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Phase Behavior of Semiinterpenetrating Polymer Networks Based on Nearly Miscible Polymer Pairs

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Introduction

As blending is the simplest and least expensive method of obtaining new materials with improved properties, the problem of the phase state of a polymer mixture is of prime interest. Most polymer pairs are immiscible as a consequence of the small entropy of mixing for macromolecules.[1] However, a few polymer pairs are relatively close to miscibility, depending on specific interactions, blending process, and molecular characteristics. A typical example is given by the polystyrene–poly(α-methylstyrene) pair: it has been well established that under certain molecular weight conditions these polymers are mutually miscible.[2–6] Also, it has been shown that block copolymers of styrene and α-methylstyrene are miscible up to considerably higher molecular weights than are mixtures of the corresponding homopolymers.[7–9] This is due to the molecular constraint of covalently bonded chains. In this context, it is reasonable to assume that the introduction of cross-links in a polymer blend would also enhance miscibility, and therefore it is of interest to examine the phase behavior of cross-linked polymer mixtures. However, it should be noted that interchain cross-linking (grafting) will not be discussed here.

In this work, we have considered the particular case of 50/50 polystyrene (PS)–poly(α-methylstyrene) (PαMS) semiinterpenetrating polymer networks (s-IPNs), i.e., interlocked systems containing one cross-linked and one linear component.[10] To ensure a better control of the molecular parameters of these s-IPNs, we made use of an anionic polymerization method. The phase behavior of these s-IPNs, as well as of the corresponding PS/PαMS blends was examined by determining their glass transition temperature, T_g, and specific heat increment, ΔC_p, by differential scanning calorimetry.

Experimental Section

The polymers were prepared by anionic synthesis in benzene at 45 °C and in THF at −78 °C for PS and PαMS, respectively. Monomers and solvents were purified and dried in the usual ways: styrene and α-methylstyrene were repeatedly distilled on sodium wire, divinylbenzene (DVB) was dried, and the inhibitor was removed by passing it twice through an aluminum oxide column. The linear polymers were prepared with *n*-butyllithium as initiator, and their average molecular weights were determined by gel permeation chromatography (GPC). The apparatus was calibrated with PS standards, and therefore the molecular weights for PαMS are not absolute values. The s-IPNs were prepared by anionic in situ polymerization: styrene was polymerized at −35 °C in a benzene–THF solution containing preformed PαMS, and cross-linked by addition of divinylbenzene at four molecules of DVB per living chain. A detailed description is given in a previous publication.[11] To obtain a network by end-linking, the disodium derivative of a α-methylstyrene tetramer was used as the difunctional initiator. The s-IPNs were dried under vacuum at 30 °C for several days until the samples were at constant weight. The average molecular weight between cross-links, $\bar{M}_c$, of the PS(DVB) network is defined as the number-average molecular weight, $\bar{M}_n$, of the PS precursor determined by GPC. The polymer blends were obtained either by dissolving PS and PαMS in benzene to make a 2% solution and subsequent freeze-drying or by directly precipitating into methanol a sample taken out from the reaction medium before the addition of DVB when preparing s-IPNs. Finally, the blends were dried under vacuum to a constant weight. Both methods gave the same result in terms of thermal behavior.

Differential scanning calorimetry, DSC, was conducted in a Perkin-Elmer DSC-4 apparatus operating at a heating rate of 20 °C/min. Initially, the samples were heated to 220 °C in nitrogen for a short period and then quenched through the glass transition region. They were then reheated at 20 °C/min. Several quenching–heating cycles were performed on each sample to ensure a uniform thermal history. Data collected from the third and subsequent scans were reproducible within less than 1 °C. The glass transition temperature, T_g, was taken at the half-height of the corresponding heat capacity change, ΔC_p. The width of the glass transition was expressed as the difference in temperature, $T_2 - T_1$, between the upper and lower points of deviation from the extrapolated liquid and glassy base lines, respectively.

Results and Discussion

The phase state was inferred from the number, location, and shape of the glass transition determined by means of differential scanning calorimetry. The criterion employed is that two polymers are immiscible if two separate glass transition temperatures characteristic of each polymer are detected, while they are miscible if only one single T_g at an intermediate temperature is observed. The intimacy of mixing is given by the width of the glass transition region.

Prior to the study of PS(DVB)/PαMS s-IPNs, the miscibility/immiscibility limit was determined for the corresponding linear polymer blends. The molecular weight of the PS was typically in the range 4000–25 000 in order to build dense networks having a reasonable chance to enhance miscibility after chain end-linking. Consequently, the molecular weight of PαMS was found to be over 140 000 to obtain phase-separated blends.[12]

We have examined nine blends located on both sides of the miscibility/immiscibility limit. The glass transition temperature, T_g, the specific heat increment, ΔC_p, and the width of the glass transition, $T_2 - T_1$, are reported in Tables I–III, respectively. The corresponding values of the individual components PαMS, PS, and PS(DVB) are included in these tables. Except ΔC_p's of PαMS, which are somewhat too high, these data are consistent with earlier literature.[2,3,13,14] In addition, note that contrary to randomly cross-linked PS, the end-linked PS(DVB) networks do not show a substantial reduction in transition height compared to linear PS, probably due to the fact that the average length of the chain elements between cross-links is nearly constant.

The experimental single T_g found for some linear blends is very close to the theoretical value calculated according to the well-known Fox equation.[15] Also, the experimental specific heat increment ΔC_p at T_g is in good agreement with the calculated value from the individual components. As expected for miscible polymer blends, the width of these single transitions is broad in comparison to that of individual PS or PαMS; see Table III.

Two transitions are observed for the remaining blends of linear polymers. The T_g values are far from the values of the individual homopolymers, indicating partial miscibility, and the reduction in ΔC_p that occurs for both transitions indicates a diffuse interfacial region. The magnitude of the shift observed for PαMS, which is greater

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Table I

Glass Transition Temperatures (°C) of 50/50 PS/PαMS Blends, s-IPNs, and Corresponding Individual Polymers

poly(α-methylstyrene)		PS and corresponding blends			PS(DVB) and corresponding s-IPNs		
$\bar{M}_n$	T_g	$\bar{M}_n = 4500$ and $T_g = 76$	$\bar{M}_n = 9500$ and $T_g = 91$	$\bar{M}_n = 22\,000$ and $T_g = 98$	$\bar{M}_c = 4500$ and $T_g = 101.5$	$\bar{M}_c = 9500$ and $T_g = 99$	$\bar{M}_c = 22\,000$ and $T_g = 98$
140 000	175	115	121.5	105.5, 144.5	128	112, 146	103, 148.5
200 000	177	112	125.5	104, 141	123.5, 145	115, 149.5	101.5, 153
300 000	176	107	95, 123	101, 157	121.5, 168	117, 174.5	99.5, 175.5

Table II

Change in Heat Capacity[a] at T_g of 50/50 PS/PαMS Blends, s-IPNs, and Corresponding Individual Polymers

poly(α-methylstyrene)		PS and corresponding blends			PS(DVB) and corresponding s-IPNs		
$\bar{M}_n$	ΔC_p	$\bar{M}_n = 4500$ and $\Delta C_p = 0.270$	$\bar{M}_n = 9500$ and $\Delta C_p = 0.288$	$\bar{M}_n = 22\,000$ and $\Delta C_p = 0.287$	$\bar{M}_c = 4500$ and $\Delta C_p = 0.284$	$\bar{M}_c = 9500$ and $\Delta C_p = 0.271$	$\bar{M}_c = 22\,000$ and $\Delta C_p = 0.280$
140 000	0.313	0.285	0.241	0.069, 0.201	0.307	0.143, 0.154	0.145, 0.148
200 000	0.309	0.289	0.269	0.071, 0.196	0.117, 0.202	0.131, 0.169	0.152, 0.161
300 000	0.318	0.299	0.139, 0.141	0.092, 0.184	0.116, 0.184	0.136, 0.173	0.147, 0.160

[a] ΔC_p in $J \cdot g^{-1} \cdot deg^{-1}$.

Table III

Width of Glass Transition (°C) of 50/50 PS/PαMS Blends, s-IPNs, and Corresponding Individual Polymers

PαMS		PS and corresponding blends			PS(DVB) and corresponding s-IPNs		
$\bar{M}_n$	$T_2 - T_1$	$\bar{M}_n = 4500$ and $T_2 - T_1 = 27$	$\bar{M}_n = 9500$ and $T_2 - T_1 = 26$	$\bar{M}_n = 22\,000$ and $T_2 - T_1 = 26$	$\bar{M}_c = 4500$ and $T_2 - T_1 = 36$	$\bar{M}_c = 9500$ and $T_2 - T_1 = 31$	$\bar{M}_c = 22\,000$ and $T_2 - T_1 = 33$
140 000	31	49	70	36, 54	88	43, 38	33, 31
200 000	29	54	63	29, 59	45, 37	37, 35	40, 27
300 000	29	68	28, 61	27, 57	42, 38	40, 29	38, 29

than that for PS, and the pronounced widening of the high-temperature transition region suggest that the immiscible blends are formed by almost pure PS and plasticized PαMS (further called the PαMS-rich phase).

Considering now the s-IPNs, except for one sample, they all exhibit two distinct glass transitions. The single transition of the s-IPN PS(DVB), $\bar{M}_c = 4500$/PαMS, $\bar{M}_n = 140\,000$, is rather broad, $T_2 - T_1 = 88$, as compared to that of the corresponding blend, $T_2 - T_1 = 49$, and hence, this sample is located close to the miscibility/immiscibility limit.

The appearance of two T_g's suggests the s-IPNs to present a multiphase system, even for the miscible blends of the linear polymers. Little work concerning this aspect was reported in the literature: to our knowledge, single-phase IPNs or s-IPNs have been reported only for PS and poly(2,6-dimethyl-1,4-phenylene oxide),[16] which are mutually miscible as linear polymers. On the contrary, s-IPNs based on PS and poly(vinyl methyl ether), another miscible polymer pair, phase separate in some cases, depending on the cross-link density of the polystyrene.[17,18] Also, Guo et al.,[19] who examined miscible blends of uncured epoxy resin and poly(ethylene oxide), have found that phase separation occurs as cross-linking proceeds.

In our case, for the two-phase PS(DVB)/PαMS s-IPNs, there is evidence of some partial miscibility, as revealed by the inward shift of T_g, compared to the T_g's of the homopolymers. Like for the blend of the linear polymers, the shift is more marked for PαMS than for PS. As expected, this shift depends on cross-link density, independently of the molecular weight of the PαMS (see Table I). The T_g displacements ΔT_g(PS) and ΔT_g(PαMS) of the PS-rich and PαMS-rich phases, respectively, are reported in Table IV for blends and s-IPNs based on PS $\bar{M}_n$ or $\bar{M}_c = 22\,000$. The shift is smaller for the s-IPN than for the blend of the linear polymers, suggesting less phase mixing.

Table IV

T_g Shift of the PS-Rich Phase and of the PαMS-Rich Phase for Blends and s-IPNs Based on PS M_n or $M_c = 22\,000$

	ΔT_g(PS)		ΔT_g(PαMS)	
$\bar{M}_n$(PαMS)	blend	s-IPN	blend	s-IPN
140 000	7.5	5	30	26.5
200 000	6	3.5	36	24
300 000	3	1.5	19	0.5

Another noticeable change is in the transition width, especially for the upper transition: in the series of PS $\bar{M}_n$ or $\bar{M}_c = 22\,000$, $T_2 - T_1$ of the PαMS-rich phase is roughly reduced by half for the s-IPNs. The width of each of the two transitions in s-IPNs is of the same order of magnitude as that for the individual components. Also, the classically observed reduction in transition height is less pronounced for s-IPNs than for linear blends. Therefore, it is probable that the majority of PS(DVB) and PαMS molecules exist in separate, well-defined phases. The change in the chemical and physical nature of polystyrene through an end-linking reaction is ineffective to overcome the unfavorable effect of the entropy of mixing. In addition, when considering the PS(DVB) network as a polymer of infinite molecular weight, the phase behavior of our s-IPNs is consistent with previous works on molecular weight dependence of PS and PαMS blends.[4,8]

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Registry No. (S)(DVB) (copolymer), 9003-70-7; PαMS, 25014-31-7; polystyrene (linear), 9003-53-6.