

On the Melting Behavior of Isothermally Crystallized 1-Octene Linear Low-Density Polyethylene Copolymers

CRISTIAN C. PUIG,¹ MARIA V. AVILÉS,¹ PABLO JOSKOWICZ,² ANTONIO DÍAZ B.²

¹ Grupo de Polímeros USB, Departamento de Ciencias de los Materiales, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

² PDVSA-INTEVEP, Los Teques, Apartado 76343, Caracas 1070-A, Venezuela

Received 24 January 2000; accepted 7 June 2000

ABSTRACT: The melting behavior of two 1-octene linear low-density polyethylene (LLDPE) copolymers is investigated. One made using Dow's INSITE constrained geometry catalyst technology (LLDPE-A) and the other using titanium-based Ziegler–Natta catalysts (LLDPE-B). Both have similar comonomer content as well as melt flow index. Differential scanning calorimetry (DSC) was used throughout the work. Isothermal crystallizations in the DSC for several times were carried out at various temperatures between 90 and 100°C for LLDPE-A and between 105 and 112.5°C for LLDPE-B. As a result of the isothermal crystallizations for both copolymers, multiple melting peaks are found in the DSC traces on subsequent heating. The melting behavior was also examined as a function of heating rate (1, 2.5, 5, 10, and 20°C/min). The multiple melting behavior indicates that they are inhomogeneous. In addition, a melting–recrystallization process was shown to be responsible for the appearance of one of the melting peaks in LLDPE-B. A lowering in heating rate from the crystallization temperature favors the occurrence of melting–recrystallization during the dynamic experiment. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2022–2028, 2001

Key words: linear low-density polyethylene; crystallization; melting–recrystallization; heterogeneous comonomer distribution

INTRODUCTION

Linear low-density polyethylene (LLDPE) resins are copolymers of ethylene and α -olefins, such as propene, 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene. The early work by Wild et al.¹ showed that when molecular species of a LLDPE, prepared using titanium-based Ziegler–Natta catalyst systems, are separated according to their crystallizabilities using a temperature rising elution fractionation (TREF) technique, a broad het-

erogeneous comonomer distribution is found. Some polymer molecules are almost completely free of comonomer while others contain extremely high comonomer levels. Same structural differences were found for other traditional LLDPE resins.^{2–14} Distributions of short chain branches were bimodal^{1,3,4,6,8,12–14} and trimodal.^{5,7}

TREF is a fractionation technique that is very little influenced by the polydispersity of the sample. When used in conjunction with other techniques that fractionates the polymer by molecular weight, it was found that in LLDPE high molecular weight fractions on average contain less short branches than the lower molecular weight fractions.^{2,3,5–7,9–13,15,16} It was also shown that at

Correspondence to: C. C. Puig (cpuig@usb.ve).

Journal of Applied Polymer Science, Vol. 79, 2022–2028 (2001)
© 2001 John Wiley & Sons, Inc.

high branching contents, comonomeric units in LLDPE are not uniformly distributed, leading to some degree of short chain branching blockiness in the chain.^{2,6,7,11–13} Then, LLDPE prepared by titanium-based Ziegler–Natta catalyst systems may show two kinds of inhomogeneity: intra- and intermolecular heterogeneity. Large differences in chain to chain heterogeneity are thought to be responsible for liquid–liquid phase separation in LLDPE^{17–19} as well as for its extraordinary fracture toughness.^{8,20,21}

Multiple melting peaks obtained by thermal analysis techniques of conventional LLDPE resins are the result of their heterogeneous molecular structure.^{6,12} Hosoda et al.²² and Defoor et al.²³ recognized by transmission electron microscopy a broad distribution of lamellar thickness and two well-differentiated populations of lamellae for LLDPE. This was associated with the broad chemical composition. Voigt-Martin et al.²⁴ had already shown for hydrogenated polybutadiene that as the concentration of the branches increases the lamellae became thinner. As a result of the small thickness of lamellae in branched polyethylene, a melting–recrystallization process may occur on heating.²⁵

Homogeneous LLDPE copolymers may be produced using Ziegler–Natta vanadium catalysts,^{26,27} metallocene catalysts,²⁸ or Dow's INSITE constrained geometry catalyst technology (CGCT).²⁹ These resins differ from conventional LLDPEs in having narrower molecular weight and composition distributions.^{29–33} Recent reports suggest that metallocene-based LLDPE may still show some intermolecular compositional inhomogeneity.^{34,35}

Single-peaked melting temperature distributions are obtained for LLDPE prepared by vanadium based catalysts,²⁷ metallocene catalysts,³⁶ and the Dow's INSITE constrained geometry catalyst technology.³⁷

A recent report classified the crystalline structures developed by CGCT ethylene–octene copolymers, of different comonomer content, into four categories. The crystalline structures varied from granular morphology for low crystalline copolymers to materials with well developed spherulitic superstructure.³⁸ Keating and Lee recently carried out a comparative study on the physical properties exhibited by commercially available metallocene and Ziegler–Natta polyethylenes. The authors concluded that the average crystallizable ethylene lengths in Ziegler–Natta 1-octene and 1-butene copolymers were at least two times

Table I Characteristics of Both 1-Octene LLDPE Resins

Characteristic	LLDPE-A	LLDPE-B
Origin	CGCT	Titanium based Ziegler–Natta
Comonomer content (mol %)	4	3
Density (kg/m ³)	907	917
Melt flow index (g/10 min)	1.1	0.9
	190/2.16	

longer than their metallocene counterparts at the same composition.³⁹

The melting behavior of a CGCT 1-octene copolymer as a function of crystallization temperature and time, and heating rate is investigated using differential scanning calorimetry in this work. The study also involved the use of a traditional 1-octene copolymer, having approximately the same comonomer content and melt flow index as the CGCT copolymer. Melting behaviors of these commercially available copolymers were examined by heating the samples from the crystallization temperature. As a result of isothermal treatments, two separate crystallization processes took place at T_c for both types of copolymers. This indicates that even for the CGCT copolymer there must be some structural heterogeneity in the material responsible for the formation of two lamellar populations. In addition, the traditional copolymer shows evidence of melting–recrystallization processes taking place during heating in differential scanning calorimetry (DSC).

EXPERIMENTAL

Two 1-octene LLDPE copolymers, whose characteristics are shown in Table I, were used. Both copolymers are commercially available, one is produced by Dow's INSITE constrained geometry catalyst technology (LLDPE-A) whereas the other by Ziegler–Natta titanium-based catalysts (LLDPE-B).

The melting behavior of isothermally crystallized copolymer samples was studied. A Perkin-Elmer DSC-7 was used for all thermal treatments. The copolymers were held at 160°C for 15 min and then cooled to the crystallization temper-

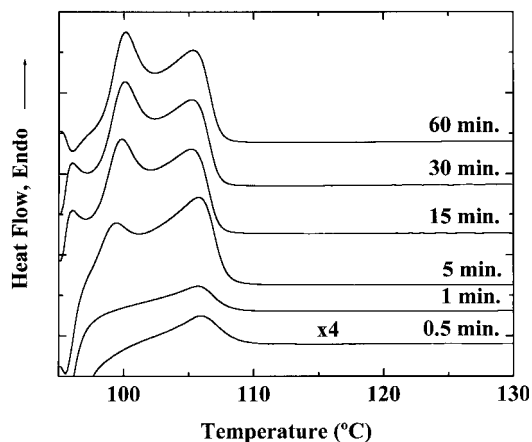


Figure 1 DSC heating thermograms from T_c of LLDPE-A after crystallizing at 95°C for various times.

ature (T_c) at 60°C/min. For LLDPE-A, the T_c used are 105, 107.5, 110, and 112.5°C and for LLDPE-B, these are 90, 92.5, 95, 97.5, and 100°C. Storage at T_c varied and lasted no longer than 60 min. Finally, the materials were heated from T_c using various rates (1, 5, 10, and 20°C/min). The DSC was used under a high purity nitrogen atmosphere and calibrated with the onset melting temperatures of indium and tin, and enthalpy of fusion of indium for each heating rate. The DSC traces are normalized to a constant mass of 1 mg.

RESULTS AND DISCUSSION

The melting behavior of LLDPE-A obtained at 10°C/min, after crystallization at 95°C for various times, is shown in Figure 1. Double melting peaks at ~100 and ~105.7°C are shown for crystallization times of 5 min or longer. At earlier stages the low melting peak is not observed, it develops later with storage at 95°C. The high melting peak is observed initially and its height becomes constant while the low melting peak continues to develop. The position of each melting peak remains constant as crystallization progresses.

The origin of double melting peaks in Figure 1 may be explained either by the presence of two populations of crystals of different thermal stabilities formed at T_c or by melting–recrystallization processes that occur on heating in the DSC.

Crystal populations with different thermal stabilities, as revealed by the presence of multiple melting endotherms in DSC thermograms, can also be formed when segregation effects at T_c

occur either by the presence of lower molecular weight material⁴⁰ or by the presence of molecules of higher degree of branching,⁴¹ and the material is cooled after completion of the isothermal treatment. Thermal segregation techniques used in branched polyethylenes are based on the selective crystallization of sequences between branch points of different length on isothermal crystallization, i.e., less branched molecules form more stable crystals and crystallize at higher temperatures. Uncompleted crystallization at T_c may also explain the presence of bimodal melting behavior on subsequent heating. Annealing of quenched branched polyethylene may also produce multiples melting peaks because of the different thermal histories of crystals, as shown by Minick et al.⁴² All treatments involve growth of crystals under more than one condition. The DSC melting endotherms, shown in Figure 1, are obtained on heating from T_c ; therefore, no additional cooling steps are carried out that could contribute to explain the presence of other crystal populations.

In order to investigate whether the origin of the multiple endotherms observed in Figure 1 is due to melting–recrystallization processes or to some structural heterogeneity present in the copolymer, a heterogeneous Ziegler–Natta titanium ethylene–octene copolymer (LLDPE-B) of similar comonomer content and melt flow index was used. It had already been reported in the past for this copolymer that melting–recrystallization occurs on heating.⁴³

Figure 2 shows DSC heating traces of LLDPE-B after storage at various T_c 's for 60 min. Multiple melting peaks are observed in the DSC traces. In this type of copolymer, it has already been

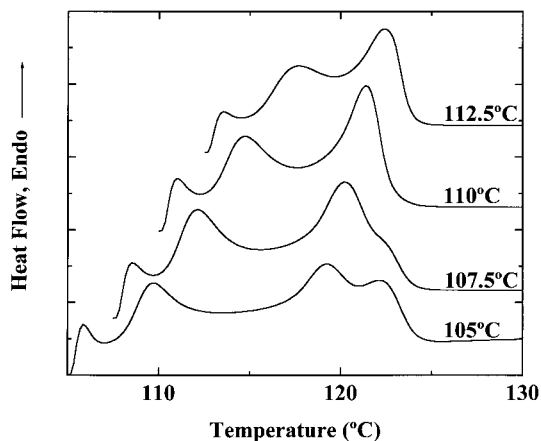


Figure 2 DSC heating thermograms from various T_c of LLDPE-B after crystallizing for 60 min.

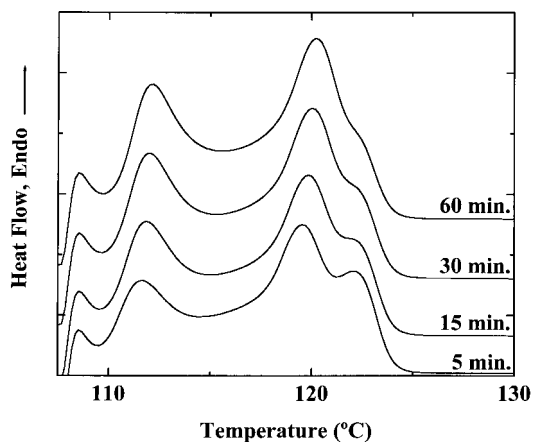


Figure 3 DSC heating thermograms from T_c of LLDPE-B after crystallizing at 107.5°C for various times.

shown that the heterogeneous intermolecular distribution of the comonomer, giving rise to different lamellar populations, is responsible for multiple melting endotherms.⁶ The comonomer is nonrandomly distributed along the chain and the amount of comonomer is a function of molecular weight. This is a result of the various kinds of active center with different activity in the polymerization with traditional high activity Ziegler-Natta catalysts.³

It is observed that by increasing the crystallization temperature the DSC traces became bimodal. The highest melting peak disappears not only with an increase in crystallization temperature but as crystallization progresses at T_c . Figure 3 shows the DSC heating traces of LLDPE-B after storage at 107.5°C for various times. It is observed that the highest melting peak located at ~122°C, clearly shown at low crystallization times, tends to disappear as time increases. Results from Figures 2 and 3 indicate that the origin of the third and highest melting peak might be related with the metastability of lamellar crystal structures formed at T_c and how close to their thermodynamic limit melt. Therefore, the occurrence of the phenomenon must depend on the heating rate used to study the melting behavior. Peeters et al. recently indicated that the time spent at a certain temperature on a dynamic experiment, given by a constant rate, along with the previous thermal history of the sample determine the magnitude of the melting–recrystallization processes.⁴⁴ Figure 4 demonstrates precisely that by showing the DSC heating traces of LLDPE-B after storage at 110°C for 60 min and heated from T_c at various rates. Results show that with de-

creasing heating rate a third peak appears at higher temperatures (~123.5°C). Its magnitude increases when the heating rate is lowered. These results, therefore, confirm that the origin of that peak in LLDPE-B is due to melting–recrystallization processes that occur during heating. This phenomenon is prone to happen for lamellae formed at lower crystallization temperatures (Fig. 2) and for short crystallization times (Fig. 3). At lower temperatures, the crystallization of the longest methylene sequences is fast and the segments in the crystals once melted (the intermediate peak) recrystallize during heating to form more stable lamellae that melt at higher temperatures. By increasing crystallization time, lamellae become stable through a process of lamellar thickening; for lamellae formed at 107.5°C there is an increase in their melting temperature from 119.5 to 120.2°C in about one hour. Yadav and Jain studied the process of isothermal lamellar thickening at T_c that occurs in branched polyethylenes.⁴⁵

Peeters et al. proposed melting–recrystallization events during heating in order to explain the higher degree of crystallinity exhibited by quenched homogeneous 1-octene copolymers when compared to slow cooled specimens.⁴⁴ In addition, using modulated temperature differential scanning calorimetry, various authors identified crystal reorganization processes that occur in 1-butene and 1-hexene copolymers by quantifying the nonreversing heat flow evolved during heating.^{46,47}

Since melting–recrystallization processes are shown to occur as a function of heating rate and crystallization temperature and time, the melting behavior of LLDPE-A held isothermally at vari-

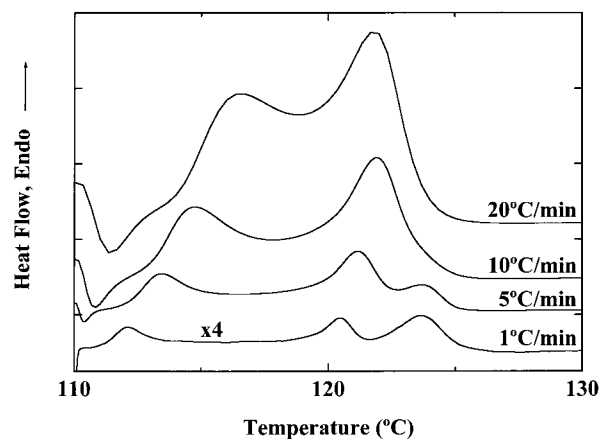


Figure 4 DSC thermograms of LLDPE-B at various heating rates after crystallizing at 110°C for 60 min.

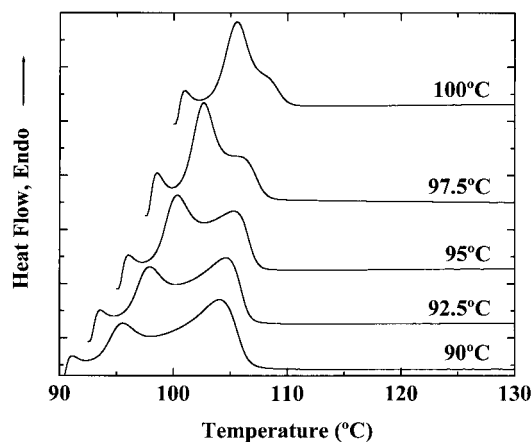


Figure 5 DSC heating thermograms from various T_c of LLDPE-A after crystallizing for 60 min.

ous crystallization temperatures for 1 h and recorded at 10°C/min was studied and the results are shown in Figure 5. It is observed that despite increasing crystallization temperature bimodal melting is always observed. The melting peaks shift to higher temperatures as the crystallization temperature increases. The same behavior was also observed in Figure 2 for LLDPE-B when attention is only drawn to those melting peaks that represent the fusion of preexisting lamellar populations. In Figure 5, the relative height of the high melting peak against that for the low melting peak decreases with increasing crystallization temperature. In addition, the lower melting peak experiences a larger displacement than the higher melting peak as found for LLDPE-B, i.e., both peaks merged each other.

The melting behavior of the LLDPE-A crystallized at 92.5°C for 60 min is examined as a function of heating rate (Fig. 6). Double melting peaks are observed for all heating rates examined, even for those heating rates that for LLDPE-B were able to suppress melting–recrystallization processes (Fig. 4).

These results suggest that double melting behavior observed in LLDPE-A is mainly due to the formation of two lamellar populations at T_c . These are of different thermal stabilities as a result of some heterogeneous distribution of the comonomer in the CGCT copolymer. Some reorganization, as indicated by the changing relative height of the peaks when heating rate is increased, must also occur.

Secondary crystallization processes in random ethylene/1-octene copolymers, synthesized using the INSITE technology, were recently investi-

gated by Alizadeh et al. The authors showed that ethylene sequences that are pinned at crystal surfaces participate in a more constrained geometry crystallization process at later stages during melt crystallization at low temperatures. Two morphological entities (i.e., lamellae and fringed micellar) are associated with different crystallization mechanisms.⁴⁸

We are concerned with the nature of heterogeneity in the CGCT copolymer. If Figures 2 and 5 are compared, just those peaks that represent the melting of lamellar populations formed at T_c , the behavior exhibited by both copolymers with changing T_c is rather different. LLDPE-B only shows a small change in their relative intensity with varying T_c whereas in the CGCT copolymer the low melting peak gains relative importance with increasing T_c . This contrasting behavior must be related to the different nature of heterogeneity in each copolymer.

Ziegler–Natta titanium based LLDPE copolymers are rather broad in polydispersity and chemical composition, and it is known that with increasing molecular weight the relative amount of strongly branched molecules and weakly branched molecules decreases.^{6,11,12} It has been reported that CGCT copolymers, however, have narrow distribution of short-chain branches and molecular weight.²⁹

A recent report on fractionation studies of a LLDPE prepared by metallocene catalysts molecular heterogeneity was detected in the copolymers. Its nature was different to that found in traditional LLDPE. It was shown using TREF–size exclusion chromatography cross-fractionation and differential scanning calorimetry that a commercial LLDPE

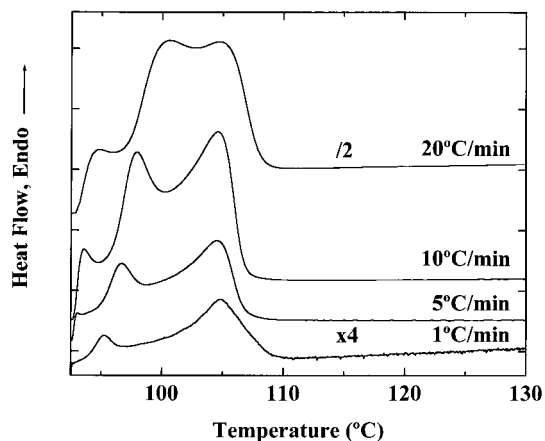


Figure 6 DSC thermograms of LLDPE-A at various heating rates after crystallizing at 92.5°C.

(ethylene/1-butene copolymer), synthesized using metallocene catalysts, possessed only intramolecular heterogeneity in short chain branch distribution.⁴⁹ We believe that CGCT copolymers might have similar structural heterogeneity. This would explain the contrasting melting behavior with the Ziegler–Natta copolymer, which has mainly intermolecular heterogeneity.

CONCLUSIONS

Evidence has been provided that led us to conclude that the investigated CGCT copolymer presents some heterogeneity on the comonomer distribution, which is responsible for the double melting endotherms observed after isothermal crystallizations. The Ziegler–Natta titanium based copolymer of similar comonomer content and melt flow index shows in addition melting–recrystallization processes that occur during heating. The DSC results on the changing melting behavior with crystallization temperature suggest that the nature of heterogeneity in each copolymer might be different.

C. C. Puig and M.V. Avilés would like to acknowledge the financial support provided by Decanato de Investigación y Desarrollo (Universidad Simón Bolívar) through Grant GID-DID-G02.

REFERENCES

- Wild, L.; Ryle, T. R.; Knobeloch, D. C.; Peat, I. R. *J Polym Sci Phys Ed* 1982, 20, 441.
- Kimura, K.; Shigemura, T.; Yuasa, S. *J Appl Polym Sci* 1984, 29, 3161.
- Usami, T.; Gotoh, Y.; Takayama, S. *Macromolecules* 1986, 19, 2722.
- Cady, L. D. *Plast Eng* 1987, 43, 25.
- Mirabella, F. M.; Ford, E. A. *J Polym Sci Phys Ed* 1987, 25, 777.
- Schouterden, P.; Groeninckx, G.; Heijden, B. V.; Jansen, F. *Polymer* 1987, 28, 2099.
- Hosoda, S. *Polym J* 1988, 20, 383.
- Mirabella, F. M.; Westphal, S. P.; Fernando, P. L.; Ford, E. A.; Williams, J. G. *J Polym Sci Phys Ed* 1988, 26, 1995.
- Mathot, V. B. F.; Pijpers, M. F. J. *J Appl Polym Sci* 1990, 39, 979.
- Wild, L. *Adv Polym Sci* 1990, 98, 1.
- Wilfong, D.; Knight, G. W. *J Polym Sci Phys Ed* 1990, 28, 861.
- Defoor, F.; Groeninckx, G.; Schouterden, P.; Heijden, B. V. *Polymer* 1992, 33, 3878.
- Zhou, X.-Q.; Hay, J. N. *Eur Polym J* 1993, 29, 291.
- Joskowicz, P. L.; Muñoz, A.; Barrera, J.; Müller, A. J. *Macromol Chem Phys* 1995, 196, 385.
- Springer, H.; Hengse, A.; Hinrichsen, G. *J Appl Polym Sci* 1990, 40, 2173.
- Mathot, V. B. F.; Scherrenberg, R. L.; Pijpers, M. F. J.; Bras, W. *J Therm Anal* 1996, 46, 681.
- Deblieck, R. A. C.; Mathot, V. B. F. *J Mat Sci Lett* 1988, 7, 1276.
- Ruiten, J.; Boode, J. W. *Polymer* 1992, 33, 2548.
- Nesarikar, A.; Crist, B.; Davidovich, A. *J Polym Sci Phys Ed* 1994, 32, 641.
- Channel, A. D.; Clutton, E. Q.; Capaccio, G. *Polymer* 1994, 35, 3893.
- Liu, T. M.; Baker, W. E. *Polym Eng Sci* 1992, 32, 944.
- Hosoda, S.; Kojima, K.; Furuta, M. *Makromol Chem* 1986, 187, 1501.
- Defoor, F.; Groeninckx, G.; Schouterden, P.; Heijden, B. V. *Polymer* 1992, 33, 5186.
- Voigt-Martin, I. G.; Alamo, R.; Mandelkern, L. *J Polym Sci Phys Ed* 1986, 24, 1283.
- Alamo, R.; Mandelkern, L. *J Polym Sci Phys Ed* 1986, 24, 2087.
- Hunter, B. K.; Russell, K. E.; Scammell, M. V.; Thompson, S. L. *J Polym Sci Polym Chem Ed* 1984, 22, 1383.
- Clas, S.-D.; McFaddin, D. C.; Russell, K. E.; Scammell-Bullock, M. V. *J Polym Sci Polym Chem Ed* 1987, 25, 3105.
- Sinclair, K.; Wilson, R. B. *Chem Ind* 1994, 7, 857.
- Sehanobish, K.; Patel, R. M.; Croft, B. A.; Chum, S. P.; Kao, C. I. *J Appl Polym Sci* 1994, 51, 887.
- Adisson, E.; Ribeiro, M.; Deffieux, A.; Fontanille, M. *Polymer* 1992, 33, 4337.
- Parker, J. A.; Bassett, D. C.; Olley, R. H.; Jaaskelainen, P. *Polymer* 1994, 35, 4140.
- Mathot, V. B. F.; Scherrenberg, R. L.; Pijpers, T. F. *J Polymer* 1998, 39, 4541.
- Marigo, A.; Zannetti, R.; Milani, F. *Eur Polym J* 1997, 33, 595.
- Fu, Q.; Chiu, F.; McCreight, K.; Guo, M.; Tseng, W. W.; Cheng, S. Z. D.; Keating, M. Y.; Hsieh, E. T.; DesLauriers, P. J. *J Macromol Sci Phys* 1997, B36, 41.
- Hsieh, E. T.; Tso, C. C.; Byers, J. D.; Johnson, T. W.; Fu, Cheng, S. Z. *J Macromol Sci Phys B* 1997, 36, 615.
- Starck, P. *Polym Int* 1996, 40, 111.
- Bensason, S.; Nazarenko, S.; Chum, S.; Hiltner, A.; Baer, E. *Polymer* 1997, 38, 3513.
- Bensason, S.; Minick, J.; Moet, A.; Chum, S.; Hiltner, A.; Baer, E. *J Polym Sci Phys Ed* 1996, 34, 1301.
- Keating, M. Y.; Lee, I. *J Macromol Sci Phys* 1999, B38, 379.

40. Mehta, A.; Wunderlich, B. *Colloid Polym Sci* 1975, 253, 193.
41. Norton, D.; Keller, A. *J Mat Sci* 1984, 19, 447.
42. Minick, J.; Moet, A.; Hiltner, A.; Baer, E.; Chum, S. P. *J Appl Polym Sci* 1995, 58, 1371.
43. Springer, H.; Hengse, A.; Höhne, J.; Schich, A.; Hinrichsen, G. *Progr Colloid Polym Sci* 1986, 72, 101.
44. Peeters, M.; Goderis, B.; Reynaers, H.; Mathot, V. *J Polym Sci Phys Ed* 1999, 37, 83.
45. Yadav, Y. S.; Jain, P. C. *Polym Commun* 1989, 30, 229.
46. R. Androsch, *Polymer* 1999, 40, 2895.
47. Janimak, J. J.; Stevens, G. C. *Thermochim Acta* 1999, 332, 125.
48. Alizadeh, A.; Richardson, L.; Xu, J.; McCartney, S.; Marand, H.; Cheung, Y. W.; Chum, S. *Macromolecules* 1999, 32, 6221.
49. Zhang, M.; Lynch, D. T.; Wanke, S. E. *J Appl Polym Sci* 2000, 75, 960.