same crystals (Scheme 1b) when quenched. In such a situation, the number of entanglements is much larger than for the polymers having homogeneous intra-molecular composition distribution. Therefore, the value of $E_t - E_i$ of *m*PE1 is higher than that of *m*PE2. After stepwise crystallization, the ethylene segments of various lengths form discrete crystals with different lamellar thickness. These lamellae are connected by tie molecules but with few entanglements (Scheme 1a) in each crystal^[15]. As there are more tie

molecules for *m*PE2, stronger slip and shear are permitted in the impact process.



Scheme 1 Crystallization of ethylene copolymer. Intra-molecular composition heterogeneity under different thermal treatments

a) Stepwise crystallization; b) Quenched

However, it should be noted that for low-density polyethylene annealing has little improvement effect on the impact properties. Since there are too many comonomer units in the polymer chains and the formed crystals are highly imperfect, annealing cannot reduce the entanglement effectively. On the contrary, the increase in crystallinity due to annealing may have a disadvantageous effect on the impact properties.

CONCLUSION

Metallocene-catalyzed ethylene- α -olefin copolymers exhibit superior impact properties than the conventional ethylene- α -olefin copolymers due to their relatively homogeneous inter-molecular composition distribution and narrow MWD. For medium- and high-density ethylene copolymers, it is found that stepwise crystallization improves the impact properties of the polymers, reflected by the larger energy absorbed in the crack propagation process. This can be explained by the reduction of entanglements, which facilitates the chain slip and shear. The effect of thermal treatment varies with different polymers. The polymer with heterogeneous intra-molecular composition distribution exhibits a more evident improvement of impact properties under stepwise crystallization.

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