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ABSTRACT

Novel 4-vinylphenyldimethylsilanol polymer (PVPDMS) and co-polymers (ST-VPDMS) were synthesized by the oxyfunctionalization re-action of the silane. The reaction was found to proceed efficiently and quantitatively. Miscibility studies indicated that about 4 mol% of 4-vin-ylphenyldimethylsilanol (VPDMS) functional group in the copolymer could achieve miscibility with poly(n-butyl methacrylate) (PBMA) and poly(N-vinylpyrrolidone) (PVPr). However, for copolymers containing more than 34 mol% VPDMS, their blends with PBMA were immiscible. The observed miscibility window of ST-VPDMS/PBMA blends was as-cribed to the competition between the self-association of dimethylsilanol groups and intermolecular hydrogen bonding of dimethylsilanol groups with the carbonyl groups of PBMA. A comparison of the efficiency of the miscibility enhancement and the miscibility windows of VPDMS, p-(hexafluoro-2-isopropyl) styrene (HFPS), and phenolic-containing polymers was made in terms of such competition. The glass transition behavior of the miscible blends involving VPDMS and HFPS-containing styrene copolymers with PBMA were analyzed by the Schneider equa-tion.

INTRODUCTION

The fundamental thermodynamics that governs polymer–polymer miscibility is the free energy of mixing:

$$\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \tag{1}$$

where ΔH_{mix} and ΔS_{mix} are the enthalpy and entropy changes on mixing and T is the absolute temperature. For a blend to be a single phase, the free energy of mixing must be negative. In addition, the stability requirement of $(\partial^2 \Delta G_{\mathrm{mix}}/\partial \phi_i^2)_{T,P} > 0$ must be fulfilled. For higher molecular weight polymers, the combinatorial entropic change of mixing is small (except in the case of strong association). Therefore, the enthalpy of mixing dominates the free energy of mixing in polymer blends. It is obvious that the miscibility of dissimilar polymers can be achieved only if the mixing is exothermic.

In many cases the observed miscibility of polymer blends is a direct result of the contribution of exothermic mixing by introducing specific interactions in polymer blends. In the past decade, the research conducted on the introduction of hydrogen bonding interactions between dissimilar polymer chains has been proven to be one of the most important and effective ways to enhance polymer–polymer miscibility [1–8]. The polymers containing hydrogen bond donor groups, such as p-(hexafluoro-2-hydroxyl isopropyl) styrene and phenolic groups, were found to be miscible with a wide variety of polymers containing hydrogen bond acceptor groups. The associated model by Coleman and Painter [9] has provided a quantitative link between miscibility behavior and intermolecular hydrogen bonding determined by infrared spectroscopy.

On the basis of the success achieved in the past, we have extended our research to macromolecules with new hydrogen bonding groups to enhance polymer–polymer miscibility. In this paper we present research conducted on the synthesis of novel silanol-containing polymers and copolymers and the results of miscibility studies. Comparisons were made with corresponding p-(hexafluoro-2-hydroxyl isopropyl) and phenolic-containing styrene copolymers with regard to miscibility windows and glass transition behaviors.

NOVEL SILANOL-CONTAINING POLYMER AND COPOLYMERS

Organosilanols

The silanols are substantially stronger acids than the corresponding alcohols. Trimethylsilanol can react with 12 N NaOH to form sodium silanolate [10], whereas trimethylcarbinol does not.

$$(CH_3)_3Si-OH + NaOH \rightarrow (CH_3)_3SiONa + H_2O \tag{2}$$

Electronegative substituents such as the phenyl group considerably increase the acidity of the silanols. It was found that triphenylsilanol is a strong acid and is only less acidic than phenol [11]. On the other hand, the basicity of the silanols does not prove to be inversely proportional to their acidity as was observed in the case of alcohols [12]. The increased acidity of the silanols is not offset by a corresponding decrease in basicity. The results were interpreted on the basis of concepts regarding

strong $p_\pi - d_\pi$ bonding between oxygen and silicon atoms [13–15]. It is proposed that oxygen has bond hybridization of sp^2, with sigma bond to Si and H and an unshared electron pair occupying one of the hybridized orbitals, and the rest of the electron pair in an unhybridized p orbital. The unhybridized electron pair in the p orbital can overlap with an unfilled $3d$ orbital of silicon (Scheme 1). The increased acidity of the silanols is due to π-bonding involving an unhybridized electron pair in the p orbital of oxygen and an unfilled $3d$ orbital of silicon which increases the positive character of the proton. The basicity of the silanols is primarily caused by the remaining unshared electron pair in the sp^2 orbital.

The silanols are known to form intermolecular hydrogen bond with phenol, ethers, ketones, etc. [15–19]. From studies of the hydrogen bonding acidity and basicity of some silanols by the measurement of the hydroxyl stretching infrared frequency shifts produced by the interaction of a silanol and a reference base diethyl ether or an acid phenol, West [15] and others [16] found that the silanols are much more strongly acidic, but only slightly less basic, than the alcohol analogues. The frequency shifts of the hetero-association of the silanols and diethyl ether are nearly twice as great as those of the corresponding alcohols. Although the proportionality constant between Δv and ΔH may be somewhat different for silanols than for alcohols, the qualitative trends indicate the relative strength of the hydrogen bonds. In the study of triphenylhydroxyl compounds of the Group IVB elements [20], it was found that the equilibrium constant for the association of triphenylsilanol to tetrahydrofuran is substantially larger than that of any other compounds in the series. Similar results were also reported for poly(diorganosiloxane)-α,ω-diols [16].

The silanols are also strongly self-associated via hydrogen bonds even in very dilute solutions [15–17]. The self-associated silanol band is characterized by a substantial width and great intensity in the silanol stretching region of infrared spectra and is shifted by 60–80 cm^{-1} toward lower wavenumbers compared with alcohol analogues.

Synthesis of Novel Silanol-Containing Polymer and Copolymers

Silanols have been shown to be stronger hydrogen bond donors than the alcohol analogues. On the basis of the consideration of the strong hydrogen bond donor ability of the silanols, we initiated research on the preparation of the novel silanol-containing polymers and copolymers and the study of the miscibility of novel silanol-containing polymer blends.
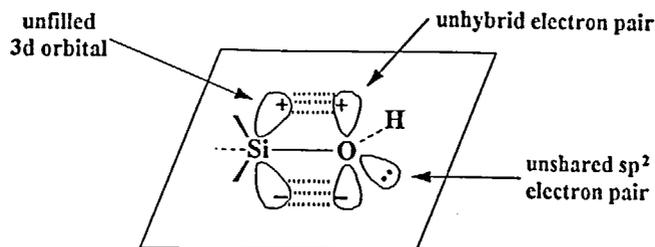
SCHEME 1.

Silanols are relatively unstable toward intermolecular condensation to form siloxanes [21]:

$$\equiv Si-OH + HO-Si\equiv \rightarrow \equiv Si-O-Si\equiv + H_2O \qquad (3)$$

Organosilanols can be obtained by the hydrolysis of organohalosilanes, organoalkoxysilanes, organoacyloxysilanes, etc. under conditions ensuring immediate neutralization of acids or bases generated during their preparation.

Previous attempts in the synthesis of poly(styrene-co-4-vinylphenyldimethylsilanol) by the hydrolysis of silanes with various silicon-functional groups have not been successfully accomplished in our laboratory.

Dioxiranes constitute a new class of reactive organic peroxides that possess great potential as oxidants [22, 23]. In 1990, Adam, Mello, and Curci [24] reported the direct conversion of silanes into silanols by oxygen atom insertion into Si—H bonds by dioxiranes (Scheme 2). The reaction was reported to be efficient, quantitative, and stereospecific. We note that this new reaction involves no acids or bases, and the silanols obtained are stabilized in acetone solution.

In order to prepare 4-vinylphenyldimethylsilanol polymer and styrene copolymers according to the reaction in Scheme 2, 4-vinylphenyldimethylsilane (VPDM-SAN) was first synthesized through the Grignard reaction of 4-vinylphenylchloride and dimethylchlorosilane. The polymerization of monomer and the copolymerization of monomer with styrene were carried out in the presence of free radical initiator 2,2'-azobisisobutyronitrile (AIBN) at 60°C as shown in Scheme 3. Novel 4-vinylphenyldimethylsilanol polymer (PVPDMS) and styrene copolymers (ST-VPDMS) were then synthesized from their silane precursors by oxygen atom insertion into the Si—H bonds (Scheme 3) [25]. Surprisingly, we found that the oxyfunctionalization of the silane is so efficient that the conversion of the dimethylsilane into dimethylsilanol is fast and quantitative, even though the reaction is carried out on the side chain of a synthetic polymer. Generally, reactions which proceed rapidly and efficiently for small molecules may not be as efficient with synthetic polymers. However, the oxyfunctionalization reaction of the silanes by dimethyldioxirane provides a new example of a rapid and efficient reaction in synthetic polymer systems.

$$
\begin{array}{ccc}
R_1 & & R_1 \\
\ \ \ \diagdown & \overset{\overset{\displaystyle O-O}{\underset{R_4\ \ R_5}{\diagup\diagdown}}}{\xrightarrow{\hspace{2cm}}} & \ \ \ \diagdown \\
\ \ \ \ \ \ Si-H & & \ \ \ \ \ \ Si-OH \\
R_2^{\prime\prime}\ \ \overset{|}{\underset{R_3}{\ }} & -20\text{-}0\ ^{\circ}C & R_2^{\prime\prime}\ \ \overset{|}{\underset{R_3}{\ }} \\
& & \\
a\text{-}c & & a\text{-}c
\end{array}
$$
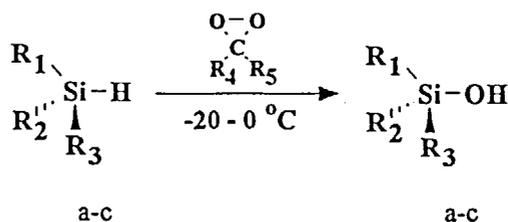
$R_4 = R_5 = CH_3$ or $R_4 = CH_3$, $R_5 = CF_3$
a: $R_1 = R_2 = R_3 = Et$;
b: $R_1 = Ph$, $R_2 = R_3 = Me$;
c: $R_1 = \alpha\text{-Naph}$, $R_2 = Ph$, $R_3 = Me$;

SCHEME 2.
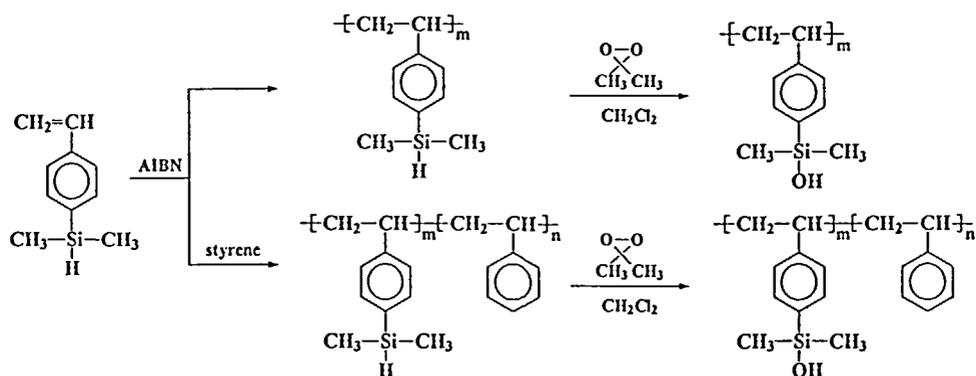
SCHEME 3.

The infrared spectra of poly(4-vinylphenyldimethylsilane) and poly(4-vinyl-phenyldimethylsilanol) is shown in Fig. 1. The absorption band at 2117 cm^{-1} (Figure 1A), due to the stretching vibration of the Si—H bond, totally disappears after the reaction, while a broad band with a weak shoulder appears in the hydroxyl stretching region, which is an indication of the formation of the silanol via the oxyfunctionalization of the silane. Figure 2 shows the hydroxyl stretching region of the infrared spectra of poly(styrene-*co*-4-vinylphenyldimethylsilanol) (ST-VPDMS) containing varying amount of 4-vinylphenyldimethylsilanol (VPDMS) in the copolymers. There are two absorption bands in the silanol stretching region of infrared spectra. The one at 3622 cm^{-1} can be attributed to the free silanol stretching vibra-
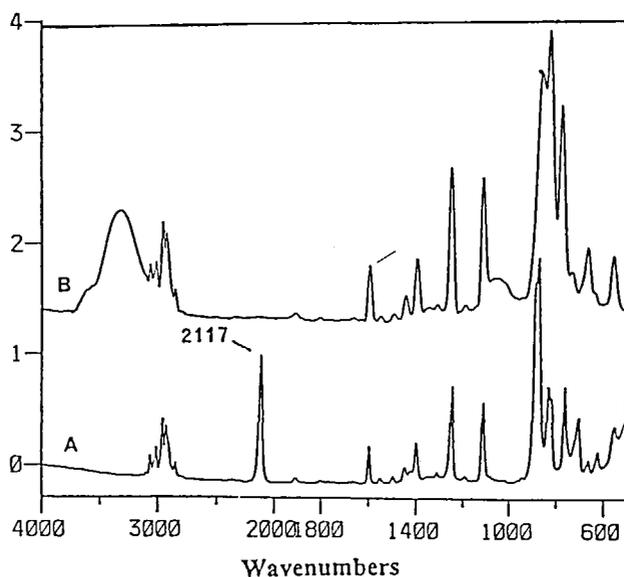
FIG. 1. FT-IR spectra of (A) poly(4-vinylphenyldimethylsilane) and (B) poly-(4-vinylphenyldimethylsilanol).
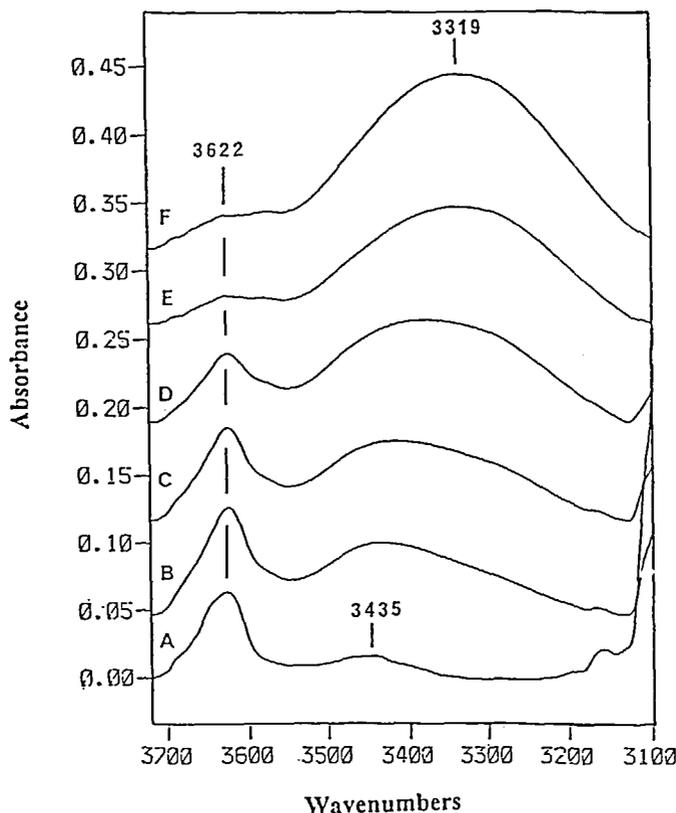
FIG. 2. FT-IR spectra in the hydroxyl stretching region for poly(styrene-*co*-4-vinylphenyldimethylsilanol) containing (A) 1.9, (B) 8.7, (C) 11.4, (D) 18.2, (E) 60.0, and (F) 100 mol% VPDMS.

tion, and the broad bands spanning 3435 to 3319 cm^{-1} are assigned to the broad distribution of the self-associated silanols [25]. The infrared absorption band of the self-associated silanol groups is characterized by a substantial width and a large integral intensity relative to the absorption band of the free silanol groups. With increasing VPDMS composition in the copolymer, the absorbance of the self-associated silanol groups increases at the expense of that of the free silanol groups. Meanwhile, the location of the maximum of the self-association band shifts to a lower wavenumber. The frequency differences between the free and the self-associated silanol bands as a function of copolymer composition are shown in Figure 3. The frequency shift ($\Delta\nu$) caused by the self-association is in the 187–303 cm^{-1} range and depends on the amount of VPDMS in the copolymers. The relatively weak self-association at low VPDMS contents is caused by the dilution effect of the unsubstituted styrene group which isolates and reduces the probability of inter- and intramolecular hydrogen bond interactions of the silanols. The magnitude of the frequency shifts and hence the strength of the self-association increase dramatically when the amount of VPDMS in the copolymer is in excess of 10 mol%. The shift is substantially larger than that reported for styrene-*co*-*p*-(hexafluoro-2-
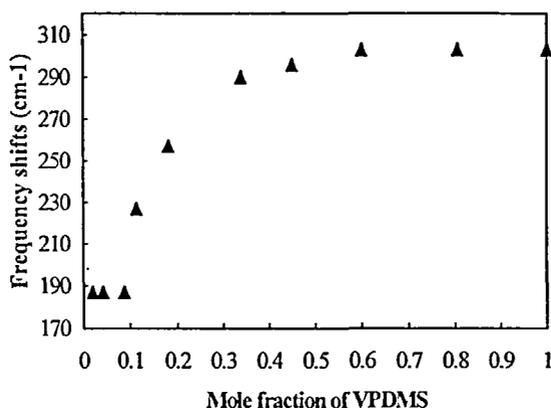
FIG. 3. Plots of the frequency shifts as a function of the VPDMS composition in the styrene copolymers.

hydroxyl isopropyl) styrene copolymers (~ 80 cm^{-1}) and poly(4-vinylphenol) (~ 175 cm^{-1}) [2, 4, 9, 26–28].

HYDROGEN BONDING INTERACTIONS IN POLYMER BLENDS

The Role of Hydrogen Bonds in Polymer–Polymer Miscibility

In the studies of polymer blends in which the driving force for miscibility is hydrogen bonding interactions, the minimum amount of the functional groups required to achieve miscibility and the competition of the hetero- and the self-associated hydrogen bonds are the subjects of considerable interest to researchers.

In binary hydrogen-bonded polymer blends, it is often the case that component Polymer A self-associates through the hydrogen bond to form dimer, trimer, or multimers (Eq. 4), while Polymer B is unassociated but has a functional group capable of forming a intermolecular hydrogen bond with Polymer B (Eq. 5). The self-association of Polymer A is caused by either the coexistence of a hydrogen bond donor in Polymer A or the basicity of the hydrogen bond donor itself, e.g., the hydroxyl group.

$$A + A \rightarrow AA$$

$$\cdots \ \cdots$$

$$A_{n-1} + A \rightarrow A_n \tag{4}$$

$$A + B \rightarrow AB \tag{5}$$

The intermolecular hydrogen bond between the hydrogen bond donor and the hydrogen bond acceptor results in a favorable contribution to the miscibility, whereas the self-association contributes endothermically to the enthalpy of mixing and competes with the intermolecular hydrogen bond between the donor and acceptor functional groups. The phase behavior of a polymer blend is controlled by the competition and balance between the self-associated hydrogen bond and the intermolecular hydrogen bond between the donor and acceptor functional groups.

Review of the Miscibility Enhancement and the Miscibility Windows of Hexafluoroisopropanol- and Phenolic-Containing Polymer Blends

Before we present the results of the novel silanol-containing polymer blends, we briefly review some research conducted on hexafluoroisopanol- and phenolic-containing polymer blends on miscibility enhancement and miscibility windows as an outcome of the competition and the balance between the hetero- and self-associated hydrogen bonds.

Hexafluoroisopropanol is known as one of the strongest hydrogen bond donors [2–4, 29–33]. The strong hydrogen bond donor ability is attributed to the inductive effects that arise from two strong electron-withdrawing trifluoromethyl substituents adjacent to the hydroxyl groups. The strong electron-withdrawing effect of the trifluoromethyl groups also reduces the basicity of hexafluoroisopropanol functional groups, and therefore significantly reduces the strength of the self-association of the hydroxyl groups. Thus hexafluoroisopropanol functional groups are present either in the form of weak self-associated or nonassociated (free) modes and are ready to associate with a hydrogen bond acceptor to form strong intermolecular hydrogen bonds. The phenolic group is another strong hydrogen bond donor [34, 36]. The strong hydrogen bond donor ability is primarily caused by the acidity of the hydroxyl (O—H) group. Although the phenol group was reported with pK_a = 9.9, comparable with 9.3 for hexafluoroisopropanol [31, 35], it is more strongly self-associated when compared with the hexafluoroisopropanol group.

The infrared spectra features [5, 28] of poly(styrene-co-4-vinylphenol) (ST-VPh) in the hydroxyl stretching region are similar to those of poly(styrene-co-4-vinylphenyldimethylsilanol) as described before. The free hydroxyl stretching vibration occurs at 3525 cm^{-1}. The frequency shifts of the self-associated hydroxyl groups vary from about 110 cm^{-1} for the styrene copolymer containing 2–4 mol% VPh to 175 cm^{-1} for the 4-vinylphenol homopolymer. The frequency shifts of the self-associated hydroxyl stretching bands in poly[styrene-co-p-(hexafluoro-2-hydroxyl isopropyl) styrene] (ST-HFPS) remain almost constant at about 80 cm^{-1} regardless of the composition of HFPS in the copolymers [4, 26]. The comparison of the self-association equilibrium constants [9, 26] for describing the formation of dimers (K_{2c} or K_2) and multimers (K_c or K_B) for the model compounds and the corresponding polymers are compiled in Table 1. It is immediately apparent that p-(hexafluoro-2-hydroxyl isopropyl) styrene is much weaker in self-association than phenol.

TABLE 1.   Comparison of the Self-Association Equilibrium Constants (L/mol)

	Model compound			Polymer	
	K_{2c}	K_c		K_2	K_B
HFPS	0.43	0.58	PHFPS	2.53	3.41
VPh	2.10	6.08	PVPh	21.0	66.8

The p-(hexafluoro-2-hydroxyl isopropyl) styrene (HFPS) functional group was found to be very effective in promoting miscibility with polymethacrylates. In studies of blends involving the HFPS-containing styrene copolymers, Pearce and Kwei [4] found that only about 1 mol% of HFPS monomer units incorporated into styrene copolymers is required to form miscible blend with poly(ethyl methacrylate) (PEMA), less than 2 mol% of HFPS for poly(n-butyl methacrylate) (PBMA), and 4 mol% of HFPS for poly(methyl methacrylate) (PMMA).

In the study of the efficiency of various hydrogen donors in promoting polymer–polymer miscibility by fluorescence techniques, Morawetz [36] further confirmed the above results and found that the 4-vinylphenol functional group is also very effective in enhancing miscibility with polymethacrylates. Over 1 mol% of 4-vinylphenol monomer units in the styrene copolymer can achieve miscibility with PMMA and PEMA, about 2 mol% for PBMA. Meanwhile, the carboxyl group has low efficiency in promoting miscibility with polymethacrylates [36]. By investigation using NMR techniques complemented with DSC, FT-IR, and cloud point measurements, Kwei and Pearce [37] found that about 4 mol% of 4-vinylphenol functional group is required to achieve miscibility with PBMA on a scale of homogeneity corresponding to a $T_{1\rho}^{H}$ value of ~ 8 ms.

Based on the association model, Coleman and Painter [38] predicted that about 0.1, 0.5, and 2 mol% of 4-vinylphenol were needed to produce a single phase with PMMA, PEMA, and PBMA, respectively. More recently, predictions [26] made on ST-HFPS and methacrylate polymer blends were coincident with the experimental observations reported by Pearce et al. [4].

We have demonstrated the effectiveness of HFPS or VPh functional groups in enhancing polymer–polymer miscibility. Only a few percent of the functional groups are necessary to form miscible blends with methacrylate polymers. However, the miscibility of a polymer blend is controlled by the relative strength and balance of the hetero- and self-associated hydrogen bonds in the blend. The intermolecular hydrogen bond between a donor and an acceptor enhances polymer–polymer miscibility whereas self-association produces an unfavorable contribution to miscibility and induces phase separation.

ST-HFPS has a much wider miscibility window than the corresponding ST-VPh copolymers. The immiscible blend of PVPh/PMMA was reported in several studies [1, 36, 66] whereas the predictions based on the association model showed that the two polymers are miscible at room temperature. Recently, Landry [29] reported that a miscible blend was formed for a melt blend of 50/50 w/w PVPh/PMMA.

In a study of blends consisting of poly(t-butyl acrylate) and poly(styrene-co-4-vinylphenol), Kwei and Pearce [34] found that the miscibility window was formed for poly(styrene-co-4-vinylphenol) containing 4-vinylphenol monomer residues in the composition range of 28 to 66 mol%.

Efficiency of the Miscibility Enhancement and the Miscibility Window of the Dimethylsilanol-Containing Polymer Blends

The structure of poly(styrene-co-4-vinylphenyldimethylsilanol) (ST-VPDMS) is shown in Scheme 4 in which the dimethylsilanol functional groups can act as a

$$-[CH_2-CH]_m-[CH_2-CH]_n-$$

$$CH_3-\underset{\underset{OH}{|}}{\overset{|}{Si}}-CH_3$$
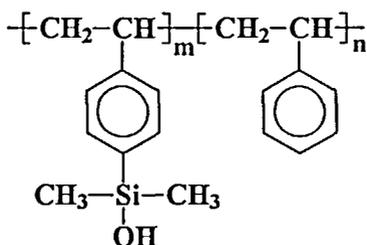
SCHEME 4.

hydrogen bond donor. The compositions and characteristics of the copolymers are listed in Table 2.

In a study of the novel silanol-containing polymer blends [39], poly(n-butyl methacrylate) (PBMA) was first chosen to blend with poly(styrene-co-4-vinylphenyldimethylsilanol). The results of 50/50 ST-VPDMS/PBMA blends are shown in Table 3. For films cast from MEK, the 50/50 blends of PVPDMS-2 and PVPDMS-4 are heterogeneous and show two distinct glass transition temperatures corresponding to those of the component polymers. The PVPDMS-60 blend is also immiscible. Miscible blends with PBMA are formed for PVPDMS-9, PVPDMS-11, PVPDMS-18, and PVPDMS-34 in the entire composition range, with a single glass transition temperature observed for each blend composition. For films cast from toluene, the 50/50 blend of PVPDMS-4 becomes miscible with PBMA whereas the 50/50 blend of PVPDMS-34 is heterogeneous and shows two distinct glass transitions. There is ample documentation in the literature about the effect of solvents on the observed miscibility behavior of polymer blends [29, 36]. MEK is capable of forming a hydrogen bond with the dimethylsilanol group and may compete with the carbonyl group of PBMA for forming hydrogen bonds with the silanol group, while

TABLE 2. Compositions and Characteristics of Poly(Styrene-co-4-Vinylphenyldimethylsilanol)

Code	VPDMS[a] composition, mol%	$[\eta]$,[b] dL/g	T_g, °C
PVPDMS-2	1.9	0.54	97
PVPDMS-4	4.1	0.58	98
PVPDMS-9	8.7	0.64	98
PVPDMS-11	11.4	0.59	99
PVPDMS-18	18.2	0.67	101
PVPDMS-34	33.9	0.70	115
PVPDMS-60	60.0	0.76	121

[a]Calculated from ^{1}H-NMR spectra.
[b]Viscosities of the precursor silane copolymers were measured in THF at 25 ± 0.01°C.

TABLE 3. Characteristics of 50/50 w/w Poly(Styrene-*co*-4-Vinyl-phenyldimethylsilanol) and Poly(*n*-Butyl Methacrylate) Blends Prepared from Toluene and MEK

		Film appearance		T_g, °C	
No.	Code	MEK	Toluene[a]	MEK	Toluene[a]
1	PVPDMS-2	Opaque	Opaque	29, 95	29, 95
2	PVPDMS-4	Opaque	Clear	30, 100	50
3	PVPDMS-9	Clear	Clear	50	52
4	PVPDMS-11	Clear	Clear	56	57
5	PVPDMS-18	Clear	Clear	63	74
6	PVPDMS-34	Clear	Opaque	70	34, 110
7	PVPDMS-60	Clear	Opaque	33, 120	35, 120

[a]For ST-VPDMS copolymers containing more than 34 mol% VPDMS functional groups, a small amount of acetone (about 10% in volume) was added into toluene.

toluene, a nonpolar solvent, will not hydrogen bond with the silanols. The solvent effects on the miscibility of ST-VPDMS/PBMA blends provide an example for using caution in the practice of the study of polymer–polymer miscibility when solvents are used in blend film casting.

From the glass transition temperature measurements we conclude that the minimum amount of the VPDMS functional group required to achieve miscibility with PBMA is about 4 mol% for films cast from toluene and about 9 mol% for films cast from MEK whereas the upper limits of the miscibility windows are in the range of 18–34 mol% for films cast from toluene and 34–60 mol% for films cast from MEK.

The FT-IR spectra of PVPDMS-9/PBMA and PVPDMS-34/PBMA blends in the silanol stretching region are shown in Fig. 4. The free silanol stretching band at 3622 cm^{-1} is hardly detectable when the concentration of PVPDMS-9 in the blend is less than 40%, but the absorption bands of the silanol–carbonyl moieties at 3528 cm^{-1} are prominent (Fig. 4a). The absorption band at 3436 cm^{-1} is an overtone of the carbonyl stretching vibration of PBMA. Apparently, almost all the free silanol groups originally present in PVPDMS-9 have been converted to the silanol–carbonyl moieties in these blends. As the concentration of PVPDMS-9 in the blend is raised to 50% or higher, the free silanol band increases in intensity. Meanwhile, the band due to the silanol–carbonyl interaction broadens and gradually shifts to a lower wavenumber, and the absorption of the self-associated silanol groups also increases in intensity. Similar results were observed for PVPDMS-34 blends as shown in Fig. 4(b). With increasing concentration of PVPDMS-34, the carbonyl bonded silanol stretching band tends to overlap with the self-associated silanol stretching band and eventually merges into a broad, unresolved band in the 70/30 blend.

As a measure of the strength of the hydrogen-bonding interactions, the frequency shift of the $\equiv$Si—OH$\cdots$O$=$C stretching band from the free silanol stretching band is about 94 cm^{-1}, which is much less than that due to the self-association
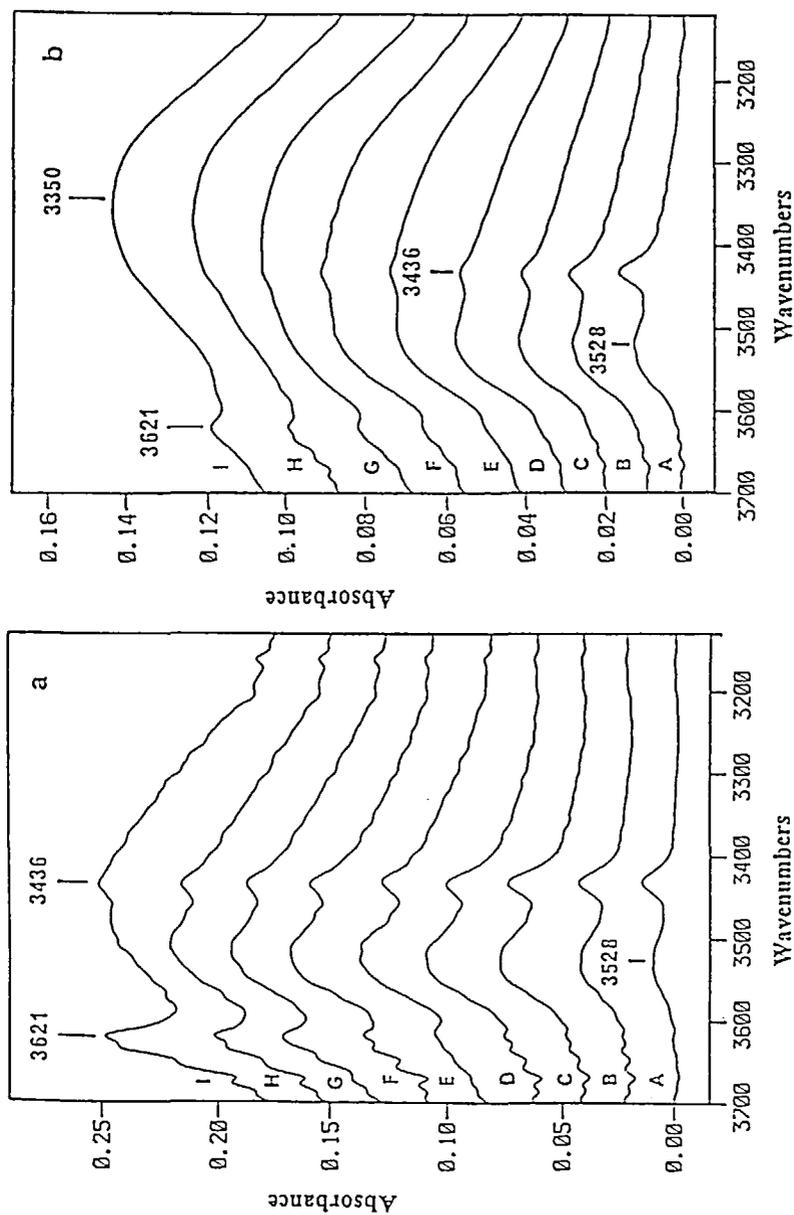
FIG. 4.   FT-IR spectra of (a) PVPDMS-9/PBMA and (b) PVPDMS-34/PBMA blends in the silanol stretching vibration region. (A) 10/90, (B) 20/80, (C) 30/70, (D) 40/60, (E) 50/50, (F) 60/40, (G) 70/30, (H) 80/20, and (I) 90/10 w/w.

of the dimethylsilanols (187 cm^{-1} for PVPDMS-9 and 290 cm^{-1} for PVPDMS-34). The result is comparable to PVPh/PBMA blends [28, 37] in which the shifts caused by $-OH\cdots O=C$ and self-associated hydrogen bonds are 105 and 175 cm^{-1}, respectively. In sharp contrast to the infrared spectra features of ST-VPDMS/PBMA and PVPh/PBMA blends [4, 26], the frequency shifts of $(CF_3)_2C-OH\cdots O=C$ in ST-HFPS/PBMA blends is about 222 cm^{-1}—much stronger than that of the self-associated HFPS band (~ 82 cm^{-1}) as shown in Fig. 5.

The FT-IR spectra of PVPDMS-9/PBMA and PVPDMS-34/PBMA blends in the carbonyl stretching region are shown in Fig. 6. The free carbonyl stretching band of PBMA is observed as a major band at 1728 cm^{-1}, while the hydrogen-bonded carbonyl stretching band at 1703 cm^{-1} appears as a weaker shoulder. Regardless of the composition, the shoulders at 1703 cm^{-1} are always weak in the PVPDMS-9 blends. They are more readily discerned in the PVPDMS-34 blends but are still much lower in intensities than for the poly(styrene-co-4-vinylphenol)/PBMA [28] or poly(styrene-co-p-(hexafluoro-2-hydroxyl isopropyl) styrene)/PBMA [26] blends.

To resolve the overlapped bands and obtain quantitative information about hydrogen bond interaction in the carbonyl stretching region of the blends, a curve-fitting program was used to deconvolute the composite spectra profiles. Representative curve-resolved spectra are shown in Fig. 7, and the results for the nine PVP-
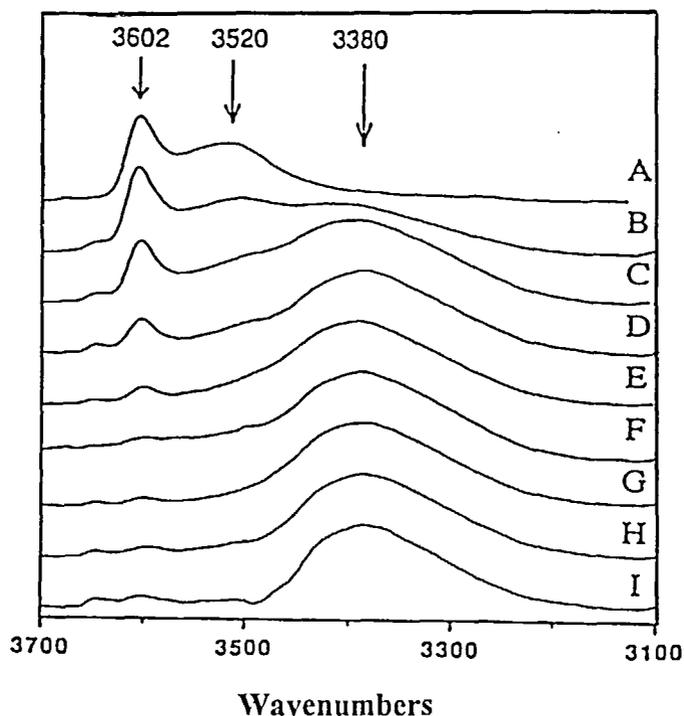
FIG. 5. Infrared spectra in the hydroxyl stretching region for ST-HFPS(80)/PBMA blends: (A) 100/0, (B) 90/10, (C) 80/20, (D) 70/30, (E) 60/40, (F) 50/50, (G) 40/60, (H) 30/70, and (I) 20/80 w/w.
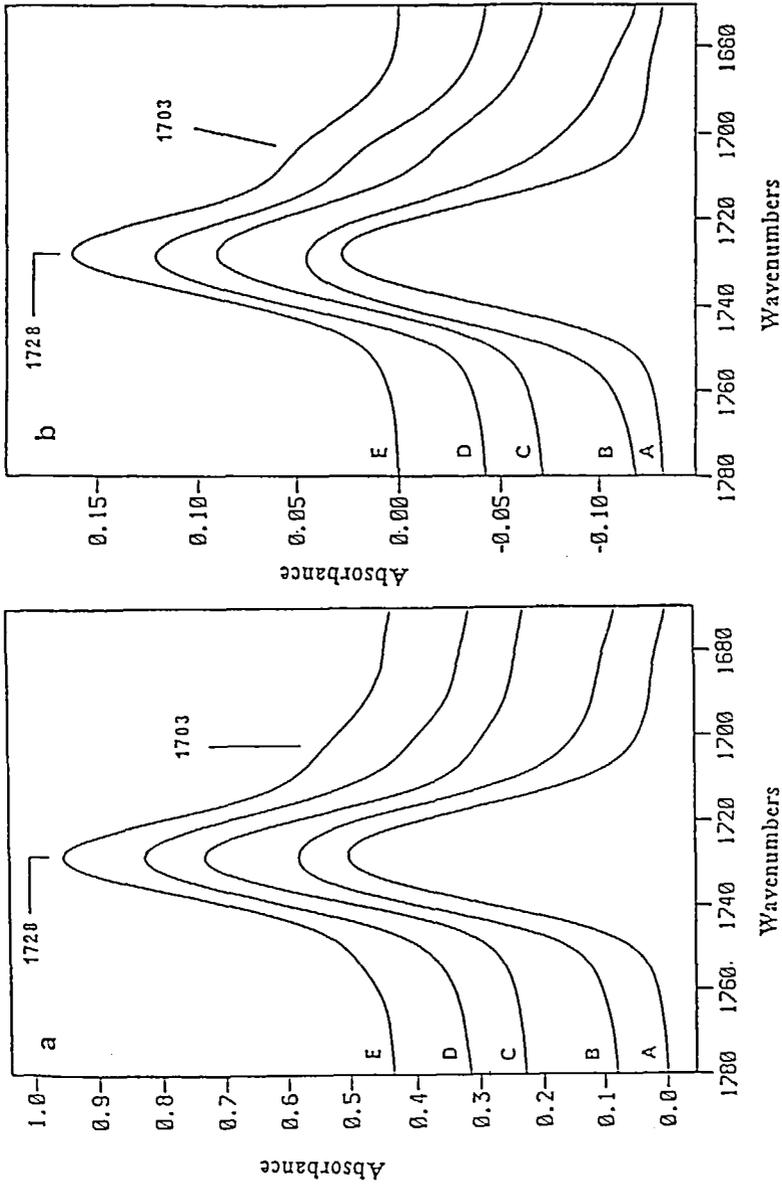
FIG. 6. FT-IR spectra of (a) PVPDMS-9/PBMA and (b) PVPDMS-34/PBMA blends in the carbonyl stretching vibration region. (A) PBMA, (B) 20/80, (C) 50/50, (D) 70/30, and (E) 90/10 w/w.
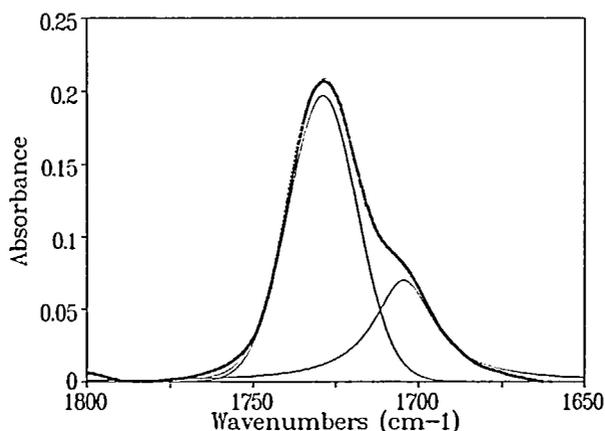
FIG. 7.   Curve-resolved spectra of 70/30 PVPDMS-34/PBMA blend in the carbonyl stretching region.

DMS-34/PBMA blends are summarized in Table 4. The areas of the 1703 cm^{-1} peak, as a percentage of the total area, increases from 12% for the 10/90 blend to 23% for the 40/60 blend. Further increases of the copolymer in the blends results in only minor variations in the areas, namely, about 26 ± 2%. To convert the area ratio to the fraction of bound carbonyl groups, we used the factor of 1.5 established by Coleman and Painter [5] for the phenol–carbonyl pair. The bound carbonyl fractions so calculated are listed in the last column of Table 4.

The results of the FT-IR study on ST-VPDMS/PBMA blends revealed that the relative weaker intermolecular hydrogen bond occurs between the dimethylsilanol group of the ST-VPDMS copolymers and the carbonyl group of PBMA com-

TABLE 4.   Curve-Fitting Results of PVPDMS-34/PBMA Blends

PVPDMS-34/PBMA	"Free" C=O band			H-bonded C=O band			
	Frequency, cm^{-1}	WHH[a], cm^{-1}	Area[b]	Frequency, cm^{-1}	WHH[a], cm^{-1}	Area[b]	Fraction of H-bonded C=O
90/10	1728	22.6	0.75	1705	18.6	0.25	0.18
80/20	1728	22.9	0.73	1705	20.3	0.27	0.20
70/30	1729	24.8	0.71	1705	22.0	0.28	0.21
60/40	1729	25.2	0.73	1705	23.5	0.27	0.20
50/50	1730	25.9	0.74	1704	24.6	0.26	0.19
40/60	1727	26.5	0.77	1702	25.0	0.23	0.17
30/70	1728	27.2	0.84	1703	25.5	0.16	0.11
20/80	1728	28.7	0.87	1703	25.5	0.13	0.09
10/90	1729	27.6	0.88	1703	24.1	0.12	0.09

[a]Width at half-height.
[b]Fraction of the total peak area.

pared with that of the self-associated silanol hydrogen bonds. The narrowness of the observed miscibility windows is an outcome of the competition between the strongly self-associated dimethylsilanol and the weaker intermolecular hydrogen bond interaction in the ST-VPDMS/PBMA blends. As we know, the strength of the intermolecular hydrogen bond not only depends on the hydrogen bond donor but also depends on the hydrogen bond acceptor. The stronger the hydrogen donor or acceptor ability, the stronger the intermolecular hydrogen bond. The amide carbonyl group of poly(N-vinylpyrrolidone) (PVPr) is known as a strong hydrogen bond acceptor. A study of ST-VPDMS/PVPr blends indicated that a strong intermolecular hydrogen bond occurred between the amide carbonyl group of PVPr and the silanol group of ST-VPDMS copolymers. The minimum amount of the VPDMS functional group required to achieve miscibility with PVPr is still 4 mol%, which is same as that observed for ST-VPDMS/PBMA blends [39]. The results may suggest that the requirement for the minimum amount of the functional groups for achieving miscibility for a random copolymer depends mainly on the number of the intermolecular interaction sites. On the other hand, mutual precipitated interpolymer complexes were formed for the copolymers containing more than 34 mol% VPDMS. Moreover, new semi-interpenetrating polymer networks (IPNs) were prepared from the complexes by the condensation of the dimethylsilanols when the composition of VPDMS exceeded 60 mol% in the copolymers without the presence of any external crosslink agents [39]. The results will be reported in future publications.

GLASS TRANSITION BEHAVIORS OF THE MISCIBLE POLYMER BLENDS

Review of the Correlation of Glass Transition Temperature and Composition

Glass transition temperature is one of the most important characteristics of polymer materials. One criterion for establishing polymer–polymer miscibility is the presence of a single and composition-dependent glass transition temperature [40, 41]. Deviations of the glass transition temperatures from calculated weight average values are frequently observed [1, 3, 7, 42–47]. Typical deviations of T_g as a function of blend composition are illustrated in Fig. 8. The T_g relation usually falls below the calculated weight-average values for many of the commercial miscible blends where strong specific interactions are absent. For blends involving strong specific interactions, such as hydrogen bonds, positive deviations of the glass transition temperature or even more complicated S-shaped curves are frequently observable.

For miscible blends, there are several classical equations that correlate the glass transition temperatures of the miscible blends with composition. The simplest relationship is the Fox equation [48] as originally written for random copolymers:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{6}$$

where T_g, T_{g1}, and T_{g2} are the glass transition temperatures of the blend, Component 1, and Component 2, respectively. w_1 and w_2 are the corresponding weight
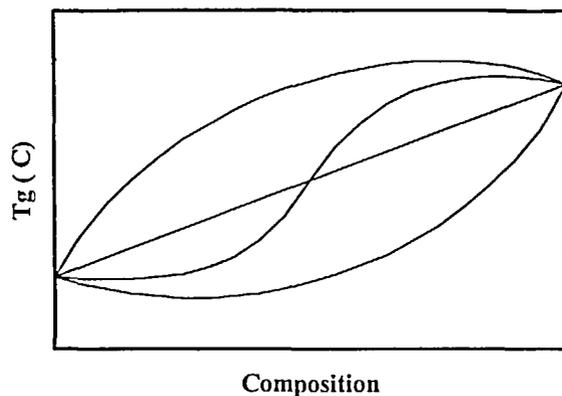
FIG. 8. Schematic representation of the typical deviations of the glass transition temperatures.

fractions. The Gordon–Taylor equation [49] was derived by assuming volume additivity to predict the T_g of binary random copolymers, and it was subsequently used to explain the composition dependence of the glass transition temperature of binary miscible polymer blends:

$$T_g = \frac{(w_1 T_{g1} + K w_2 T_{g2})}{w_1 + K w_2} \tag{7}$$

where K is defined as the ratio of the differences of the coefficients of expansion, $\Delta\alpha$, at T_g of the glass and rubbery states. For a blend, the K parameter includes, in addition, the ratio of their respective densities [50], ρ_i:

$$K = \rho_1 \Delta\alpha_2 / \rho_2 \Delta\alpha_1 \tag{8}$$

Simultaneous with Gordon and Taylor's derivation, Jenckel and Heusch [51] proposed an equation to explain the lowering of the T_g of polymers by plasticizers:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + w_1 w_2 b (T_{g2} - T_{g1}) \tag{9}$$

where b is a parameter than can be adjusted to give the best fit. All the above equations predict T_g values lower than the calculated weight-average values and cannot explain the observed positive deviations of the glass transition temperature. Later Kwei [52] proposed an equation by introducing a quadratic correction term $(q w_1 w_2)$ into the Gordon–Taylor equation:

$$T_g = \frac{(w_1 T_{g1} + K w_2 T_{g2})}{w_1 + K w_2} + q w_1 w_2 \tag{10}$$

where K is the parameter in the Gordon-Taylor equation and the $q w_1 w_2$ term represents the contribution of the specific interaction to the glass transition temperature of a blend. It was found that the Kwei equation represents a number of blend systems in which either a positive or an S-shaped T_g-composition relationship was observed [29, 45–47, 53, 54].

Recently, several other equations [55–60] have been derived to correlate the T_g-composition relationship for miscible blends. One of the most successful ap-
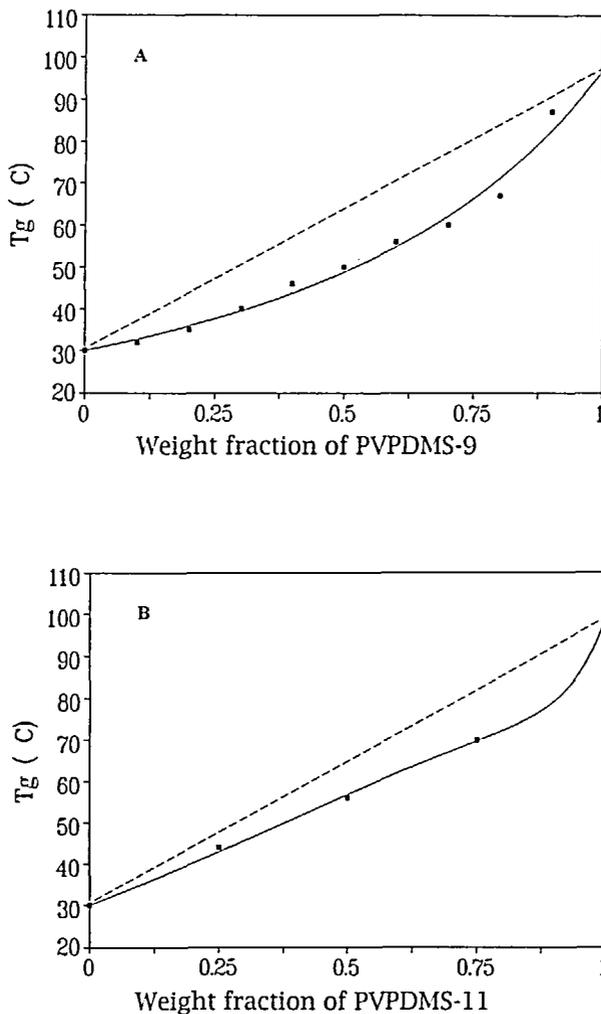
FIG. 9. Composition dependence of the glass transition temperatures for miscible ST-VPDMS/PBMA blends. (A) PVPDMS-9, (B) PVPDMS-11, (C) PVPDMS-18, and (D) PVPDMS-34.

proaches to the glass transition behavior of miscible blends was developed by Schneider et al. [58–60] by the use of a third-power equation. It is based on the assumption that the binary contact influences both conformation and "free-volume" distribution in the polymer blends.

$$\frac{T_g - T_{g1}}{T_{g2} - T_{g1}} = (1 + k_1)w_{2c} - (k_1 + k_2)w_{2c}^2 + k_2 w_{2c}^3 \qquad (11)$$

where $w_{2c} = Kw_2/(w_1 + Kw_2)$ represents the corrected weight fraction of the component with the higher glass transition temperature (T_{g2}). In the above definition, w_1 and w_2 are the weight fractions of Components 1 and 2, respectively. The parameter K is given by $K = k'(T_{g1}/T_{g2})$, where k' accounts for the ratio of the
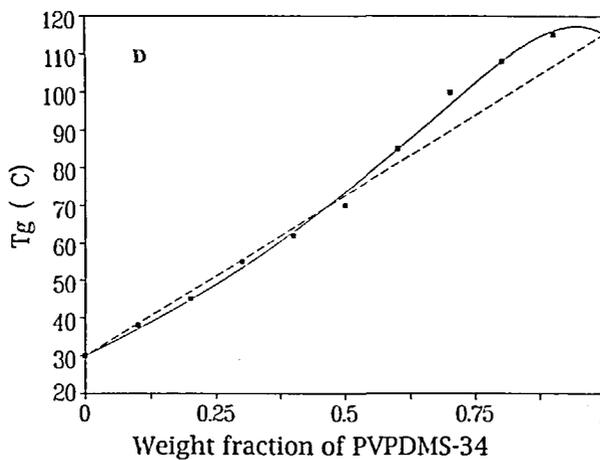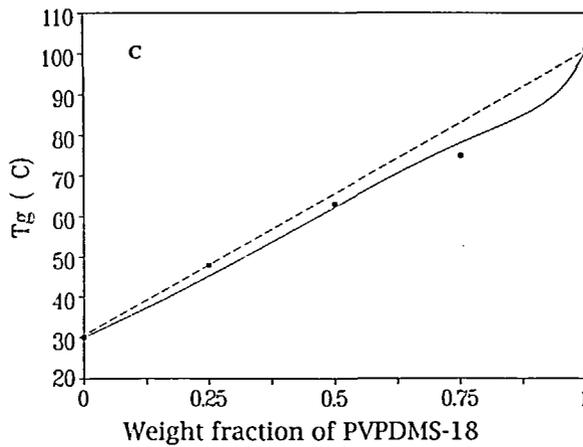
densities of the two polymers and for possible deviations from the Simha–Boyer [61] rule relating $\Delta\alpha$ (the difference between the thermal expansion coefficients in the glassy and liquid states) and T_g. The parameter k_1 is related primarily to the interaction energy differences between hetero- and homomolecular contacts, whereas k_2 represents the differences only between the energetic perturbations in the molecular surroundings of the binary contacts (as defined by Schneider, k_1 indicates some of the perturbation effects as well). Both can be related to orientation effects of the hetero-interactions in the blends and are affected by molecular weights. For identical effects of the neighborhood perturbations, $k_2 = 0$ and Eq. (11) is equivalent to the Kwei equation (Eq. 10). The interaction parameter, q, is related to the parameter k_1 by

$$q = Kk_1(T_{g2} - T_{g1})/(w_1 + Kw_2)^2 \tag{12}$$
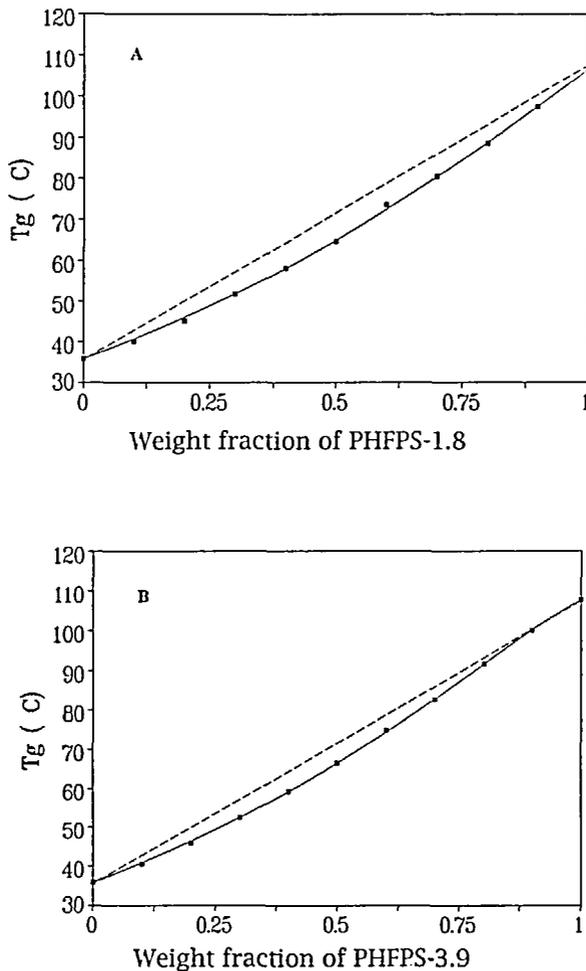
FIG. 10.   Concentration dependence of the glass transition temperatures for miscible ST-HFPS/PBMA blends. (A) PHFPS-1.8, (B) PHFPS-3.9, (C) PHFPS-9.7, and (D) PHFPS-16.7.

The Schneider equation satisfactorily describes the composition dependence of the glass transition temperature for a wide variety of miscible polymer blends [58, 59, 62, 63].

Glass Transition Behavior of ST-VPDMS/PBMA and ST-HFPS/PBMA Miscible Blends

The composition dependence of the glass transition temperatures of the miscible ST-VPDMS/PBMA blends [39] is shown in Fig. 9. The glass transition temperatures of the blends fall below the weight-average values and become gradually closer to the weight-average values as the composition of the VPDMS increases in the copolymers. Finally, for PVPDMS-34 blends, the T_g's of the blends exceed the

Weight fraction of PHFPS-9.7

Weight fraction of PHFPS-16.7
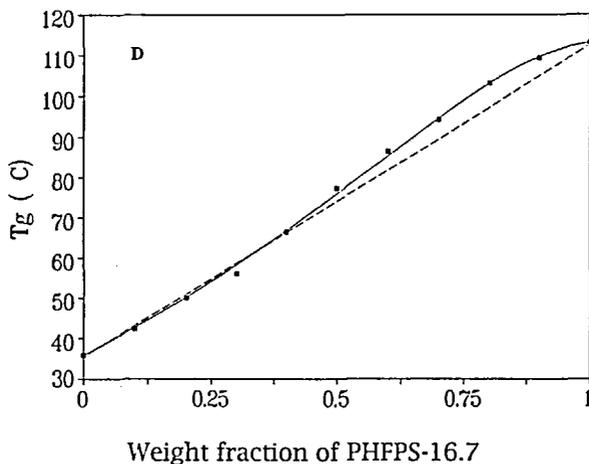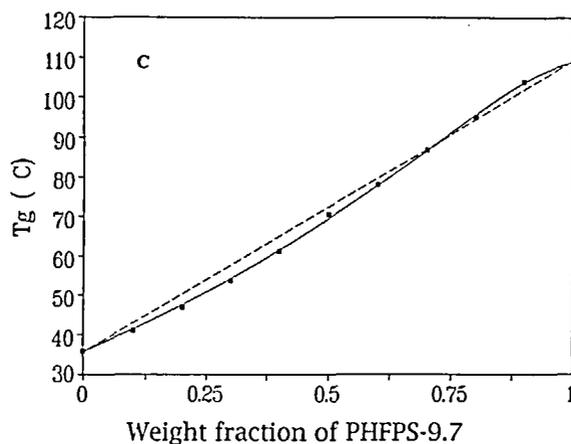
weight-average values for several blend compositions. Similar results [4] were re-ported for ST-HFPS/PBMA blends as shown in Fig. 10.

The results of the composition dependence of the glass transition temperature of the miscible blends were analyzed by use of Schneider's third-power equation (Eq. 11). In the curve-fitting process, k' was set equal to unity. A good fit of the experimental data was obtained for each blend. The fitting parameters k_1 and k_2 for ST-VPDMS/PBMA and ST-HFPS/PBMA miscible blends are listed in Table 5. We noted that the values of the fitting parameter k_1 consistently increase with increasing amounts of the functional group in the copolymers. The k_1 parameter, as defined originally by Schneider et al., is related primarily to the interaction energy differ-ences between hetero- and homomolecular contacts. Since the copolymers in the blends contain increased amounts of the functional groups, it is apparent that the increased values of the k_1 parameter for ST-VPDMS/PBMA or ST-HFPS/PBMA

TABLE 5. Fitting Parameters of the Schneider Equation for
ST-HFPS/PBMA and ST-VPDMS/PBMA Miscible Blends

Fitting parameters	PHFPS-1.8	PHFPS-3.9	PHFPS-9.7	PHFPS-16.7
k_1	0.94	1.04	1.23	1.70
k_2	0.39	0.36	0.36	0.80
	PVPDMS-9	PVPDMS-11	PVPDMS-18	PVPDMS-34
k_1	0.24	1.32	1.70	2.03
k_2	-0.02	1.93	1.84	0.77

miscible blends reflect the increased intensity of the intermolecular hydrogen bond interaction in the blends.

As Schneider has noted for other blends, it is tempting to speculate the physical reasons responsible for the "surrounding" effect in the hydrogen-bonded blend system. Schneider's equation can also be derived by defining the k_1 and k_2 parameters in terms of volume changes instead of energy differences between hetero and homo binary contacts. There is a certain advantage in using volume as the molecular parameter because it is experimentally measurable. In previous publications [64, 65] we measured the excess volume of mixing of poly(methyl methacrylate) (PMMA) with two other styrene copolymers containing 4-vinylphenol or p-(hexafluoro-2-hydroxyl isopropyl) styrene groups as hydrogen bond donors. The excess volume was found to change from negative to positive as the hydroxyl content of the copolymer increased. The explanations proposed in References 64 and 65 were based on considerations of chain packing. It was reasoned that the volume shrinkage to be expected from the formation of a hydrogen bond between a free hydroxyl group and a carbonyl group was diminished to some extent by the poor packing of the styrene and methyl methacrylate segments in the immediate neighborhood of the interacting sites. Consequently, the net volume shrinkage resulting from this type of hetero contact is small. When an exchange of hydrogen bonding takes place between the self-associated hydroxyl groups and carbonyl groups, the combined effect of breakup of the self-association and the inability for the neighboring styrene and methacrylate units to pack efficiently results in a net increase in volume. If we adopt this line of reasoning, it is easy to see that the volume increase incurred by the breakup of a given hydroxyl–hydroxyl contact is influenced by whether there are other hydroxyl–hydroxyl contacts in the neighborhood which exert a constraining effect to volume change. This can be viewed as one of the contributing factors to the "surrounding" effect through the e_{11-1} term in Schneider's derivation. It also appears reasonable that the k_1 and k_2 parameters change with the $\equiv$Si—OH content of the copolymer because the distribution between the free and self-associated hydroxyl species alters with composition.

In contrast to the glass transition behaviors of p-(hexafluoro-2-hydroxyl isopropyl) styrene (HFPS) or 4-vinylphenyldimethylsilanol (VPDMS) containing polymer blends, most of the phenolic-containing polymer blends exhibited positive devi-

ations of the T_g's from the calculated weight-average values or even more complicated S-shaped curves. The large positive deviations of the T_g's were reported for a series of blends involving phenolic-containing polymers, such as poly[styrene-co-4-vinylphenol] [43] and poly(tert-butyl acrylate) [34], poly(4-vinylphenol) and poly(vinylpyridine) [47], and novolac resins and isotactic poly(methyl methacrylate) blends [44]. S-shaped curves were reported for blends of novolac and syndiotactic poly(methyl methacrylate) [44]. For para-substituted poly[(1-hydroxyl-2,6-phenylene) methylene] (PHMP) and poly(methyl methacrylate) blends, Pennacchia et al. [46] observed positive derivations of the T_g's for p-Cl-PHMP, negative derivations of T_g's for p-NO$_2$-PHMP and p-tert-butyl-PHMP, and S-shaped curves for p-H-PHMP.

Although some successes have been achieved for a number of equations derived from either fundamental arguments or empirical observation to rationalize the deviations of the T_g's of miscible blends involving specific interactions, there is still much more work to be done for the satisfactory interpretation of the glass transition behaviors of miscible polymer blends.

CONCLUSIONS

Novel 4-vinylphenyldimethylsilanol polymer and styrene copolymers were synthesized from their silane precursors by oxygen atom insertion in the Si—H bond. The oxyfunctionalization of the silane on the side chain of the polymer is rapid and efficient. The reaction provided a new example for a fast and quantitative reaction in a synthetic polymer system.

Poly(styrene-co-4-vinylphenyldimethylsilanol) (ST-VPDMS) has been shown to be capable of forming intermolecular hydrogen bonding to enhance polymer-polymer miscibility. The results of glass transition temperature measurements indicated that the minimum amount of the VPDMS functional group required to achieve miscibility with poly(n-butyl methacrylate) (PBMA) or poly(N-vinylpyrrolidone) (PVPr) is about 4 mol%. The efficiency of the miscibility enhancement of the dimethylsilanol group is comparable with that reported for p-(hexafluoro-2-hydroxyl isopropyl) styrene (HFPS) or 4-vinylphenol (VPh). Immiscible blends of ST-VPDMS/PBMA were formed for copolymers containing more than 34 mol% VPDMS. The observed upper limit of the miscibility window is a direct result of the strong self-associated hydrogen bond of the dimethylsilanol group and the weaker intermolecular hydrogen bond between the carbonyl group of PBMA and the dimethylsilanol group of the copolymer in the blends. From the point of view of molecular structure, the strength of the self-associated silanols depends on the electronegativity and the steric effect of the substituents bound to the Si atom. The research conducted in this laboratory has already shown that the strength of the self-associated silanol group is reduced markedly with a phenyl substituent bound directly to the Si atom [39]. Moreover, the properties of the blends, such as positive or negative deviations of the glass transition temperatures, can be tailored by changing the substituents bound to the Si atom.

The glass transition behaviors of miscible ST-VPDMS/PBMA blends are very similar to those reported for ST-HFPS/PBMA blends. It was found that the T_g-composition relationships of miscible ST-VPDMS/PBMA or ST-HFPS/PBMA

blends can be reasonably fitted well by the third-power equation proposed by Schneider et al. The physical meaning of the fitting parameters and the possible physical reasons responsible for the "surrounding" effect have been discussed, and they may offer a possible interpretation for the specific interactions in hydrogen-bonded blend systems.

ACKNOWLEDGMENT

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