

CRYSTALLIZATION KINETICS OF ETHYLENE-PROPYLENE COPOLYMERS PREPARED BY LIVING COORDINATION POLYMERIZATION*

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Abstract In this paper, crystallization kinetics of a series of ethylene-propylene copolymers prepared by living polymerization coordination catalyzed by a fluorinated bis(phenoxyimine) Ti catalyst (FI-EP copolymers) was studied, and was compared with that of ethylene-propylene copolymers prepared by a conventional Ziegler-Natta catalyst (ZN-EP copolymers). It is found that, the Avrami exponent and the crystallization rate constant of the FI-EP and ZN-EP copolymer show similar dependence on crystallization temperature, but the FI-EP copolymers exhibit a larger Avrami exponent than corresponding ZN-EP copolymers at high crystallization temperature and at low propylene content level. The crystallization temperature, equilibrium melting temperature and crystallinity of the FI-EP copolymers decrease more rapidly with propylene content than those of the ZN-EP copolymers. This can be attributed to their different comonomer distributions and partially to the different molecular weight distributions at low propylene content level.

Keywords: Comonomer distribution; Crystallization; Ethylene-propylene copolymer.

INTRODUCTION

For ethylene- α -olefin copolymers, short chain branching distribution is an important structure parameter, since it has a great influence on crystallization behavior and mechanical properties of the ethylene- α -olefin copolymers. For example, ethylene copolymers prepared by metallocene catalysts usually have a more homogeneous comonomer distribution than those prepared by conventional Ziegler-Natta catalysts, thus at the same comonomer content level, metallocene-based ethylene copolymers may exhibit a different crystallization behavior and better mechanical property of toughness^[1–23]. Compared with other ethylene- α -olefin copolymers, the effect of comonomer distribution on crystallization behavior of ethylene-propylene copolymers is rarely reported^[24]. The major difference between ethylene-propylene copolymer and other ethylene- α -olefin copolymers is that the methyl branches can be easily incorporated into the crystal lattice of polyethylene, whereas other branches bulkier than methyl are difficult to be incorporated^[25–30]. However, we speculate that short chain branching distribution still can exert effect on crystallization behavior of ethylene-propylene copolymers. To verify this speculation, in the present work two series of ethylene-propylene copolymers with different propylene contents were prepared by a fluorinated bis(phenoxyimine) Ti catalyst (FI-EP copolymers)^[31, 32] and a conventional Ziegler-Natta catalyst (ZN-EP copolymers), respectively. The FI-EP copolymers have a narrow molecular weight distribution and a random comonomer distribution^[33], while the ZN-EP copolymers have a heterogeneous comonomer distribution. The crystallization kinetics of FI-EP and ZN-EP copolymers were compared.

* This work was supported by the National Basic Research Program of China (No. 2005CB623804).

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Oral lecture presented at the Asian Polyolefin Workshop 2007, 2007, Hangzhou, China

Received March 13, 2008; Revised May 5, 2008; Accepted May 8, 2008

EXPERIMENTAL

Synthesis of Ethylene-Propylene Copolymers

Copolymerization of ethylene and propylene catalyzed by a fluorinated bis(phenoxyimine) Ti (FI) catalyst was described elsewhere^[33]. Copolymerization was carried out at 25°C under atmospheric pressure in a 100 mL glass reactor equipped with a propeller-like stirrer and thermostat water bath. Toluene (50 mL) was introduced into the nitrogen-purged reactor and stirred (600 r/min), then the ethylene/propylene mixed gas were rapidly bubbled through the reactor. The flow rates of ethylene and propylene were regulated to levels that are much larger than the monomer consumption rate during the polymerization, so the monomer concentrations in the solution can be kept at a constant level. After 10 min, polymerization was initiated by adding a toluene solution of MAO (1.0 mol/L, 4.0 mL) and then a toluene solution of catalyst (10 mmol/L, 1.0 mL) into the reactor with stirring (600 r/min). Polymerization was terminated by addition of *sec*-butyl alcohol (10 mL), followed by introduction of ethanol (250 mL) and concentrated HCl (2 mL). The polymer was collected by filtration, washed with ethanol (200 mL), and dried in vacuum at 80°C overnight. Copolymers with different propylene content were prepared by changing the flow rates of ethylene and propylene.

Ethylene-propylene copolymers were also prepared by a conventional Ziegler-Natta (ZN) catalyst in a similar way. The catalyst is $\text{TiCl}_4/\text{MgCl}_2/\text{SiO}_2/\text{di-butyl phthalate}$ with a Ti content of 3.0 wt%. The concentration of the ZN catalyst was 0.5 mg/mL. The cocatalyst was AlEt_3 ($x(\text{Al})/x(\text{Ti}) = 150$) and dimehtoxy diphenyl silane was used as external donor ($x(\text{Si})/x(\text{Ti}) = 7.5$).

The ethylene-propylene copolymers prepared by FI and ZN catalysts are denoted as FI-EP and ZN-EP copolymers, respectively. The molecular weight, molecular weight distribution and propylene content are listed in Table 1.

Table 1. Molecular weight, molecular weight distribution and propylene content for FI-EP and ZN-EP copolymers^a

Samples	E/P feed ratio (mL/min) ^b	$M_w \times 10^{-3}$	M_w/M_n	[P] (mol%)	T_c (°C)
FI-EP0	300/0	239.7	1.29	0	116.8
FI-EP1	600/300	76.5	1.27	2.12	110.3
FI-EP2	300/60	17.11	1.27	5.09	91.8
FI-EP3	300/150	16.55	1.25	8.08	86.6
FI-EP4	300/300	13.25	1.19	11.40	67.3
FI-EP5	300/600	11.57	1.16	14.93	nd
ZN-EP1	400/30	247.3	28.1	2.40	108.1
ZN-EP2	400/40	410.1	46.6	5.55	108.1
ZN-EP3	300/40	339.3	39.0	8.00	107.8
ZN-EP4	300/100	366.5	24.6	11.62	105.8
ZN-EP5	150/50	186.9	25.6	14.76	104.8

^a Polymerization conditions for FI-EP copolymers: $[\text{Ti}] = 10.0 \mu\text{mol}$, $x(\text{Al})/x(\text{Ti}) = 400$, 0.1 MPa, 50 mL toluene, 25°C, polymerization time $t_p = 5$ min; Polymerization conditions for ZN-EP copolymers: 40 mg Ziegler-Natta catalyst, $x(\text{Al})/x(\text{Ti}) = 150$, $x(\text{Si})/x(\text{Ti}) = 7.5$, 0.1 MPa, 80 mL *n*-heptane, 60°C, polymerization time $t_p = 30$ min;

^b Flow rate of ethylene and propylene feeds

Characterization

Molecular weight and molecular weight distribution of the ethylene-propylene copolymers were measured by GPC in a PL 220 GPC instrument (Polymer Laboratories Ltd.) at 150°C in 1,2,4-trichlorobenzene. Three PL mixed-B columns (500–107) were used. Universal calibration against narrow polystyrene standards was adopted. Quantitative ^{13}C -NMR spectra were recorded on a Varian Mercury 300-plus spectrometer at 120°C in 100 g/L solution of *o*- $\text{C}_6\text{D}_4\text{Cl}_2$. $\text{Cr}(\text{acac})_3$ was used to reduced the relaxation time of carbon atoms and the delay time was set as 3 s. The pulse angle was 90°, and 8000 scans were collected.

Differential Scanning Calorimetry (DSC)

DSC analysis was performed on a Perkin-Elmer Pyris-1 DSC calorimeter. The polymer samples were heated to

200°C and held for 5 min to remove thermal history. Subsequently the samples were cooled to pre-set crystallization temperature at a rate of 100 K/min to complete crystallization. After crystallization, the samples were heated to 180°C at a rate of 10 K/min.

RESULTS AND DISCUSSION

Isothermal Crystallization Kinetics

The isothermal crystallization temperatures were chosen based on non-isothermal crystallization. The crystallization peak temperatures for the FI-EP and ZN-EP copolymers, which are obtained by cooling the polymer samples from 200°C at a cooling rate of 10 K/min, are listed in Table 1. One can see that the crystallization temperature of the FI-EP copolymers decreases rapidly as the propylene content increases, and thus the crystallization temperature varies in a wide range. For FI-EP5, even no crystallization peak is detected in non-isothermal crystallization. As a result, for FI-EP copolymers isothermal crystallization is only conducted for four samples (from FI-EP1 to FI-EP4). In contrast, the crystallization temperature of the ZN-EP copolymers varies in a limited range (4°C). This is mainly due to the presence of long crystallization segments in all ZN-EP copolymers and the length of these segments almost does not change with increasing in propylene content, whereas the crystallizable segments becomes shorter gradually as the propylene content increases^[34].

The isothermal crystallization kinetics of the ethylene-propylene copolymers can be interpreted in terms of Avrami equation^[35]:

$$1 - X(t) = \frac{\Delta H_{t=\infty}^c - \Delta H_t^c}{\Delta H_{t=\infty}^c - \Delta H_{t=0}^c} = \exp(-Kt^n) \quad (1)$$

Where $X(t)$ is the relative crystallinity at time t , $\Delta H_{t=\infty}^c$, $\Delta H_{t=0}^c$ and ΔH_t^c are the crystallization enthalpies on complete crystallization, at $t = 0$ and after time t , respectively. Therefore, we have:

$$\ln[-\ln(1 - X(t))] = \ln K + n \ln t \quad (2)$$

The crystallization rate constant K and Avrami exponent n can be determined from the intercept and slope in the plot of $\ln[-\ln(1 - X(t))]$ versus $\ln t$, respectively.

The derived Avrami exponents and crystallization rate constants are shown in Figs. 1 and 2, respectively. It is found that, as crystallization temperature increases, the Avrami exponent increases but the crystallization rate constant decreases, which is a common trend for all the FI-EP and ZN-EP copolymers. For ZN-EP copolymers,

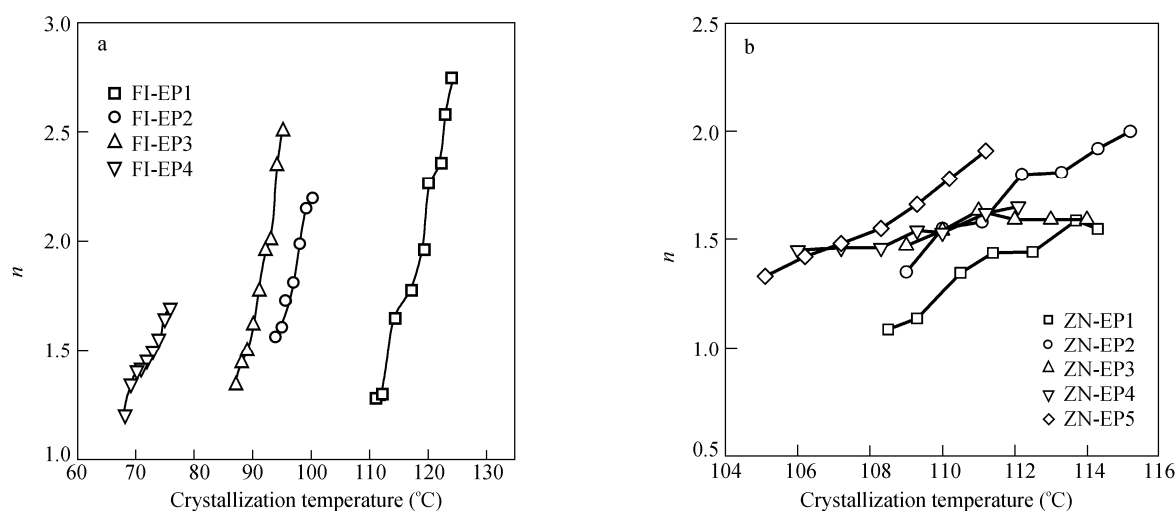


Fig. 1 Avrami exponents for FI-EP copolymers (a) and ZN-EP copolymers (b) at various crystallization temperatures

the Avrami exponent varies between 1.0 and 2.0 in the crystallization temperature range studied. In contrast, The Avrami exponent of the FI-EP copolymers with lower propylene content can exceed 2.0 at higher crystallization temperatures.

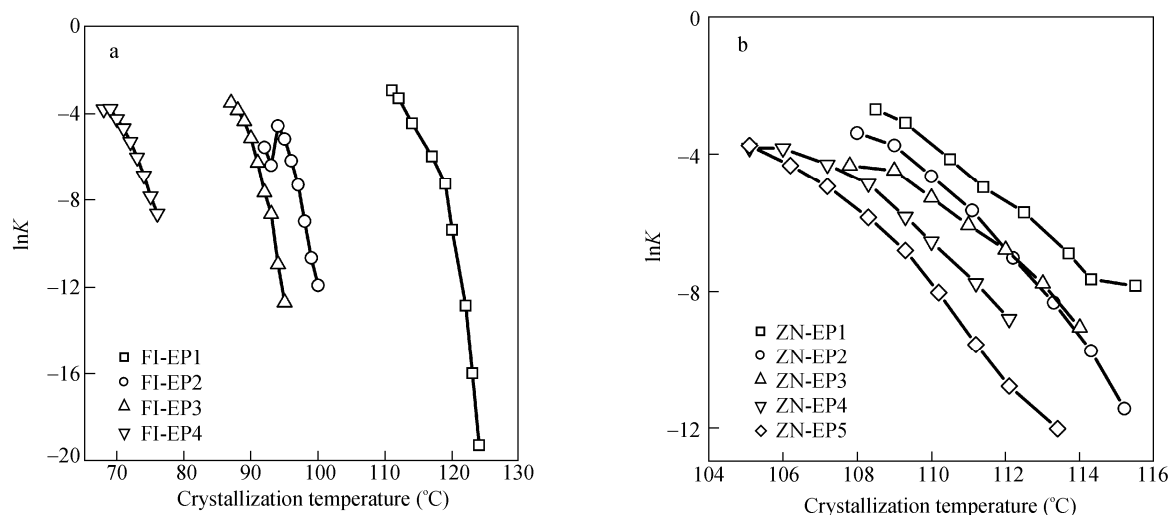


Fig. 2 Plots of $\ln K$ versus crystallization temperature for FI-EP copolymers (a) and ZN-EP copolymers (b)

Crystallinity

The crystallinity of the ethylene-propylene copolymers (X_c) was calculated from the fusion enthalpy according to following equation:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100\% \quad (3)$$

Where ΔH_f is the measured fusion enthalpies for the ethylene-propylene copolymers and ΔH_f^0 is the fusion enthalpies of perfect polyethylene (289 J/g).

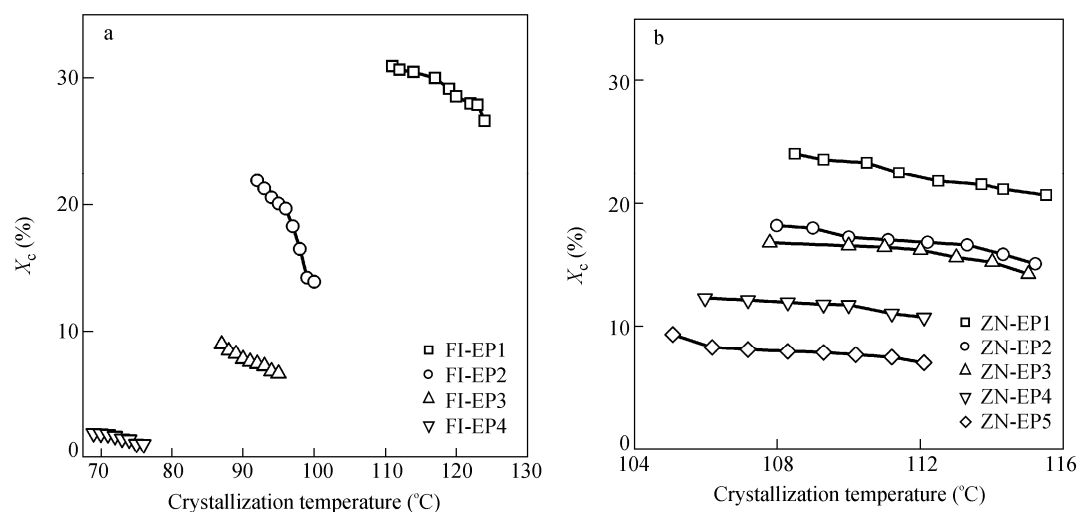


Fig. 3 Crystallinity of FI-EP copolymers (a) and ZN-EP copolymers (b) at various crystallization temperatures

Figure 3 shows crystallinity of the FI-EP and ZN-EP copolymers after isothermal crystallization at different crystallization temperatures. It is found that crystallinity decreases as crystallization temperature increases for all FI-EP and ZN-EP copolymers. This is because there exist crystallizable segments of different lengths, which have different crystallizability in both FI-EP and ZN-EP copolymers. The shorter crystallizable segments with weaker crystallizability can not crystallize at higher crystallization temperatures, leading to lower crystallinity. Examining crystallinity of the copolymers with different propylene content, one can see that crystallinity of the FI-EP copolymers decreases with propylene content more rapidly than the ZN-EP copolymers. For the FI-EP copolymers, crystallinity changes from 30% of FI-EP1 ([P] = 2.1 mol%) to about zero of FI-EP4 ([P] = 11.4 mol%), while for the ZN-EP copolymers, crystallinity changes from 25% of ZN-EP1 ([P] = 2.40 mol%) to 8% of ZN-EP5 ([P] = 14.76 mol%). At low propylene content level the FI-EP copolymers have higher crystallinity than the ZN-EP copolymers, but at high propylene content level the crystallinity of the FI-EP copolymers is lower than that of the ZN-EP copolymers, when the FI-EP and ZN-EP copolymers have similar propylene content. This difference mainly arises from the different comonomer distributions of the FI-EP and ZN-EP copolymers. Our previous results show that the FI-EP copolymers have a random comonomer distribution, but the ZN-EP copolymers have a blocky comonomer distribution^[34]. In the ZN-EP copolymers, there are segments of weak crystallizability (high local propylene content) even at low propylene content level, leading to their lower crystallinity, but at high propylene content level the ZN-EP copolymers still contains some segments of strong crystallizability (low local propylene content), leading to their higher crystallinity. On the other hand, we also notice that the ZN-EP copolymers have a much broader molecular weight distribution than the corresponding FI-EP copolymers. As a result, there are polymer fractions of low molecular weight ($< 10^4$) in the ZN-EP copolymers, which may also partially responsible for the lower crystallinity of ZN-EP copolymers at low propylene content level.

Equilibrium Melting Temperature

Figure 4 shows the plots of crystallization temperature (T_c) versus melting temperature (T_m) for the FI-EP and ZN-EP copolymers. Based on Hoffman-Weeks equation^[36], the equilibrium melting temperature (T_m^0) of the polymers can be obtained by extrapolating this plot to $T_c = T_m = T_m^0$:

$$T_m = (1 - 1/\gamma)T_m^0 + T_c/\gamma \quad (4)$$

Where γ is the ratio of the crystal thickness to the thickness of the initial nucleus at crystallization temperature T_c .

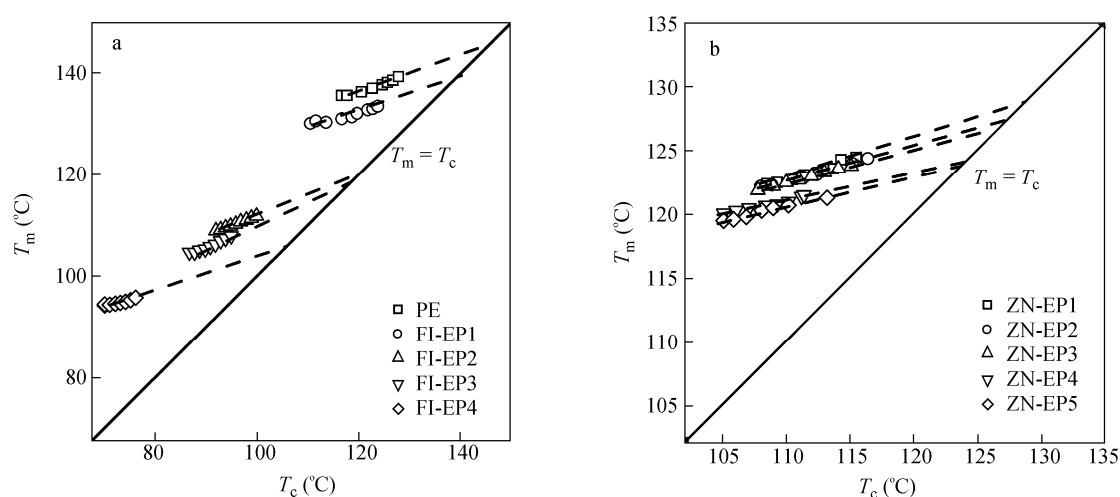


Fig. 4 Plots of melting temperatures versus crystallization temperature for FI-EP copolymers (a) and ZN-EP copolymers (b)

The extrapolated equilibrium melting temperatures for all FI-EP and ZN-EP copolymers are shown in Fig. 5. One can see that, the equilibrium melting temperature of the FI-EP copolymers decreases with propylene content more rapidly than that of the ZN-EP copolymers, which similar to the crystallization temperature. This is also due to the presence of long crystallizable segments in the ZN-EP copolymers, which become shorter very slowly as propylene content increases. However, when the lines in Fig. 5 are extrapolated to zero propylene content, we can find that the neat PEs from FI and ZN catalyst have different equilibrium melting temperatures. This can be attributed to their different molecular weight distributions, *i.e.* the presence of fractions with low molecular weight in the ZN-PE.

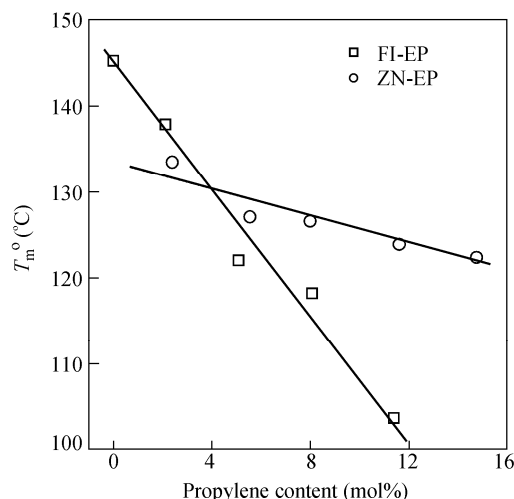


Fig. 5 Change of equilibrium melting temperature with propylene content for FI-EP and ZN-EP copolymers

CONCLUSIONS

Our results show that crystallization behavior of ethylene-propylene copolymers is affected by the comonomer distribution. The FI-EP copolymers, which have a random comonomer distribution, exhibit a larger Avrami exponent at high crystallization temperature and low propylene content level. The ZN-EP copolymers, which have a blocky comonomer distribution, exhibit smaller crystallinity, lower T_c and T_m at low propylene content level due to the presence of short crystallizable segment with weak crystallizability, while at high propylene content level the ZN-EP copolymers have larger crystallinity, higher T_c and T_m due to the presence of long crystallizable segment with strong crystallizability. Their different molecular weight distributions are also partially responsible for these differences, especially at low propylene content.

REFERENCES

- 1 Sehanobish, K., Patel, R.M., Croft, B.A., Chum, S.P. and Kao, C.I., *J. Appl. Polym. Sci.*, 1994, 51: 887
- 2 Kennedy, M.A., Peacock, A.J., Failla, M.D., Lucas, J.C. and Mandelkern, L., *Macromolecules*, 1995, 28: 1407
- 3 Graham, J.T., Alamo, R.G. and Mandelkern, L., *J. Polym. Sci. Part B: Polym. Phys.*, 1997, 35: 213
- 4 Gaucher-Miri, V., Elkoun, S. and Seguela, R., *Polym. Eng. Sci.*, 1997, 37: 1672
- 5 Marigo, A., Zannetti, R. and Milani, F., *Eur. Polym. J.*, 1997, 33: 595
- 6 Simanke, A.G., Galland, G.B., Neto, R.B., Quijada, R. and Mauler, R.S., *J. Appl. Polym. Sci.*, 1999, 74: 1194
- 7 Xu, J.T., Xu, X.R., Chen, L.S. and Feng, L.X., *J. Mater. Sci. Lett.*, 2000, 19: 1541
- 8 Xu, X.R., Xu, J.T., Feng, L.X. and Chen, W., *J. Appl. Polym. Sci.*, 2000, 77: 1709
- 9 Xu, J.T., Xu, X.R., Feng, L.X., Chen, L.S. and Chen, W., *Macromol. Chem. Phys.*, 2001, 202: 1524

- 10 Xu, J.T., Xu, X.R., Chen, L.S., Feng, L.X. and Chen, W., *Polymer*, 2001, 42: 3867
- 11 Xu, X.R., Xu, J.T. and Feng, L.X., *Polym. Int.*, 2002, 51: 458
- 12 Xu, J.T., Li, B.T., Fan, Z.Q. and Ryan, A.J., *Chinese J. Polym. Sci.*, 2004, 22: 279
- 13 Shan, C.L.P., Soares, J.B.P. and Penlidis, A., *Polymer*, 2002, 43: 767
- 14 Hussein, I.A., *Macromolecules*, 2003, 36: 2024
- 15 Mirabella, F.M. and Crist, B., *J. Polym. Sci. Part B: Polym. Phys.*, 2004, 42: 3416
- 16 Islam, M.A., Hussein, I.A. and Atiqullah, M., *Eur. Polym. J.*, 2007, 43: 599
- 17 Fu, Q., Chiu, F.C., McCreight, K.W., Guo, M.M., Tseng, W.W., Cheng, S.Z.D., Keating, M.Y., Hsieh, E.T. and DesLauriers, P.J., *J. Macromol. Sci.-Phys.*, 1997, B36: 41
- 18 Zhang, F.J., Liu, J.P., Xie, F.C., Fu, Q. and He, T.B., *J. Polym. Sci. Part B: Polym. Phys.*, 2002, 40: 822
- 19 Zhang, F.J., Song, M., Lu, T.J., Liu, J.P. and He, T.B., *Polymer*, 2002, 43: 1453
- 20 Wang, H.P., Khariwala, D.U., Cheung, W., Chum, S.P., Hiltner, A. and Baer, E., *Macromolecules*, 2007, 40: 2852
- 21 Peng, Y. and Fu, Q., *Chinese J. Polym. Sci.*, 2004, 22: 431
- 22 Teng, H.X., Tang, W.H., Shi, Y. and Jin, X.G., *Chinese J. Polym. Sci.*, 2002, 20: 339
- 23 Teng, H.X., Shi, Y., Jin, X.G. and Cheng, S.Z.D., *Chinese J. Polym. Sci.*, 2002, 20: 347
- 24 Zhang, M.Z. and Duhamel, J., *Macromolecules*, 2007, 40: 661
- 25 Bassi, I.W., Corradini, P., Fagherazzi, G. and Valvassori, A., *Eur. Polym. J.*, 1970, 6: 709
- 26 Shirayama, K., Kita, S. and Watabe, H., *Makromol. Chem.*, 1972, 151: 97
- 27 Pérez, E. and Vanderhart, D.L., *J. Polym. Sci. Part B: Polym. Phys.*, 1987, 25: 1637
- 28 Hosoda, S., Nomura, H., Gotoh, Y. and Kihara, H., *Polymer*, 1990, 31: 1999
- 29 Bracco, S., Comotti, A., Simonutti, R., Camurati, I. and Sozzani, P., *Macromolecules*, 2002, 35: 1677
- 30 Hu, W.G., Srinivas, S. and Sirota, E.B., *Macromolecules*, 2002, 35: 5013
- 31 Mitani, M., Mohri, J., Yoshida, Y., Saito, J., Ishii, S., Tsuru, K., Matsui, S., Furuyama, R., Nakano, T., Tanaka, H., Kojoh, S., Matsugi, T., Kashiwa, N. and Fujita, T., *J. Am. Chem. Soc.*, 2002, 124: 3327
- 32 Mitani, M., Furuyama, R., Mohri, J., Saito, J., Ishii, S., Terao, H., Nakano, T., Tanaka, H. and Fujita, T., *J. Am. Chem. Soc.*, 2003, 125: 4293
- 33 Du, Z.X., Xu, J.T., Wang, X. and Fan, Z.Q., *Polym. Bull.*, 2007, 58: 903
- 34 Du, Z. X., Thesis, Zhejiang University, 2007
- 35 Avrami, M., *J. Chem. Phys.*, 1939, 7: 1103
- 36 Hoffman, J.D. and Weeks, J.J., *J. Res. Natl. Bur. Stand.*, 1962, 66A: 13