

Nonisothermal Crystallization of Poly(phenylene sulfide) in Presence of Molten State of Crystalline Polyamide 6

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ABSTRACT: The nonisothermal crystallization and melting behavior of a poly(phenylene sulfide) (PPS) blend with polyamide 6 (PA6) were investigated by differential scanning calorimetry. The results indicate that the crystallization parameters for PPS become modified to a greater extent than those for PA6 in the blends. The PPS and PA6 crystallize at high temperature as a result of blending. The crystallization temperatures of PPS in its blends are always higher than that of pure PPS and are independent of the melting temperature and the residence time at that temperature. The PPS crystallization peak becomes narrower and the crystallization temperature shifts to a higher temperature, suggesting a faster rate of crystallization as a result of blending with PA6. This enhancement in the nucleation of PPS could be attributed to the possible presence of interfacial interactions between the component polymers to induce heterogeneous nucleation. On the other hand, the increase in the crystallization temperature of PA6 can be attributed to the heterogeneous nucleation provided by the already crystallized PPS. The heterogeneous nucleation induced by interfacial interactions depends on the temperature at which the polymers remain in the molten state and on the storage time at this temperature. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3033–3039, 1999

Key words: polyphenylene sulfide; polyamide 6; polymer blends; crystallization behavior; heterogeneous nucleation

INTRODUCTION

The ultimate properties of semicrystalline poly(phenylene sulfide) (PPS) are highly determined by its degree of crystallinity, as well as its crystalline morphology and structure, which in turn is dependent on its crystallization behavior. Much effort has been expended to study the effect of blending on the crystallization behavior of PPS. In the PPS blends with other crystalline thermoplastics the crystallization behavior and morphol-

ogy of the PPS in its blends is influenced by the blending. There are a number of factors that govern the extent and direction of change. These include the miscibility of the component polymers, their relative amounts, their relative melt viscosities at the temperature of crystallization, chemical compatibility, relative crystallizabilities, and the level of dispersion achieved in the compounding process. Also, the melting points and the temperature range of crystallization of the component polymers determines the physical conditions of crystallization.¹ Thus, if the crystallization temperatures are comparable, depending on the crystallizability of the individual component polymers, the polymers may crystallize concurrently or sequentially. On the other hand, if the crystallization temperature of PPS is higher

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than that of the other component, then PPS crystallizes in the presence of the molten state of the other component whereas the second component crystallizes in the presence of the solidified phase of the PPS component. If the crystallization temperature of PPS is lower than that of the other component, PPS crystallizes in the presence of the solidified phase of the other component. The crystallization conditions of a polymer in a blend are different from those involved in its crystallization from the virgin melt. The presence of a second component either in the molten or solid state affects both the nucleation and crystal growth of the crystallizing polymer. The effect of blending on the overall crystallization rate is the net combined effect of nucleation and growth. The presence of a second fluid or solid phase influences the crystallization behavior and the degree of crystallinity, thereby modifying the morphology and mechanical properties of PPS. Therefore, a scientific understanding of the influence that other thermoplastics have on the crystallization behavior of PPS is an essential step in the optimization of the compounding and processing conditions for effective manipulation and control of the ultimate properties of PPS blends.

There have been a number of reports on the crystallization and melting behavior of PPS in its blends with other thermoplastics²⁻¹⁴ and liquid crystalline polymers.¹⁵⁻²⁰ In the present article the crystallization behavior of PPS in the presence of a molten state of crystalline polyamide 6 (PA6) is reported. The results of nonisothermal crystallization experiments show that the crystallization behavior of PPS and PA6 is modified as a result of blending. The PPS and PA6 are both found to crystallize at higher temperature in the presence of the other component. However, the extent of the increase in the crystallization temperature for PPS is more pronounced than that for PA6.

EXPERIMENTAL

The powdered PPS sample (sieved through 40 mesh/in², number average molecular weight of 2200 g/mol) used in this study was obtained from Changshou Chemical Factory (China). The PA6 was obtained from UBE Industries Ltd. (Japan, UBE 1013B). Powder of PPS and PA6 pellets were dried at 100°C for 3 h prior to use and were mechanically mixed at different compositions at room temperature. The mixture was added to a

preheated roll mill (model xss-300, Shanghai) at 300°C and then mixing was continued for 8 min with a rotor speed of 32 rpm. After mixing thoroughly the mixture was removed from the mixing head and cooled to room temperature.

Thermal analysis was carried out by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 in a nitrogen atmosphere. Samples were heated from room temperature to 320°C at a rate of 20°C/min and held at that temperature for 3 min. The nonisothermal crystallization process was recorded from 320 to 50°C at a rate of 20°C/min, followed by heating from 50 to 320°C at a rate of 20°C/min for the second heating run. The thermal parameters were obtained from the cooling and reheating scans for the crystallization and melting behavior of PPS. The transition temperature and heat of crystallization and fusion were calibrated using an indium standard.

RESULTS AND DISCUSSION

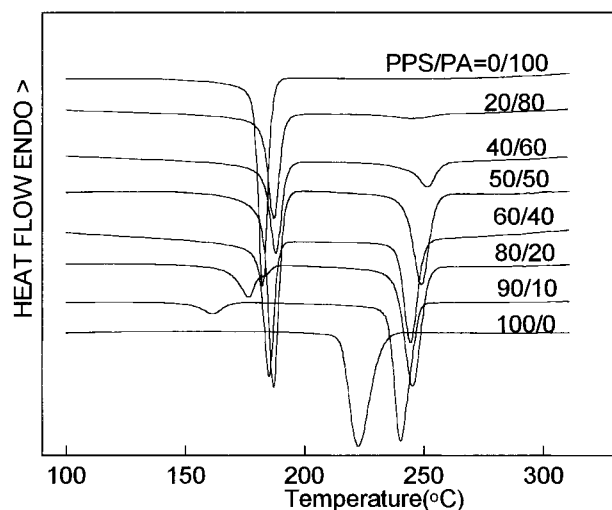
Effect of PA6 Content

The difference in the melting points and crystallization temperatures of two components is significant in the case of PPS/PA6 blends; the crystallization of PPS takes place in the presence of the melt of the PA6 component, whereas the PA6 crystallizes in the presence of the solidified phase of the PPS component. The crystallization and melting parameters determined from the cooling and reheating scans of the PPS component in the binary blends are summarized in Table I. The blends exhibited two distinct crystallization peaks corresponding to the crystallization of the component polymers during cooling. The peak appearing at the higher temperature was assigned to PPS whereas that at the lower temperature was assigned to PA6. It was found that blending significantly changed the onset temperature of crystallization (T_{co}) and peak crystallization temperature (T_c) of PPS. It was observed that the PPS crystallized at a higher temperature over the entire composition range in its blends. The T_{co} and T_c showed a significant increase upon the addition of PA6, followed by a gradual increase with increasing PA6 content. By adding 10 wt % PA6, in which the PA6 component was dispersed in a continuous phase of PPS, the T_{co} and T_c of PPS increased from 232 and 228°C to 248 and 240°C, respectively. The overall crystallization process of PPS was accelerated as evidenced by

Table I DSC Results of PPS Component in PPS/PA6 Blends

PPS/PA6	T_{co} (°C)	T_c (°C)	ΔH_c (J/g)	T_{mo} (°C)	T_m (°C)	ΔH_m (J/g)	ΔT (°C)
100/0	232.4	228.0	49.4	264.5	280.6	44.9	52.6
90/10	248.2	240.6	50.0	270.2	279.8	44.9	39.2
80/20	252.1	245.7	50.1	271.5	280.5	44.1	34.8
60/40	250.3	244.8	45.0	272.1	280.3	41.9	35.5
50/50	255.4	249.4	43.0	273.3	281.1	39.4	31.7
40/60	257.9	251.8	42.8	273.1	281.9	41.0	30.1
20/80	259.9	244.8	32.9	272.9	281.3	24.5	36.5

the narrowing of the crystallization peak width in the nonisothermal DSC cooling scans (Fig. 1). As the PA6 concentration increased up to 60 wt %, the T_c of PPS continued to increase. Even in the case of PPS/PA6 (80/20) blend in which PPS formed the dispersed phase in a continuous phase of PA6, the T_c of the PPS component was 16°C higher than that of pure PPS. This suggests that the PPS crystallization becomes accelerated as a result of blending. The heat of crystallization (ΔH_c) of PPS remained unchanged in the PPS blends containing less than a 40% weight of PA6. At blend compositions higher than 40 wt % PA6, the heat of crystallization of PPS decreased with the increase in the content of PA6. This could be attributed to the mobility constraints on PPS due to the major volume filling by the PA6 phase. The degree of supercooling ($\Delta T = T_m - T_c$) required for the PPS crystallization in the blends was significantly lower (30–40°C) compared to that required for pure PPS (53°C). The drop in the de-

**Figure 1** DSC cooling curves of PPS/PA6 melt blends.

gree of supercooling indicates an accelerated nucleation process for PPS in the presence of the PA6 melt.

The onset temperature of melting of PPS in the blends was also found to increase significantly with increasing amounts of PA6. The increase in the temperature at the onset of melting indicates that the stability of the least-stable crystallites in the blend was increased by blending. Because the PPS crystallization takes place at significantly higher temperature as a result of blending, it is likely that this relates to an overall increase in the crystallite thickness. The higher thickness of the crystallites could be the result of facilitated crystal growth because the crystallization of PPS takes place in the presence of the molten phase of the PA6.

The melting peak temperature (T_m) for PPS in its blend with PA6 was found to be comparable with that of neat PPS and did not show significant composition dependence, indicating that the PPS and PA6 components were not miscible. The melting peak width (Fig. 2) became narrower on adding PA6, suggesting that the crystallite size distribution of PPS became narrow as a result of blending. The heat of fusion (ΔH_m) of PPS was found to remain unchanged as the content of PA6 increased up to 40 wt % and then decreased with an increase in the PA6 content.

Because the crystallization temperature of PA6 is lower than that of PPS, the crystallization of the PA6 component takes place in the presence of solidified PPS. It can be seen from Table II that the T_{co} and T_c of PA6 in the blends containing less than 60% by weight of PPS is higher than those in the PA6 homopolymer. The degree of supercooling required for the PA6 crystallization in the blends containing less than 80% by weight of PPS is lower (31–36°C) than that required for pure PA6 (39°C). The decrease in the degree of supercooling could be attributed to an accelerated

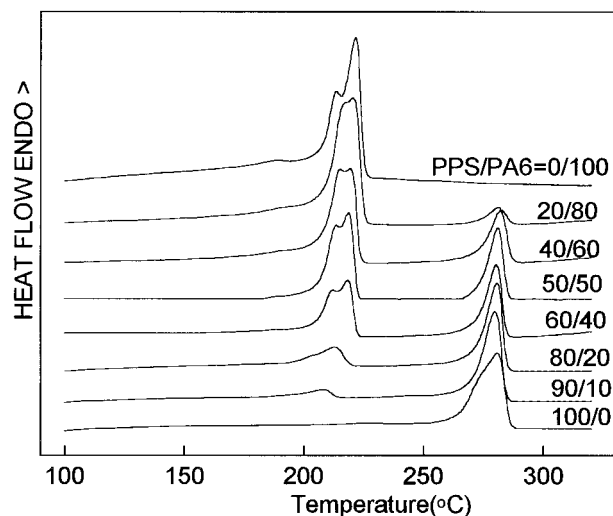


Figure 2 DSC heating curves of PPS/PA6 melt blends.

nucleation process for PA6 in the presence of solidified PPS. The acceleration in the nucleation of PA6 crystallization could be attributed to the presence of heterogeneous nucleation of already crystallized PPS particles. These PPS crystallites with a finite surface area can act as heterogeneous nuclei during PA6 crystallization. The diminishing effect of heterogeneous nucleation in the PPS-rich blends could be attributed to the constraints on crystal growth of PA6 in the presence of higher amounts of PPS. The heat of crystallization and fusion of PA6 in the blend containing lower than 60% by weight of PPS was found to increase as a result of blending with PPS. The increase in the heat of crystallization and fusion can be attributed to the nucleating effects of already crystallized PPS. The drop in the heat of crystallization and fusion for PA6 in the blends containing higher than 60% by weight of PPS can be due to the mobility restrictions imposed by PPS solid particles for the PA6 crystal growth.

Based on the above observed results concerning crystallization and melting parameters in the PPS/PA6 blend, we concluded that the effect of blending on the crystallization process of PPS was more significant than on that of PA6 whereas the effect of blending on the melting temperature of PA6 was greater than that of PPS. Similar results were obtained by Shingankuli et al.⁷ in PPS/poly(ethylene terephthalate) (PET) blends. The PPS and PET were both found to crystallize at a faster rate in the presence of the other component. However, the extent of acceleration in the rate of crystallization for PET was more pronounced compared to that for PPS.

In the polymer blends the thermal and chemical environment under which a polymer crystallizes is modified as a result of the presence of the second component. The critical factors governing the extent and direction of change in the overall crystallization rate and crystallization temperature of two components include miscibility, relative melt viscosities, chemical compatibility, amounts of the component polymers, and their phase morphology.⁸ In the PPS/PA6 blends the observed change in the crystallization temperature could be attributed to the interfacial interactions between PPS and PA6, which induce the heterogeneous nucleation and enhance the nucleation of PPS. On the other hand, the possibility of interfacial interactions in the blends may lead to an increase in the local ordering of the polymer chains in the molten state of the blends due to the higher interfacial tension for the PPS/PA6 blend. Yoon and White²¹ examined the interfacial tension of PPS with other polymer melts and reported the order of the interfacial tensions of PPS with other polymers as PPS/PA6 > PPS/PE > PPS/PP \approx PPS/PET > PPS/PC > PPS/PS > PPS/PSF. The presence of such local ordering would therefore facilitate the nucleation of PPS. The extent of the interfacial interactions depends

Table II DSC Results of PA6 Component in PPS/PA6 Blends

PPS/PA6	T_{co} (°C)	T_c (°C)	ΔH_c (J/g)	T_{mo} (°C)	T_m (°C)	ΔH_m (J/g)	ΔT (°C)
90/10	168.3	161.6	45.8	196.5	207.8	46.0	46.2
80/20	182.3	176.8	62.5	199.5	212.6	53.8	35.8
60/40	189.3	185.4	77.3	204.6	218.3	77.0	32.9
50/50	191.5	187.3	72.6	206.2	218.2	69.2	30.9
40/60	192.7	188.3	69.8	207.1	219.2	81.0	30.9
20/80	191.7	187.4	71.8	208.3	220.5	77.2	33.1
0/100	186.6	182.8	71.2	211.3	221.5	68.6	38.7

Table III DSC Results of Pure PPS and PPS Component in Its Blend Melted at Different Temperatures for 10 min

	T_{melt} (°C)	T_{m_o} (°C)	T_m (°C)	ΔH_m (J/g)	T_{co} (°C)	T_c (°C)	ΔH_c (J/g)	ΔT (°C)
PPS	300	265.5	278.3	42.3	232.2	220.9	46.5	57.4
	320	265.8	279.7	42.0	228.7	219.5	46.6	60.2
	340	260.9	281.1	40.6	224.9	205.7	45.0	75.4
	350	263.9	282.9	40.4	229.5	211.1	43.7	71.8
	360	268.3	282.4	34.7	234.8	221.0	36.3	61.4
PPS/PA6 80/20	300	267.7	279.2	46.5	256.8	251.3	44.8	27.9
	320	264.7	279.8	47.3	255.4	247.3	47.8	32.5
	340	267.6	281.9	39.0	256.1	251.6	38.6	30.3
	350	270.3	282.5	30.3	253.5	248.6	37.6	33.9
	360	265.6	278.9	24.8	251.2	239.0	28.4	39.9

on the interfacial area between the PPS and PA6 in the blends, which in turn depends on the phase morphology. A continuous/dispersed phase morphology may be formed in the blends containing less than 50% by weight of PA6, whereas the blends containing about 60% by weight of PA6 will form a cocontinuous phase morphology. The interfacial area between the continuous PPS and the dispersed PA6 domains will increase on increasing the content of PA6. The highest interfacial area was obtained in the cocontinuous phase morphology. The crystallization temperature of the PPS component depends on the interfacial area between the PPS and PA6. Thus, the highest temperature of PPS crystallization was attributed to the highest interfacial area between the PPS phase and the PA6 phase in the cocontinuous phase morphology.

Effect of Melting Temperatures

In order to study the influence of the interfacial interactions between PPS and PA6, the effect of the melting temperatures on the nonisothermal crystallization and melting behavior of PPS and its blends was investigated. Table III shows the DSC results of pure PPS and the PPS component in the blend (PPS/PA6 = 80/20) at different melting temperatures for 10 min, followed by quenching in ice water. It can be seen from Table III that the melting point (T_m) of pure PPS increases on increasing the melting temperature (T_{melt}), indicating better crystal perfection. The onset temperature of crystallization (T_{co}) and crystallization temperature (T_c) of PPS decreases as T_{melt} is increased from 300 to 340°C. This is due to a decrease in the unmelted PPS crystal fragments acting as nucleation sites, which can cause self-

nucleation during crystallization of PPS. Budgell and Day²² suggested that complete melting of PPS occurs between 320 and 350°C. Estimates of the equilibrium melt temperature for PPS range from 301 to 357°C, depending on the sample and method of determination.^{23–26} The heat of crystallization and fusion of pure PPS remain unchanged for a T_{melt} below 340°C. In this region the number of crystalline entities that remain in the melt are reduced when the T_{melt} is increased. As the T_{melt} is increased to a temperature above 340°C, the observed high values of T_{co} and T_c are likely the result of degradation. Because of the reduction in the molecular weight, the molecular rearrangements become easier, resulting in an increase in T_c . Higher melting temperatures cause the formation of more of the degraded materials, which increases the T_{co} and T_c . However, the heat of crystallization and fusion decrease significantly at the highest melting temperature (360°C), indicating that at temperatures higher than 340°C, the PPS undergoes chemical alterations like crosslinking or oxidative damage.⁶ Such phenomena were observed by Caramaro et al.¹³ They suggested that variation of the T_c as a function of T_{melt} can be divided into three regions: at low treatment temperature the T_c decreases with the T_{melt} ; the T_c does not change with the T_{melt} in the region where all the crystallization entities are destroyed and the number of crystallization nuclei (stable heterogeneous nuclei) is constant; and at high T_{melt} the T_c slightly increases.

Similar results were observed in the PPS/PA6 (80/20) blend. The T_m of the PPS component in the blend also slightly increases with increasing the T_{melt} . The T_{co} and T_c remain unchanged with

Table IV DSC Results of Pure PPS and PPS Component in Its Blend Melted at 340°C for Different Times

	t_{melt} (min)	T_m (°C)	ΔH_m (J/g)	T_{co} (°C)	T_c (°C)	ΔH_c (J/g)	ΔT (°C)
PPS	10	281.1	40.6	224.9	205.7	45.0	75.4
	20	281.9	45.5	230.1	211.0	45.1	70.9
	40	281.7	28.2	228.7	214.0	22.4	67.7
	80	280.9	19.7	233.6	214.7	19.6	66.2
PPS/PA6 80/20	10	281.9	39.0	256.1	251.6	38.6	30.3
	20	281.0	32.8	253.1	240.9	34.8	40.1
	40	278.9	25.0	249.2	236.7	26.0	42.2
	80	278.3	33.5	234.2	220.9	32.0	57.4

increasing the T_{melt} from 300 to 340°C and are 20–40°C higher than that of pure PPS due to the interfacial nucleation induced by the interfacial interaction between PPS and PA6. At high T_{melt} (above 340°C) the decrease in the crystallization temperature could be attributed to the chemical changes (branching and crosslinking) of the PPS that diminish the interfacial nucleation induced by interfacial interaction. As the T_{melt} increases the decrease in the heat of crystallization and fusion of the PPS component in the blend was more significant than those of pure PPS. This was due to the presence of the chemical and physical interaction (crosslinking and interpenetrating) in the interface between the two components.

Effect of Residence Time in Melt

The storage time at the melting temperature may play an important role in the crystallization behavior of PPS in its blends. Table IV shows DSC results of pure PPS and PPS/PA6 (80/20) blend melted at 340°C for different times, followed by quenching in ice water. It is clear that the T_{co} and T_c of pure PPS depend on the storage time in the melt at 340°C. The crystallization temperature shifts to a higher temperature and the degree of supercooling decreases. Auer et al.⁶ found that the crystallization peak shifts to a shorter time and its half-width is lessened with the storage time at the melting temperature, suggesting that this was caused by such molecular processes in the melt as postpolymerization, depolymerization, change of molecular weight distribution, and crosslinking. As the melting time is longer than 20 min, the heat of crystallization and fusion decreases on increasing the melting time (t_{melt}), although the T_m of PPS was independent of the t_{melt} .

In the PPS/PA6 blends the effect of melting time on the crystallization process of the PPS component is more significant than that of pure PPS. As the t_{melt} is increased the T_c and T_m decrease, and the decrease in T_c is greater than that in T_m . However, the T_c of the PPS component in the blend is always higher than that of pure PPS in the same treatment. The higher crystallization temperature of the PPS component in its blends proves that the heterogeneous nucleation effect of the interfacial interactions due to surface-induced nucleation/crystallization by the PA6 melt is dominant. The extent of heterogeneous nucleation will decrease on increasing the melting temperature and the residence time in the melt. Therefore, the observed results suggest that the interfacial interactions between PPS and PA6 induce the heterogeneous nucleation, which depend on the temperature at which the polymer remains in the molten state and on the storage time at this temperature.

REFERENCES

1. Nadkarni, V. M.; Jop, J. P. In *Two-Phase Polymer Systems*; Utracki, L. A., Ed.; Hanser Publishers: Berlin, 1991; p 213–240.
2. Mai, K.; Zhang, M.; Zeng, H.; Qi, S. *J Appl Polym Sci* 1994, 51, 57.
3. Mai, K.; Mei, Z.; Xu, J.; Zeng, H. *J Appl Polym Sci* 1998, 69, 637.
4. Mai, K.; Mei, Z.; Xu, J.; Zeng, H. *J Appl Polym Sci* 1997, 63, 1001.
5. Lim, S.; Kim, J.; Park, M.; Chou, C.; Lee, J.; Kim, D. *Polym Eng Sci* 1996, 36, 2502.
6. Auer, C.; Kalinka, G.; Krause, J.; Hinrichsen, G. *J Appl Polym Sci* 1994, 51, 407.
7. Shingankuli, V. L.; Jog, J. G.; Nadakarni, V. M. *J Appl Polym Sci* 1994, 51, 1463.

8. Jog, J. P.; Shingankali, V. L.; Nadkarni, V. M. *Polymer* 1993, 34, 1966.
9. Song, S. S.; White, J. L.; Cakmak, M. *Polym Eng Sci* 1990, 30, 944.
10. Bhardwaj, I. S.; Das, A.; Kumar, V. *Thermochim Acta* 1989, 144, 165.
11. Radhakrishnan, S.; Joshi, S. G. *Eur Polym J* 1987, 23, 819.
12. Nadkarni, V. M.; Jop, J. P. *J Appl Polym Sci* 1986, 32, 5817.
13. Caramaro, L.; Chabert, B.; Chauchard, J. *Polym Eng Sci* 1991, 31, 1279.
14. Shingankuli, V. L.; Jop, T. P.; Nadkarni, V. M. *J Appl Polym Sci* 1988, 36, 335.
15. Gopakumar, T. G.; Ghadage, R. S.; Ponrathnam, S.; Rajan, C. R.; Fradet, A. *Polymer* 1997, 38, 2209.
16. Gabellini, G.; Bretas, R. E. S. *J Appl Polym Sci* 1996, 61, 1803.
17. Hong, S. M.; Kim, B. C.; Kim, K. V.; Chung, I. J. *Polym J* 1992, 24, 727.
18. Minkova, L. I.; Paci, M.; Procella, M.; Magagnini, P. *Polym Eng Sci* 1992, 32, 57.
19. Gopakumar, T. G.; Ponrathnam, S.; Rajan, C. R.; Fradet, A. *Polymer* 1998, 39, 2221.
20. Gopakumar, T. G.; Ponrathnam, S.; Rajan, C. R.; Fradet, A. *Polym J* 1998, 29, 884.
21. Yoon, P. J.; White, J. L. *J Appl Polym Sci* 1994, 51, 1515.
22. Budgell, D. R.; Day, M. *Polym Eng Sci* 1991, 31, 1271.
23. Lovinger, A. J.; Davis, D. D.; Padden, F. J., Jr. *Polymer* 1985, 26, 1595.
24. Lopez, L. C.; Wilkes, G. L. *Polymer* 1988, 29, 106.
25. Lopez, L. C.; Wilkes, G. L. *Polymer* 1989, 30, 147.
26. Cheng, S. Z. D.; Wu, Z. Q.; Wunderlich, B. *Macromolecules* 1987, 20, 2802.