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Pseudo Interpenetrating Polymer Networks of Crystalline Polystyrene

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ABSTRACT: Pseudo interpenetrating polymer networks (IPN's) of linear syndiotactic polystyrene (syn-PS) and cross-linked atactic polystyrene (c-PS) were prepared and characterized. The crystalline behavior of syn-PS in polymer networks and the morphology of pseudo-IPN's of syn-PS/c-PS have been studied by DSC and SEM. Pseudo-IPN's of linear isotactic polystyrene and c-PS as well as linear syn-PS and cross-linked atactic poly(methyl methacrylate) were also prepared for comparison with the pseudo-IPN's of syn-PS and c-PS.

I. Introduction

Binary interpenetrating polymer networks (IPN's) composed of two chemically identical components have been known as Millar IPN's.[1] One type of Millar IPN is obtained when the degrees of cross-linking of the two chemically identical networks are different. Polystyrene/polystyrene IPN's of this type were prepared by polymerizing and cross-linking of the first component, followed by swelling, polymerizing, and cross-linking of the second component with the same cross-linking reagent.[2] Another type of Millar IPN can be prepared with two chemically identical polymers of different tacticities which was less reported. In this paper we describe the synthesis and characterization of pseudo-IPN's (P-IPN's) of atactic and syndiotactic polystyrene (PS).

Syndiotactic PS, a recently synthesized polymer, is a new semicrystalline thermoplastic material with high melting temperature (~270 °C) and excellent chemical resistance. The rate of crystallization of syndiotactic PS is several orders of magnitude higher than that of isotactic PS and similar to that of poly(ethylene terephthalate).[3] A wide range of products have been formulated with syndiotactic PS including glass-reinforced resins and impact-modified grades for specific applications.

This paper is concerned with the crystalline behavior of syndiotactic PS in polymer networks and the morphology of pseudo-IPN's composed of linear syndiotactic PS and cross-linked atactic PS. Pseudo-IPN's of linear isotactic PS and cross-linked atactic PS as well as linear syndiotactic PS and cross-linked atactic poly(methyl methacrylate) are prepared for comparison.

II. Experimental Section

1. Synthesis of Syndiotactic PS[4-6] (syn-PS). Toluene solvent (AR grade; Malline Prodt Specialty Chemicals) was refluxed with CaH_2 for 4-5 h and then distilled and kept over CaH_2. Styrene monomer (99%; Aldrich Chemical Co.) was washed with a 10% NaOH solution followed by distilled water, dried over $MgSO_4$ and CaH_2, and then distilled under vacuum and kept over CaH_2. Both toluene and styrene were distilled for a second time and stored over 4-Å molecular sieves 24 h before the polymerization.

The synthesis of syndiotactic PS was carried out in a dry flask baked with a heat gun and cooled under vacuum. A total of 16 mL of a methylaluminoxane (MAO) solution (10% solution in toluene; Scherine Co.) and 7 mg of pentamethylcyclopentadienyltitanium trichloride[7,8] were added to the flask in a glovebox. Toluene (35 mL) and styrene (15 mL) were then added, and the reaction mixture was stirred for 4-5 h at 50 °C under N_2 and then put into a water bath at 50 °C for 3 days. The reaction mixture was then hydrolyzed with the addition of 40 mL of methanol and was poured into 100 mL of a 1 M aqueous HCl solution while stirring slowly. In a separatory funnel, the water layer was removed. The resultant polystyrene was collected by vacuum filtration, washed with methanol, and vacuum dried at 90 °C for 24 h. The yield was 1.8 g. After extraction with methyl ethyl ketone (MEK) at room temperature for 24 h, 1.25 g of syndiotactic PS was obtained; the percentage yield of the syndiotactic PS was ~70%.

Table 1. P-IPN's of the Same Composition but Different Degrees of Cross-Linking

sample no.	divinylbenzene (g)	$\overline{M}_c$[a]	percentage yield (%)	wt percentage of syn-PS (%)
1	0.074	500	68	37.0
2B	0.037	1000	75	33.3
3	0.019	2000	65	38.5
4	0.009	4000	78	32.3
5	0 (blend)		63	40.0

[a] $\overline{M}_c$ is the average molecular weight between cross-linking points. $\overline{M}_c$ values were estimated from the initial molar ratio of styrene and divinylbenzene.

2. Synthesis of Pseudo-IPN's of Linear Syndiotactic PS and Cross-Linked Atactic PS. A typical synthesis of a pseudo-IPN was carried out in the following manner: In a reaction vial, 0.1 g of syn-PS was dissolved in 1.5 g of 1,2,4-trichlorobenzene at 170 °C with stirring. The solution was then cooled down to 110 °C. To this solution was added a premixed solution which was made by dissolving 0.01 g of AIBN initiator in 0.3 g of styrene and 0.037 g of divinylbenzene. The vial was degassed, filled with N_2, and then stirred for 4 h at 100 °C. The reaction continued in a 100 °C oven for 5 days before termination by the addition of methanol. The product was washed with methanol, filtered, and dried under vacuum at 90 °C for 24 h. The amounts of syn-PS and divinylbenzene were varied to form IPN's with different compositions and cross-linking densities, respectively. The synthesis of syn-PS/c-PMMA pseudo-IPN was carried out in a similar way except styrene was replaced by MMA. Similar procedures were also employed to synthesize isotactic PS/c-PS pseudo-IPN's. However, the addition of the monomer as well as the reaction was performed at a lower temperature of 80 °C so that the reactions were easily controlled. Due to the high molecular weight of isotactic PS, about 50% more solvent than was described above was used to decrease the viscosity of the reaction mixture. Information about the P-IPN's is listed in Tables 1-3.

III. Characterizations

1. Differential Scanning Calorimetry (DSC). The DSC data were obtained with a DuPont Instrument DSC

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Table 2. P-IPN's of Different Compositions but Similar Degrees of Cross-Linking[a]

sample no.	syn-PS (g)	percentage yield (%)	wt percentage of syn-PS (%)
2A	0.225	91	46.9
2C	0.060	89	18.8
2D	0.030	91	10.0

[a] $\overline{M}_c$ = 1000 for each sample.

Table 3. P-IPN's of Linear Isotactic PS and Cross-Linked Atactic PS

sample no.	divinylbenzene (g)	$\overline{M}_c$	percentage yield (%)	wt percentage of iso-PS (%)
1	0.037	1000	100	26.8
2	0.019	2000	95	28.2

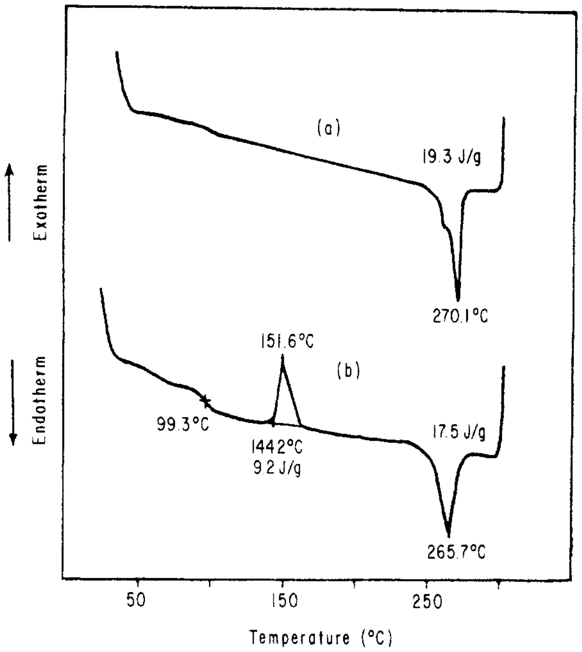

Figure 1. DSC thermograms of (a) syn-PS and (b) partially quenched syn-PS.

2910. A 7-mg sample was used in the DSC scanning in the temperature range of 25–300 °C. The heating rate of the first scan was 40 °C/min, and the cooling rate was 20 °C/min. The heating rate of the second scan was 20 °C/min. For partially quanched IPN samples, which were prepared by heating the sample at 300 °C for 6 min and moving it into liquid nitrogen, the heating rate of 20 °C/min was used. The T_g's were determined by the midpoint of the transition region. The T_m's and T_c's were determined by the peak maximum temperatures. The areas of the peaks were integrated based on the linear base line.

2. Infrared Spectra (IR). Infrared spectra were obtained at room temperature by using a Perkin-Elmer 1600 Series FTIR spectrophotometer with a resolution of 4 cm^{-1}; 16 scans were collected for each sample. A 1,2,4-trichlorobenzene solution of ~3% (by weight) syndiotactic PS was used for the syndiotactic PS sample.

3. NMR Measurements. ^{1}H-NMR and ^{13}C-NMR spectra were obtained from a XL-300 NMR instrument at 100 °C. Deuterated tetrachloroethane was used as the solvent to make up a 15% (by weight) testing solution. The ^{13}C-NMR spectra were obtained at a frequency of 75.5 MHz with ^{1}H decoupling.

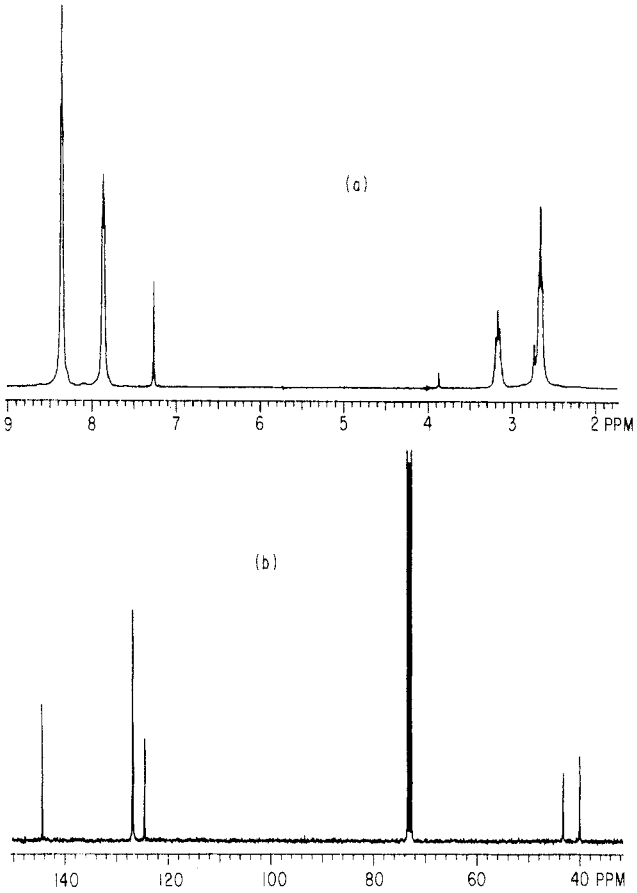

Figure 2. (a) ^{13}C-NMR spectrum of syn-PS. (b) ^{1}H-NMR spectrum of syn-PS.

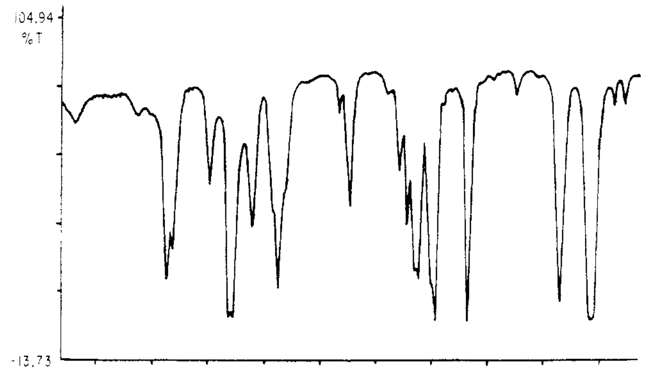

Figure 3. IR spectrum of syn-PS in 1,2,4-trichlorobenzene within the range of 1700–800 cm^{-1}.

4. Gel Permeation Chromatography (GPC). The relative molecular weight of the linear syn-PS was obtained from GPC measurement. Instrument: Waters 150C. Eluant: trichlorobenzene. Temperature: 145 °C. Flow rate: 1.5 mL/min. Void volume: 45 mL. Column type: μ-Styragel. A narrow-M_w PS standard sample was used to get the calibration curve.

5. Scanning Electron Microscopy (SEM). The phase morphological characteristics of the samples were studied by means of SEM. The specimens for SEM were bent in air. Then, they were mounted on a stub with silver paint and coated with platinum in a Hummer V sputter coater. They were then observed with a digital scanning microscope (DSM 940; Zeiss, Germany) operating at low voltage (5 kV). The electron images were recorded directly from the cathode ray tube on Polaroid 55 film.

IV. Results and Discussion

1. Characterization of Syndiotactic PS. Syndiotactic PS is a white powder. From Figure 1 we found the melting temperature (T_m) of syndiotactic PS to be 270.1 °C and the amount of heat evolved during crystal melting

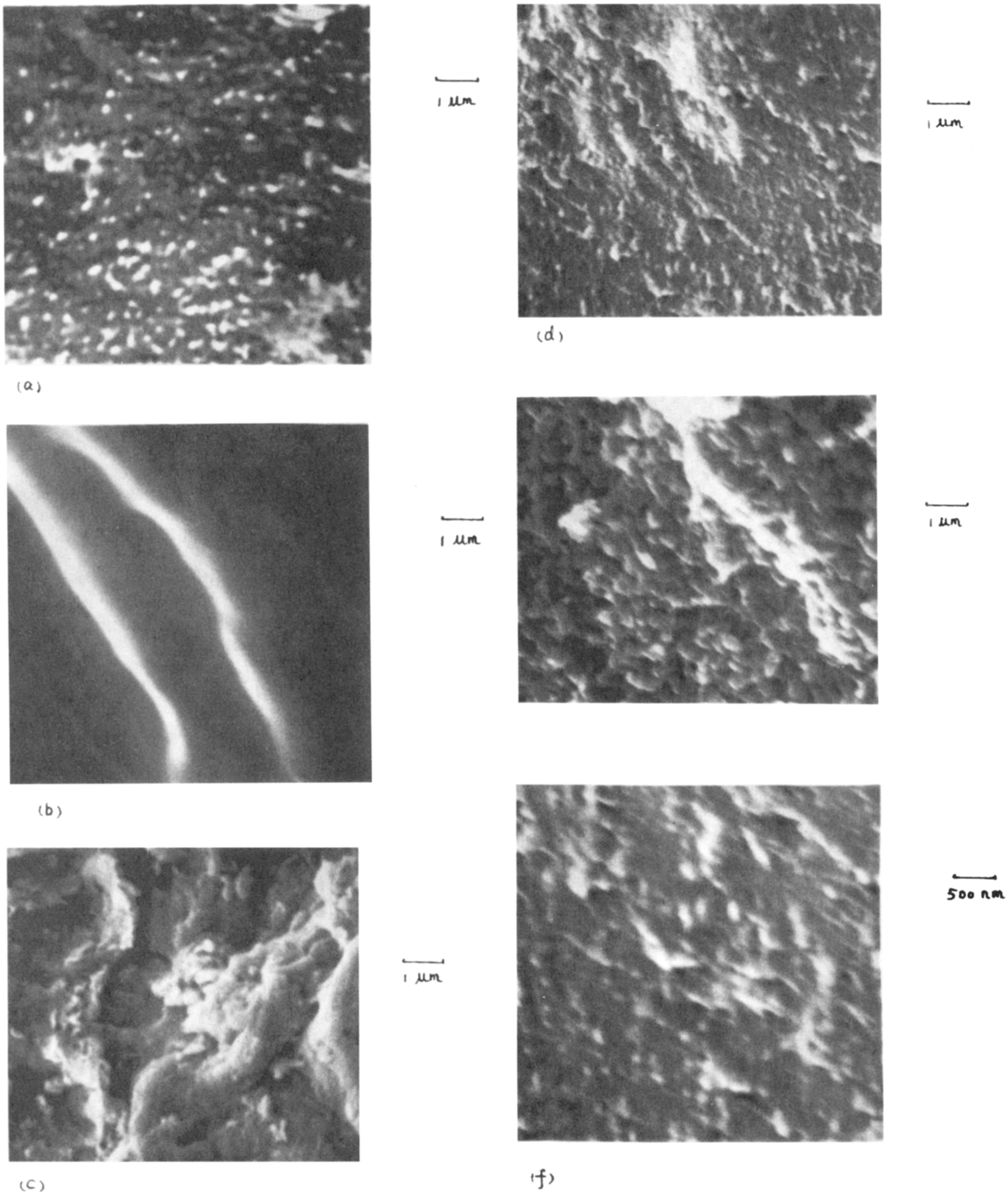

Figure 4. SEM micrographs of: (a) syn-PS; (b) cross-linked atactic PS; (c) pseudo-IPN of linear syn-PS and cross-linked atactic PS (18.8% syn-PS, $\overline{M}_c$ = 1000); (d) pseudo-IPN of linear isotactic PS and cross-linked atactic PS (28.2% isotactic PS, $\overline{M}_c$ = 2000); (e) pseudo-IPN of linear syn-PS and cross-linked atactic PMMA (25% syn-PS, $\overline{M}_c$ = 1000); (f) same as d, but with a higher magnification.

(ΔH_f) to be 19.3 J/g. For partially quenched syndiotactic PS, T_m = 265.7 °C, ΔH_f = 17.5 J/g, and the crystallization exotherm has a maximum at 144.2 °C.

Figure 2 shows the ^{1}H- and ^{13}C-NMR spectra of syndiotactic PS; the main resonances correspond to those reported in the literature for highly syndiotactic PS.[9,10] The absence of any additional detectable resonances in the region of the quaternary carbons indicates a very high stereoregularity of the polymer. Figure 3 shows the IR spectrum of syn-PS in 1,2,4-trichlorobenzene; a band at about 1250 cm^{-1} is associated with the presence of chains in the zigzag conformation[9,11] which are not present in the amorphous syn-PS sample.

The weight-average molecular weight ($\overline{M}_w$), the number-average molecular weight ($\overline{M}_n$), and the quotient of weight- to number-average molecular weight ($\overline{M}_w/\overline{M}_n$) were obtained from GPC as 97 300, 52 900, and 1.8, respectively, for syn-PS.

Table 4. DSC Data of P-IPN's of the Same Composition but Different Degrees of Cross-Linking[a]

sample no.	T_g (°C)	T_m (°C)	ΔH_f* (J/g)	ΔH_f	T_{gQ} (°C)	T_{mQ} (°C)	T_c (°C)	ΔH_f*$_Q$ (J/g)	ΔH_{fQ}
1	122.7	268.7	14.50	5.37		270.3	154.5	17.46	6.47
2B	116.6	268.6	15.15	5.05	114.1	266.0	153.3	18.51	6.17
3	102.4	266.7	16.26	6.25	97.7	266.4	154.8	21.29	8.19
4	100.0	266.4	21.70	7.00	98.3	265.7	155.5	27.11	8.75
5	97.7	264.4	20.23	8.09	94.7	263.7	152.8	22.23	8.90
sps	99.7	269.9	19.92		98.4	271.1	141.5	20.15	

[a] T_g is the glass transition temperature. T_m is the melting temperature of crystalline polymer. T_c is the temperature of crystallization. ΔH_f* is the amount of heat evolved during crystal melting (ΔH_f* values have been modified to be comparable to pure syn-PS sample). ΔH_f is the original value from DSC measurements. sps is the pure syn-PS sample with the same treatment as for the preparation of the P-IPN's. T_g, T_m, and T_c values are from the second run of DSC for unquenched samples. T_{gQ}, T_{mQ}, T_c, and ΔH_{fQ} values are from the first run of the DSC for partially quenched samples.

Table 5. DSC Data of P-IPN's of Different Compositions but Similar Degrees of Cross-Linking[a]

sample no.	T_g (°C)	T_m (°C)	ΔH_f* (J/g)	ΔH_f	T_{gQ} (°C)	T_{mQ} (°C)	T_c (°C)	ΔH_f*$_Q$ (J/g)	ΔH_{fQ}
2A	118.7	268.8	15.38	7.21	118.3	268.5	154.4	18.27	8.57
2B	116.6	268.6	15.15	5.05	114.1	266.0	153.3	18.51	6.17
2C	117.5	267.1	15.55	2.92	112.9	267.0	162.3	15.96	3.00
2D	115.9	267.0	7.52	0.75	115.8	266.7		8.68	0.87

[a] The symbols have the same meaning as in Table 4.

2. DSC Results and Discussion of P-IPN's of Linear Syn-PS and Cross-Linked Atactic PS. From the DSC results shown in Tables 4 and 5, the following apply:

(a) As $\overline{M_c}$ decreases, the T_g goes up due to the reduction of the chain flexibility (the differences are 6.1, 4.2, 2.4, and 2.3 °C, respectively). For the P-IPN's of different compositions but similar degrees of cross-linking, the differences are smaller (2.1, 0.9, and 1.6 °C).

(b) As $\overline{M_c}$ decreases, ΔH_f values decrease too, since the crystallinity of syn-PS declines because of the presence of the atactic PS networks. The higher the degree of cross-linking, the lower the value of ΔH_f when the degree of cross-linking is changed from $\overline{M_c} = 500$ to $\overline{M_c} = 4000$. For the P-IPN's of similar degrees of cross-linking, the ΔH_f values of 2A–C are almost the same, while the ΔH_f value of 2D is much smaller. This tells us that for the P-IPN's of similar degrees of cross-linking, when the weight percentage of linear syn-PS increases in P-IPN's, there are more chances for linear syn-PS chains to come together and fold to form crystals, so crystallization is easier. After the weight percentage reaches a certain point, the crystallinity tends to be constant because of the limited ability for syn-PS to be crystallized.

(c) Compared to the pure syn-PS sample, T_m values of the P-IPN's are lower; the presence of the atactic PS networks makes it easier for the syn-PS crystals to melt. We find the lower the $\overline{M_c}$ value, the higher the T_m value. Thus the degree of cross-linking seems to effect the crystallinity and the T_m of crystalline syn-PS in different ways: As the degree of cross-linking increases, the crystallinity of syn-PS declines, while the melting point generally increases for both partially quenched samples and unquenched samples. For P-IPN's of different compositions, as the weight percentage of syn-PS increases, the T_m value goes up, which suggests to us that the more syn-PS is present in the P-IPN, the easier it is to have high T_m crystals formed. The possible reason for this is that the presence of the atactic PS network causes the formation of imperfections in the crystals.

(d) Compared to the pure syn-PS sample, the T_c values of P-IPN's are about 10 °C higher. This indicates that due to the presence of an atactic PS network the formation of syn-PS crystals is more difficult and only occurs at the higher temperature.

3. SEM Results and Discussion. SEM micrographs show surface topographical and chemical contrast of the samples. Some phase domains in IPN's can be resolved on SEM micrographs.[12] SEM micrographs of the individual polymers and pseudo-IPN's are shown on Figure 4. Linear syn-PS (Figure 4a) exhibits clearly resolvable domains with an average domain size of 0.3 μm in diameter which is due to the partial crystallization of the syn-PS sample (with the melting point at 270.1 °C). The pure cross-linked atactic PS which has no melting point reveals a homogeneous single-phase morphology (Figure 4b). On micrograph c in Figure 4 we see diffuse circular regions and less well-defined spherical domains. This result shows that the formation of this P-IPN affects the crystallinity of linear syn-PS.

Micrograph d in Figure 4 exhibits the phase morphology of P-IPN of linear isotactic PS and cross-linked atactic PS. Many dispersed domains are resolved with an average domain diameter of about 1000 Å. This is more clearly revealed at higher magnification as shown in Figure 4f. Figure 4e exhibits the morphology of P-IPN of cross-linked atactic PMMA and linear syn-PS with an average domain size of 0.4 μm in diameter.

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