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Sequential Interpenetrating Polymer Networks of Isotactic Polystyrene and Heterotactic Polystyrene

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ABSTRACT: The synthesis and characterization of sequential interpenetrating polymer networks (SIPN's) of isotactic polystyrene and heterotactic polystyrene are reported in this paper. SIPN's with different cross-linking degrees or different compositions of isotactic PS networks show single T_g's in DSC thermograms, while in SEM micrographs the SIPN's exhibit a heterogeneous phase morphology.

Introduction

In a previous paper,[1] we reported the synthesis and characterization of pseudointerpenetrating polymer networks of syndiotactic polystyrene and heterotactic polystyrene. In this paper, we describe sequential interpenetrating polymer networks (SIPN's) of isotactic polystyrene and heterotactic polystyrene which are different from the Millar SIPN's of polystyrene synthesized by Siegfried et al.[2]

Polymers with aromatic character can be prepared by the condensation of α,α′-dichlor-*p*-xylene in the presence of Friedel−Crafts catalysts.[3,4] It has also been demonstrated[5] that polystyrene (PS) may be cross-linked in the same way through its aromatic substituents, and the reaction can be monitored by the evolution of hydrogen chloride and the increase in glass transition temperature of the polystyrene. A Friedel−Crafts catalyst was used in this research to obtain cross-linked networks of isotactic polystyrene.

Experimental Section

I. Synthesis. The raw materials used are listed in Table 1. The cross-linker, α,α′-dichloro-*p*-xylene, was recrystallized from methanol and vacuum dried at 60 °C. The initiator, lauroyl peroxide, was purified by dissolving in tetrachloromethane, precipitating in methanol, and then drying under vacuum at room temperature. Styrene and divinylbenzene were washed with dilute NaOH solution followed by distilled water and then dried over CaH_2. After vacuum distillation, styrene and divinylbenzene were kept over 4Å molecular sieves. Other chemicals were used without further purification.

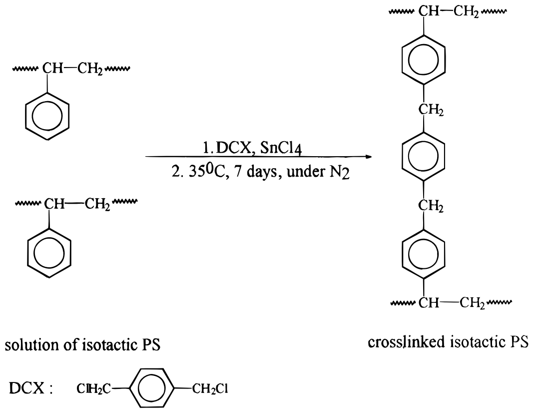
1. Cross-Linked Isotactic PS. The cross-linking reaction (shown in Scheme 1) was carried out within a sealed reaction flask which was dried and filled with N_2. First, the isoPS solution and DCX were mixed in the flask, allowing the DCX to be dissolved completely. Then the flask was degassed and filled with N_2. The $SnCl_4$ catalyst was added by syringe under a N_2 flow, and finally the reaction flask was sealed. The reaction proceeded at 35 °C for 7 days. The cross-linking mixture went from a slightly yellow solution to the final deep red gel, and the reaction was terminated by the addition of a mixture of methanol and distilled water. The solid product was a pale yellow powder, which was washed with methanol and vacuum dried at 90 °C. The liquid supernatant was saved for analysis of HCl evolution.

2. SIPN of Isotactic PS and Heterotactic PS. To make the SIPN, we swelled the cross-linked isotactic PS with St, DVB, and LPO (0.6 wt %). The mixture of St, DVB, LPO, and cross-linked isotactic PS was allowed to equilibrate at 5 °C for 25 h, and then heated at 75 °C for 7 days in a reaction vial. The blends were made from the mixture of linear isotactic PS, St, and LPO under similar conditions. The resulting SIPN's were opaque after they were washed by toluene and vacuum dried. The reaction was virtually complete as indicated by the small weight loss.

Table 1. Materials and Their Abbreviations

designation	name and description	source
isoPS solution	3% solution of 90% isotactic PS in 1,2-dichloroethane, MW = 400 000 by GPC	Scientific Polymer Products, Inc.
DCX	α,α′-dichloro-*p*-xylene, 98%	Aldrich Chemical Co.
$SnCl_4$ catalyst	1.0 M solution of $SnCl_4$ in heptane	Aldrich Chemical Co.
LPO	lauroyl peroxide, 97%	Aldrich Chemical Co.
St	styrene, 99%	Aldrich Chemical Co.
DVB	divinylbenzene, 55%, mixture of isomers	Aldrich Chemical Co.
methanol	reagent grade	Aldrich Chemical Co.
toluene	reagent grade	Aldrich Chemical Co.

Scheme 1. Cross-Linking Reaction of Isotactic PS



II. Characterization. 1. Differential Scanning Calorimetry (DSC). The DSC thermograms were obtained from a DuPont DSC 2910 and Thermal Analyst 2000 within the temperature range 25−300 °C. The first scan was at 20 °C/min, followed by equilibration to 25 °C, and the second scan was at 40 °C/min. The glass transition temperature (T_g's) and the melting temperature (T_m's) were determined by the midpoint of the transition region and the peak maximum temperatures, respectively. The areas of the peaks were integrated based on the linear base line.

2. NMR Measurement. The ^{13}C NMR spectrum of isotactic PS was recorded at 25 °C using a Varian Gemini-300 spectrometer operating at 75.5 MHz. The solution was made in $CDCl_3$ (∼5 wt %) and heated to 50 °C to enhance solubility. At room temperature, some of the dissolved polymer precipitated into a suspension.

3. UV−vis Spectra. UV−vis spectra were obtained at room temperature from a HP 8452A diode-array spectrophotometer with a wavelength accuracy of ±1 nm. The measure-

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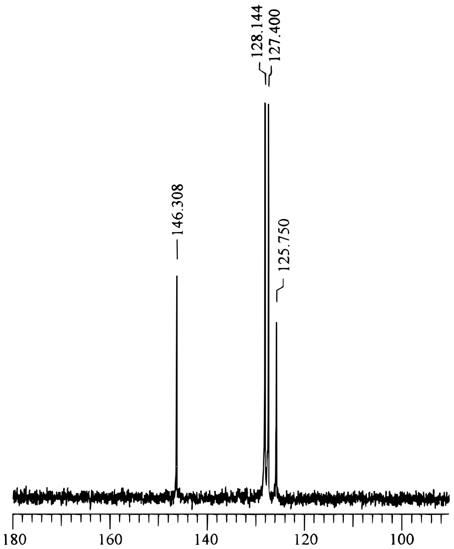

Figure 1. ^{13}C NMR spectrum of linear isotactic polystyrene.

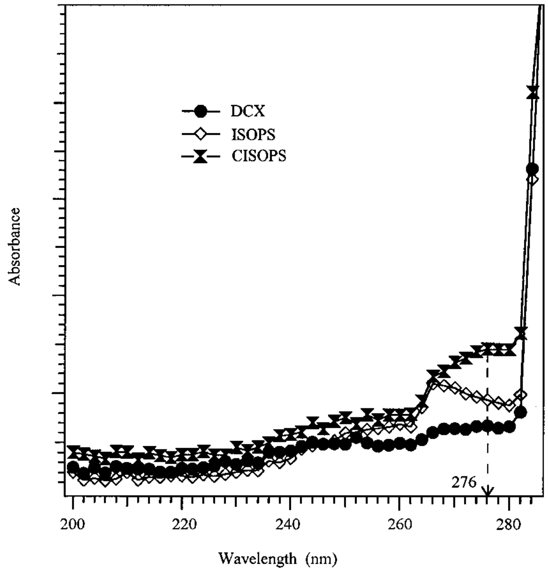

Figure 2. UV spectra of C-isoPS, isoPS, and DCX.

Table 2. Cross-Linked Isotactic PS Samples

sample no.	T_g[a] (°C)	M_c (titration)	M_c[b] (theory)	wt loss[c] (%)
c-isoPS(I)	123	1.1×10^3	0.9×10^3	<10.0
C-isoPS(II)	107	1.6×10^3	1.5×10^3	<25.0
C-heteroPS	125		1.0×10^3	<5.0
L-isoPS	100			

[a] Scanning rate: 40 °C/min (the second run). [b] Calculated from the stoichiometry. [c] After 72 h of Soxhlet extraction.

ments were made using ~0.1 % solutions of the samples in toluene in quartz cells. The cross-linked isotactic PS sample was taken from the cross-linking reaction medium before gelation.

4. Scanning Electron Microscopy (SEM). The specimens for SEM were fractured in air, mounted on a stub with silver paint, and then coated with platinum in a Hummer V sputter coater. The electron images were observed on a Zeiss DSM 940 operating at low voltage (5 kV), and the pictures were taken directly from the cathode ray tube on Polaroid 55 films.

5. Analysis of HCl. A mixture of methanol, distilled water, and the supernatant reaction mixture obtained after the cross-linking reaction (see synthesis section) was titrated against standard 0.1 N NaOH solution to estimate the amount of HCl evolved in the condensation between DCX and isotactic PS. The results were corrected for the amount of HCl formed by hydrolysis of the $SnCl_4$.

Results and Discussion

For the isotactic PS used in making the SIPN's, the ^{13}C NMR spectrum (Figure 1) displayed the main resonances corresponding to those reported for highly isotactic PS.[6-8] The single sharp peak at $\delta = 146.3$ ppm is attributed to the mmmm pentad configuration of isotactic PS.[8] DSC revealed a T_g of 100 °C and a T_m at 220 °C. The crystallinity is 30% if the crystallinity of the isotactic PS is defined as

$$\% \text{ crystallinity} = (\Delta H_f / \Delta H_f^\circ) \times 100$$

where ΔH_f is the amount of heat evolved during crystal melting and $\Delta H_f^\circ = 86.32$ J/g for a pure crystalline sample.[9]

1,2-Dichloroethane (DCE) was chosen as the solvent for the cross-linking reaction since DCE accelerates the reaction between DSX and benzene.[3] Although it has been reported[10] that PS can be cross-linked by DCE with the use of $AlCl_3$ as catalyst, under the conditions applied to the cross-linking reaction of isotactic PS, no significant cross-linking occurred in the mixture of St, $SnCl_4$, and DCE. No self-condensation of DCX could be detected under the same conditions.

The cross-linking of the isotactic PS was monitored by the color change, HCl evolution, UV spectra, etc. during the cross-linking reaction. The appearance of the reaction medium changes from a slight yellow solution to a deep red gel. The nature of the coloration suggests the formation of a complex between $SnCl_4$ and the disubstituted benzene rings. Coloration does not occur with DCX because the disubstituted benzene nucleus is deactivated by the chloromethyl groups[11] while the solutions of both *p*-xylene and *p*-benzylbenzene with $SnCl_4$ in DCE are also deep red. The cross-linking is also associated with the HCl evolution and the formation of the *p*-benzylbenzene structure in the networks. The absorption at 276 nm (as shown in Figure 2) is the maximum absorption of *p*-dibenzylbenzene in the UV−vis spectra.

Using the $SnCl_4$ catalyst under our conditions, the M_c values of the isotactic PS network were limited to the range of 1.0×10^3 to 3.0×10^3. Two kinds of isotactic PS network have been synthesized, having different T_g's as indicated in Table 2 due to the different degrees of cross-linking of the networks. For different SIPN's, the cross-linking degree of C-heteroPS is the same ($M_c = 1.0 \times 10^3$) and the T_g value of the C-heteroPS is 125 °C. No melting peaks were observed for the cross-linked isotactic PS samples C-isoPS(I) or C-isoPS(II), even after they were annealed at 150 and 180 °C for 4 weeks.

All the IPN's with different compositions of C-isoPS-(I) or C-isoPS(II) showed single T_g's after Soxhlet extraction (shown in Table 3), and the T_g values of IPN-3 and -4 are lower than those in IPN-1 and -2 because of the lower T_g value of C-isoPS(II). The samples without extraction gave either a lower T_g or two T_g's indicating the effects of the tiny amount of monomer left in the IPN's and the inhomogeneity of the samples at that time. The relatively low T_g's of the blend 40/60 and the blend 25/75 are due presumably to some presence of linear heterotactic PS in the blends which possess a lower average molecular weight.

Some phase information about the IPN's can be resolved in the SEM micrographs.[12-14] SEM micro-

Table 3. IPN's of Isotactic and Heterotactic PS ($M_c = 1.0 \times 10^3$ for C-heteroPS)

sample no.	$T_g{}^a$ (°C)	$T_g{}^b$ (°C)	wt loss^c (%)	C-isoPS (wt %)
IPN-1	83, 134	122	<2.0	26(I)
IPN-2	121	123	<2.0	45(I)
IPN-3	115	118	<2.0	21(II)
IPN-4	72, 117	120	<2.0	38(II)
blend 25/75	82			25 (linear)
blend 40/60	70			38 (linear)

[a] Scanning rate: 50 °C/min (the second run). [b] After 72 h of Soxhlet extraction. Scanning rate: 40 °C/min (the second run). [c] Soxhlet extraction for 72 h.

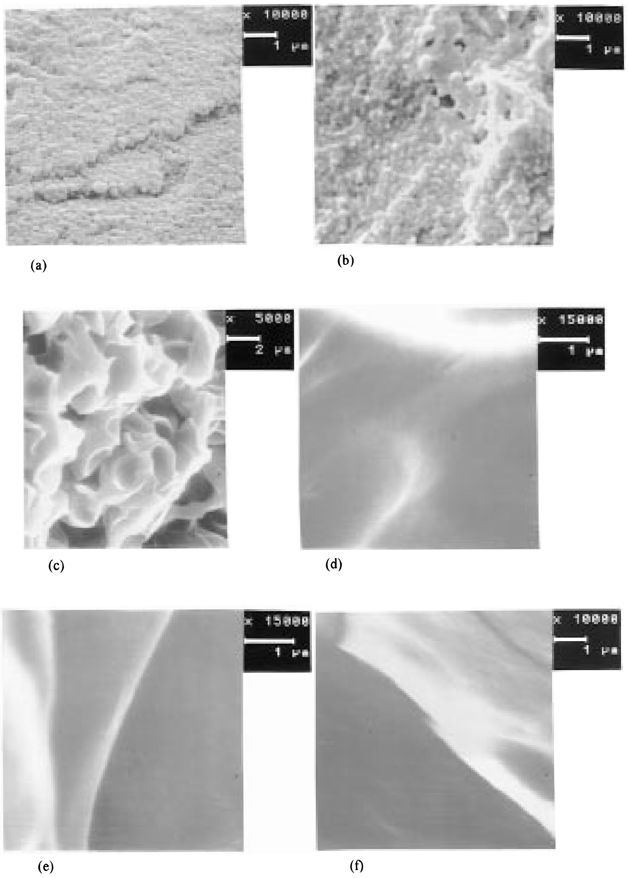

Figure 3. SEM micrographs of (a) IPN-1, (b) IPN-4, (c) blend 25/75, (d) C-isoPS(I), (e) C-isoPS(II), and (f) C-aPS.

graphs of the SIPN's, blends and pure cross-linked isoPS or heteroPS are shown in Figure 3. The pure cross-linked isotactic PS or heterotactic PS reveals a homogeneous single-phase morphology (Figure 3d–f). On the other hand, a binary phase morphology structure of the blend 25/75 is clearly indicated in Figure 3c with a layer thickness of about 0.2 μm, and for the pseudo-IPN of linear isotactic and cross-linked heterotactic PS, dispersed domains were resolved with an average domain diameter of about 0.1 μm.[1] IPN-1 exhibited a ball-like two-phase morphology in which isotactic PS formed the continuous phase. The average domain diameter of heterotactic PS is about 0.3 μm (Figure 3a). The smaller heterotactic PS domains (mean linear dimension of about 0.2 μm) are also found in the isotactic PS continuous phase of IPN-4 as indicated in Figure 3b. All the above SEM information gave a picture of a heterogeneous phase morphology for IPN's of isotactic and heterotactic PS. Previous work[15] has shown that the network first synthesized controls the morphology of the IPN's and is the more continuous phase. Even though the polymers are chemically the same and while only a very small heat of mixing is expected, entropic effects can cause phase separation.

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