

Synthesis and Characterization of Polymethylphenylsilane–Polystyrene Block Copolymers

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SYNOPSIS

Block copolymers of polymethylphenylsilane (PMPS) and polystyrene (PS) have been successfully prepared by the condensation of α,ω -dichloro-polymethylphenylsilane with polystyryl-lithium. These new materials have been characterized by UV spectroscopy, ²⁹Si-NMR, and size exclusion chromatography. These block copolymers show a good emulsifying activity to compatibilize blends of the two homopolymers (PMPS and PS). © 1993 John Wiley & Sons, Inc.

Keywords: polysilane • polystyrene • blends • block copolymers

INTRODUCTION

Despite their relative novelty, soluble polysilanes have already found a number of areas in which they may play a practical role.¹ They are commercially used as thermal precursors to β -silicon carbide² and are intensively studied as photoresists for microlithography,³ as photoinitiators for free radical vinyl polymerization,⁴ and as a new class of photoconductors⁵ and nonlinear optical materials.⁶

Thus far, the scientific interest in the substituted polysilanes was mostly centered on their very unusual spectral properties as well as their photosensitivity. However, we recently observed that polysilane films are brittle and that they crack rather rapidly under the action of internal stresses.⁷ To improve the polysilanes' mechanical resistance while reducing their cost and preserving their exceptional electronic properties, we have considered the incorporation of polysilanes in blends and in block copolymers with other polymer units. The first polymer pair studied as a model system was constituted of polymethylphenylsilane and polystyrene.

In this article, we describe the preparation and the characterization of polymethylphenylsilane (PMPS)–polystyrene (PS) block copolymers. The synthesis process consists of the coupling of α,ω -dichloro-polymethylphenylsilane with polystyryl-lithium. We also show the emulsifying ability of these block copolymers to compatibilize physical blends of the two homopolymers.

EXPERIMENTAL

Synthesis of α,ω -Dichloro-Polymethylphenylsilane

Dichloromethylphenylsilane was purchased from Alfa Products and distilled under argon prior to use. The polymerization was carried out in brown glassware under argon atmosphere. A dry 500 mL three-necked-round bottom flask equipped with a reflux condenser, an argon inlet, and a lateral pressure-equalized flask was charged with freshly distilled toluene (100 mL), and sodium chunks (20% weight excess). The mixture was brought to reflux and magnetically stirred, producing a fine dispersion. The monomer (0.163 mol) was then added dropwise. Addition required 25–30 min during which the reaction mixture turned from grey to dark purple. After the addition was completed the mixture was heated to reflux for 6 h. Thereafter, the system was cooled to room temperature and the reaction mixture

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was filtered without adding any alcohol nor water to remove excess of sodium. The polymer was obtained by two precipitations into an inert nonsolvent: petroleum ether to preserve chloro-ended chains. The precipitate was dried in a vacuum oven at 110°C for 1 day.

Synthesis of Polystyryl-Lithium

In a dry flask fitted with a magnetic stirrer, freshly distilled toluene was introduced together with styrene under nitrogen atmosphere. Styrene monomer was dried over CaH₂ and then distilled under nitrogen prior to use. *sec*-Butyllithium was added dropwise, at room temperature, until the reaction mixture turned from colorless to yellow. Then the catalytic quantity of *sec*-butyllithium was introduced and the mixture became dark orange. The reaction was continued for 2 h at room temperature. Solvent, monomer, and initiator of polymerization were all added by syringe under nitrogen.

Synthesis of Polymethylphenylsilane-Polystyrene Block Copolymer

The α,ω -dichloro-polymethylphenylsilane was redissolved in dry toluene (10% wt/vol) in brown glassware and dried carefully by azeotropic distillation. Then the freshly prepared polystyryl-lithium solution was transferred through a capillary into the PMPS solution. The mixture was stirred under nitrogen for 18 h at room temperature. The copolymer was obtained by precipitation into methanol. The precipitate was dried overnight at 60°C under vacuum.

Characterization Techniques

Molecular weights of the polymers and copolymers were determined by size exclusion chromatography (SEC) at 25°C, using 6 Ultrastaygel Waters columns calibrated by polystyrene standards (porosity ranges: 10⁶, 10⁵, 10⁴, 10³, 500, 100 Å) and with THF as eluent at a flow rate of 0.8 cm³ min⁻¹. The detection system was a variable wavelength UV detector (WATERS 484). Data analyses were performed on a Digital Microvax 2000 computer with handling treatment by Millipore Waters.

²⁹Si-NMR spectra were recorded on a Bruker 500 MHz FT-NMR instrument, at room temperature. Polymers were dissolved in chloroform-*d* (solution 15% wt/vol) with chromium(III) acetylacetonate [Cr(Acac)₃, 0.02M] as relaxing agent. Chemical shifts are quoted in ppm from TMS.

The UV spectra were recorded on a Philips 8720 UV/VIS scanning spectrophotometer.

A Hitachi S570 scanning electron microscope was used to examine fractures of cast films prepared from polymer solutions in dichloromethane. Polymer films were fractured in liquid nitrogen and coated with gold prior to analysis.

RESULTS AND DISCUSSION

Syntheses

Polymethylphenylsilane was synthesized by the most common and effective preparative technique of polysilanes⁸ which consists of the condensation of methylphenyldichlorosilane with sodium metal (Fig. 1). The Würtz-type coupling reaction, run at elevated temperature (110°C) in toluene, is difficult to reproduce and polymodal molecular weight distributions invariably result. A typical distribution is trimodal with \bar{M}_w fractions: (1) < 1500; (2) 4000–30,000; and (3) 10⁵ to several millions.⁹ To preserve chloro-ended chains, the polymer was precipitated into an inert nonsolvent: petroleum ether. In our reaction conditions, described in the Experimental section, very few high molecular weight PMPS was formed and by a second precipitation of the material into petroleum ether, we eliminate low molecular weight polymer. Thus, the resulting product is a fraction of intermediate molecular weight PMPS (\bar{M}_w of 20,000–30,000) with chloro-ended chains.

This chlorine end-functionalization was confirmed by ²⁹Si-NMR. Indeed, the ²⁹Si-NMR spectrum of polymethylphenylsilane obtained by this way consists of the three usual resonances at -39.2, -39.8, and -41.1 ppm corresponding to chain-silicons, and a peak at +15 ppm characteristic of Si-Cl chain-ends.¹⁰

The synthesis of polystyryl-lithium was carried out by anionic polymerization in toluene with *sec*-butyllithium as initiator (Fig. 2).

PMPS-PS block copolymers were prepared by condensation of α,ω -dichloro-polymethylphenylsi-

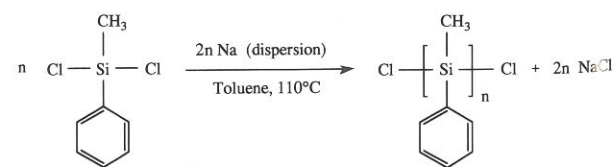


Figure 1. Synthesis of α,ω -dichloro-polymethylphenylsilane.

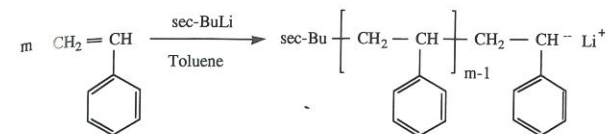


Figure 2. Synthesis of polystyryl-lithium.

lane with polystyryl-lithium in toluene. The synthetic scheme is shown in Figure 3.

Physicochemical Characterization

Molecular weight data for precursor polymers PMPS and PS and for the products of copolymerization PMPS-PS are gathered in Table I. Molecular weights at the top of chromatographic peak (M_p), weight-average molecular weights (\bar{M}_w), and number-average molecular weights (\bar{M}_n) were determined by size exclusion chromatography (SEC) with polystyrene standards.

The molecular weight distribution was found to be monomodal for the PMPS-PS (I) product and trimodal for the PMPS-PS (II) product. In the first synthesis, equivalent moles number of each precursor polymer PMPS (I) and PS (I) were mixed together, so that $y = x$ (Fig. 3).

In this case, the expected product of reaction is a statistical mixture of triblock copolymer (25%),

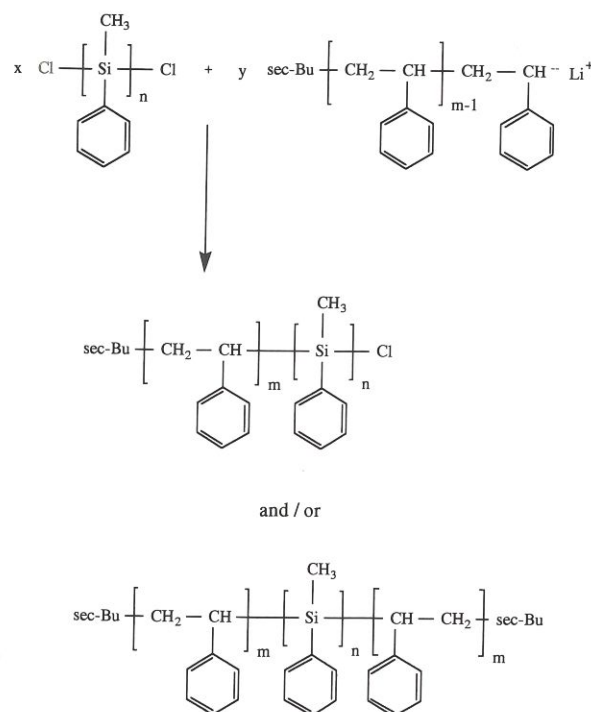


Figure 3. Synthesis of PMPS/PS block copolymers.

Table I. Molecular Weights in PS Equivalents of PMPS and PS Precursor Polymers and of the Products of Copolymerization PMPS-PS, with UV Detector at 254 nm

Reference	M_p	\bar{M}_w	\bar{M}_n
PMPS (I)	7400	20,200	3300
PS (I)	3800	3800	3500
PMPS-PS (I)	12,300	19,300	4800
PMPS (II)	6700	27,900	2700
PS (II)	22,000	19,500	14,900
PMPS-PS (II)	8000 (first peak) 28,400 (second peak) 49,900 (third peak)	45,200	21,000

diblock copolymer (50%), and the remaining PMPS (I) homopolymer (25%). The results presented in Table I and (later in Fig. 6) show that only one peak is detected on the PMPS-PS (I) chromatogram. However, the molecular weight at the top of the chromatographic peak (M_p) almost corresponds to M_p [PMPS (I)] + M_p [PS (I)] which indicates the formation of a block copolymer. The reason why three peaks on the chromatogram remain undistinguishable is due to the fact that the PS (I) precursor polymer is a low molecular weight one (Table I) and therefore M_p [PMPS (I)], M_p [PMPS-PS (I)] diblock copolymer, and M_p [PMPS-PS (I)] triblock copolymer lie too close to one another.

In the second synthesis, the relation between the numbers of moles of each precursor polymer PMPS (II) and PS (II) is $y = 1.32x$ (Fig. 3). Therefore, the expected statistical mixture of products is: 44% of PMPS-PS (II) triblock copolymer, 45% of PMPS-PS (II) diblock copolymer, and 11% of the remaining PMPS (II) precursor polymer. As can be seen on Figure 4 and in Table I, the molecular weight of the PS (II) precursor polymer is now large enough to allow the distinction of three peaks. Nevertheless, the separation of these three peaks is not very good, then a deconvolution of the PMPS-PS (II) chromatogram was performed. Molecular weights at the top of the chromatographic peak (M_p) and areas (in %) of each peak obtained by the deconvolution are given in Table II.

The results of the deconvolution clearly indicate the obtainment of PMPS-PS (II) diblock and triblock copolymers and the presence of the remaining PMPS (II) homopolymer after the second synthesis. The M_p values for the three peaks obtained by deconvolution (Table II) are similar to the values measured on the chromatogram (Table I). More-

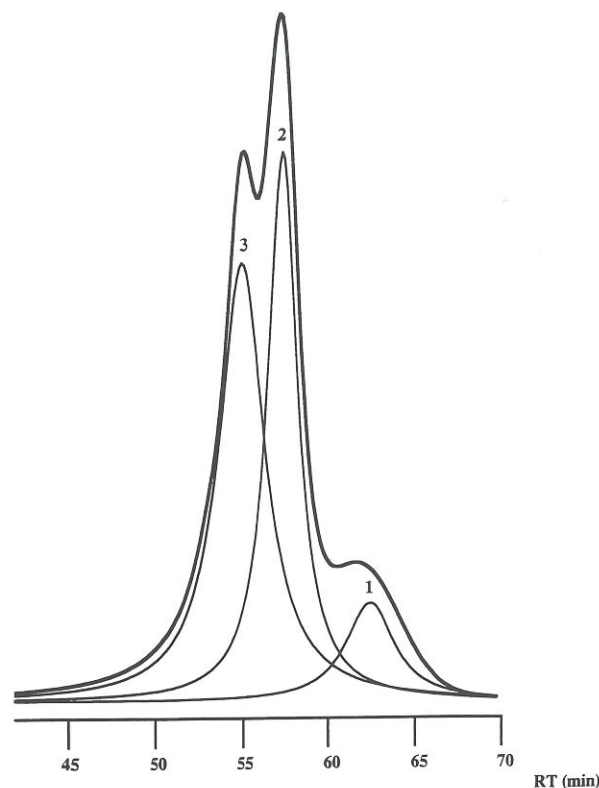


Figure 4. PMPS-PS (II) chromatogram and the three peaks resulting from the deconvolution: (1) PMPS (II) precursor polymer, (2) PMPS-PS (II) diblock copolymer, (3) PMPS-PS (II) triblock copolymer.

over, M_p [PMPS-PS (II)] for the second peak is close to M_p [PMPS (II)] + M_p [PS (II)] as well as M_p [PMPS-PS (II)] for the third peak is almost equal to M_p [PMPS (II)] + $2M_p$ [PS (II)]. It must also be noticed that the proportions of each component obtained by the deconvolution of the chromatogram are very close to those predicted by the statistics.

Further proof that the products of the copolymerization were genuine block copolymers and not

Table II. Molecular Weights at the Top of the Chromatographic Peak (M_p) and Areas (in %) of Each Peak Obtained by the Deconvolution of PMPS-PS (II) Chromatogram

Reference	M_p	Area (%)
First peak	6500	11.5
Second peak	27,700	40.5
Third peak	50,400	48

simple physical blends were provided by different SEC analyses. First of all, during the synthesis of the PMPS-PS (I) block copolymer, an aliquot was removed after 1 h of reaction for SEC analysis. The chromatogram of that sample exhibits a peak with a shoulder corresponding respectively to the PMPS-PS (I) block copolymer and to the PMPS (I) precursor polymer as well as a peak at lower molecular weight corresponding to the PS (I) precursor polymer (Fig. 5). However, the chromatogram of the product obtained after 18 h of reaction exhibits only one peak assigned to the PMPS-PS (I) block copolymer (Fig. 6). That observation indicates that a coupling between the two precursor homopolymers was achieved.

Furthermore, the precursor polymers PMPS (I and II), and PS (I and II) as well as the products of the copolymerization PMPS-PS (I and II) were also characterized by SEC with a UV detector set successively at different wavelengths between 254 and 325 nm. We report here the molecular weight data obtained with UV detector set at 254 nm (Table I) and at 300 nm (Table III). With the detector at the wavelength of 254 nm, which is the maximum absorption wavelength characteristic of the phenyl aromatic group, PMPS and PS absorb and thus both polymers can be detected and analysed by SEC. However, if the detector is set at 300 nm, only PMPS absorbs and can be characterized by SEC. Therefore two different situations have to be considered. First, if no chemical bond between PS and PMPS exists in the products of copolymerization, at 300 nm, the

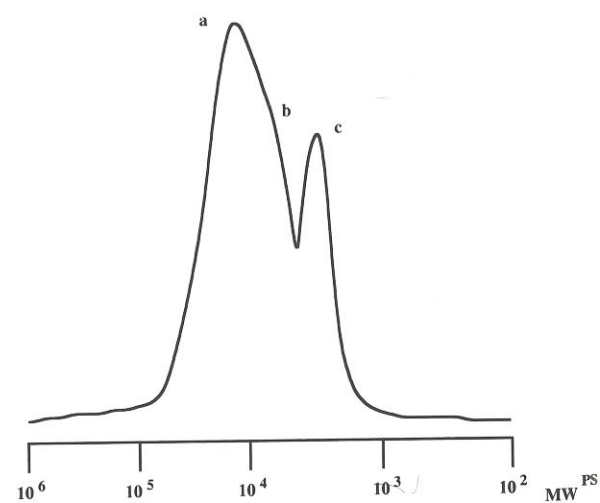


Figure 5. SEC curve of the product obtained after 1 h of coupling reaction: (a) PMPS-PS (I) block copolymer, (b) PMPS (I) precursor polymer, (c) PS (I) precursor polymer.

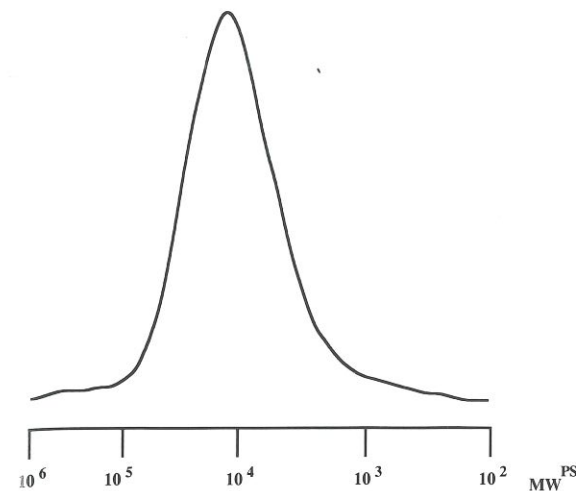


Figure 6. SEC curve of the product obtained after 18 h of copolymerization reaction.

chromatogram corresponding to the PMPS precursor should be displayed. Secondly, if a chemical bond exists between PS and PMPS in the products of copolymerization, the chromatograms and molecular weights should be similar with the detector set at 254 or at 300 nm. The situation observed is the second one. If we compare the results listed in Table I with those reported in Table III, we remark that the different molecular weights (M_p , \bar{M}_n , and M_w) of PMPS-PS (I and II) remain almost constant whether we detect at 254 or at 300 nm. This original method allowed us to demonstrate the existence of chemical bonds between the two precursor polymers PS and PMPS in the compounds PMPS-PS (I and II).

PMPS-PS (I and II) were also characterized by ^{29}Si -NMR and by UV spectroscopy. The ^{29}Si -NMR spectra of these compounds do not show anymore

Table III. Molecular Weights in PS Equivalents of PMPS and PS Precursor Polymers and of the Products of Copolymerization PMPS-PS, with UV Detector at 300 nm

Reference	M_p	\bar{M}_w	\bar{M}_n
PMPS (I)	7300	20,900	3600
PS (I)	— ^a	— ^a	— ^a
PMPS-PS (I)	12,400	20,500	5100
PMPS (II)	6800	28,500	3200
PS (II)	— ^a	— ^a	— ^a
PMPS-PS (II)	8000 (first peak) 28,800 (second peak) 49,400 (third peak)	49,600	18,700

^a Undetectable at this wavelength.

the characteristic resonance of chloro-ended PMPS chains at +15 ppm. This seems to indicate that the chloro end groups have actually reacted. This observation is thus in good agreement with previous results obtained by SEC. The ^{29}Si -NMR spectra will be published in a future article. The UV spectra of PMPS-PS (I and II) show a strong absorption at 339 nm (λ_{max}) which is the characteristic absorption band of PMPS.¹ This value of λ_{max} shows that polymethylphenylsilane does not degrade during copolymer syntheses.

Morphological Observations

A scanning electron microscopy study on fracture surfaces of PMPS/PS blend films shows that those two homopolymers form a two-phase system. The SEM micrograph of a 50% PMPS/50% PS ($\bar{M}_n = 125,000$) blend sample (Fig. 7) shows a coarse dispersion of polymethylphenylsilane in polystyrene matrix. The particle size can reach 5–10 μm and the interfacial adhesion is bad. The poor interphase adhesion characteristic of incompatible blends usually results in very poor mechanical properties. This behavior is presumably related to a high degree of stress concentration in the vicinity of the interface.¹² One widely practiced way to obtain a finer dispersion and to improve adhesion between incompatible polymers is to use a block copolymer that will tend to localize preferentially at the homopolymer-homopolymer interface.¹³ We have applied this concept to our system and we have compared by SEM the morphology of PMPS/PS blends compatibilized by the incorporation of a small quantity of PMPS-PS block copolymer with the morphology of the same

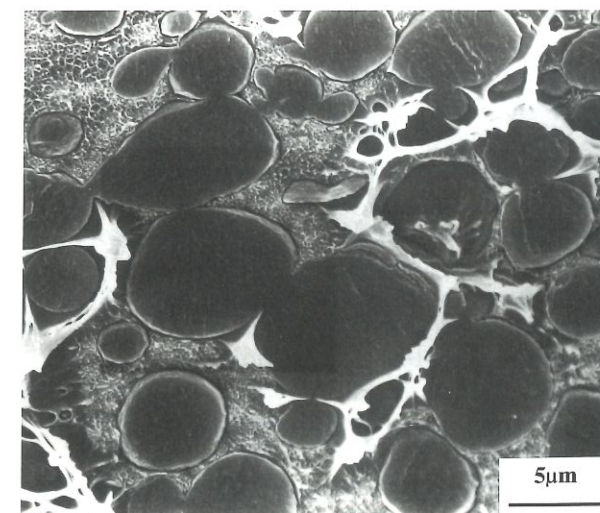


Figure 7. Scanning electron micrograph of the fractured surface of a 50% PMPS/50% PS blend film.

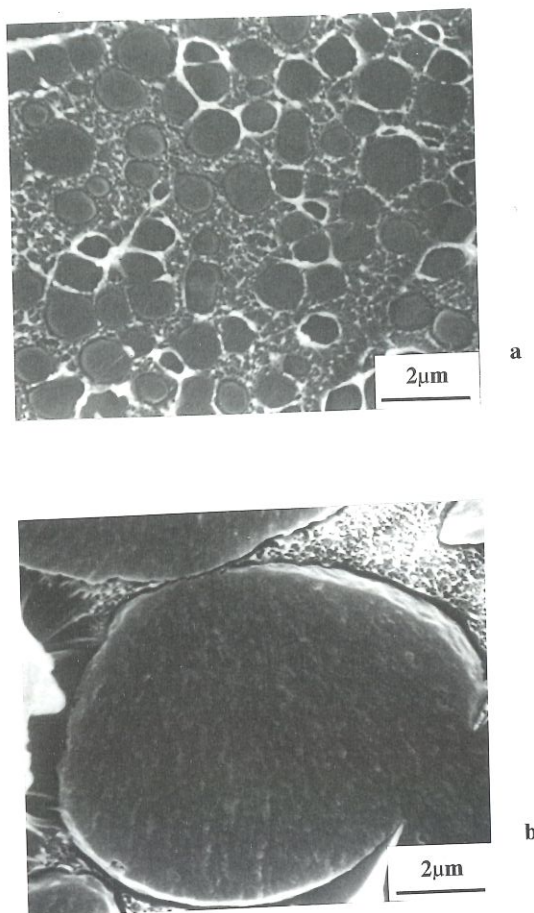


Figure 8. Scanning electron micrographs of fractured surfaces of: (a) a 45% PMPS/45% PS + 10% PMPS-PS (I) block copolymer sample, and (b) a 50% PMPS/50% PS blend film.

blends not compatibilized. The morphology of a ternary blend composed of 45% PMPS (I), 45% PS ($\bar{M}_n = 125,000$), and 10% PMPS-PS (I) block copolymer is totally different from that of a binary blend 50% PMPS/50% PS [Figs. 8 (a) and (b)]. The SEM micrographs of Figures 8 (a) and (b) are taken at the same magnification ($\times 10,000$) whereas the SEM micrograph on Figure 7 was taken at a lower magnification ($\times 3000$). As discussed earlier, examination of the fractured surface of PMPS/PS blend films without any compatibilizing agent reveals a coarse particle dispersion ($5\text{--}10\ \mu\text{m}$). On the contrary the fracture surface of blend films with a compatibilizing agent shows a finer dispersion with particles size $\leq 1\ \mu\text{m}$. Thus, the addition of a PMPS-PS block copolymer as a compatibilizing agent results, as expected, in a significant decrease in particle size.

Further investigations on the morphology of such blends, including a study of the morphology of melt blended systems are now in progress.

CONCLUSION

We have demonstrated that PMPS-PS block copolymers can be prepared by the coupling of α,ω -dichloro-polymethylphenylsilane with polystyryl-lithium. UV spectroscopy, ^{29}Si -NMR, and SEC clearly indicate the formation of block copolymers as opposed to simple physical mixture of the two precursors. A morphological study by SEM reveals a significant decrease in particle size when a PMPS-PS block copolymer is incorporated into a PMPS/PS (50/50) blend. This aspect provides evidence for the interfacial activity of the block copolymer and also provides additional proof for the existence of blockiness.

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