

Preparation of Polypropylene/Poly(styrene-*co*-(butyl methacrylate)) Nanoblends by Diffusion and Subsequent Copolymerization of Monomers in Isotactic Polypropylene Pellets*

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Abstract The diffusion and subsequent copolymerization of styrene (St)/butyl methacrylate (BMA) mixed monomers in *i*PP pellets to prepare copolymer nanoblends were investigated. The diffusion step was carried out at 90 °C for 2 h in water, and the copolymerization was initiated by the addition of BPO with the aid of a small amount of St. The diametrical distributions of both St and BMA units and their ratio St/BMA were investigated by micro FTIR. Both St and BMA can diffuse into the centres of *i*PP pellets. The diametrical distribution of St/BMA ratio is constant in all the copolymer blends. The copolymer composition depends on the comonomer feed ratio. The molecular weights of the copolymers were measured by GPC after extraction with tetrahydrofuran. The phase morphology of the copolymer blends was investigated by FESEM, showing the average particle sizes of less than 100 nm. DSC measurements show that the diffusion and subsequent copolymerization of St/BMA monomers only occur in the amorphous regions of *i*PP pellets.

Keywords: Polypropylene; Polymer blend; Diffusion; Copolymerization.

INTRODUCTION

Diffusion and subsequent polymerization of monomers in polymer matrices is a well-known solid state modification method with many advantages such as minimum degradation of the matrix polymer and feasibility for large scale production. The main purposes are to prepare polymer blends or graft copolymers used as compatibilizers for traditional melt blending^[1]. Polypropylene (PP) is the most frequently used polymer in solid state modification. The reactor alloy process of *i*PP is a well-known industrial process to produce PP-based alloys such as high impact PP containing random ethylene-propylene copolymer as the elastomer to toughen PP^[2,3]. The process usually uses porous *i*PP powders as the reactors^[1,4]. Polymer films and sheets (or discs) have also been successfully used as the matrices to prepare polymer blends by the method of diffusion and subsequent polymerization with or without the aid of supercritical carbon dioxide^[5–17]. However, the commercially available *i*PP pellets^[18,19] are rarely used as the matrices to prepare polymer blends which have the interest of direct use in plastic production.

Previously, our research group reported the diffusion and subsequent polymerization of styrene and BMA in commercial *i*PP pellets having a diameter of 4.5 mm using water as the diffusion and polymerization medium^[20,21]. When used separately, both monomers can diffuse into the centres of the pellets and the newly

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formed dispersed phases are very small (their average sizes are close to nanometre range). But, their diffusion coefficients and maximum absorptions are significantly different. The diffusion coefficient of BMA is smaller than that of St ($1.14 \times 10^{-10} \text{ m}^2/\text{s}$ versus $1.93 \times 10^{-10} \text{ m}^2/\text{s}$), and the maximum absorption of BMA (10% to *i*PP) is considerably lower than that of St (17%) under similar diffusion and polymerization conditions, due to its bigger molecular size and the more polar nature^[21].

In this work, mixtures of styrene and BMA were used for diffusion and subsequent copolymerization in *i*PP pellets. The purpose is to find out whether the two types of comonomers with different diffusion coefficients can both reach the centres of the pellets and in what composition when they are used together. Blend pellets were synthesized using different monomer compositions. The diametrical distribution of each monomer unit and the ratio of the two monomer units St/BMA were determined by micro FTIR. The molecular weights of the copolymers were measured by GPC and the phase morphology of the blend pellets was investigated by FESEM.

EXPERIMENTAL

Materials

Commercial grade isotactic polypropylene pellets S1003 with a diameter of approximately 4.5 mm were purchased from Yanshan Petroleum and Chemical, China. Styrene (St) and *n*-butyl methacrylate (BMA) were distilled under reduced pressure. Benzoyl peroxide (BPO) was purified by recrystallization from chloroform/methanol. Chloroform and methanol were analytical grade and used as received. Tetrahydrofuran (THF) was chromatographically pure.

Typical Procedure for Copolymer Blend Synthesis

The copolymerization of styrene and BMA in *i*PP pellets proceeds with the following procedure: 60 mL of deionized water was added to a 250 mL flask equipped with a mechanical stirrer and a condenser. The flask was then heated to and maintained at 90 °C. 20 g of *i*PP as well as 5.5 g of mixture of styrene and BMA were added. After the diffusion of the monomers for 2 h, the pellets were separated by vacuum filtration and washed with water, then transferred into another 250 mL flask containing 60 mL of deionized water preheated to 90 °C. 0.06 g of BPO, served as the initiator and dissolved in 0.5 g of styrene, was added into the system. After 3 h of copolymerization, the flask was cooled to room temperature, and the pellets were isolated by vacuum filtration and washed with water, then dried to a constant weight.

Measurement of Copolymer Contents

The total copolymer formed in the blend synthesis consists of two parts: copolymer formed at the surface and that inside *i*PP pellets. The total and inner copolymer contents were defined as follows:

$$\text{Total copolymer content (\%)} = \frac{m_{\text{total copolymer}}}{m_{\text{iPP}}} \times 100\% \quad (1)$$

$$\text{Inner copolymer content (\%)} = \frac{m_{\text{inner copolymer}}}{m_{\text{iPP}}} \times 100\% \quad (2)$$

where m_{iPP} is the initial mass of the *i*PP pellets, and $m_{\text{total copolymer}}$ is the mass of the total copolymer formed during the synthesis. They were determined by weighing the pellets before and after the copolymerization. $m_{\text{inner copolymer}}$ was determined gravimetrically after the removal of surface copolymer by ultrasonic treatment with chloroform for 5 min.

Extraction of the Copolymer from the Blend Pellets

The copolymer blend pellets were cut into tiny fragments with a pair of scissors and immersed in THF. The mixture was stirred for 24 h. After filtration through a membrane filter with pore size of 0.25 microns, THF was removed by rotary evaporation.

Characterization

Micro Fourier transform infrared spectroscopy (Micro FTIR)

Micro FTIR was performed with a Nicolet 6700 FTIR Microscope. Samples were cut through the centre of the copolymer blend pellet by a microtome (YD-1508R, Zhejiang Jinhua Yidi Medical Equipment Factory), with a thickness of 20 μm . The step length was 100 μm and the microsampling area was 100 $\mu\text{m} \times 100 \mu\text{m}$ at each detected position. Infrared spectra were recorded along the diameter of the pellets. The peak of benzene ring at 699 cm^{-1} was taken to characterize St units in the copolymer and its peak area was denominated as A_{St} . The peak of ester band at 1728 cm^{-1} was taken to characterize BMA units, which was denominated as A_{BMA} . The two peaks at 972 and 997 cm^{-1} were taken as characteristic peaks of *i*PP because they do not overlap with any peak of PBMA and PS, and the summation of the two peak areas was denominated as A_{iPP} . The ratios $A_{\text{St}}/A_{\text{iPP}}$ and $A_{\text{BMA}}/A_{\text{iPP}}$ were used to express the contents of St and BMA units in the copolymer relative to *i*PP. $A_{\text{St}}/A_{\text{BMA}}$ represents the copolymer composition.

Field emission scanning electron microscopy (FESEM)

A JSM-7401 field emission scanning electron microscope (FESEM) was used to visualize the morphology of the blends at an accelerating voltage of 3 kV. For sample preparation, the blend pellets were cut into two symmetry parts and then etched for 45 min with stirring in an aqueous mixture of sulfuric acid, orthophosphoric acid and potassium permanganate^[22] to remove the amorphous phase of the cross section of *i*PP. After cleaning ultrasonically with water and methanol for 5 min with each solvent, the samples were dried in an oven and gold coated (30 s) before observation.

Gel permeation chromatography (GPC)

The molecular weights of the copolymers and their distributions were determined by a gel permeation chromatography (GPC) apparatus using THF as eluent (1 mL/min) at room temperature. The instrument was equipped with a refractive index detector (Wyatt Optilab rEX) as well as a PLgel 5 μm mixed-D column. Calibration was achieved by means of polystyrene narrow standards.

Differential scanning calorimetry (DSC)

DSC (TA Instrument model Q100) measurements were carried out to verify if the diffusion and subsequent copolymerization only occur in the amorphous regions of *i*PP pellets. The samples were round slices (about 8 mg) cut through the centre of the copolymer blend pellets. The samples were then heated from room temperature to 200 °C at a rate of 10 K/min under nitrogen. The melting temperature (T_{m}) was defined as the maximum of the melting peak and the enthalpy of melting (ΔH_{m}) was calculated as the integral of melting peak divided by the weight percent of PP in the blend.

RESULTS AND DISCUSSION

Copolymer Blend Synthesis

Diffusion and subsequent copolymerization of St/BMA mixed monomers in *i*PP pellets are illustrated in Fig. 1. When *i*PP pellets and St/BMA mixed monomers are suspended in water, most of the monomers is immediately adsorbed on the surface of *i*PP pellets because both St/BMA mixture and *i*PP are of hydrophobic nature, and a small amount of St/BMA mixture is in the form of droplets in water^[20], as shown in Fig. 1(a). After diffusion at 90 °C for a certain time, some monomers (not all of the monomers, because they are in excess) diffuse into the amorphous regions of *i*PP pellets such as the core of the spherulites and regions between two neighbouring lamellae as seen in Fig. 1(b). Then, the monomer-swollen *i*PP pellets are separated and transferred into another flask containing water to remove excess monomers (Fig. 1c). After the addition of BPO with the aid of a small amount of St followed by polymerization for 3 h, the blend pellets with random copolymer^[23] of styrene and butyl-methacrylate as the dispersed phase are formed (Fig. 1d).

Referenced to our previous work^[20, 21], the amounts of total comonomers and initiator BPO were set at 30 wt% relative to *i*PP and 1 wt% relative to monomer, respectively. The diffusion temperature was fixed at

90 °C to get a reasonable and detectable amount of monomer diffusion by ensuring sufficient segmental mobility of *i*PP chains. The polymerization temperature and time are 90 °C and 3 h, respectively. Compared to the previously reported ‘902’ procedure, where ‘90’ means diffusion temperature of 90 °C and ‘2’ means separation and transfer of the *i*PP pellets after diffusion step into another flask for polymerization, slight modifications were envisaged. Firstly, PVA was not used in the diffusion step because no caking was encountered during polymerization in ‘902’ procedure. Secondly, BPO was dissolved in a small amount of St instead of chloroform to avoid the evaporation of the assistant solvent in order to assist diffusion of BPO into *i*PP pellets.

The effect of diffusion time (t_d) on total copolymer content was investigated, and the results are shown in Fig. 2. Total copolymer content increases with t_d and levels off at about 2 h, and its equilibrium value is 12% (to *i*PP). Therefore, t_d is fixed at 2 h in subsequent investigation.

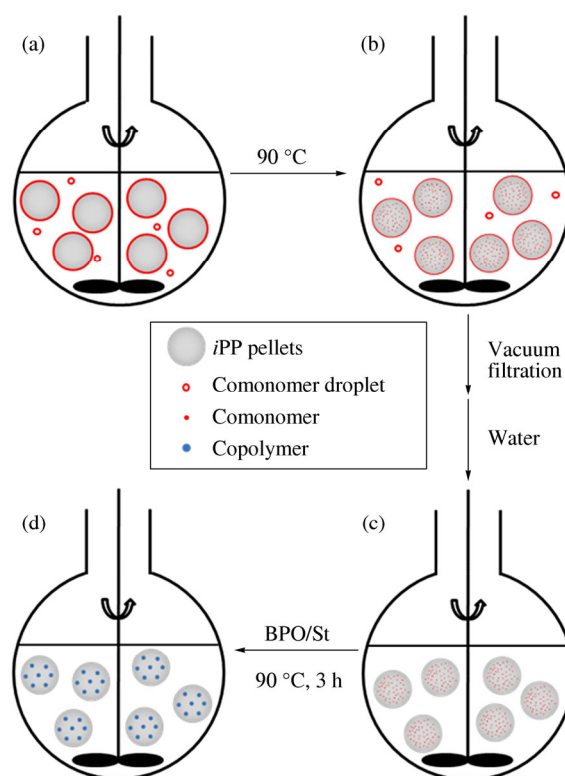


Fig. 1 Illustration of the copolymer blend synthesis

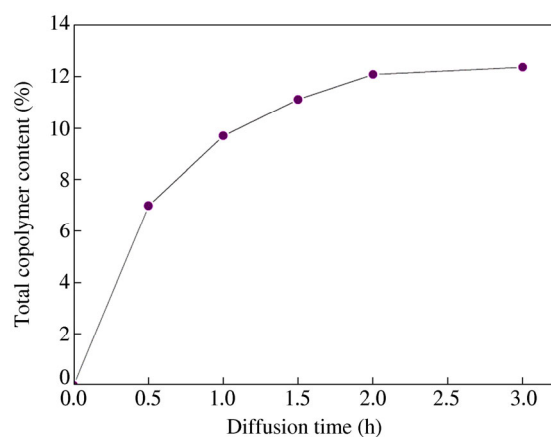


Fig. 2 Total copolymer content as a function of diffusion time with a comonomer feed ratio St:BMA 1:1

Effect of Comonomer Feed Ratio on Copolymer Contents

Figure 3 shows total and inner copolymer contents at various St/BMA feed ratios. When mixed monomers are used, the copolymer contents are always lower than those with neat St and higher than those with neat BMA, and decrease when St/BMA feed ratio decreases. This can be understood from the fact that BMA is more polar and bigger in size than St. Because the difference in polarity between BMA and *i*PP is bigger than that between St and *i*PP, the degree of swelling of *i*PP is less with BMA than with St, meaning less BMA can diffuse into the amorphous regions of *i*PP pellets than St. It is noted that all the values of total copolymer contents are very close to those of inner copolymer contents, revealing very little amount of copolymer formed on the surface of the pellets. This is advantageous to direct use of the copolymer blend pellets.

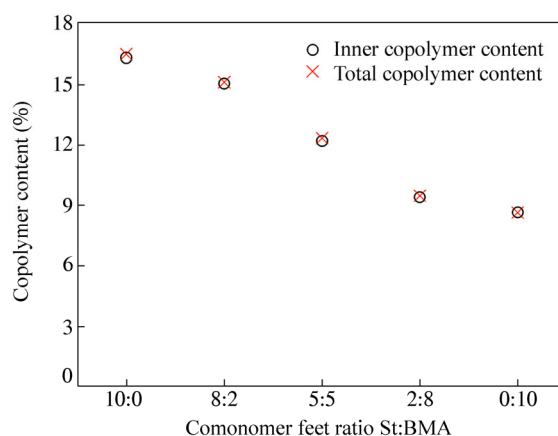


Fig. 3 Total and inner copolymer contents in *i*PP pellets obtained from different comonomer feed ratios

Micro FTIR

In order to investigate if the two monomers can both diffuse into the centres of *i*PP pellets, Micro FTIR was used so that the spectra can be taken at 100 μm interval from one end to the other along the diameter of a slice cut through the centre of a pellet. Figure 4 shows the spectra of the blend pellets with different comonomer feed ratios at about 200 μm distance to the surface. Taking the characteristic peaks of *i*PP at 972 and 997 cm^{-1} as the reference, the characteristic peak of St unit at 699 cm^{-1} decreases and that of BMA unit at 1728 cm^{-1} increases when St/BMA feed ratio decreases, indicating a decrease in St units in the copolymer when its proportion in the feed decreases.

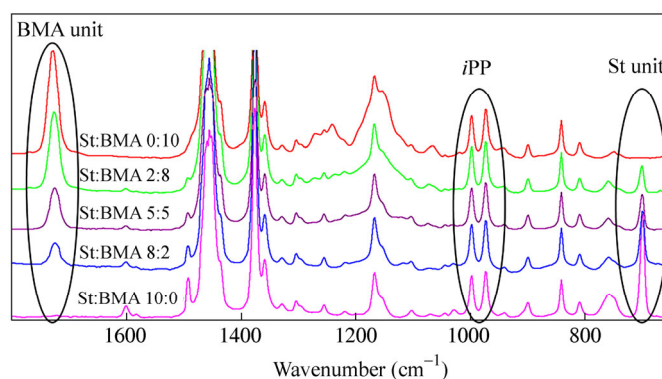


Fig. 4 Original FTIR spectra of the blends with different comonomer feed ratios (at about 200 μm distance to the surface)

Figures 5(a) and 5(b) show the diametrical distributions of St and BMA units in the blend pellets with different comonomer feed ratios, deduced from the micro FTIR spectra along the diameter. The distance 0 is the

centre of the pellet. The vacancy of data in the central regions of some pellets is due to the hole formed during granulation of *i*PP, and indicates that the monomers do not diffuse into this hole due to the lack of thermodynamic driving force. Clearly, both St and BMA can diffuse upto the centres of the *i*PP pellets. The curves are typically saddle-shaped with a maximum at about 200 μm distance to the surface and a minimum in the central region of a pellet. The minimum can be easily understood since the monomers diffuse from the surface towards the centre with the farthest travel distance to the centre. The maximum could be related to the inhomogeneous crystallization behavior of *i*PP pellets formed during their production process.

Figure 5(c) shows the diametrical distributions of the ratios of the two monomer units in the three blend pellets investigated. The distribution is almost constant for all the three samples. Although the diffusion coefficient of St is bigger than that of BMA when they are used alone^[20], St and BMA are miscible, St/BMA ratio shows no diametrical gradient. The average values of $A_{\text{St}}/A_{\text{BMA}}$ for the three samples are in the same tendency to their feed ratios, indicating that more BMA is needed if one wants to incorporate more BMA into the copolymer.

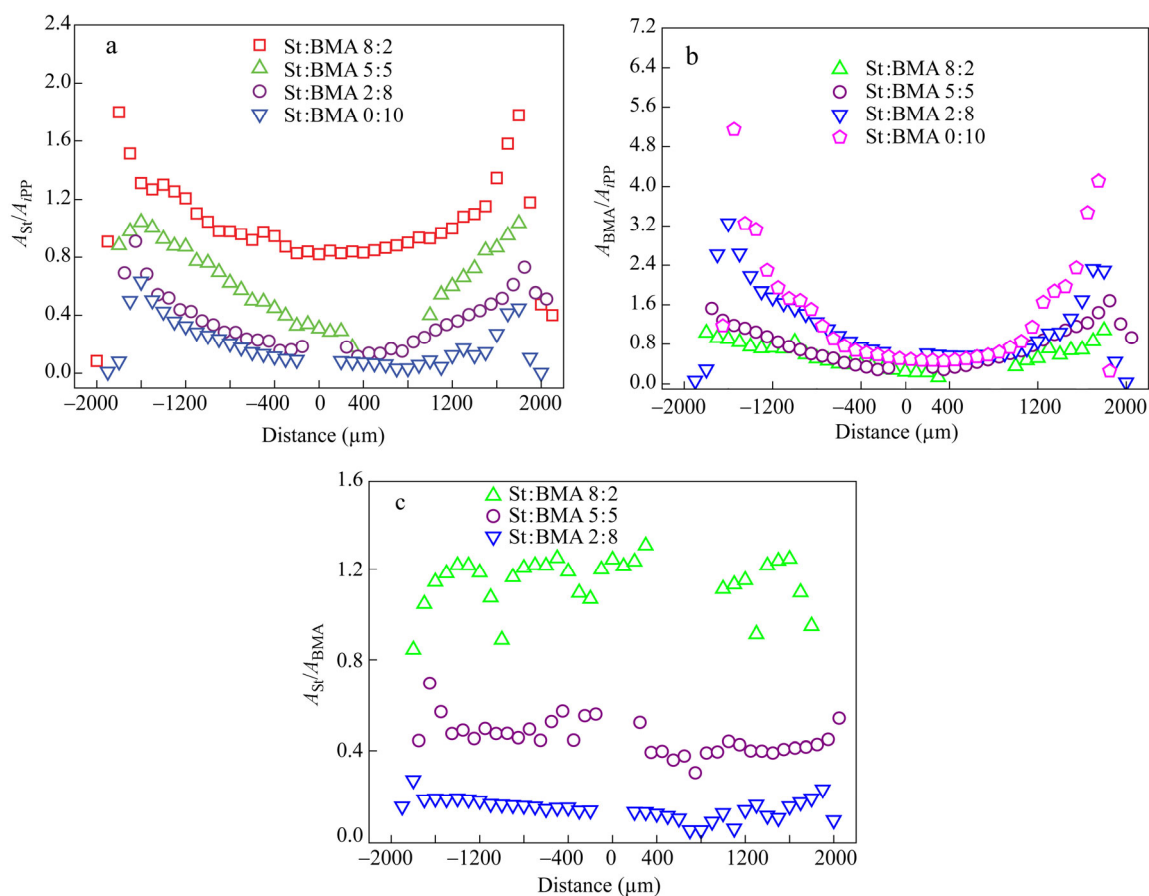


Fig. 5 Micro FTIR profiles along pellet diameter: (a) $A_{\text{St}}/A_{i\text{PP}}$, (b) $A_{\text{BMA}}/A_{i\text{PP}}$ and (c) $A_{\text{St}}/A_{\text{BMA}}$ for different comonomer feed ratios

Molecular Weights of the Copolymers

GPC measurements of the THF extracts were carried out to determine the molecular weights of the copolymers formed inside *i*PP pellets, and the results are listed in Table 1. The weight average molecular weights of the copolymers are about 100000 and their number average molecular weights are more than 40000 with a polydispersity index around 2. There are no significant differences among molecular weights of different samples except for PBMA homopolymer whose molecular weight is about two times of those of the copolymers.

It is noted that the values are relative to polystyrene standards, and did not take into account of the differences in molecular size between PS and PBMA.

Table 1. Average molecular weights and polydispersity indexes of the copolymers

Comonomer feed ratio St:BMA	M_w	M_n	PDI
10:0	79000	42000	1.9
8:2	85000	42000	2.0
5:5	97000	42000	2.3
2:8	125000	48000	2.6
0:10	267000	128000	2.1

Phase Morphology of the Copolymer Blends

Figure 6 shows FESEM photos of the PP/poly(St-co-BMA) blends at about 200 μm distance to the surface of the pellets after permanganic etching of the amorphous regions of the cross section of *i*PP. Poly(St-co-BMA) appears as spherical particles in the amorphous regions of *i*PP in a wide range of sizes. Many small particles are of the order of a few nanometers. The maximum particle size is around 400 nm. The average particle sizes in the blends with different comonomer feed ratios are listed in Table 2. They are less than 100 nm except for PP/PBMA blend where the PBMA particle size is a bit over 100 nm although its copolymer content is the lowest. The formation of nano-structured spherical particles can be attributed to the surface tension and the limited inter-lamella spacing.

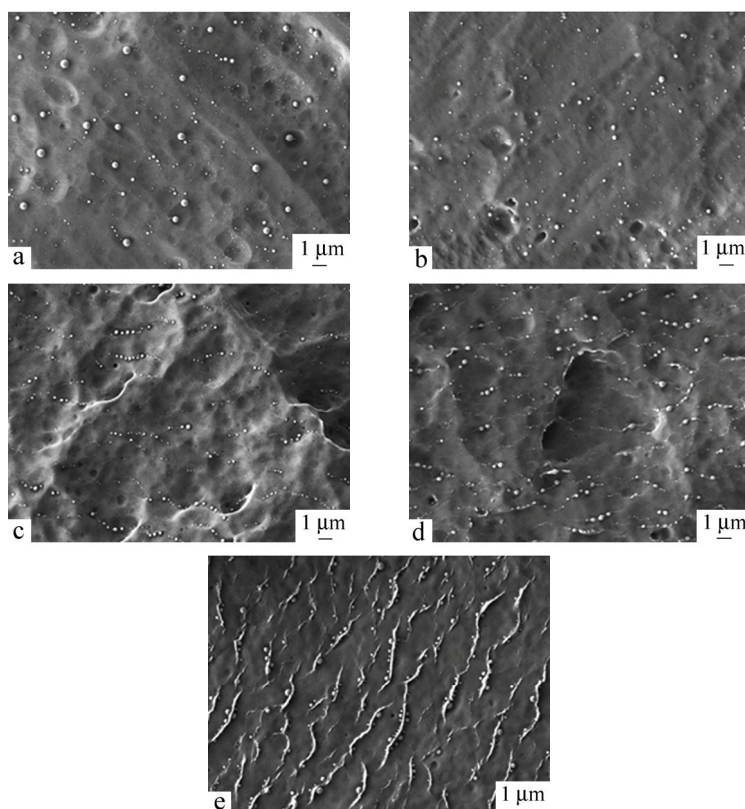


Fig. 6 FESEM micrographs of the blend pellets at about 200 μm distance to the surface after etching of the amorphous regions of *i*PP with different feed ratios St:BMA: (a) 10:0 (b) 8:2 (c) 5:5 (d) 2:8 and (e) 0:10

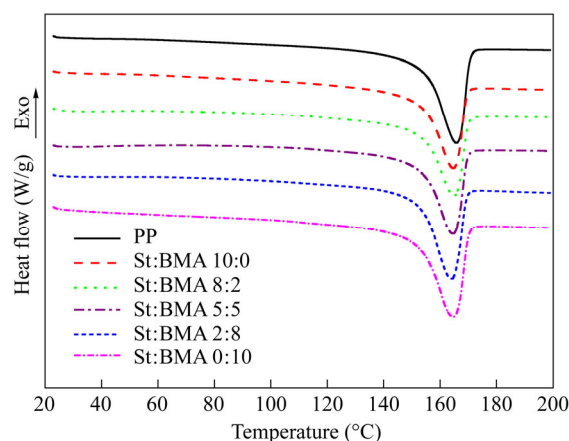
The copolymer blends obtained in this work cannot be found in the literature. However, nano-structured PP/PS blends in the form of film and sheets have been reported through supercritical carbon dioxide-assisted diffusion and subsequent polymerization of St with conventional initiator AIBN or γ -ray pre-irradiation^[9, 16].

Table 2. Average sizes of the dispersed phases, and T_m and ΔH_m of PP in the blend pellets

Sample	Average particle size (nm)	T_m (°C)	ΔH_m (J/g)
St:BMA 10:0	75	164.7	103.2
St:BMA 8:2	85	165.0	108.8
St:BMA 5:5	90	164.6	106.4
St:BMA 2:8	93	164.4	110.8
St:BMA 0:10	121	164.4	104.3
Neat <i>i</i> PP	–	165.7	103.6

DSC Measurements

In order to verify if the diffusion and subsequent copolymerization of St/BMA monomers only occur in the amorphous regions of *i*PP pellets, DSC measurements were carried out on commercial *i*PP pellet and the blend pellets with different poly(St-co-BMA) copolymer compositions. The DSC curves are given in Fig. 7, and the data of melting temperature (T_m) and enthalpy of melting (ΔH_m) are listed in Table 2. The melting behavior of *i*PP in all the samples is similar with a T_m around 165 °C and ΔH_m around 100 J/g, confirming that the diffusion and subsequent copolymerization of the St/BMA monomers do not disturb the crystalline regions of *i*PP pellets. This is in agreement with the results reported in the literature on diffusion and subsequent polymerization of St in PP films with the assistance of supercritical carbon dioxide^[9].

**Fig. 7** DSC curves of commercial *i*PP pellet and the blend pellets with different poly(St-co-BMA) copolymer compositions

CONCLUSIONS

St/BMA mixed monomers can be used to prepare copolymer blend pellets by diffusion and subsequent copolymerization in *i*PP pellets in water medium. Although the diffusion coefficients of St and BMA are different when each is used alone, both St and BMA can diffuse into the centres of the pellets when they are used together, and the diametrical distribution of St/BMA ratio is constant from the edge to the centre of the pellet. The copolymer composition can be altered by varying the comonomer feed ratio. As revealed by GPC analysis, the number average molecular weights of the copolymers are 42000–48000 with a polydispersity of 2.0–2.6. The average particle sizes in the copolymer blend pellets are less than 100 nm, showing advantage of this method over the conventional melt blending. The melting behavior of the blend pellets is similar to that of neat *i*PP pellet, confirming that the copolymerization occurs in the amorphous regions of *i*PP pellets. The method reported in this paper can be extended to prepare a range of different copolymer nanoblend pellets by varying the type of comonomers and the comonomer feed ratio.

REFERENCES

- 1 Rätzsch, M., Arnold, M., Borsig, E., Bucka, H. and Reichelt, N., *Prog. Polym. Sci.*, 2002, 27: 1195
- 2 Dong, Q., Wang, X.F., Fu, Z.S., Xu, J.T. and Fan, Z.Q., *Polymer*, 2007, 48: 5905
- 3 Li, R.B., Zhang, X.Q., Zhao, Y., Hu, X.T., Zhao, X.T. and Wang, D.J., *Polymer*, 2009, 21: 5124
- 4 Picchioni, F., Goossens, J.G.P., van Duin, M. and Magusin, P., *J. Appl. Polym. Sci.*, 2003, 89: 3279
- 5 Pluta, M., Milczarek, P., Wlochowicz, A. and Kryszewski, M., *Acta Polymerica*, 1991, 42: 306
- 6 Pluta, M., Milczarek, P., Wlochowicz, A. and Kryszewski, M., *Acta Polymerica*, 1991, 42: 485
- 7 Trznadel, M., Milczarek, P. and Kryszewski, M., *J. Appl. Polym. Sci.*, 1991, 43: 1125
- 8 Pluta, M., Morawiec, J., Kryszewski, M. and Kowalewski, T., *J. Therm. Anal.*, 1996, 46: 1061
- 9 Liu, Z.M., Dong, Z.X., Han, B.X., Wang, J.Q., He, J. and Yang, G.Y., *Chem. Mater.*, 2002, 14: 4619
- 10 Watkins, J.J. and McCarthy, T.J., *Macromolecules*, 1994, 27: 4845
- 11 Watkins, J.J. and McCarthy, T.J., *Macromolecules*, 1995, 28: 4067
- 12 Zhang, J.X., Busby, A.J., Roberts, C.J., Chen, X.Y., Davies, M.C., Tendler, S.J.B. and Howdle, S.M., *Macromolecules*, 2002, 35: 8869
- 13 Li, D., Liu, Z.M., Han, B.X., Song, L.P., Yang, G.Y. and Jiang, T., *Polymer*, 2002, 43: 5363
- 14 Busby, A.J., Zhang, J.X., Naylor, A., Roberts, C.J., Davies, M.C., Tendler, S.J.B. and Howdle, S.M., *J. Mater. Chem.*, 2003, 13: 2838
- 15 Naylor, A. and Howdle, S.M., *J. Mater. Chem.*, 2005, 15: 5037
- 16 Wang, Y.M., Wang, Y.J. and Lu, X.B., *Polymer*, 2008, 49: 474
- 17 Kung, E., Lesser, A.J. and McCarthy, T.J., *Macromolecules*, 1998, 31: 4160
- 18 Su, Z.Q., Dong, M., Guo, Z.X. and Yu, J., *Macromolecules*, 2007, 40: 4217
- 19 Su, Z.Q., Chen, X.N., Yu, Z.Z. and Zhang, L., *J. Appl. Polym. Sci.*, 2009, 111: 786
- 20 Yao, X.R., Yu, J. and Guo, Z.X., *Polymer*, 2011, 52: 667
- 21 Yao, X.R., Chen, F., Guo, Z.X. and Yu, J., *Chinese Chem. Lett.*, 2012, 23: 753
- 22 Patrick, M., Bennett, V. and Hill, M.J., *Polymer*, 1996, 37: 5335
- 23 Kim, N.S. and Seul, S.D., *J. Ind. Eng. Chem.*, 1996, 2: 122