A Survey of Polyvinylphenol Blend Miscibility

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SYNOPSIS

The effect of polymer structure on blend miscibility with polyvinylphenol (PVPh) has been studied for at least one polymer from a variety of polymer classes with potential hydrogen-bond accepting groups: polyesters (aliphatic and aromatic), polycarbonates, polyimides, polyamides, polysulfones, polyurethanes, polyethers, polysiloxanes, poly(amide-imides), and cellulose esters. Many of the polyesters, polyamides, and cellulose esters showed evidence of interaction and miscibility with PVPh. In most of the other cases, there was no sign of miscibility. Generally good correlation exists between thermal behavior and infrared spectral data. Where there is significant interaction seen between the polymers by FTIR, substantial miscibility is seen by DSC analysis. In some cases, the phase behavior depended on the blend preparation scheme. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends are known to be a route to the design of novel materials having extended and improved ranges of physical characteristics, such as processing, toughness, barrier properties, and chemical resistance. In some instances, blending affords a cost advantage as well. Blends may be miscible (single-phase) or immiscible, often with the target property dictating the optimal morphology. For example, in applications where optical clarity is needed, thermodynamic miscibility between blend components is usually required owing to turbidity that often arises from phase separation. Miscibility is also desired in compatibilizer design, such as with a copolymer (block, graft, or random) added to a mixture of immiscible polymers.[1,2]

The equilibrium state of a polymer mixture is understood in terms of the free energy of mixing, which for a generic mixture is represented by the well-known thermodynamic expression

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1)$$

where ΔG_m is the free-energy change upon mixing and ΔH_m and ΔS_m are the enthalpic and entropic contributions, respectively. For a blend to be a single phase, the requirements of $\Delta G_m < 0$ and $(\partial^2 \Delta G_m / \partial \phi_i^2)_{\phi_{j \neq i},T} \geq 0$ must be fulfilled. Using the simplistic Flory–Huggins lattice theory, eq. (1) can be rewritten on a volume basis for polymers 1 and 2 with volume fractions ϕ_i as[3]

$$\frac{\Delta G_m}{VkT} = \frac{g}{V_s}\,\phi_1\phi_2 + \left[\frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2\right] \qquad (2)$$

The first term on the right-hand side represents the enthalpic contribution per segment volume V_s; experimentally, the interaction term g has been shown to depend on composition and temperature. The term in brackets demonstrates that for polymers the entropic contribution (which is strictly combinatorial in the Flory–Huggins lattice picture) to the total free energy of mixing has only a small effect on enhancing miscibility, owing to the large molecular volumes V_1 and V_2 of macromolecules. Therefore, enthalpic contributions usually dominate in polymeric blends. In H-bonding blends, noncombinatorial entropy must also be considered for accurate analysis of the total free energy.

In all but a few rare instances, miscibility is observed only when there is a significant interaction between constituent polymers, i.e., when the en-

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thalpic interaction term in eq. (2) is negative.[4] Hence, a common means of designing thermodynamic miscibility for a blend of two or more polymers is through incorporation of specific attractive interacting groups.[1,3,5] This may be done by either copolymerizing with monomers containing interacting groups or by postfunctionalizing an existing polymer. Additionally, homopolymer pairs can be selected that have the potential for positive interactions. Examples of strong interactions are dipole-dipole, hydrogen bonding, charge transfer, ionic, and acid–base.[3,5] It is also important to note that the effects of crystallization have not been considered in the balance of enthalphic interactions.

There exists a wealth of literature with respect to enhancing polymer–polymer miscibility through hydrogen-bond interactions. Of particular interest to our laboratory is work concerning miscible blends with poly(4-vinylphenol), otherwise referred to as poly(p-hydroxystyrene) or polyvinylphenol (PVPh) and its random copolymer with styrene. Several polymers containing H-bond acceptor groups have been found to be miscible with PVPh, e.g., ester and carbonyl groups in poly(vinyl acetate) and poly(ethylene-co-vinyl acetate),[6] main-chain aliphatic polyesters [e.g., poly(ε-caprolactone) and poly(β-propiolactone),[6] and poly(ethylene succinate) and poly(ethylene adipate)[7]], aliphatic polyketones,[8,9] and numerous polyacrylates.[10–13] Amide-, imide-, and amine-containing polymers such as poly(N-vinylpyrrolidone),[14,15] poly(N,N-dimethylacrylamide),[13] poly(4-vinylpyridine),[16] and polypeptides[17] also exhibit miscibility with PVPh. Many etheric polymers such as poly(ethylene oxide),[14,18] poly(vinyl alkyl ethers),[14,19] etheric polyphosphazenes,[20] and polyitaconates[21] also form miscible blends. Finally, PVPh has also been found to be compatible with a number of other thermoplastics.[22]

The goal of this study was to survey the phase behavior of blends of PVPh with several polymers in some of the classes listed above and to determine if other possible H-bond-accepting polymers could be found. In particular, we scanned additional aliphatic and aromatic polyesters, polyimides, polyamides, and polyethers. Moreover, at least one polymer from the following classes was also probed, including cellulose esters, polycarbonates, polysulfones, polyurethanes, and polysiloxanes. Each type of polymer has etheric (or siloxane), carbonyl (from ester, amide, imide, carbonate, or urethane groups), or sulfonyl groups that have the potential of interacting with the proton-donating VPh polymer. Future reports from our laboratory will provide a more

in-depth look at the thermal and spectroscopic behavior of miscible blends of PVPh with a variety of aromatic polyesters[23] and polyamides.[24] We note that Pearce et al.[25] conducted a similar study on a series of solution-made blends with another hydrogen-bonding polymer, poly(styrene-co-vinylphenyl hexafluorodimethyl carbinol).

The experimental approaches utilized were differential scanning calorimetry (DSC), solid-state NMR, and FTIR spectroscopy. These techniques permit us to probe the phase behavior (i.e., determine whether a blend is miscible or immiscible) and to examine the origins of miscibility (or lack thereof). Mixtures were prepared by either solvent-blending or melt-blending methods.

We note that, in some of the previously listed studies,[6,9,10c,11,14,16–18,22] the PVPh polymer had quite a low molecular weight, typically M_w = 1500–7000 g mol^{-1}, and a broad molecular weight distribution. As seen in eq. (2), the lower the molecular weight (i.e., the smaller the molecular volume V_i), the larger the favorable combinatorial entropy contribution to the total free energy of mixing, hence, a tendency toward miscibility independent of the favorable hydrogen-bonding interactions that are also present. Often for polymer blends in practical applications requiring mechanical strength, higher molecular weights than those reported above for PVPh are required. Thus, for the study that follows, a high molecular weight PVPh (M_w = 68,000 g mol^{-1}) was synthesized and employed throughout the experiments, which should afford a more accurate indication of the inherent miscibility of PVPh with the other polymers due to specific interactions.

EXPERIMENTAL

Materials

The polymers studied are compiled and described in Tables I–III. The polyester and polyamide samples are listed in Tables II and III, respectively, whereas Table I lists the remaining polymers, along with available molecular weight characterization data. Except where noted, the polymers were of moderately high molecular weight and inherent viscosity (IV), so that their blend phase behavior would not be dominated by molecular weight effects. All the polyesters were obtained in-house; they are referred to in this report by the abbreviations in Table II. The polyamides were purchased from Scientific Polymer Products, Ontario, NY, and the remaining polymer sources are given in Table I.

The nomenclature for many of the copolyesters has been generalized so that the first part represents the diacid monomer and the symbol after the hyphen is for the diol portion. In the case of mixed diacids or diols, the quantity enclosed by parentheses gives the mol % of the monomer that follows. Thus, T-C(X)E is a copolymer prepared from terephthalic acid (T) and an X to 100-X mol % ratio of ethylene glycol (E) to 1,4-cyclohexane dimethanol (C).

Blends of each of the polymers with PVPh were prepared by one of the following techniques: For solution blending, each polymer was dissolved separately in a solvent common to both. The solutions were then combined in the ratios of 1 : 3, 1 : 1, and 3 : 1 by volume. The solution mixtures were either precipitated into a nonsolvent (usually hexane) or were knife-coated. Following coating or precipitation, the blends were dried, typically at 60–70°C under vacuum for 48 h. Specifics about the precipitation or knife-coating procedures are given in Table IV.

The second method involved blending by laboratory-scale melt extrusion. For this, the polymers were first ground into fine powders using a Retsch grinder with liquid nitrogen cooling when necessary. The powders were mixed by hand in the appropriate weight ratio, then dried under vacuum at 105°C for at least 1 day. Samples were removed from the vacuum oven only prior to extrusion. Melt extrusions were carried out with a Microtruder (Randcastle, Inc.) laboratory extruder equipped with a single $\frac{1}{4}$-in. screw, operating at 75 rpm, and a 2-in. slit die. Amounts ranging from 4 to 20 g of each blend sample were prepared. The blending conditions for all of the melt-prepared samples are supplied in Table V.

Methods

DSC

The onset and midpoint of the glass transition temperature (T_g), melting point temperature (T_m), and change in heat capacity at T_g (ΔC_p) for each blend (when a single phase) and homopolymer were measured on a Perkin-Elmer DSC7 or a DuPont 990 thermal analyzer equipped with a Laboratory Microsystems data analysis program. The thermal data were taken from the DSC trace of the second or subsequent runs that were scanned at a heating rate of 20°C/min. Semicrystalline homopolymers and their blends with PVPh were quenched in liquid N_2 prior to recording their DSC profile. All thermal data are reported in Table IV for the solution-prepared blends and in Table V for the melt-extruded ones.

FTIR

FTIR spectra were collected using a Bio-Rad (Digilab Division) FTS-7 spectrometer (3240-SPC) at a 4 cm^{-1} resolution. For solvent-cast polymers and blends, thin-film samples on a KBr disk were prepared by spin-casting a 5 wt % polymer solution at 1000 rpm followed by several hours of vacuum drying at 70°C. Photoacoustic spectroscopy was used to obtain FTIR spectra of the melt-processed blends, which were first ground into powdered form. The data for the melt-processed blends shown in the figures that follow were the accumulation of 2048 scans per sample, then statistically smoothed using a Savitsky-Golay smoothing algorithm.

The analysis of infrared spectra is intended to provide information to complement thermal data. The anticipated interaction between PVPh and polymers miscible with it is hydrogen bonding, which is readily seen by FTIR. The carbonyl stretch region for esters and carbonates (1700–1800 cm^{-1}) and the amide absorption near 1640 cm^{-1} provide the most quantitative information about the H-bond interaction. For polymers that do not contain carbonyl or amide groups, the hydroxy stretching mode band of PVPh (3000–3600 cm^{-1}) can also be studied. This band is present in all of the blends and is affected by hydrogen-bond formation. Frequency shifts in this band have been shown to provide information on relative strengths of interactions.[14,15]
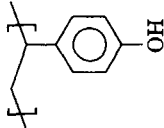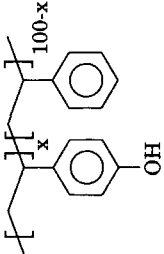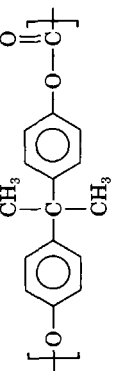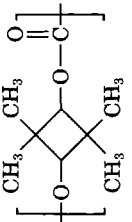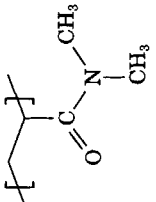
For each blend studied by FTIR, an addition spectrum was made by adding the spectra for the individual components and compared with the corresponding blend spectrum.

NMR

A few blend samples with similar constituent glass transition temperatures were examined by solid-state NMR spectroscopy. NMR spin-lattice relaxation times T_1 and $T_{1\rho}$ were measured on a Bruker CXP-100 spectrometer using previously described techniques.[26] The samples were from portions of those prepared for DSC analysis.

The spin-lattice relaxation time T_1 (laboratory reference frame) characterizes the return of the nuclear system to equilibrium following a single inverting rf pulse. The spin-lattice relaxation time $T_{1\rho}$ (rotating reference frame) measures the rate of relaxation while rf irradiation is being applied and the nuclear magnetization is locked along the effective magnetic field. Measurement of these proton relaxation times in the blends was done indirectly by transferring proton magnetization to the carbons after partial relaxation of the proton nuclei. In this

Table I Polymer Structures and Characterization

Polymer	Abbreviation	Chemical Structure	Molecular Weight	Source
Polyvinylphenol	PVPh		$M_w = 67.8$ K; $M_n = 37.9$ K[a]	Synthesized in-house
Poly(styrene-co-vinylphenol)	P(S-VPh(X)) X = 52, X = 42, X = 34, X = 22, X = 14, X = 5		$M_w = 116$ K; $M_n = 46.4$ K[a]; $M_w = 157$ K; $M_n = 66.2$ K[a]; $M_w = 89.5$ K; $M_n = 44.9$ K[a]; $M_w = 95.6$ K; $M_n = 48.4$ K[a]; $M_w = 98.9$ K; $M_n = 50.0$ K[a]; $M_w = 74.7$ K; $M_n = 40.7$ K[a]	Synthesized in-house
Poly(tetramethylene oxide)	PTMO		$M_w = 106.5$ K[b]; $M_w/M_n = 1.07$	Polymer Laboratories Lot 20935-1
Bisphenol-A polycarbonate	BPA-PC		$M_w = 47.7$ K; $M_n = 19.4$ K[c]	General Electric Lexan 145
Poly(dimethylsiloxane)	PDMS		$M = $ ca. 28 K[c]	Petrarch PS034
2,2,4-tetramethylcyclo-butane-1,3-diol polycarbonate	Cb-PC		—[d]	Eastman Chemical
Poly(N,N-dimethyl-acrylamide)	PDMA		IV = 0.50 g/dL[e]; $M_w = 490$ K; $M_n = 48$ K[f]	Polysciences
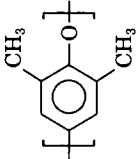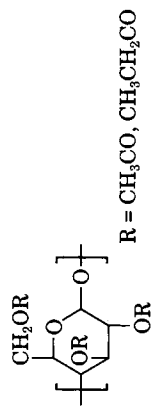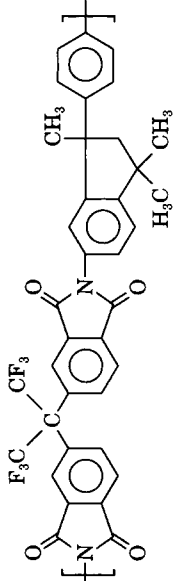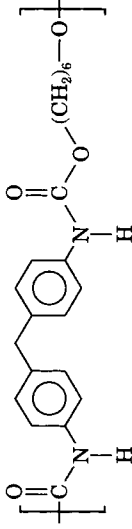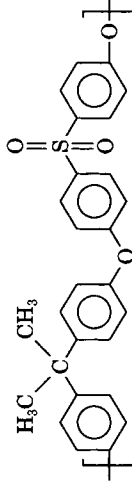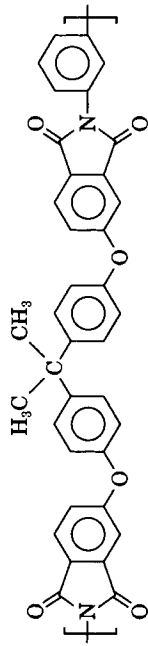
Name	Abbreviation	Structure	Property	Source
Poly(2,6-dimethyl-phenylene oxide)	PPO	CH_3 / CH_3 (2,6-dimethylphenylene oxide repeat unit)	IV = 0.46[c]	General Electric
Cellulose tripropionate	CTP	CH_2OR / OR / OR, R = CH_3CO, CH_3CH_2CO	—[d]	Eastman Chemical
Cellulose acetate propionate	CAP		—[d]	Eastman Chemical
Diaminophenylindane hexafluoroisopro-pylidene polyimide	DAPI-6F	CH_3, H_3C CH_3, F_3C CF_3 C (polyimide structure)	IV = 0.55 g/dL[g]	Synthesized in-house
Polyurethane	MDI-6	$(CH_2)_6$—O (polyurethane structure)	—[d]	Synthesized in-house
Poly(ether sulfone)	PES	H_3C CH_3 C, $O=S=O$ (poly(ether sulfone) structure)	—[d]	Union Carbide P1700 NT11
Polyetherimide	Ultem® PEI	H_3C CH_3 C (polyetherimide structure)	—[d]	General Electric Ultem 1010

Table I (Continued from the previous page)

Polymer	Abbreviation	Chemical Structure	Molecular Weight	Source
Poly(amide–imide) [from condensation of hexa-fluoroisopropylidene with p-aminobenzoic acid and bis-amino-phenoxyphenyl propane]	6F-BAPP PAI		$M_w = 65.5$ K[h] $M_n = 30.1$ K[h]	

[a] Absolute molecular weight of methylated phenol.
[b] GPC polystyrene equivalents.
[c] Manufacturer's specifications.
[d] No information available.
[e] Inherent viscosity, measured in MeOH.
[f] GPC, polysaccharide equivalents.
[g] Inherent viscosity, measured in N,N-dimethylacetamide, 25°C.
[h] GPC PMMA equivalents.

manner, the inherently high resolution of ^{13}C-NMR spectra of solids taken with magic-angle spinning is utilized for the measurement of ^{1}H relaxation times.

RESULTS AND DISCUSSION

Thermal Properties

The thermal properties of the solvent-prepared polymer blends are summarized in Table IV, and the melt extruded blends, in Table V.

Immiscible Blends

It can be seen that several of the binary blends listed in Table IV, the solution-blended samples, are immiscible as revealed by two glass transition temperatures. Blends of PVPh with T(60)A-Nb polyester, BPA polycarbonate (BPA-PC), Ultem® polyetherimide, DAPI polyimide, a fully aromatic polyamide (ODA-TA), a polyamide-imide (6F-BAPP), polydimethylsiloxane (PDMS), and poly(phenylene oxide) (PPO) each show two distinct T_g's. The knife-cast PVPh/PPO blend initially showed a very broad transition temperature, but, after annealing above the glass temperature of PPO, was confirmed immiscible by the appearance of two T_g's. The 1 : 1 PVPh/PPO blend was confirmed to be two-phased by solid-state NMR, as discussed below in the section NMR Relaxation Time Measurements.

Two of the solvent-precipitated blends in Table IV, PVPh with poly(ether sulfone) (PES) and Ardel-D100 (T(50)I-BPA polyarylate), exhibited one apparent T_g by DSC. However, the constituent homopolymer T_g's are too close to be resolved. The 1 : 1 blends were examined further by NMR and each were concluded to be two-phased. A more detailed analysis of the PES blend is provided in the NMR Relaxation Time Measurements on NMR results and the polyarylate blend is discussed elsewhere.[23] Another solution-prepared blend, PVPh with MDI-6 polyurethane, showed gross phase separation in each of the 1 : 3, 1 : 1, and 3 : 1 mixtures, with two physically separated phases forming upon coating. Because of this observation, none of these samples was examined further by DSC.

Of the solution-prepared, immiscible blends, melt blending was also carried out with T(60)A-Nb, BPA-PC, Ultem, 3Me6T (Trogamid-T®), and PPO. The melt-blending procedure was used as a double check, as it is known that solvent-induced phase separation, often referred to as the $\Delta\chi$ effect,[27,28] can occur when blends are prepared from solution.
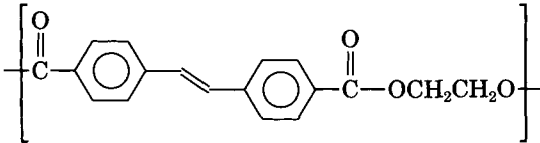
Table II   Polyester Structures

Abbreviation	Chemical Structure
PET[a]	$-[C(=O)-C_6H_4-C(=O)-OCH_2CH_2O]-$
PCT[b]	$-[C(=O)-C_6H_4-C(=O)-OCH_2-C_6H_{10}-CH_2O]-$
T-C(X)E X = 17, 29, 50, 66 (PET, X = 100) (PCT, X = 0)	$-[C(=O)-C_6H_4-C(=O)]-[-OCH_2CH_2O-]_X[-OCH_2-C_6H_{10}-CH_2O-]_{100-X}$
PBT	$-[C(=O)-C_6H_4-C(=O)-O-(CH_2)_4-O]-$
PEN	$-[C(=O)-C_{10}H_6-C(=O)-O-CH_2CH_2-O]-$
PBA	$-[O(CH_2)_4O-C(=O)-(CH_2)_4-C(=O)]-$
T-Ne	$-[C(=O)-C_6H_4-C(=O)-OCH_2C(CH_3)_2CH_2O]-$
T(17)I-C (Kodar A150)	$[C(=O)-C_6H_4-C(=O)]_{83}[C(=O)-C_6H_4-C(=O)]_{17} [-OCH_2-C_6H_{10}-CH_2O-]$
T(50)I-BPA (Ardel D100)	$[C(=O)-C_6H_4-C(=O)]_{50}[C(=O)-C_6H_4-C(=O)]_{50} [-O-C_6H_4-C(CH_3)_2-C_6H_4-O-]$

Table II *(Continued)*

Abbreviation	Chemical Structure
T(60)A-Nb	
TB-(60)Hb	
T(13)G-P(5)GL[c]	
T-E(50)BPAE	
Cy-E(50)BPAE	
T-E(50)Nbe	
Cy-Cb(30)C Cy-C (X = 100)	

Table II   (*Continued*)

Abbreviation	Chemical Structure
S-E	

^a IV = 0.621, measured in 60/40 phenol/1,1,2,2-tetrachloroethane (TCE), 25°C, 0.5% solution.
^b IV = 0.775, measured in 60/40 phenol/TCE, 25°C, 0.5% solution.
^c IV = 0.4, measured in 50/50 phenol/chlorobenzene, 25°C, 0.5% solution.

The preferential strong interaction between one polymer and the solvent can exclude the other polymer from the solution phase during drying, thus obscuring the equilibrium phase behavior of the dried blend. This effect has been noted for blends with PVPh using proton-accepting solvents.[13] With the exception of the Trogamid-T blends, each of these blends was deemed immiscible, regardless of the preparation procedure.

There has been some solvent-induced phase separation for the blend with the polyamide Trogamid-T. Table IV reports two values for the glass transition temperature. However, the melt blend of this pair only exhibits one T_g intermediate to those of
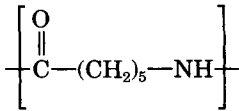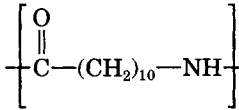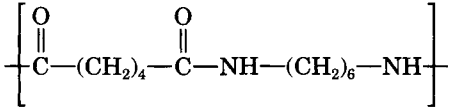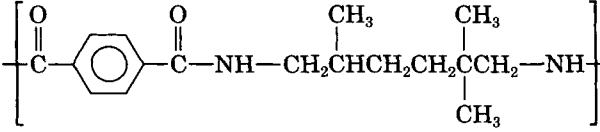
Table III   Polyamide Structures
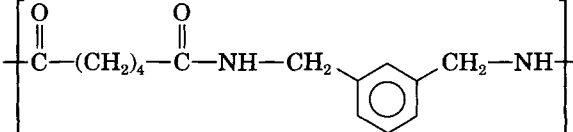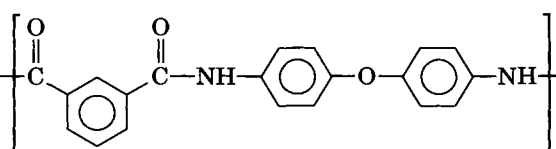
Name	Chemical Structure
Nylon-6	
Nylon-11	
Nylon-6,6	
3Me6T (Trogamid-T®)	
MXD6	
Poly(4,4'-oxydianiline–terephthalamide (ODA–TA)	

Table IV   Solution Blend Preparation Methods and Thermal Data

Polymer	Common Solvent[a]	PVPh : Polymer	1st T_g (°C) Onset	1st T_g (°C) Midpoint	ΔC_p (J/g °C)	2nd T_g (°C) Onset	2nd T_g (°C) Midpoint	Preparation Method and Comments
PVPh	THF	Pure	183.0	188.0	0.415	—	—	
PBA	THF, 5%	Pure	−66.5	−64.0	0.48	—	—	Precipitated into cold hexane; vacuum-dried at 60°C for 48 h (miscible blends)
		1 : 3	−46.0	−37.0	0.45	—	—	
		1 : 1	−2.0	19.0	0.45	—	—	
		3 : 1	97.0	109.0	0.27	—	—	
T-C(50)E	60/40 v/v CH$_2$Cl$_2$/THF, 3%	Pure	81.0	85.0	0.24	—	—	Precipitated in hexane; vacuum-dried at 65°C for 24 h (miscible blends)
		1 : 3	114.0	125.0	0.32	—	—	
		1 : 1	137.0	145.0	0.34	—	—	
		3 : 1	145.0	172.0	0.40	—	—	
T(50)I-BPA (Ardel D100)	THF, 5%	Pure	183.0	191.0	0.18	—	—	Precipitated into hexane; vacuum-dried at 65°C for 24 h (immiscible blends, see text for NMR data)
		1 : 3	183.5	190.0	0.22	—	—	
		1 : 1	181.0	188.0	0.37	—	—	
		3 : 1	181.5	187.0	0.39	—	—	
T(60)A-Nb	THF, 5%	Pure	149.0	156.0	0.166	—	—	Knife-cast at room temperature; vacuum-dried at 70°C for 7.5 days, follwed by 130°C for 4 h (immiscible blends)
		1 : 3	135.0	144.0	—	183.0	187.0	
		1 : 1	136.0	145.0	—	181.0	186.0	
		3 : 1	137.0	144.0	—	183.0	187.0	
CTP	MEK, 5%	Pure	121.0	127.0	0.34	—	—	Precipitated into hexane; vacuum-dried at 120°C for > 28 h; partial crystallinity in 1 : 3 blend, T_m = 225°C (miscible blends) (also see Table V)
		1 : 3	123.0	131.0	(0.35)	—	—	
		1 : 1	139.0	146.0	0.37	—	—	
		3 : 1	158.0	166.0	0.44	—	—	
BPA-PC	THF, 5%	Pure	137.0	144.0	0.24	—	—	Precipitated into hexane; vacuum-dried at 65°C for 24 h (immiscible blends) (also see Table V)
		1 : 3	140.0	144.0	—	180.0	184.0	
		1 : 1	137.0	141.0	—	184.0	189.0	
		3 : 1	135.0	139.0	—	184.0	188.0	
PTMO	THF 3.3%	Pure	−98.0	−74.0	—	—	—	Knife-cast at room temperature or at 40°C; vacuum-dried at 60–80°C for 3 days (partially miscible, see text)
	5%	1 : 1	−19.0	−8.0	—	—	—	
		3 : 1	ca. 160	ca. 168	—	—	ca. 155	

Polymer	Solvent	Blend						Comments
Ultem® PEI	Pyridine, 5%	Pure	199.0	206.0	0.26	—	—	Precipitated into hexane; vacuum-dried at 70°C for 65 h (immiscible blends) (also see Table V)
		1:3	185.0	189.0	—	213.0	216.0	
		1:1	186.0	190.0	—	206.0	213.0	
		3:1	184.0	189.0	—	212.0	221.0	
3Me6T	DMF, 5%	Pure	136.0	144.0	0.40	—	—	Knife-cast at 35°C; vacuum-dried at 70°C for 65 h (immiscible due to solvent effect) (see text, also see Table V)
		1:3	149.0	153.0	—	—	—	
		1:1	148.0	151.0	—	181.0	186.0	
		3:1	149.0	152.0	—	173.0	182.0	
PDMA	DMF, 5%	Pure	116.0	123.0	0.29	—	—	Knife-cast at 43°C; vacuum dried at 90°C for 24 h (miscible blends)
		1:3	151.0	157.0	0.33	—	—	
		1:1	170.0	177.0	0.43	—	—	
		3:1	187.0	193.0	0.46	—	—	
DAPI-6F	THF, 5%	Pure	317.0	324.0	0.164	—	—	Precipitated into hexane; vacuum-dried at 65–70°C for 2.5 days (immiscible blends)
		1:3	183.0	188.0	—	316.0	321.0	
		1:1	182.0	186.0	—	311.0	317.0	
		3:1	180.0	185.0	—	334.0	336.0	
PES	THF, 5%	Pure	175.0	181.0	0.23	—	—	Precipitated into hexane; vacuum-dried at 65°C for 24 h (immiscible blends) (see text for NMR data)
		1:3	180.0	185.0	0.30	—	—	
		1:1	184.0	188.0	0.30	—	—	
		3:1	181.0	187.0	0.38	—	—	
PPO	THF, 5% at 50°C	Pure	206.0	211.0	0.15	—	—	Knife-cast at room temperature; vacuum-dried at 70°C for 2 days (immiscible blends) (also examined by NMR)
		1:3	174.0	180.0	—	197.0	203.0	
		1:1	181.0	186.0	—	208.0	213.0	
		3:1	182.0	186.5	—	208.0	215.0	
PDMS	MEK, 5%	Pure	−120.0	−119.0	—	—	—	Knife-cast at room temperature; vacuum-dried at 70°C for 2 days (immiscible blend)
		1:1	−124.0	−121.5	—	166.0	170.0	
IPC-ODA polyamide	DMF, 5%	Pure	244	251	—	—	—	Precipitated into water; vacuum-dried at 83°C for 12 h (immiscible blend)
		1:1	182	189	—	247	252	
6F-BAPP PAI	DMF, 5%	Pure	262	269	—	—	—	Precipitated into water; vacuum-dried at 83°C for 12 h (immiscible blend)
		1:1	190	197	—	246	258	

a THF: tetrahydrofuran; MEK: methyl ethyl ketone (2-butanone); DMF: dimethylformamide.

Table V   Melt-extruded Blends and Thermal Data

Polymer	Extrusion Temp. (°C)	PVPh : Polymer	1st T_g (°C) Onset	1st T_g (°C) Midpoint	ΔC_p (J/g °C)	2nd T_g (°C) Onset	2nd T_g (°C) Midpoint	Physical State[a]
PVPh	—	Pure	183	188	0.42	—	—	(A)
PET	—	Pure	77	80	0.33	—	—	(C) $T_c = 168°C$, $T_m = 249°C$
	254	1 : 1	117	126	0.42	—	—	(M), (C) $T_c = 200°C$, $T_m = 236°C$
PCT	—	Pure	92	103	—	—	—	(C) $T_m = 286°C$
	293	1 : 1	96	107	—	175	181	(I), (C) $T_c = 145°C$, $T_m = 288°C$
T-C(66)E	—	Pure	78	82	0.28	—	—	(A)
	260	1 : 1	122	129	0.36	—	—	(M), (A)
T-C(29)E	—	Pure	86	89	0.25	—	—	(A) ($T_m = 236°C$)
	260	1 : 1	136	144	0.35	—	—	(M), (A)
T-C(17)E	—	Pure	88	92	—	—	—	(C), $T_m = 257°C$
	282	1 : 1	94	105	—	158	165	(I), (C) $T_c = 158°C$, $T_m = 264°C$
PBT	—	Pure	39	42	—	—	—	(C) $T_m = 223°C$
	293	1 : 1	94	103	0.34	—	—	(M), (A) ($T_c = 163°C$, $T_m = 216°C$)
PEN	—	Pure	119	124	—	—	—	(C) $T_m = 260°C$ (small)
	230	1 : 1	141	149	—	—	—	(M), (C) $T_m = 260°C$ (small)
T(17)I-C	—	Pure	89	93	—	—	—	(C)$T_c = 166°C$, $T_m = 265°C$
(Kodar A150)	277	1 : 1	92	101	—	168	177	(I), (C) $T_c = 172°C$, $T_m = 264°C$
T(60)A-Nb	—	Pure	149	156	0.17	—	—	(A)
	293	1 : 1	141	148	—	182	187	(I), (A) (also see Table IV)
T-Ne	—	Pure	47	50	0.29	—	—	(A)
	210	1 : 1	109	118	0.34	—	—	(M), (A)
Cy-C	—	Pure	60	65	0.18	—	—	(C) ($T_c = 130°C$, $T_m = 212°C$)
	254	1 : 1	128	135	0.26	—	—	(M), (A)
Cy-Cb(30)C	—	Pure	100	108	0.13	—	—	(A)
	254	1 : 1	158	164	0.29	—	—	(M), (A)
T(13)G-P(5)GL	—	Pure	59	63	0.32	—	—	(A)
	210	1 : 1	107	116	0.37	—	—	(M), (A)
T-E(50)BPAE	—	Pure	79	82	0.35	—	—	(A)
	254	1 : 1	74	78	—	156	167	(I), (A)
Cy-E(50)BPAE	—	Pure	45	48	0.27	—	—	(A)
	254	1 : 1	100	108	0.34	—	—	(M), (A)
T-E(50)Nbe	—	Pure	114	119	0.28	—	—	(A)
	254	1 : 1	111	116	—	171	178	(I), (A)
S-E	—	Pure	—	—	—	—	—	(LC) $T_{m1} = 250°C$, $T_{m2} = 276°C$
	282	1 : 1	—[b]	—[b]	—	—	—	(I), (LC) $T_{m1} = 251°C$, $T_{m2} = 279°C$
TB-(60)Hb	—	Pure	—	—	—	—	—	(LC)
	282	1 : 1	—[b]	—[b]	—	—	—	(I), (LC)
3Me6T	—	Pure	149	153	0.40	—	—	(A)
(Trogamid-T®)	260	1 : 1	168	173	0.42	—	—	(M), (A) (also see Table IV)

Table V Continued

Polymer	Extrusion Temp. (°C)	PVPh : Polymer	1st T_g (°C)		ΔC_p (J/g °C)	2nd T_g (°C)		Physical State[a]
			Onset	Midpoint		Onset	Midpoint	
Nylon-MXD6	—	Pure	84	88	(0.44)	—	—	(C), $T_c = 167°C$, $T_m = 231°C$
	230	1 : 1	115	120	0.43	—	—	(M); (A)
Nylon-6	—	Pure	40	43	—	—	—	(C), $T_m = 222°C$
	260	1 : 1	90	97	0.40	—	—	(M), (A)
Nylon-11	—	Pure	—	33 (lit.)	—	—	—	(C), $T_m = 191°C$
	260	1 : 1	88	96	0.42	—	—	(M), (A)
Nylon-6,6	—	Pure	—	45 (lit.)	—	—	—	(C), $T_m = 254°C$
	271	1 : 1	96	103	(0.38)	—	—	(M), (C), $T_m = 162, 217°C$
CAP[c]	—	Pure	127	142	0.28	—	—	(A)
	249	1 : 1	137	147	0.35	—	—	(M), (A)
CTP	—	Pure	121	127	0.34	—	—	(C) or (A), $T_c = 175°C$, $T_m = 245°C$
	254	1 : 1	136	144	0.38	—	—	(M), (A) (also see Table IV)
BPA-PC	—	Pure	137	141	0.24	—	—	(A)
	293	1 : 1	143	147	—	183	187	(I), (A) (also see Table IV)
Cb-PC	—	Pure	116	122	0.17	—	—	(C), $T_m = 257°C$
	254	1 : 1	115	122	—	180	187	(I), (C), $T_c = 202°C$, $T_m = 253°C$
PEI (Ultem®)	—	Pure	199	206	0.26	—	—	(A)
	277	1 : 1	182	187	—	210	213	(I), (A)
PPO	—	Pure	206	211	0.15	—	—	(A)
	277	1 : 1	—	—	—	—	—	(I) (see text for NMR result) (also see Table IV)

[a] (A) amorphous; (C) semicrystalline; (LC) liquid crystalline; (M) miscible; (I) immiscible.

[b] Grossly phase-separated as extruded.

[c] Contains plasticizer (see text).

the component polymers. Note that the T_g for the pure solvent-cast Trogamid-T appears lower by ca. 10°C (Table IV vs. V), probably due to retained DMF solvent. This blend is concluded to be miscible.

Other melt-processed PVPh blends that could not be prepared by solution methods owing to lack of solubility in a common solvent were found to be immiscible. In the blends with a crystalline component, immiscibility was seen by the presence of two glass temperatures in liquid N_2-quenched samples. These include the Cb polycarbonate, several polyesters and copolyesters [PCT, Eastman Kodar® A150, T-E(50)BPAE, T-E(50)Nbe], and two liquid crystalline polyesters TB-(60)Hb and S-E. The structures for all of these polymers are given in Tables I and II, and DSC data, in Table V.

Final examples of immiscible blends are those containing random copolymers of styrene and VPh, P(S-VPh(X)), where X represents the mol % VPh (Table VI). One such blend is PPO with P(S-VPh(42)). This is an interesting example in that there should be a transition in the phase behavior when going from a VPh/PPO to a styrene/PPO blend. Pure polystyrene is known to be miscible with PPO, whereas PVPh is not. The two distinct T_g's for the 1 : 1 blend of PPO/P(S-VPh(42)) show that at this particular copolymer composition the two polymers are immiscible; however, note that the blend of PPO and P(S-VPh(22)) appears to be miscible (Table VI). Two other random copolymer blends of P(S-VPh(5)) and P(S-VPh(14)) with the polyamide nylon-6 are also immiscible, not surprising due to the small amounts of the VPh comonomer present.

Partially Miscible Blend with PTMO

The semicrystalline polymer poly(tetramethylene oxide) (PTMO) exhibited partial miscibility with PVPh. A significant interaction was seen but it did

Table VI Thermal Data for Poly(styrene-co-vinylphenol) Blends

Copolymer	Polymer	Copolymer : Polymer	Extrusion T (°C)	1st T_g (°C) Onset	1st T_g (°C) Midpoint	ΔC_p (J/g °C)	2nd T_g (°C) Onset	2nd T_g (°C) Midpoint	Physical State
P(S-VPh(42))	PPO	Pure	—	141	146	0.42	—	—	(A)
		1 : 1	260	144	148	—	210	213	(A), (I)
P(S-VPh(22))	PPO	Pure	—	122	127	0.34	—	—	(A)
		1 : 1	260	146	157	(0.22)	—	—	(C), (M) T_m = 242°C
P(S-VPh(5))	Nylon-6	Pure	—	107	110	0.30	—	—	(A)
		1 : 1	260	49	59	—	107	110	(C), (I) T_m = 221°C
P(S-VPh(14))	Nylon-6	Pure	—	113	116	0.34	—	—	(A)
		1 : 1	260	47	56	—	109	114	(C), (I) T_m = 220°C
P(S-VPh(34))	Nylon-6	Pure	—	—	—	—	—	—	(A)
		1 : 1	260	72	83	0.36	—	—	(C), (M) T_m = 213°C
P(S-VPh(52))	Nylon-6	Pure	—	148	153	0.42	—	—	(A)
		1 : 1	260	76.5	85	0.38	—	—	(C), (M) T_m = 199°C

a (A) amorphous; (C) semicrystalline; (M) miscible; (I) immiscible.

not result in completely miscible films under the blend preparation conditions employed. In solution, the 1 : 1 blend was phase-separated at 10% solids concentration in tetrahydrofuran, but was homogeneous at 5%. When allowed to dry slowly at room temperature, the 1 : 3, 1 : 1, and 3 : 1 PVPh/PTMO compositions separated into semicrystalline PTMO-rich and PVPh-rich phases. The crystallinity was dependent upon sample preparation history. Only the 3 : 1 sample became a single phase when heated above 200°C in the DSC and would not recrystallize after heating and cooling. When knife-coated at about 40°C, however, a 1 : 1 blend dried to a tacky film that had a large glass transition at 8°C, as shown in Table II, but also showed evidence of a minor second phase with a T_g of ca. 155°C. The T_g of the majority phase is close to what one would predict from the Fox[29] equation, $1/T_g = w_1/T_{g1} + w_2/T_{g2}$, where T_{gi} are the glass temperatures of the pure homopolymers and w_i are the weight fractions (Fig. 1). This rough agreement suggests that the composition is not far from 1 : 1. The thermal evidence, then, is that the two polymers show substantial miscibility but may not be completely miscible, owing either to the crystallizability of PTMO or possibly to the presence of a critical phase transition that would, if present, affect the phase behavior when heated. Additional experiments employing special annealing and thermal history cycles are required for full characterization. This system is discussed further in the section FTIR Measurements on the IR results.

Miscible Blends with Cellulose Esters

Extensive work has been done previously by Kelley and Zimmerman[30] on blends of PVPh with cellulose diacetates (CA). Miscibility was found for the CA/PVPh blends over a range where the acetyl content in CA was varied between 32.0 and 42.5 wt %. The work presented here is a continuation with cellulose propionate and a cellulose acetate propionate mixed ester.

Figure 2 shows the composition dependence of T_g for the miscible blend of PVPh with cellulose tripropionate (CTP). Samples prepared both by precipitation and by melt blending yielded identical T_g data. Although most of these blends were amorphous, the blend containing 75% CTP was semicrystalline. The melting point was depressed by approximately 20°C from that of pure CTP. As extruded, both CTP and the CTP/PVPh blends provided good quality clear films.
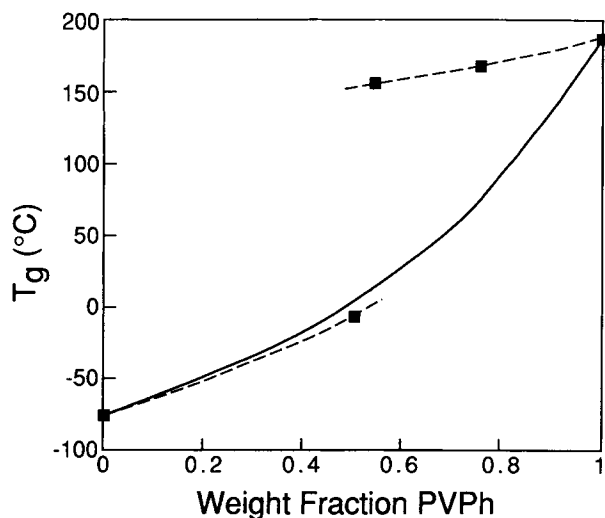
Other cellulose esters are not as thermally stable

Figure 1 Composition dependence of PVPh/PTMO blend T_g data. The solid curve represents the Fox equation prediction, and the symbols are from DSC data. The dashed lines are included only to show the general trend of the data.

as is CTP, and often difficulty was encountered during melt-extrusion steps. A 50/50 blend with cellulose acetate propionate (CAP) mixed ester that had been precompounded with ca. 15 wt % plasticizing agents was prepared. These additives were necessary to decrease the high melt viscosity of CAP to allow extrusion at a reasonable temperature. The DSC results for the melt blend (Table V and Fig. 2) reveal a single, intermediate T_g, indicating miscibility of the two polymers. It is not known how the presence of the plasticizers affected this observation.

Miscible Blends with Polyesters

Two of the PVPh/polyester blends prepared via solution techniques showed a single T_g over all compositions: poly(butylene adipate) (PBA) and the copolyester of terephthalic acid and 50/50 ethylene glycol/cyclohexane dimethanol (T-C(50)E). PBA is an all aliphatic polyester and is used for comparison since this blend has already been reported in the literature.[7] Each blend exhibits some broadening of T_g at intermediate compositions, possibly revealing a degree of heterogeneity at the segmental level to which the DSC glass transition is sensitive. Such broadening is a common phenomenon in blends of miscible polymers.[1]

Most of the melt-blended polyesters were found to be miscible with PVPh (see Table V), especially several containing aliphatic diol monomers. Each of

the single-phase blends exhibited one T_g in the DSC runs, so long as the crystallization temperature was not reached. Many of the blends recrystallized near T_m of the polyesters during thermal analysis. For these cases, the crystallization and melting temperatures are included in Table V. To outline, PVPh was found to be miscible with poly(butylene terephthalate) (PBT), poly(2,2-dimethylpropylene terephthalate) (T-Ne), poly(ethylene 2,6-naphthalenedicarboxylate) (PEN), Cy-E(50)BPAE, a copolymer of terephthalic and pentanedioic acids with 1,2-propanediol and glycerol [T(13)G-P(5)GL], two aliphatic but cyclic copolyesters [Cy-Cb(30)C and Cy-C], and several copolyesters from the poly(ethylene-co-cyclohexanedimethylene terephthalate) series, T-C(X)E. The structures of these polymers are found in Table II.

The glass transition temperatures for many of the miscible polyester/PVPh pairs are plotted in Figure 3. Only 1 : 1 compositions were studied for these blends, necessitated by the limited quantity of PVPh available for the extrusion experiments (roughly 5 g per blend). No fits to any theoretical equations were employed, and the dashed lines are drawn as visual guides. It is interesting to note that two of the blends with cycloaliphatic copolyesters, Cy-Cb(30)C and Cy-C, show strong positive deviations from additivity.
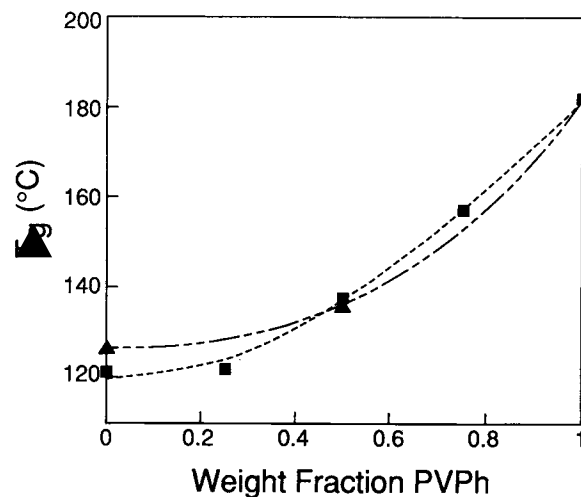

Figure 2 Composition dependence of T_g (DSC onset) for blends of PVPh with cellulose esters. The symbols are for (■) blends with cellulose tripropionate (CTP) prepared by solution methods and (▲) for cellulose acetate propionate with plasticizer prepared by melt blending. The melt-blended 50/50 CTP sample coincides with the solution-prepared one. The curves are spline fits through the data.
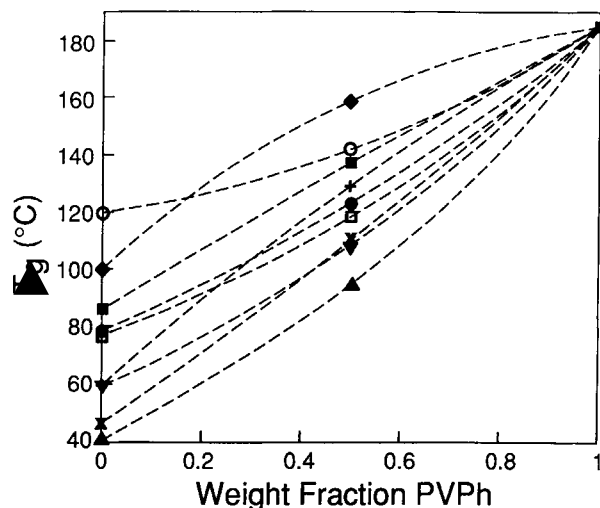
Figure 3 General trends in the composition dependence of T_g (DSC onset) for melt blends of PVPh with polyesters: ($\square$) PET; ($\bigcirc$) PEN; ($\blacktriangle$) PBT; ($\times$) T-Ne; ($\blacksquare$) T-C(29)E; ($\bullet$) T-C(66)E; ($\blacktriangledown$) T(13)G-P(5)GL; (+) Cy-C; ($\blacklozenge$) Cy-Cb(30)C.

The rationale for why PVPh is not miscible with all of the polyesters is not known at this time. Possibly, an optimum density of ester groups in polyesters is necessary for achieving the strongest interaction, as suggested for another H-bonding polymer, phenoxy.[31] It appears that, in particular, copolyesters derived from aliphatic diol monomers, rather than from aromatic diols, have a greater tendency to be miscible with PVPh. A more detailed investigation is beyond the scope of this survey.

To investigate whether crossreactions play a role in introducing miscibility into the melt-extruded PVPh/polyester blends, annealing studies were performed on some of the extruded blends. Changes were observed in the crystalline and melting behavior of some of the blends, but only after extended annealing for periods approximately five to 10 times the extrusion residence time, which was about 1.5 min. For example, the PBT/PVPh blend still showed spontaneous crystallization upon heating followed by melting, even after 8 min of annealing at 290°C. T_c and T_m eventually disappeared after 16 min. The blend with PET was less robust, with changes in the crystalline and melting behavior occurring after 8 min at 265°C, which was 10°C higher than the extrusion temperature. Similar experiments on immiscible blends such as with PCT and T-C(17)E still resulted in having two T_g's after up to 10 min at 305 and 295°C, respectively. These annealing experiments, we believe, signify that the ob-

served miscibility of the polyesters with PVPh is not a result of chemical reaction under normal extrusion conditions.

Miscible Blends with Polyamides

Poly(N,N-dimethylacrylamide), which contains pendant tertiary amide groups, was studied in addition to one amorphous (Trogamid-T) and several crystalline "backbone" polyamides. The crystalline nylons had to be melt-blended due to their lack of solubility. All were found to be miscible with PVPh with the exception of the polyaramide ODA-TA and the 6F-BAPP polyamide–imide. It was stated in the section Immiscible Blends that the solution-prepared Trogamid sample was two-phased because of preferential solvation. The DSC results for five representative polyamides are plotted in Figure 4 in the same manner as in Figure 3. Each blend shows negative additivity in the composition dependence of T_g. This is in contrast to earlier work[13] with the amorphous polyamide PDMA, which showed a strong positive deviation from additivity.

As indicated in Table V, most of the melt blends were amorphous as extruded and did not crystallize upon heating. This is in contrast to the pure polyamides themselves, which were highly crystalline and difficult to quench to an amorphous state. For example, pure nylon-6 can be quenched in liquid N_2, but nylon-11 still crystallizes even after quenching in liquid N_2. Blends of these two polymers
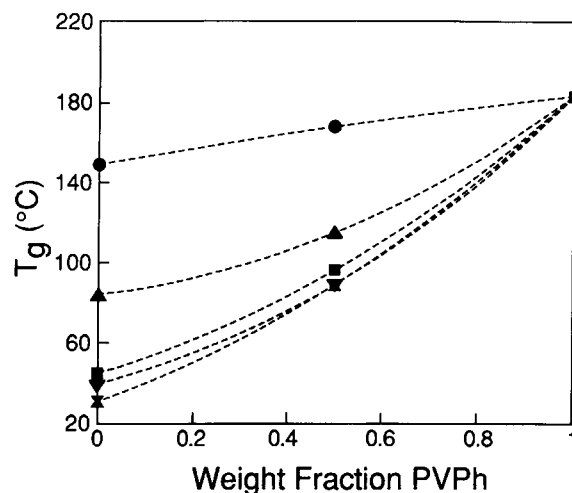

Figure 4 General trends in the composition dependence of T_g (DSC onset) for melt blends of PVPh with polyamides: ($\bullet$) 3Me6T (Trogamid-T); ($\blacktriangle$) MXD6; ($\blacksquare$) nylon-6,6; ($\blacktriangledown$) nylon-6; ($\times$) nylon-11.

with PVPh were both amorphous, indicating a strong interaction between the constituent polymers.

Although the nylon-6,6/PVPh blend exhibited a single T_g intermediate to the homopolymers, its DSC trace also showed two small, broadened melting peaks at 162 and 217°C. Nylon-6,6 itself has a melting point at 254°C. Complications in the interpretation of the DSC observation for this melt blend may be the result of thermal instability of nylon-6,6, since this polyamide homopolymer is known to undergo chain scission and cross-linking when heated above 260°C in air.[32,33]

A total of four styrene–VPh random copolymer 1 : 1 blends were made with nylon-6. The VPh comonomer contents were 5, 14, 34, and 52 mol %. Of these blends, two [P(S-VPh(34)) and P(S-VPh(52))] were miscible as deduced by a single T_g of the amorphous portion for each. All four P(S-VPh)/nylon-6 blends were semicrystalline, but only the miscible ones had melting points lower than pure nylon-6 (see Table VI).

NMR Relaxation Time Measurements

Spin-lattice relaxation time measurements were employed to determine the state of blends that had constituent glass transition temperatures too close to be resolved by DSC. Three 1 : 1 PVPh blends were examined with Ardel D100 ($T_g = 191°C$), PES ($T_g = 181°C$), and PPO ($T_g = 211°C$). Our conclusion from these measurements is that all three blends were immiscible.

The spin-lattice relaxation times T_1 and $T_{1\rho}$ for protons of each component in a few of the blends were measured indirectly by ^{13}C-NMR. Two proton T_1 values, which typically fall in the range of 50–500 ms, is a clear indication of phase separation at a scale exceeding 100–300 Å.[25] A single relaxation time usually suggests, but does not unconditionally prove, intimate mixing within the blend. Moreover, separate $T_{1\rho}$'s (range 1–50 ms) suggest phase separation above 30–60 Å.[26]

Analysis of relaxation curves of the PVPh/Ardel D100 blend revealed two distinct sets of nuclear relaxation times: $T_1 = 495 \pm 17$ ms and 180 ± 10 ms and $T_{1\rho} = 8.2 \pm 0.3$ ms and 7.0 ± 0.5 ms. The uncertainties arise from statistical analysis and should be considered as lower limits to the actual deviations. The proton T_1 value of pure Ardel D100 is 160 ± 13 ms, clearly different from that of pure PVPh: 528 ± 27 ms. The $T_{1\rho}$ values for the pure components are slightly different: 6.0 ± 0.4 ms for Ardel and 8.1 ± 0.4 ms for PVPh. Seeing that the relaxation times

for the components within the blend are nearly the same as for the pure materials, complete phase separation of this blend is indicated.

Pure PPO has a $T_{1\rho}$ that is distinctly different from that of PVPh (17.7 ± 0.6 vs. 8.1 ± 0.4 ms, respectively), whereas the T_1 value for pure PVPh (528 ± 27 ms) falls within a range of observed PPO proton relaxation times (507–645 ms) measured from different carbon signals. This broad range for pure PPO is unexpected, as each carbon nucleus, from which the relaxation times were obtained, is buried in the same proton "bath" in the pure polymer. The discrepancy may be related to impurities in our PPO sample that contribute from 10 to 15% of the carbon spectrum. Impurity peaks underlying the PPO signals would skew the apparent relaxation times. Despite the uncertainties related to the T_1 values, the $T_{1\rho}$ number for the PPO protons in the blend is decidedly different from that of the VPh polymer. It appears that there is slight mixing of PPO and PVPh in the initially prepared blend, although there are two separate phases.

Only a limited quantity of the PES/PVPh blend was available, making it difficult to perform a complete measurement of relaxation times. In lieu of a full determination of ^{1}H relaxation times, single spectra were taken after partial relaxation. If the relative peak intensities in the carbon spectra of a partially spin-relaxed material are the same as in the fully relaxed sample, then all protons relax at the same rate as well—hence, a single phase blend. If the protons relax at different rates, then the carbon spectra will appear different. Figure 5 shows the ^{13}C-NMR spectra from such an experiment.

In Figure 5(a), the standard spectrum for the 1 : 1 solvent-prepared mixture of PES/PVPh taken with the protons at equilibrium, prior to cross-polarization, shows a resolvable peak at about 30 ppm due to the methyl carbons of the bisphenol-A (BPA) unit in PES. The larger signal at 40 ppm is from the backbone carbons in PVPh and also the quaternary carbon in the BPA moiety. After allowing the proton bath to relax in a T_1 experiment (see the section Methods), one can see from Figure 5(b) that the methyl signal at 30 ppm is relatively more intense than in Figure 5(a). This means that the T_1 of the protons around the PES methyl group is shorter than for those around the PVPh carbons. Figure 5(c) shows the spectrum taken during a $T_{1\rho}$ experiment. The methyl signal has become less intense than the 40 ppm peak in the standard spectrum, signifying that $T_{1\rho}$ for the protons in PES is less than that of PVPh. Because the protons of the
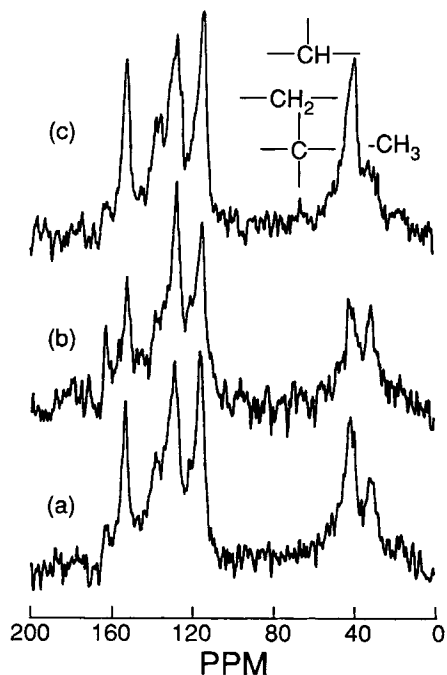
Figure 5 ^{13}C-NMR spectra of a 1 : 1 blend by weight of PVPh and PES: (a) standard spectrum acquired with the proton bath at complete equilibrium before cross-polarization; (b) spectrum acquired after recovery in the absence of irradiation (T_1 experiment); (c) spectrum obtained after relaxation, but during irradiation for 10 ms before cross-polarization ($T_{1\rho}$ experiment).

two components in the polymer mixture relax at different rates, we conclude that this pair of polymers is immiscible as prepared.

FTIR Measurements

For all of the solvent-cast blends that were deemed to be immiscible, no differences were observed between the synthesized addition spectra and the blend spectra; therefore, no evidence of hydrogen-bonding interactions was seen. The one exception was the blend with T(60)A-Nb (see Table II for structure) where a very small interaction was seen. Interactions were observed in the miscible solution-prepared blends of PVPh with PBA, PDMA, and PTMO. Several of the miscible melt-blended polyesters exhibited H-bond interactions as well. The components in the PVPh/PCT melt blend, although immiscible, exhibited some interaction by FTIR. No measurements were carried out on the cellulose ester/PVPh blends, although observations on cellulose diacetate blends have shown specific interactions between the phenolic group and the carbonyl

and ether groups.[30] Only one of the melt-prepared polyamides, MXD-6, was examined and observed to have H-bond interactions present. In this survey report, FTIR results for the PBA, MXD-6, and PTMO 1 : 1 blends with PVPh will be summarized. A more detailed analysis of and commentary on the levels of hydrogen bonding in the other miscible polyester/PVPh[23] and PDMA/PVPh[13] blends can be found in other reports.

In Figure 6 are shown the carbonyl (a) and hydroxyl (b) stretching regions for the solvent-cast PBA/PVPh blend and the pure components. The free ester carbonyls in pure crystalline PBA present themselves in the primary IR band at 1729 cm^{-1}, and the amorphous phase causes the slight shoulder at higher wavenumbers. Upon introduction of PVPh, a new band at 1708 cm^{-1} appears, indicating that
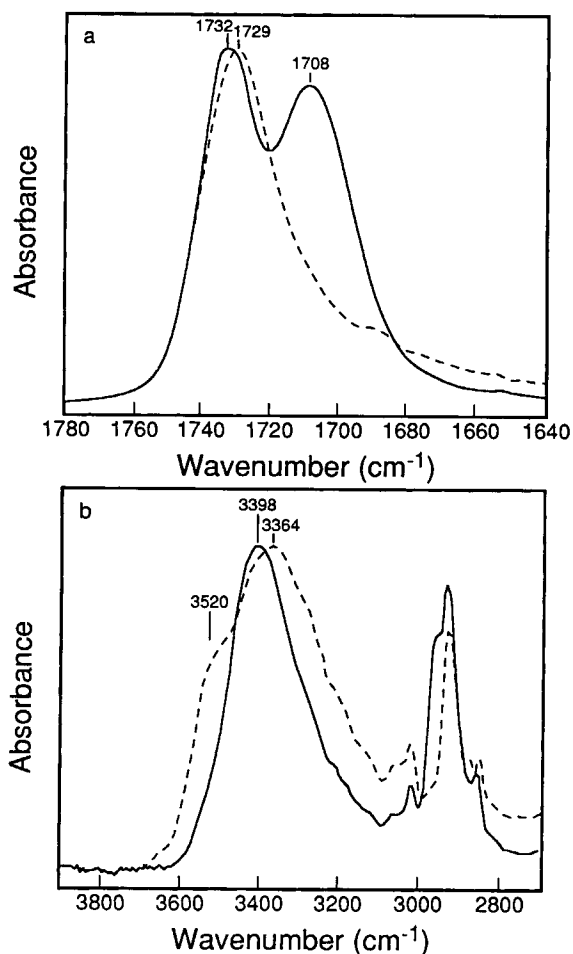

Figure 6 FTIR spectra (solid lines) for a 1 : 1 blend of PVPh/PBA. In (a), the carbonyl stretching region, the dotted line is pure PBA; in (b), the hydroxyl stretching region, the dotted line is pure PVPh.

some hydrogen bonding has occurred between the ester carbonyl and PVPh. At the same time, the free carbonyl peak has shifted toward higher wavenumbers, most likely from the decrease of the PBA crystallinity. The pure PVPh OH stretching region in Figure 6(b) shows a nonbound band (3520 cm^{-1}) and a broad band attributed to self-association (3364 cm^{-1}). The appearance of a new, intermediate IR absorption at 3398 cm^{-1} likewise signifies interaction between some of the PVPh hydroxyl groups and the polyester in the blend.

As mentioned at the start of this section, some interactions were seen by FTIR for the immiscible PCT blend. Some increase in the fraction of free hydroxyl groups in PVPh was seen, as well as a shift in the ester carbonyl peak, although to a lesser degree than with the other polyesters.[23] This observation appears consistent with those of Coleman et al.[10] for PVPh/polyacrylate blends, in that hydrogen-bound carbonyls were present in phase-separated mixtures. The favorable carbonyl/hydroxyl interactions in the PCT/PVPh blend are apparently not enough to overcome enthalpic repulsions.

The carbonyl and hydroxyl absorbance regions of the infrared spectrum for the miscible blend of PVPh with the polyamide MXD-6 are shown in Figure 7. Figure 7(a) contains the pure carbonyl spectrum for MXD-6. Unfortunately, the interpretation of the results for the amide carbonyl region is more ambiguous than for the ester one due to the presence of overlapping bands. The broad amide carbonyl band has a peak value at 1652 cm^{-1}; a new band appears at 1610 cm^{-1} in the blend with PVPh. However, PVPh itself has absorbances associated with ring vibrations at 1510, 1592, and 1610 cm^{-1}, which make it difficult to ascertain the state of H-bonding in the blend. The other peaks observed in the 1500–1580 cm^{-1} region of the pure amide and blend spectra are associated with the amide-II (C — N) vibrations.

Examination of the hydroxyl region [Fig. 7(b)] of both the VPh homopolymer and the blend is complicated by the N — H vibrations of the polyamide at 3294 cm^{-1}. However, it is clear that in the miscible blend essentially no free hydroxyl groups remain, as evidenced by the lack of absorption bands in the 3500–3600 cm^{-1} region and the shift of the main peak to lower frequencies. This indicates that the interactions present in this blend are stronger than those observed in the polyester blends. One could potentially perform a subtraction of the MXD-6 spectrum from that of the blend to extract more information. With the noisiness of the data in Figure
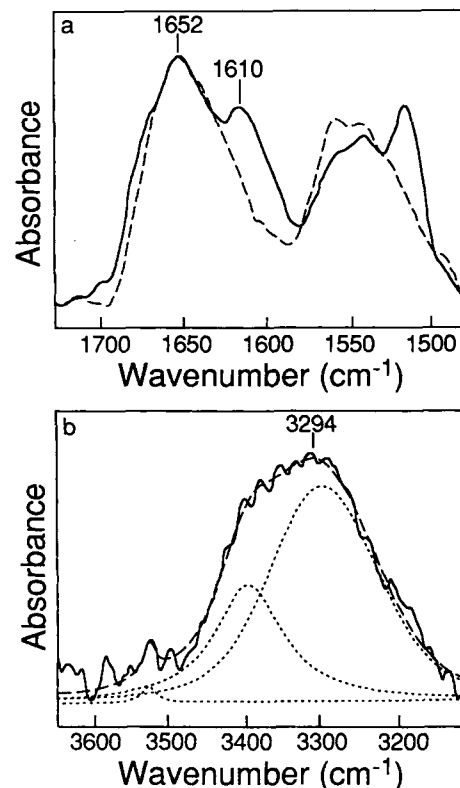

Figure 7 FTIR spectra for 1 : 1 melt blends of PVPh with the polyamide MXD6: (a) the carbonyl stretching region for pure MDX6 (dashed) and the blend (solid); (b) a band fit of the hydroxyl stretching region for the blend. The solid curve is the smoothed data, and the dashed envelope is the sum of the component bands (dotted).

7(b), however, this method would be qualitative at best.

The FTIR spectra for the PVPh hydroxyl stretching region for the 1 : 1 PVPh/PTMO blend and the individual components are shown in Figure 8. Once again, the amount of free hydroxyls is decreased in the blend relative to that present in pure PVPh. The center of the bound OH peak has shifted to 3318 cm^{-1}, indicating the presence of strong hydrogen bonding between PVPh and PTMO. In fact, the strength of interaction is comparable to that observed in PDMA/PVPh blends.[13] Many changes also occur in the frequency region between 1000 and 1300 cm^{-1} (not shown) when the two polymers are blended. These changes, however, are difficult to interpret since these bands correspond to C — O — C modes and other stretches that are very sensitive to changes in the local environment and molecular conformation.
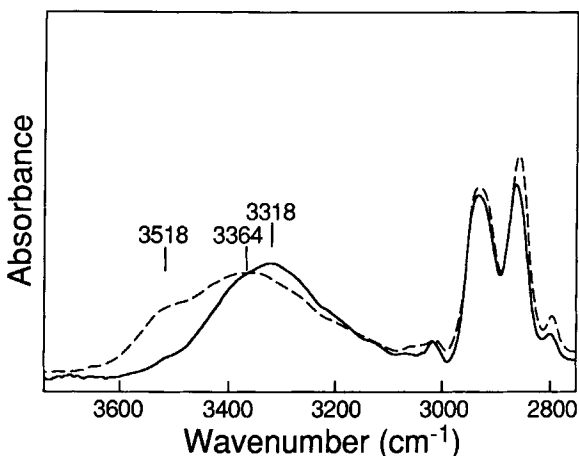
Figure 8 FTIR spectra for a 1 : 1 blend of PVPh and PTMO. The solid curve is for the blend and the dashed curve is the addition spectrum for the pure components.

SUMMARY AND CONCLUSIONS

The polymer polyvinylphenol (PVPh) was combined by either melt blending or solution mixing with at least one polymer from the following classifications to determine whether miscible blends could be prepared: cellulose esters, polycarbonates, polysulfones, polyurethanes, polysiloxanes, aliphatic and aromatic polyesters, polyamides, polyimides, and polyethers. Each type of polymer has either ether- or carbonyl-containing groups that were thought to have a possibility of interacting with the proton-donating VPh polymer. Of this list, several polyesters, polyamides, cellulose esters, and the polyether PTMO were found to be either fully or partially miscible with PVPh. Polymers found to be immiscible were bisphenol-A polycarbonate, 2,2,4,4-tetramethylcyclobutane-1,3-diol (Cb) polycarbonate, Ultem polyetherimide, poly(phenylene oxide), poly(dimethylsiloxane), MDI-6 polyurethane, poly(ether sulfone), DAPI polyimide, ODA-TA polyamide, and 6F-BAPP poly(amide–imide). Since these represent limited examples of the various types of polymers, the results are not meant to be indicative of PVPh miscibility with others from these classes.

Among the polyesters found to be miscible were poly(ethylene terephthalate), poly(butylene terephthalate), poly(2,2-dimethylpropylene terephthalate), poly(ethylene 2,6-naphthalenedicarboxylate), a copolymer of terephthalic and pentanedioc acids with 1,2-propanediol and glycerol, several cyclic aliphatic copolyesters containing 1,4-cyclohexanedicarboxylic acid, and a range of co-

polyesters of terephthalic acid and ethylene glycol/1,4-cyclohexane dimethanol, containing up to about 80 mol % of the cycloaliphatic diol. Miscibility was not seen for blends with several polyesters having high aromatic content, poly(1,4-cyclohexane dimethylene terephthalate) (PCT), Ardel D100, Kodel A150, and two liquid crystalline samples. From the series of polyesters studied, it appears that an appreciable percentage of the diol portion must be noncyclic and aliphatic in order to be miscible with PVPh. Apart from PCT, the immiscible polyester/PVPh blends showed little interaction between components. The miscible blends, on the other hand, showed intermolecular hydrogen-bond formation between ester carbonyls and the phenol hydroxy groups by FTIR.

Binary blends with the crystalline polyamides nylon-6, nylon-11, nylon-6,6, and poly(hexylene-m-xylenedicarboxamide) (MXD-6), as well as the amorphous poly(2,2,5-trimethyleneterephthalamide) (Trogamid-T) and poly(N,N-dimethyl-acrylamide) were also completely or, in the case of nylon-6,6, partially miscible in that some residual crystallinity remained in the latter. It is interesting to note that Trogamid-T was only found to be miscible from a melt-prepared sample. A two-phase mixture was obtained when blends were solution mixed, then knife-cast, due to a preferential solvation effect. Although the FTIR spectral evidence for the presence of hydrogen bonding was not as clear for the polyamide blends due to the existence of overlapping bands, favorable interactions were observed in both the hydroxyl and carbonyl regions. The elimination or significant reduction of crystallinity in these blends also suggests a disruption of self-interactions in the bulk polyamide phase. At the same time, loss of the crystallinity resulted in an increase of optical clarity of some of the nylon blends.

Although many pure cellulose esters decompose below temperatures suitable for melt extrusion, cellulose tripropionate was able to be melt-blended with PVPh to give miscible blends. Identical results were observed in blends obtained by coprecipitation. A cellulose acetate proprionate, precompounded with a plasticizer to lower its melt viscosity, was also found to be miscible.

In the solvent-prepared blend with the polyether poly(tetramethylene oxide), the IR results showed evidence for strong hydrogen bonding, even though thermal analysis showed only partial miscibility. A convincing dependence of phase behavior on thermal and coating history was observed.

Random copolymers of styrene and vinylphenol,

P(S-co-VPh), were blended with poly(phenylene oxide) (PPO) and the polyamide nylon-6 to determine their miscibility limits. In the case of the PPO/P(S-co-VPh) blends, phase separation occurs somewhere between 22 and 42 mol % VPh, with the styrene-rich copolymers being miscible. For the nylon-6 blends, the transition window is between 34 and 14 mol % VPh, with the VPh-rich copolymers showing miscibility.

In general, there is a good correlation between the thermal and IR data in that when there is evidence of significant interaction single-phase behavior is seen by thermal analysis. The expectation that H-bonding is a significant requirement (though not necessarily sufficient) for miscibility with PVPh is confirmed.

REFERENCES

1. D. R. Paul, and S. Newman, Eds., *Polymer Blends*, Academic Press, New York, 1978, Vols. 1 and 2.
2. N. G. Gaylord, *J. Macromol. Sci. Chem.*, **A26**(8), 1211 (1989).
3. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, San Diego, 1979.
4. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
5. M. M. Coleman, J. F. Graf, and P. C. Painter, *Specific Interactions and the Miscibility of Polymer Blends*, Technomic, Lancaster, PA, 1991.
6. E. J. Moskala, S. E. Howe, P. C. Painter, and M. M. Coleman, *Macromolecules*, **17**, 1671 (1984).
7. L. A. Belfiore, C. Qin, E. Ueda, and A. T. N. Pires, *J. Polym. Sci. Polym. Phys. Ed.*, **31**, 409 (1993).
8. D. L. Handlin, Jr., US Pat. 4,812,522 (1989) (to Shell Oil Co.).
9. C. Qin, A. T. N. Pires, and L. A. Belfiore, *Macromolecules*, **24**, 666 (1991).
10. (a) M. M. Coleman, A. M. Lichkus, and P. C. Painter, *Macromolecules*, **22**, 586 (1989). (b) C. J. Serman, Y. Xu, P. C. Painter, and M. M. Coleman, *Macromolecules*, **22**, 2015 (1989). (c) C. J. Serman, P. C. Painter, and M. M. Coleman, *Polymer*, **32**, 1049 (1991). (d) Y. Xu, P. C. Painter, and M. M. Coleman, *Macromolecules*, **25**, 7076 (1992).
11. S. H. Goh and K. S. Siow, *Polym. Bull.*, **17**, 453 (1987).
12. K. J. Zhu, S. F. Chen, T. Ho, E. M. Pearce, and T. K. Kwei, *Macromolecules*, **23**, 150 (1990).
13. C. J. T. Landry and D. M. Teegarden, *Macromolecules*, **24**, 4310 (1991).
14. E. J. Moskala, PhD Thesis, Pennsylvania State University, 1984.
15. E. J. Moskala, D. F. Varnell, and M. M. Coleman, *Polymer*, **26**, 228 (1985).
16. M. Vivas de Meftahi and J. M. J. Fréchet, *Polymer*, **19**, 477 (1988).
17. W.-L. Tang, B. Thompson, M. M. Coleman, and P. C. Painter, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **31**(1), 541 (1990).
18. C. Qin, C. Cheng, A. T. N. Pires, and L. A. Belfiore, *Polym. Mater. Sci. Eng.*, **61**, 945 (1989).
19. C. J. Serman, Y. Xu, P. C. Painter, and M. M. Coleman, *Polymer*, **32**, 516 (1991).
20. C. J. T. Landry, W. T. Ferrar, D. M. Teegarden, and B. K. Coltrain, *Macromolecules*, **26**, 35 (1993).
21. C. J. T. Landry, B. K. Coltrain, D. M. Teegarden, and W. T. Ferrar, to appear.
22. M. Shimizu, *Maruzen Oil Co., Research Report*, Tokyo, 1987.
23. C. J. T. Landry, D. J. Massa, D. M. Teegarden, M. R. Landry, P. M. Henrichs, R. H. Colby, and T. E. Long, *Macromolecules*, **26**, 6299 (1993).
24. D. M. Teegarden, T. E. Long, M. R. Landry, R. H. Colby, C. J. T. Landry, and D. J. Massa, unpublished results.
25. E. M. Pearce, T. K. Kwei, and B. Y. Min, *J. Macromol. Sci.-Chem.*, **A21**, 1181 (1984).
26. P. M. Henrichs, D. J. Massa, J. Tribone, and J. M. Hewitt, *Macromolecules*, **21**, 1282 (1988).
27. L. Zeman and D. Patterson, *Macromolecules*, **5**, 513 (1972).
28. A. Robard, D. Patterson, and G. Delmas, *Macromolecules*, **10**, 706 (1977).
29. T. G. Fox, *Proc. Am. Phys. Soc.*, **1**, 123 (1956).
30. S. S. Kelley and R. L. Zimmerman, unpublished results.
31. J. E. Harris, S. H. Goh, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **27**, 839 (1982).
32. H.-R. Schulten and B. Plage, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 2381 (1988).
33. *Encyclopedia of Polymer Science and Engineering*, 2nd ed., vol 11, Wiley, New York, 1985.