Morphology Stabilization of the Polypropylene/Polystyrene Nanoblends Prepared by Diffusion and Polymerization of Styrene in Isotactic Polypropylene Pellets During Melt Mixing by the Incorporation of Divinylbenzene

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ABSTRACT: Divinylbenzene (DVB) was used as a comonomer of styrene (St) during the preparation of polypropylene/polystyrene (PP/PS) nanoblends by diffusion and polymerization of St in isotactic PP pellets to make the PS domains crosslinked and further to reduce the coalescence of the PS domains during melt mixing. Different morphologies were obtained after melt mixing with different amounts of the initiator benzoyl peroxide (BPO) and DVB, which was explained by different morphology evolutions during melt mixing with different crosslinked structures of the PS chains. With relatively high amounts of BPO and DVB, the nanosized PS domains almost kept their shape and size, and only simple aggregates of a few PS particles with an average size of 130 nm were observed after melt mixing of the PP/PS blends. It can be concluded that DVB is useful for morphology stabilization of the PP/PS nanoblends during subsequent melt processing. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Nanoblends, in which dispersed-phase domains exhibit length scales of order 100 nm or less, are of growing interest due to the potential for enhanced properties.[1–3] For most polymer blends processed under traditional extrusion conditions, it is hard to achieve nanoblends as a limited dispersed-phase particle size exists due to the equilibrium between drop breakup and coalescence during melt processing.[4,5] In contrast, *in situ* polymerization of one monomer inside a polymer matrix is demonstrated to be a feasible and promising method to produce nanoblends.[6–9] For example, Picchioni et al.[6,7] prepared isotactic polypropylene/polystyrene (iPP/PS) blends with PS particle size of 10–50 nm in the amorphous phase of iPP microparticles via diffusion and *in situ* polymerization of styrene (St) in porous iPP powders. Han et al.[8,9] achieved nanoblends via supercritical CO_2-assisted impregnation of monomer and subsequent polymerization in PP films.

In our previous work,[10] PP/PS blends have been successfully prepared by diffusion and subsequent polymerization of St in commercial iPP pellets, with an average size of the PS domains less than 100 nm. However, during subsequent melt processing, the nanosized PS domains will collide and coalesce to bigger domains at a low capillary number.[11] To reduce the extent of coalescence, a crosslinking agent divinylbenzene (DVB) was used as a comonomer of styrene (St) during the preparation of PP/PS nanoblends to introduce crosslinked structure to the PS domains. By crosslinking of the PS chains, the diffusion and interpenetration of the PS chains will be restricted, and it will be hard for the PS chains in different dispersed droplets to make contact on a microscopic scale and flow together, so actual coalescence will be retarded.[12] The morphology evolutions during melt mixing of the PP/PS nanoblends prepared with different amounts of the initiator benzoyl peroxide (BPO) and DVB are discussed in detail.

EXPERIMENTAL

Materials

Commercial grade iPP S1003 with a pellet diameter of approximately 4.5 mm, a crystallinity of 40% (determined by differential scanning calorimetry (DSC)), was purchased from Yanshan Petroleum and Chemical (Beijing, China). Styrene (St) was distilled under reduced pressure. DVB, chemically pure, was used without
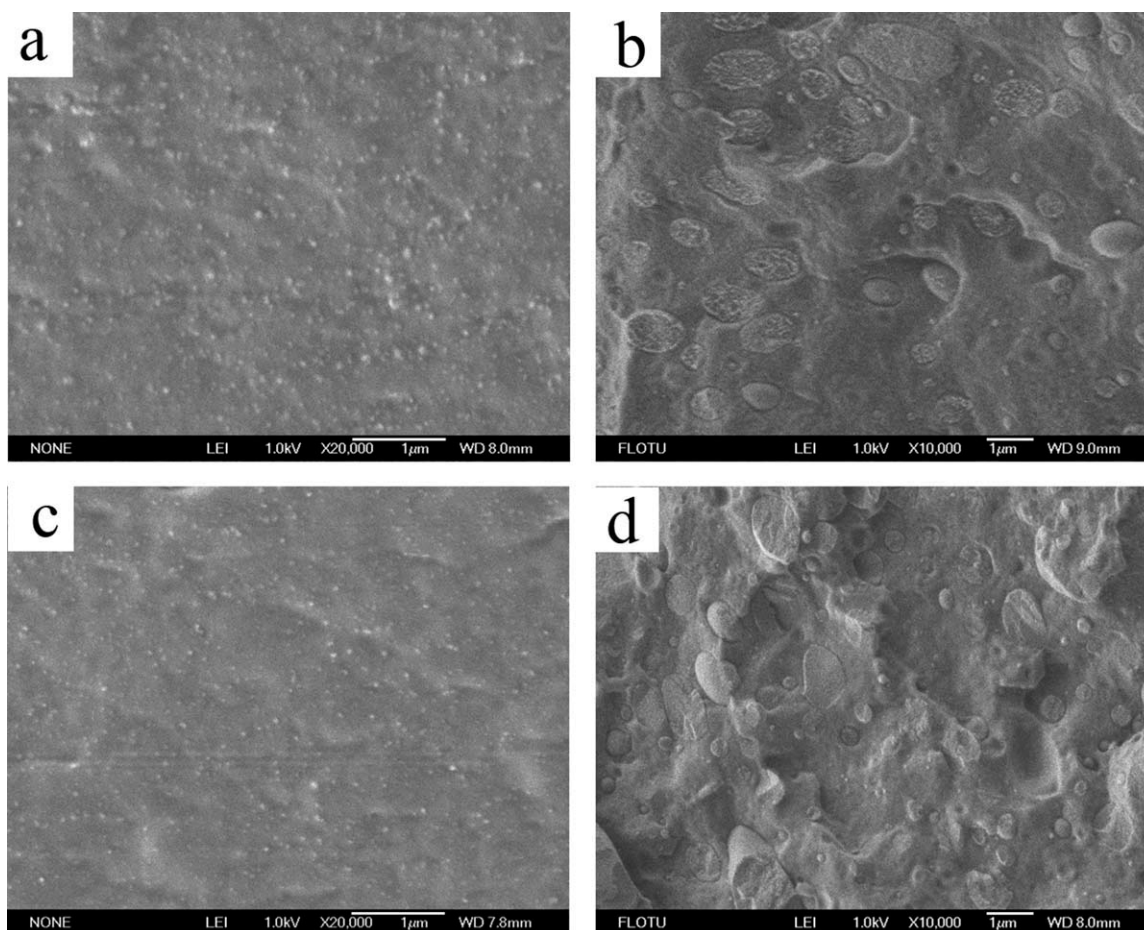
Figure 1. FESEM photographs of the PP/PS blends prepared without DVB before (a,c) and after melt mixing (b,d). (a,b): 1% BPO; (c,d): 5% BPO.

further purification. BPO was purified by recrystallization from chloroform/methanol. Polyvinyl alcohol (PVA) was provided by Beijing Organic Chemical Plant (Beijing, China), with a degree of polymerization of 1750 ± 50 and a degree of alcoholysis of 88%. Chloroform was analytical grade and used as received.

Preparation of PP/PS Blend Pellets

To a 250 mL flask equipped with a condenser and a mechanical stirrer were added 20 g of PP, 7.5 mL of 0.8 wt % aqueous PVA as a suspending agent, and 52.5 mL of deionized water. The mixture was heated with a water bath while stirring and then maintained at 90°C. Afterward, 6 g of St (or with 1% or 5% DVB, to the weight of St) was added to the flask and diffusion proceeded for 1 h. Subsequently, the diffusion systems were added initiator BPO (1% or 5% to the weight of St) dissolved in 2 mL of chloroform and maintained at 90°C for 3 h to complete polymerization. In latter discussion, different PP/PS blends are denominated with a system "xByD," where "xB" symbolizes addition of x% BPO and "yD" symbolizes addition of y% DVB. After polymerization, pellets were separated from the suspension, washed, and dried to a constant weight.

Characterization of the Initial Morphology of the PP/PS Blend Pellets

As the PP/PS pellets were too small to be directly fractured, they were hot pressed into platelets at 160°C (below the melting point of PP) and then cryofractured in liquid nitrogen. Field emission scanning electron microscopy (FESEM) analysis was performed with a JSM-7401F (Japan Electron Optics Laboratory CO., LTD) apparatus operating at an accelerating voltage of 1 kV.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed with a TA instrument dynamical analyzer (model 2980) at a fixed frequency of 1 Hz from −100°C to 150°C with a heating rate of 2.5°C/min. Samples for DMA were all prepared by melt mixing of the PP/PS blend pellets in a MS-II melt mixer and extruder (Beijing University of Aeronautics and Astronautics, Beijing, China) followed by compression molding into films of 75 μm thickness. For DMA test, a rectangle of 10 mm width and 40 mm length was cut from the film for characterization.

Determination of the Gel Content

The PP/PS pellets with DVB were extracted in a Soxhlet Extractor with xylene for 2 weeks, and the insoluble residue was defined as gel. The gel content of the blends was calculated using the following equation:

$$\text{Gel content}(\%) = \frac{m}{m_0} \times 100\%$$

where m is weight of the gel, and m_0 is the weight of the sample used in the extraction.
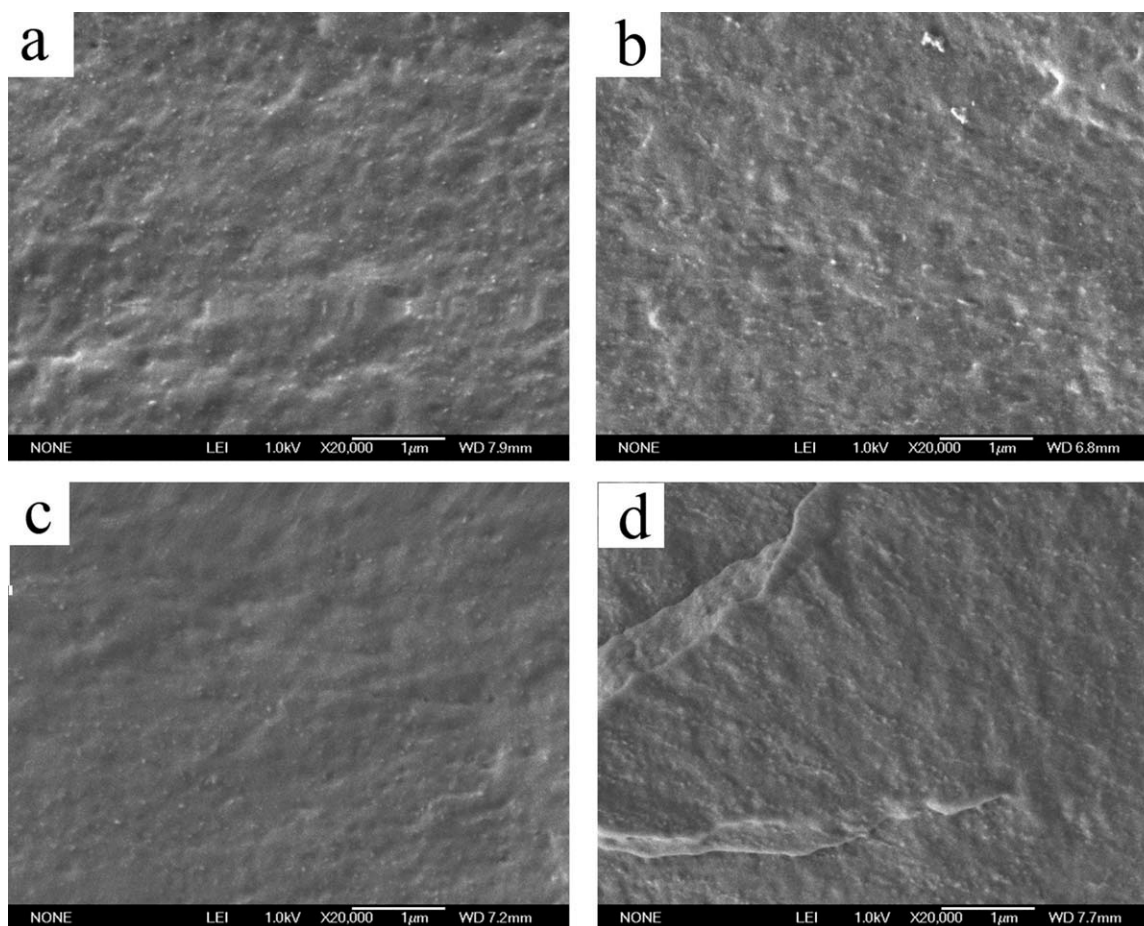
Figure 2. FESEM photographs of the PP/PS blends prepared with DVB before melt mixing. (a) 1B1D; (b) 1B5D; (c) 5B1D; (d) 5B5D.

Melt Mixing of the PP/PS Blend Pellets

Melt mixing of the PP/PS blend pellets was performed in a Haake torque rheometer (Thermo Fisher Scientific, Germany) at the temperature of 200°C for 3 min, with a screw speed fixed at 60 rpm. Samples of the PP/PS blends after melt mixing for FESEM were obtained by cryofracture in liquid nitrogen.

RESULTS AND DISCUSSION

Morphology of the PP/PS Blends Prepared without DVB Before and After Melt Mixing

The morphologies of the PP/PS blends prepared without DVB before and after melt mixing have been visualized by FESEM (Figure 1). The average sizes of the primary PS domains are 50 nm [Figure 1(a,c)]. However, after melt mixing, the PS domains coalesce into bigger domains with an average size of 0.5 μm [Figure 1(b,d)]. There is no obvious difference between the morphologies with 1 and 5% BPO addition. The results clearly show that the initial nanoscopic morphology of the PP/PS blends is not stable during melt mixing.

Morphology of the PP/PS Blends Prepared with DVB Before and After Melt Mixing

To reduce the coalescence of the PS domains and improve the stability of the initial nanoscopic morphology of the PP/PS blends during melt processing, crosslinked structures were introduced into the PS domains by diffusion and subsequent polymerization of a mixture of St and a crosslinking agent DVB in PP pellets. With addition of DVB, absorption of St is almost unchanged, as reflected by the almost unchanged total and inner PS contents in the PP/PS blends. The nanoscopic morphology of the polymerized PP/PS blends prepared with different amounts of BPO and DVB before melt mixing is similar to the PP/PS blends prepared without DVB (Figure 2).

Morphologies of the PP/PS blends after melt mixing were shown in Figure 3. In the case of "5B1D" [Figure 3(c)], the nanosized PS domains coalesce into bigger domains with an average size of 200 nm, which is much smaller than the average size of the PS domains in PP/PS blends prepared without DVB after melt mixing [Figure 1(d)]. In the case of "5B5D" [Figure 3(d)], aggregates of a few PS particles with an average size of 130 nm are observed. Preliminary conclusion can be reached from the results above that crosslinking is useful for reducing coalescence and achieving a finer morphology. However, unexpected morphologies are observed in the cases of "1ByD" [Figure 3(a,b)]. Microsized islands with irregular shape and heterogeneous structure are found in "1B1D" [Figure 3(a)] while networks with sizes of several micrometers built by fibrillar PS domains are found in "1B5D" [Figure 3(b)]. It can be conferred that the amounts of BPO and DVB do affect the morphology evolution during melt mixing.
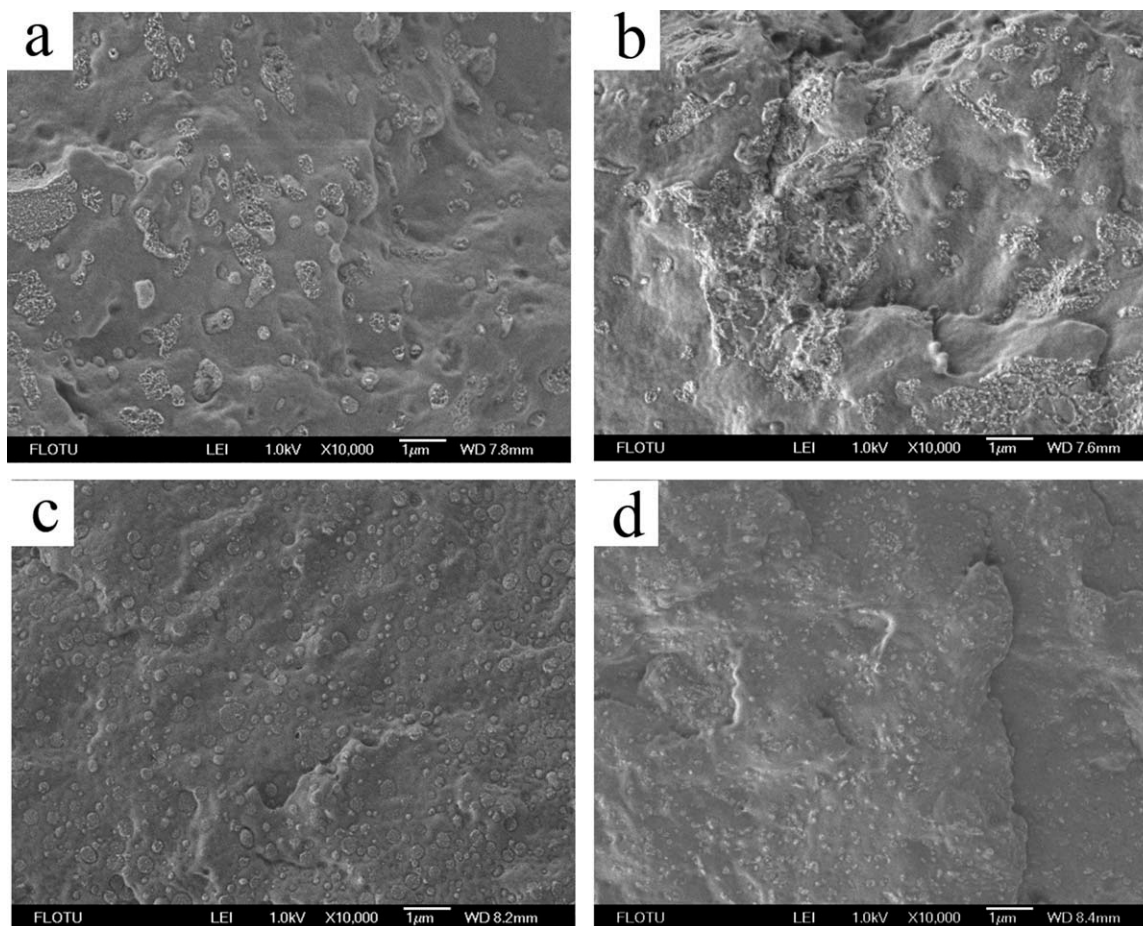
Figure 3. FESEM photographs of the PP/PS blends prepared with DVB after melt mixing. (a) 1B1D; (b) 1B5D; (c) 5B1D; (d) 5B5D.

Morphology Evolutions of the PP/PS Blends During Melt Mixing

The different morphology of the PP/PS blends with different levels of BPO and DVB after melt mixing must be resulted from different morphology evolutions with different crosslinked structure of the PS chains during melt mixing.

Free radical copolymerization of St and DVB has been studied for years, and it is commonly accepted that the formation of the crosslinked structure involves intermolecular and intramolecular crosslinking.[13–15] An ideal homogeneous crosslinked structure forms when intermolecular crosslinking dominates, whereas the intramolecular crosslinking will leads to the formation of regions of relative high segmental density which are called "microgels" and final inhomogeneous crosslinked structure. And the weight-average length of the primary polymer chain during copolymerziation (equivalent to the kinetic chain length of the radical homopolymerization) was demonstrated crucial to the competition between intermolecular and intramolecular crosslinking.[15] Longer primary polymer chains lead to promoted intramolecular crosslinking, and shorter primary polymer chains are beneficial to intermolecular crosslinking. And variation of the initiator BPO content will affect the length of the primary molecules and finally influence the homogeneity of the crosslinked structure.[13] In this work, when 5% BPO is added, the primary polymer chains are much shorter than that when 1% BPO is added. The crosslinked structures of the PS chains in the cases of "1ByD" are apt to be more heterogeneous and "microgels" linked less densely probably exist, whereas the crosslinked structures of the PS chains in the cases of "5ByD" are more homogeneous.

The extent of crosslinking is expected to increase as the ratio of DVB/St increases.[13] This is evidenced by the DMA results shown in Figure 4 and the gel contents shown in Table I. In Figure 4, the peak above 100°C is assigned to the glass transition of PS. The glass transition temperatures (T_g) of PS are 109.0, 109.2, and 116.2°C for samples 1B0D, 1B1D, and 1B5D, respectively, and 100.1, 101.3, and 107.2°C for samples 5B0D, 5B1D, and 5B5D, respectively, indicating an increase in T_g as the DVB content increases, and thus an increase in the extent of crosslinking. The T_g of PS is higher in series of "1ByD" than "5ByD" probably due to the higher PS molecular weight at a lower amount of the initiator BPO.[16] In Table I, the gel contents of samples 1B5D and 5B5D are bigger than those of samples 1B1D and 5B1D, revealing an increase in gel content and thus an increase in the extent of crosslinking with more DVB addition.

During melt mixing, the collision and coalescence of the nano-sized PS domains happens initially, while breakup of the small
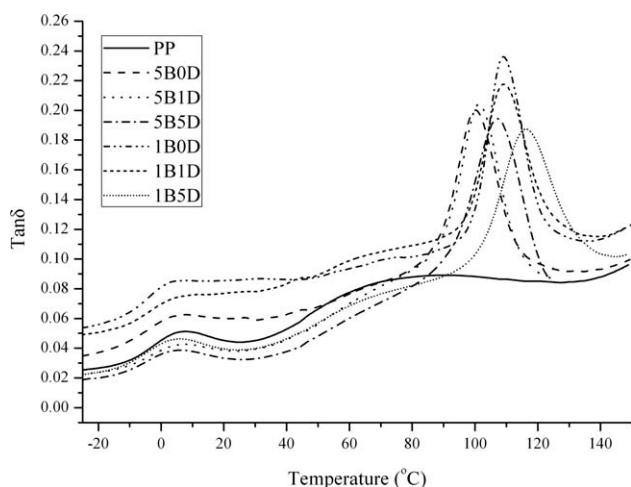
Figure 4. DMA results of the PP/PS blends prepared with different amounts of BPO and DVB.

Table I. Gel Contents of the PP/PS Blends

Samples	1B1D	1B5D	5B1D	5B5D
Gel content (%)	12	19	0[a]	18

[a]The extent of crosslinking is too small to be detected.

domains hardly happens at a low capillary number.[11] According to the discussion above, different crosslinked structures of the PS chains with different amounts of BPO and DVB and the possible initial morphology evolutions of the PP/PS blends are illustrated in Figure 5. In the case of "1ByD" [Figure 5(a,b)], the PS chains have inhomogeneous structures with densely crosslinked microgels that are less densely linked externally.[13] The less densely crosslinked polymer chains linking the microgels can still have ability to coalesce. And the extent of coalescence decreases with the increase in the amount of DVB due to the increase in the extent of crosslinking. In the case of "1B1D" [Figure 5(a)], the nanosized PS domains collide and coalesce into bigger domains due to the coalescence of the polymer chains linking the microgels. However, it is hard for the newly

formed PS domains to retract to spheres due to the existence of microgels. Such irregular shaped PS domains will further coalesce into microscale domains [Figure 3(a)] as the melt mixing proceeds. In the case of "1B5D" [Figure 5(b)], coalescence happens in the same way as "1B1D." However, the contact between two droplets is weaker and the retraction dynamics[17,18] of the newly formed PS domains after coalescence is slower than "1B1D" due to the higher extent of crosslinking. As a result, PS domains with higher aspect ratios form and are benefit for the formation of final networks [Figure 3(b)][19]. Both in the above two cases, as the coalescence of the domains continue to carry out, the breakup of the domains still hardly happen due to the big viscosity of the PS phase with microgels,[20] so final microsized PS domains or networks are finally achieved [Figure 3(a,b)]. In the case of "5ByD" [Figure 5(c,d)], the PS chains have homogenous structures and the extent of crosslinking increase as the amount of DVB increases. When the extent of crosslinking is low, as in the case of "5B1D" [Figure 5(c)], the coalescence and retraction of the PS domains are similar to those of PS domains without crosslinking. And the spherical PS domains go on coalescing to a steady domain size depending on the viscosity ratio and the capillary number that describes the relative importance of viscous stresses and interfacial tension.[12] As the viscosity ratio between the dispersed phase and the matrix is higher in "5B1D" than "5B0D," the steady domain size is smaller in "5B1D" [200 nm, Figure 3(c)] than "5B0D"
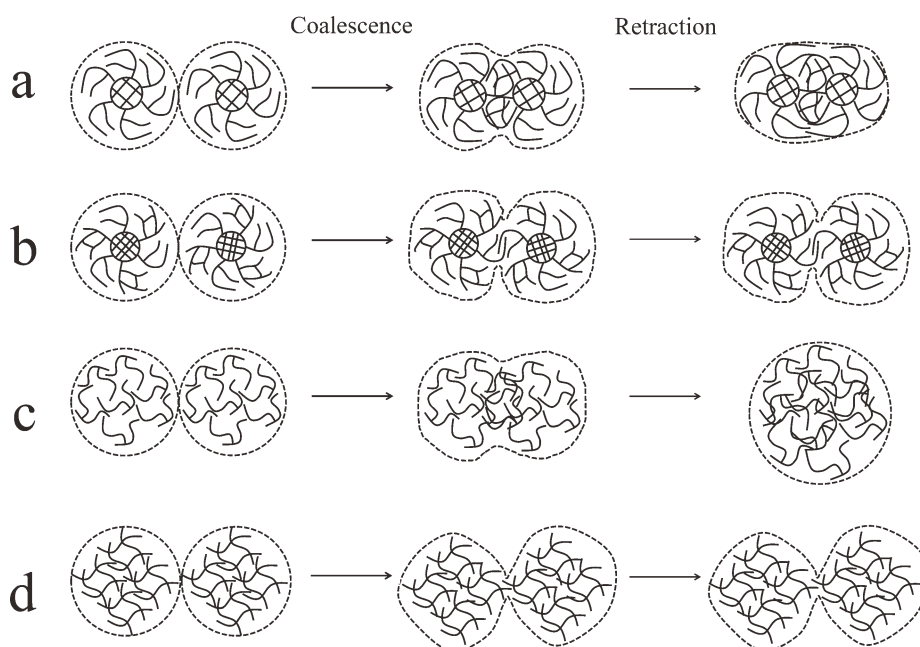

Figure 5. Schematic illustration of initial morphology evolutions of the PS domains with different chain structures during melt mixing. (a) 1B1D; (b) 1B5D; (c) 5B1D; (d) 5B5D.

[0.5 μm, Figure 1(d)] according to influence of the viscosity ratio on the steady drop size given by the partially mobile interface (PMI) theory.[11] In the case of "5B5D" [Figure 5(d)], the extent of crosslinking of the PS domains is high and the extent of coalescence is low. Therefore, the nanosized PS domains are apt to accumulate and aggregates of a few PS particles with an average size of 130 nm are finally observed after melt mixing [Figure 3(d)].

CONCLUSIONS

The use of a crosslinking agent DVB as a comonomer of St in the preparation of PP/PS nanoblends by diffusion and polymerization of St in iPP pellets is an effective way to stabilize the initial nanoscopic morphology of the PP/PS blends during subsequent melt processing. Both the amounts of BPO and DVB used in the copolymerization have great effects on the morphology evolutions of the PP/PS blends during subsequent melt mixing and different morphologies were achieved after melt mixing. When the amounts of BPO and DVB were both high, the nanosized PS domains initially formed by polymerization almost kept their shape and size, and simple aggregates of a few PS particles with an average size of 130 nm were observed after melt mixing of the PP/PS blends.

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