

Microstructure Characterization of Short-chain Branching Polyethylene with Differential Scanning Calorimetry and Successive Self-nucleation/Annealing Thermal Fractionation*

Yan-hu Xue^{a,b}, Yan-hui Wang^a, Yan-di Fan^a, He-ran Yang^a, Tao Tang^a,
Shu-qin Bo^a and Xiang-ling Ji^{a**}

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b University of Chinese Academy of Sciences, Changchun 130022, China

Abstract A series of the copolymers of ethylene with 1-hexene (M1–M9) synthesized by metallocene catalyst $\text{Et}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ was studied by differential scanning calorimetry and successive self-nucleation and annealing (SSA) thermal fractionation. The distribution of methylene sequence length (MSL) in the different copolymers was determined using the SSA method. The comonomer contents of samples M4 and M5 are 2.04 mol% and 2.78 mol%, respectively. Both M4 and M5 have low comonomer content and their MSL distribution profiles exhibit a monotonous increase trend with their MSL. The longest MSL of M5 is 167, and its corresponding molar percent is 43.95%, which is higher than that of M4. Moreover, the melting temperature (T_m) of M5 is also higher than that of M4. The comonomer contents of samples M7, M8, and M9 are 8.73 mol%, 14.18 mol% and 15.05 mol%, respectively. M7, M8, and M9 have high comonomer contents, and their MSL distribution profiles display unimodality. M7 has a lower peak value of 33 and a narrow MSL distribution, resulting in a T_m lower than that of M8 and M9. The MSL and its distribution are also key points that influence the melting behavior of copolymers. Sometimes, MSL and its distribution of copolymers have a greater impact on it than the total comonomer contents, which is different from traditional views.

Keywords: Polyethylene; Methylene sequence length(MSL); Microstructure; successive self-nucleation and annealing (SSA); SCB.

INTRODUCTION

Polyethylene (PE) is the major commodity polymer worldwide. Its versatility has been greatly expanded by the control of chain microstructure that can be achieved by copolymerizing ethylene with α -olefins^[1, 2]. The distribution of α -olefin along the chain is particularly important because these copolymers can exhibit a highly heterogeneous intramolecular and/or intermolecular comonomer distribution. The short-chain branching (SCB) PE has elicited great interest industrially and academically because it affects numerous physical and mechanical properties, including density, crystallinity, rigidity, permeability and environmental stress crack resistance^[3–7]. The common methods for characterizing SCB include Fourier transform infrared spectroscopy^[8, 9] and ^{13}C nuclear magnetic resonance (^{13}C -NMR) spectroscopy^[10, 11].

Less time-consuming methods, such as thermal fractionation techniques, have been developed recently^[12–17]. Such methods are based on the differences in the crystallizability of structurally heterogeneous

* This work was financially supported by the National Natural Science Foundation of China (Nos. 20734006 and 50921062).

** Corresponding author: Xiang-ling Ji (姬相玲), E-mail: xlji@ciac.ac.cn

Received September 9, 2013; Revised October 29, 2013; Accepted November 19, 2013

doi: 10.1007/s10118-014-1444-7

polymer chains. These techniques are much more sensitive to chain structural differences rather than to difference in molecular weight. Two main methods include step-crystallization (SC) and successive self-nucleation and annealing (SSA).

SC induces molecular segregation by repeating isothermal crystallization steps at progressively lower temperatures in the cooling fractionation stage. Mandelkern studied the influence of molecular weight on the melting and phase structure of random copolymers of ethylene. He also calculated lamellar thickness distributions in linear polyethylene and ethylene copolymers from the endotherms obtained by DSC^[18, 19]. Keating *et al.* reported sequence length calibration curves based on melting points and statistical terms to describe ethylene sequence length distribution^[20]. Chen *et al.* investigated the molecular structure of ethylene copolymers synthesized with different types of catalysts and employing 1-butene, 1-hexene and 1-octene as comonomers. Thermal analysis after SC has shown that the Ziegler-Natta catalyzed linear low density polyethylenes have broad bimodal SCB, lamellar thickness and MSL distributions with less SCB, while the single-site catalyzed very low density polyethylene shows a much narrower distribution of SCB, lamellar thickness and MSL with more SCB^[21]. Starck and Löfgren have found similar results when they evaluated the effect of the side chain size in 1-octene, 1-tetradecene and 1-octadecene comonomers^[22].

SSA is based on the sequential application of self-nucleation and annealing steps. SSA was first presented by Müller and coworkers. They fractionated ethylene/ α -olefin copolymers using SSA^[23]. Cho *et al.* proposed a modified Gibbs-Thomson equation to predict the lamellar thickness from DSC data^[24]. And Müller and coworkers used it and obtained the results consistent with those derived from SAXS^[25]. Wanke conducted quantitative determination of SCB content and distribution in commercial PEs. In addition, the relationship between DSC melting temperature (T_m) and SCB content has been determined^[26]. SSA is performed at substantially shorter times than SC or temperature rising elution fractionation and with better resolution^[27, 28].

In this study, the SSA method was utilized to characterize the heterogeneity in the comonomer distribution of ethylene/1-hexene copolymers. The distribution of methylene sequence length (MSL) was determined using the SSA method. Furthermore, the influences of MSL and its distribution on the melting behavior of copolymers were discussed in detail.

EXPERIMENTAL

Materials

The polymerization of samples was conducted in a 150 mL glass reactor which was dried in vacuum. And then it was loaded with toluene, 1-hexene and metallocene catalyst $\text{Et}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ solution ($\text{Al}/\text{Zr} = 2000$). The total volume of the feeding liquid was 100 mL. The polymerization was initiated by introducing ethylene gas. The reaction glass was stirred and maintained at 60 °C for 60 min. The polymerization was terminated by venting ethylene gas and adding acidified ethanol solution. The product was filtered, washed with a large amount of ethanol and acetone, and then dried under vacuum at 60 °C for 24 h. The samples used in this study were synthesized *via* the different additive amount of 1-hexene (0 mol%~16 mol%) and were coded as samples M1, M4, M5, M6, M7, M8, and M9. M1 was an ethylene homopolymer. M4, M5, M6, M7, M8, and M9 were copolymers obtained through the copolymerization of ethylene with 1-hexene.

¹³C-NMR Spectroscopy

The polymer solutions were prepared with ~80 mg of the sample in 0.5 mL of *o*-dichlorobenzene- d_4 at 125 °C. ¹³C-NMR spectra were recorded at 125 °C using a Bruker AV400 NMR spectrometer at 100.58 MHz. The *o*-dichlorobenzene- d_4 solvent was used to provide the internal lock signal with its highest peak at $\delta = 133.22$ as the standard reference. In all measurements, the inverse gated decoupling was used to remove NOE and ¹³C-¹H couplings, the pulse angle was 90°. The number of scans was 5000, and the delay time was 8 s.

Differential Scanning Calorimetry (DSC)

The DSC curves were recorded using a TA Instrument model DSC Q100. The temperature calibration of the instrument was performed by using indium. The sample (about 6 mg) was sealed in an aluminum sample pan,

initially heated from 20 °C to 200 °C at a rate of 10 K/min, held at 200 °C for 5 min to remove its thermal history, cooled down from 200 °C to 20 °C at a rate of 10 K/min, held at 20 °C for 5 min, and finally heated again to 200 °C at a rate of 10 K/min. The T_m and the heat of fusion (ΔH_m) were measured during the reheating experiments.

SSA Method

The SSA thermal-fractionation process was carried out on a TA DSC, Q100. The specimens were about 6 mg. The temperature calibration of the instrument was performed using standard indium. The complete thermal treatment comprised the following steps. (a) The previous thermal history was erased. The sample was initially heated from 20 °C to 200 °C at a rate of 10 K/min, and then held at 200 °C for 5 min to remove its thermal history. (b) The sample was cooled at a rate of 10 K/min to 0 °C and held for 5 min. (c) The sample was heated at a rate of 10 K/min from 0 °C to a selected self-seeding temperature (T_s). Fillon *et al.* suggested that this first T_s temperature must be determined previously by performing separate DSC experiments in order to determine the so-called self-nucleation domains of the sample^[29]. The sample was kept at T_s for 5 min. (d) DSC cooling was performed at a rate of 10 K/min from T_s to 0 °C, in which the effects of the thermal treatment reflected on the crystallization of the sample. (e) The sample was heated to a new T_s that was 5 K lower than the previous T_s and held for 5 min. (f) Steps “c” to “e” were repeated at T_s . (g) Finally, the sample was heated at a rate of 10 K/min from 0 °C to 200 °C, and a multiple-melting endotherm was obtained.

RESULTS AND DISCUSSION

SCB Contents of the Samples

The content and distribution of SCB are important factors that determine the physical properties of ethylene/1-hexene copolymers. The SCB contents, *i.e.*, the comonomer contents of the samples listed in Table 1, were calculated from ¹³C-NMR spectra^[10, 11]. The comonomer content gradually increased from 2.04 mol% to 15.05 mol% corresponding to the samples M4–M9. M4 had the lowest 1-hexene content of 2.04 mol% among all the copolymers, whereas M9 had the highest 1-hexene content of 15.05 mol%. The homopolymer M1 had no 1-hexene, which was included only for comparison.

Table 1. The 1-hexene contents of samples

Sample	M1	M4	M5	M6	M7	M8	M9
1-hexene (mol%)	0	2.04	2.78	4.86	8.73	14.18	15.05

Melting Behavior of the Original Samples Based on DSC Analysis

Figure 1 shows the DSC melting curves of the samples, and the related data are listed in Table 2. As shown in Fig. 1, the homopolymer M1 had a sharp melting peak at about 131.0 °C, melting enthalpy of 170.8 J/g, and crystallinity of 59.3%. For the ethylene/1-hexene copolymers (M4, M5, M6, M7, M8, and M9), the melting peak of different samples generally shifted toward lower temperatures with the increase of 1-hexene content from 2.04 mol% to 15.05 mol%. The melting enthalpy of copolymers exhibited the same trend, *i.e.*, it decreased with the 1-hexene content. The crystallinity of copolymers gradually decreased from 32.2% to 1.7%, with the increase in 1-hexene content from 2.04 mol% to 15.05 mol%. M4 had the lowest 1-hexene content of 2.04 mol% and the highest crystallinity of 32.2%. By contrast, M9 had the highest 1-hexene content of 15.05 mol% and the lowest crystallinity of 1.7%. When 1-hexene content increases, the possibility of 1-hexene inserting crystallizable ethylene sequence increases, the lamellar thickness of crystals becomes thinner, and T_m gradually decreases^[30, 31].

Meanwhile, M5 and M7 exhibited special situations. M5 had 2.78 mol% 1-hexene and its T_m was 123.2 °C, which are both higher than those of M4 (2.04 mol% 1-hexene and 120.4 °C, respectively). M7 had 8.73 mol% 1-hexene, which is much lower than those of M8 (14.18 mol%) and M9 (15.05 mol%). However, T_m of M7 was only 82.8 °C, which is obviously lower than those of M8 (98.1 °C) and M9 (89.0 °C). This unusual phenomenon is discussed in the succeeding section.

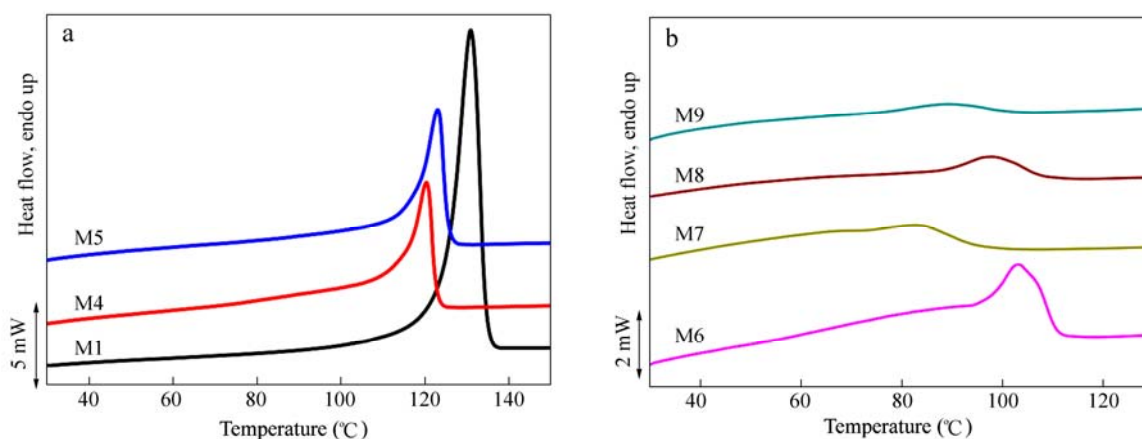


Fig. 1 DSC melting curves of the samples: (a) M1, M4 and M5, (b) M6, M7, M8, and M9

Table 2. Thermal properties of the samples

Sample	T_m (°C)	ΔH_m (J/g)	$W_{c,h}$ (%) ^a
M1	131.0	170.8	59.3
M4	120.4	92.8	32.2
M5	123.2	71.6	24.9
M6	103.2	44.0	15.3
M7	82.8	26.4	9.2
M8	98.1	9.4	3.3
M9	89.0	4.8	1.7

^a Observed heat of fusion divided by 288 J/g^[32]

MSL and Its Distribution Based on SSA Thermal Fractionation

Thermal fractionation techniques offer quick and practical ways to evaluate chain heterogeneity in semicrystalline thermoplastic materials by employing carefully designed thermal cycles in a differential scanning calorimeter. They are particularly useful in studying the degree and distribution of short-chain branches produced by the copolymerization of ethylene with α -olefins. SSA is based on the sequential application of self-nucleation and annealing steps to a polymer sample. After thermal conditioning a final DSC heating run reveals the distribution of melting points induced by the SSA treatment as a result of the heterogeneous nature of the chain structure of the polymer under analysis. The SSA curves of the samples reflect the differences in the SCB distribution of ethylene copolymers in more detail, in comparison with the DSC results.

Figure 2 shows the final DSC heating curves of the samples after the SSA thermal fractionation. The homopolymer M1 showed a main melting peak and several shoulder peaks, which were due to the formation of crystallites with different lamellar thicknesses when the sample underwent the SSA procedure. For ethylene/1-hexene copolymers (M4, M5, M6, M7, M8, and M9), SCB 1-hexene units interrupted the ethylene crystalline sequences and formed crystalline methylene sequences with different lengths. Given that the crystalline methylene sequence distribution was broad, multiple melting peaks formed during each step of isothermal crystallization. The multiple melting peaks of every sample were ascribed to intramolecular heterogeneity. The number and intensity of the melting peaks in the heating curves qualitatively showed the differences of the MSL distributions among the samples^[33, 34]. The multiple melting peaks of different samples shifted toward lower temperatures with the increase of the comonomer content, which was due to intermolecular heterogeneity. In particular, the multiple melting peaks of M7 were lower than those of M8 and M9.

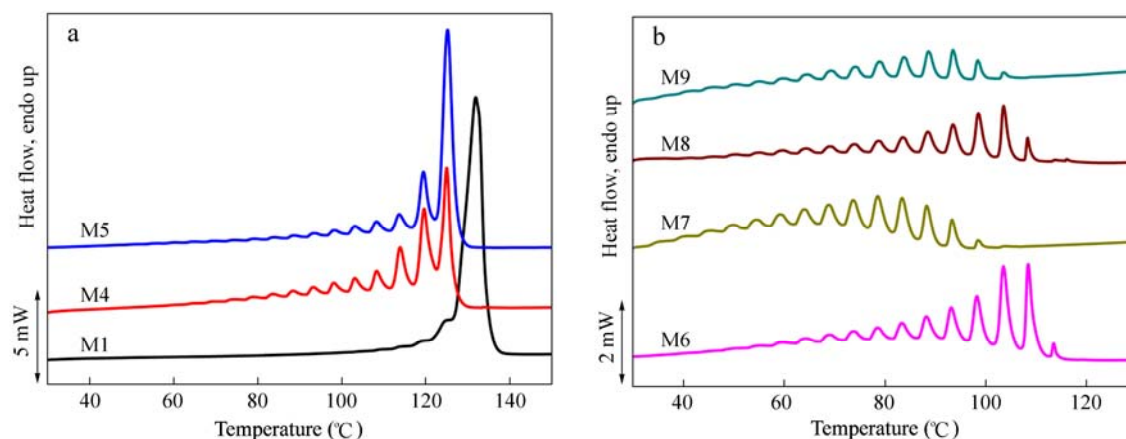


Fig. 2 DSC heating scans for samples after SSA thermal fractionation: (a) M1, M4 and M5, (b) M6, M7, M8 and M9

We used the calibration curve obtained by Zhang and Wanke to calculate the MSL for each fraction. They obtained the calibration curve that related MSL to melting temperatures, in which the curve was based on the DSC measurements after the SSA treatments. The plot of $\ln(\text{CH}_2 \text{ molar fraction})$ against $1/T$ showed a linear relationship (Eq. 1)^[26]. Based on this curve, the MSL of fractionated ethylene copolymers can be assigned through the T_m of the fractions. Moreover, the distribution curves of MSL for various copolymers were obtained.

$$\ln(\text{CH}_2 \text{ molar fraction}) = 0.3451 - 142.2/T_m \quad (1)$$

The values of CH_2 molar fraction can be converted to MSL using Eq. (2)^[26].

$$\text{MSL} = \frac{2X}{1-X}, X = \text{CH}_2 \text{ molar fraction} \quad (2)$$

The overlapped melting peak in Fig. 2 can be separated by the fitting of multiple Gaussian functions by the peak resolving software. The MSL can then be calculated using Eqs. (1) and (2). Finally, the MSL distribution maps of all samples can be drawn. The MSL distributions of M1, M4, and M5 are shown in Fig. 3. The molar percents monotonously increased with their MSL. M1 was a homopolymer and its MSL distribution focused on 334 with approximately 83%. M4 and M5 contained 2.04 mol% and 2.78 mol% 1-hexene, respectively. Although their comonomer contents were only approximately 2.0 mol%, their MSL distributions were broad, *i.e.*, from 20 to 170. Furthermore, the longest MSL of M5 was 167 and its corresponding percent was 43.95%. Meanwhile, M4 had the longest MSL of 165, which accounted for 24.55%. This result explains why M5 had higher 1-hexene content and T_m than M4.

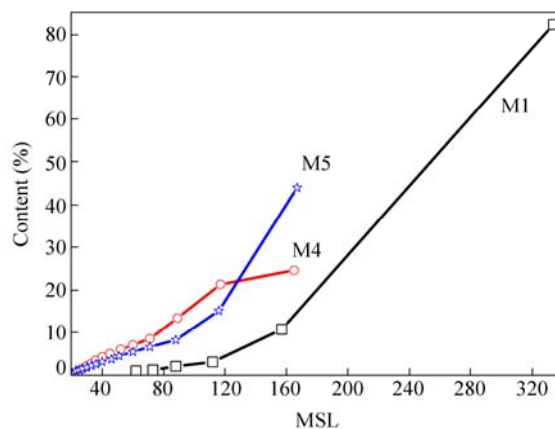


Fig. 3 MSL distributions of M1, M4 and M5

Figure 4 shows the MSL distributions of M6, M7, M8, and M9, which displayed a unimodal distribution different from those of M4 and M5. M6 had a higher peak value at 61, and its MSL varied from 19 to 87. M7 had a lower peak value at 30, and its MSL varied from 15 to 52. The peak of M8 was at 61, and its MSL varied from 16 to 71. The peak of M9 was located at 41, and its MSL varied from 15 to 61. Accordingly, 1-hexene content in these three samples (M6, M8, and M9) gradually increased but their longest MSL decreased. M7 had a lower peak value at 33 and a narrow MSL distribution, which led to a lower T_m compared with those of M8 and M9.

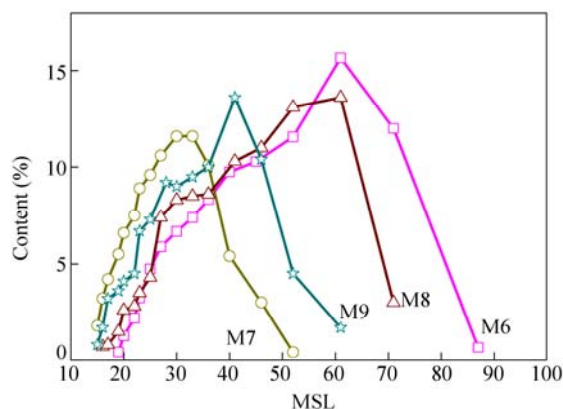


Fig. 4 MSL distributions of M6, M7, M8 and M9

According to the above results, the content and distribution homogeneity of 1-hexene (SCB) significantly affect its melting behavior. Therefore, MSL and its distribution are key factors that influence the melting behavior of copolymers.

CONCLUSIONS

The SSA method is a quick and effective thermal fractionation technique used to study the distribution of the SCB of ethylene/1-hexene copolymers. The MSL and its distribution significantly affect the melting behavior of copolymers. The average MSL and distribution of M5 and M7 significantly influenced their melting behaviors rather than the total comonomer content. Therefore, the thermal fractionation provides a facile method to analyze the structural heterogeneity of SCB ethylene/ α -olefin copolymers.

REFERENCES

- 1 Usami, T., Gotoh, Y. and Takayama, S., *Macromolecules*, 1986, 19: 2722
- 2 Xu, J., Xu, X. and Feng, L., *Eur. Polym. J.*, 1999, 36: 685
- 3 Starck, P., *Polym. Int.*, 1996, 40: 111
- 4 Zhang, F.J., Liu, J.P., Fu, Q., Huang, H.Y., Hu, Z.J., Yao, S., Cai, X.Y. and He, T.B., *J. Polym. Sci. Part B: Polym. Phys.*, 2002, 40: 813
- 5 Liu, Y.G., Bo, S.Q., Zhu, Y.J. and Zhang, W.H., *J. Appl. Polym. Sci.*, 2005, 97: 232
- 6 Gabriel, C. and Lilge, D., *Polymer*, 2001, 42: 297
- 7 Fan, Y.D., Xue, Y.H., Nie, W., Ji, X.L. and Bo, S.Q., *Polym. J.*, 2009, 41: 622
- 8 Gulmine, J.V., Janissek, P.R., Heise, H.M. and Akcelrud, L., *Polym. Test*, 2002, 21: 557
- 9 Blitz, J.P. and Mcfaddin, D.C., *J. Appl. Polym. Sci.*, 1994, 51: 13
- 10 Galland, G.B., Souza, R.F., Mauler, R.S. and Nunes, F.F., *Macromolecules*, 1999, 32: 1620
- 11 Galland, G.B., Quijada, R., Rojas, R., Bazan, G. and Komon, Z.J., *Macromolecules*, 2002, 35: 339

- 12 Lorenzo, A.T., Arnal, M.L., Müller, A.J., Fierro, A.B. and Abetz, V., *Macromol. Chem. Phys.*, 2006, 207: 39
- 13 Zhang, F.J., Fu, Q., Lv, T.J., Huang, H.Y. and He, T.B., *Polymer*, 2002, 43: 1031
- 14 Ma, Y. and Xu, M., *Chinese J. Polym. Sci.*, 2000, 18: 557
- 15 Fu, Q., Chiu, F.C., He, T.B., Liu, J.P. and Hsieh, E.T., *Macromol. Chem. Phys.*, 2001, 202: 927
- 16 Müller, A.J. and Arnal, M.L., *Prog. Polym. Sci.*, 2005, 30: 559
- 17 Arnaldo T.L., Arnal, M.L., Müller, A.J., Fierro, A.B. and Abetz, V., *Macromol. Chem. Phys.*, 2006, 207: 39
- 18 Lu, L., Alamo, R. and Mandelkern, L., *Macromolecules*, 1994, 27: 6571
- 19 Alamo, R., Chan, E. and Mandelkern, L., *Macromolecules*, 1992, 25: 6382
- 20 Keating, M., Lee, I. and Wong, C., *Thermochim. Acta.*, 1996, 284: 47
- 21 Chen, F., Shanks, R. and Amarasinghe, G., *Polym. Int.*, 2004, 53: 1795
- 22 Starck, P. and Löfgren, B., *Eur. Polym. J.*, 2002, 38: 97
- 23 Müller, A.J., Hernández, Z.H., Arnal, M.L. and Sánchez, J.J., *Polym. Bull.*, 1997, 39: 465
- 24 Cho, T.Y., Heck, B. and Strobl, G., *Colloid. Polym. Sci.*, 2004, 282: 825
- 25 Arnaldo, T. L., Arnal, M.L., Müller, A.J., Lin, M.C. and Chen, H.L., *Chem. Phys.*, 2011, 212: 2009
- 26 Zhang, M.Q. and Wanke, S.E., *Polym. Eng. Sci.*, 2003, 43: 1878
- 27 Kong, J., Fan, X.D., Xie, Y.C. and Qiao, W.Q., *J. Appl. Polym. Sci.*, 2004, 94: 1710
- 28 Müller, A.J., Lorenzo, A.T. and Arnal, M.L., *Macromol. Symp.*, 2009, 277: 207
- 29 Fillon, B., Wittmann, J.C., Lotz, B. and Thierry, A., *J. Polym. Sci. Part B: Polym. Phys.*, 1993, 31: 1383
- 30 Bensason, S., Minick, J., Moet, A., Chum, S., Hiltner, A. and Baer, E., *J. Polym. Sci. Part B: Polym. Phys.*, 1996, 34: 1301
- 31 Sarzotti, D.M., Soares, J. and Penlidis, A., *J. Polym. Sci. Part B: Polym. Phys.*, 2002, 40: 2595
- 32 Mirabella, F.M. and Bafna, A., *J. Polym. Sci. Part B: Polym. Phys.*, 2002, 40: 1637
- 33 Zhang, M., Lynch, D.T. and Wanke, S.E., *Polymer*, 2001, 42: 3067
- 34 Du, Z.X., Xu, J.T., Dong, Q. and Fan, Z.Q., *Polymer*, 2009, 50: 2510