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Functional Group Accessibility in Hydrogen Bonded Polymer Blends

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ABSTRACT: Accessibility of functional groups is an important concept in the mixing of polymers and involves factors such as chain connectivity, steric shielding, etc., all of which tend to limit the number of interchain contacts formed. Infrared spectroscopy is well suited to study functional group accessibility in carefully selected miscible hydrogen bonded polymer blend systems, because the fraction of interchain hydrogen bonded groups can be measured quantitatively. Such measurements have been made on blends consisting of a wide range of carbonyl containing (co)polymers with a 2,3-dimethylbutadiene-*stat*-4-vinylphenol containing 24 wt % 4-vinylphenol. Evidence has been obtained for decreasing accessibility of the carbonyl groups of the poly(*n*-alkyl methacrylate)s due to steric shielding from bulky side groups. Conversely, when these groups are spaced further apart in an ethylene-*stat*-vinyl acetate or ethylene-*stat*-methyl methacrylate copolymer chain, they become much more accessible. The effect of functional group accessibility on the scaling and transferability of self- and interassociation equilibrium constants is discussed, together with ramifications in terms of the prediction of miscibility windows and maps for hydrogen bonded polymer blends.

Introduction

At the conclusion of our 1991 monograph (ref. 1: pp 485−487), we predicted that the one phase region in the miscibility map of butadiene-*stat*-4-vinyl phenol (BD-VPh) copolymer blends with the homologous series of poly(*n*-alkyl methacrylate)s (PAMA) or ethylene-*stat*-vinyl acetate (EVA) copolymers should be much greater than that of the analogous styrene-*stat*-4-vinyl phenol (STVPh) copolymer blends. For expository purposes, calculated miscibility maps (at 25 °C) for STVPh and 2,3-dimethylbutadiene-*stat*-4-vinylphenol (DMBVPh) blends are reproduced in a slightly different format in Figure 1. We recently embarked on extensive studies to test the validity of these predicted miscibility maps, and initial results indicate that the essential features are consistent with experiment. However, before these studies were completed, we obtained experimental results that have a number of implications, and these are reported here.

As we have noted many times,[1,2] miscibility in hydrogen bonded polymer blends is primarily determined by the balance between unfavorable "physical" and (usually) favorable "chemical" forces, as expressed by the following free energy equation (on a per mole of lattice site basis):

$$\frac{\Delta G_{\mathrm{m}}}{RT} = \left\{\frac{\Phi_{\mathrm{A}}}{M_{\mathrm{A}}}(\ln \Phi_{\mathrm{A}}) + \frac{\Phi_{\mathrm{B}}}{M_{\mathrm{B}}}(\ln \Phi_{\mathrm{B}})\right\} + \Phi_{\mathrm{A}}\Phi_{\mathrm{B}}\chi + \frac{\Delta G_{\mathrm{H}}}{RT} \qquad (1)$$

This free energy of mixing equation can be thought of as consisting of three major contributions. Combinatorial entropy is a very small but nonetheless favorable contribution to the free energy of mixing which is contained in the first two logarithmic terms, with Φ_A and Φ_B being the volume fractions of (co)polymer A and (co)polymer B in the blend and M_A and M_B the degrees of polymerization of the respective polymers. If the favorable free energy contribution derived from the formation of specific interactions (the $\Delta G_H/RT$ term in eq 1) is sufficient to overcome that of the unfavorable contribution from "physical" (dispersion and weak polar) forces (the $\Phi_A\Phi_B\chi$ term), then a miscible system is predicted.

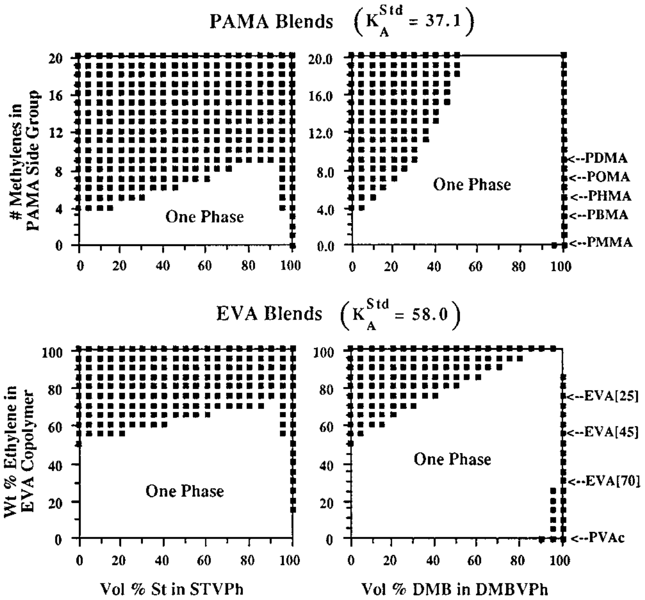

Figure 1. Theoretical miscibility maps calculated at room temperature. Top: PAMA blends with STVPh (left) and DMBVPh (right) using a constant K_A^{Std} value of 37.1. Bottom: EVA blends with STVPh (left) and DMBVPh (right) using a constant K_A^{Std} value of 58.0.

Returning to Figure 1, the enhanced single phase region predicted for the PAMA (or EVA) blends with DMBVPh over that of the analogous STVPh copolymers is primarily caused by the difference in the values of the non-hydrogen bonded solubility parameters of the styrene (ST) and 2,3-dimethylbutadiene (DMB) segments (δ = 9.5 and 8.1 (cal cm^{-3})$^{0.5}$, respectively). The ST and DMB comonomers are effectively "inert diluents" (i.e., non-hydrogen bonding) for the VPh segment, and it follows that the favorable free energy contribution from the $\Delta G_H/RT$ term (eq 1) for a particular PAMA (or

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EVA) blend with either a STVPh or DMBVPh copolymer, containing the *same volume fraction* of VPh, is essentially identical. In marked contrast, however, statistical copolymers of STVPh or DMBVPh containing the same volume fraction of VPh have very different average solubility parameter values (the latter being significantly less than the former). Moreover, the magnitude of the unfavorable (to mixing) $\Phi_A\Phi_B\chi$ term is proportional to the square of the solubility parameter difference ($\Delta\delta$) between a given PAMA or EVA copolymer and the particular VPh copolymer. If we use poly(*n*-hexyl methacrylate) (PHMA) as a typical example, which has a $\delta = 8.5$ (cal cm^{-3})$^{0.5}$, it is immediately apparent that the magnitude of $\Delta\delta$ (and thus χ) is considerably less for the DMBVPh blend compared to that of the comparable STVPh blend (containing the same volume fraction of VPh in the copolymers). This then implies that the contribution from the favorable $\Delta G_H/RT$ term to the free energy of mixing that is required to overwhelm the unfavorable $\Phi_A\Phi_B\chi$ term (eq 1) is less in the case of the DMBVPh blend compared to that of the corresponding STVPh blend. This explains, in simple terms, the enhanced single phase regions predicted for the PAMA and EVA blends with DMBVPh.

In this present study we focus our attention on polymer blends involving a DMBVPh copolymer containing 24 wt % (18 vol %) VPh, denoted DMBVPh[24]. A comparison of the predicted miscibility gaps for the STVPh and DMBVPh copolymer blends containing ≈20 vol % VPh is germane to this study and worthy of emphasis. As can be seen from Figure 1, PAMA homologues higher than poly(*n*-octyl methacrylate) (POMA) are predicted to be immiscible with the STVPh copolymer, which was indeed found to be the case experimentally.[1] On the other hand, the corresponding DMBVPh copolymer is predicted to be miscible with all PAMA homologues containing up to well in excess of 20 methylene groups in the side chain! A larger miscibility gap is also predicted in the case of the analogous EVA blends.

The extensive miscibility gaps of PAMA and EVA blends with DMBVPh[24] copolymers, coupled with their relatively low glass transition temperatures (which facilitates attainment of equilibrium conditions), permits us to test with reasonable precision one of the major assumptions that we have used in the calculation of miscibility windows and maps. This assumption pertains to the scaling and transferability of equilibrium constants, which are intimately tied to the relative accessibility of the functional groups in polymer blends. This is the major focus of this present paper.

The determination of self-association and interassociation equilibrium constants has been discussed in detail in our monograph[1] and a recent review article[2] so that only a brief summary necessary for coherence is presented here. In essence, the determination of self-association equilibrium constants for low molecular weight materials such as phenol or 4-ethylphenol is conceptually straightforward. Sampling cells of known thickness are used to obtain infrared spectra of these materials as a function of dilution in a non-hydrogen bonded hydrocarbon solvent such as cyclohexane. Self-association equilibrium constants can be calculated from measurements of the fraction of non-hydrogen bonded hydroxyl "monomers" using such spectral data.[1,2] A minimum of two dimensionless equilibrium constants is necessary to adequately describe the self-association of molecules that contain hydroxyl groups:[1–3] one that describes the formation of dimers (K_2) and a second that describes higher multimers or "chain-like" complexes (K_B), as follows:

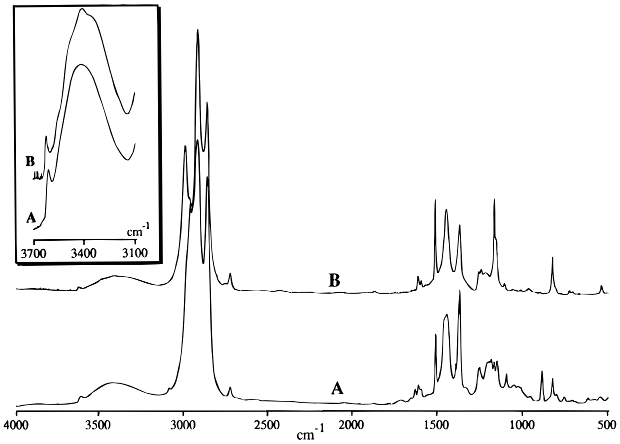


Figure 2. Infrared spectra of (A) DMBVPh[5] and (B) an analogous solution of EPh and 2,3-dimethyl-2-butene normalized to an equivalent hydroxyl content recorded at room temperature in the range from 500 to 4000 cm^{-1}. Insert: scale expanded spectra in the O–H stretching region (3100–3800 cm^{-1}).

$$B_1 + B_1 \xrightleftharpoons{K_2} B_2$$

$$B_h + B_1 \xrightleftharpoons{K_B} B_{h+1} \qquad (h > 1) \tag{2}$$

It is important to recognize that this methodology cannot be used for polymers such as poly(4-vinylphenol) (PVPh) because they will not dissolve in a non-hydrogen bonding solvent. Moreover, dilute solutions of polymers are not equivalent to low molecular weight analogs, as the segments are not randomly dispersed throughout the solution, but localized as a consequence of chain connectivity. In our work, we have assumed that self-association equilibrium constants are the same for low molar mass and analogous polymers (when normalized to the same number of OH groups per unit volume).[1,2] This is not unreasonable because in a PVPh melt there is no distinction between interchain and intrachain contacts. Furthermore, in Figure 2 we compare the infrared spectra of a DMBVPh copolymer containing ≈5 mol % VPh to a low molecular weight analog mixture of 4-ethylphenol (EPh) and 2,3-dimethyl-2-butene, normalized to equivalent OH concentrations. As illustrated in the insert to Figure 2, the relative intensities of the bands attributed to "free" and hydrogen bonded hydroxyl groups (the relatively sharp band at ≈3625 cm^{-1} and the broad band centered at ≈3400 cm^{-1}, respectively) are, within experimental error, essentially the same. This implies that dimensionless self-association equilibrium constants for low and high molar mass phenols are very similar (when based upon the same reference molar volume).

Furthermore, implicit in the calculation of miscibility maps, such as those shown in Figure 1, is the assumption that the self-association equilibrium constants of copolymers, such as STVPh and DMBVPh, composed of two different segments, one that self-associates and the other which is essentially an inert diluent, can be simply scaled with respect to the molar volume of an average repeat unit containing one self-associating functional group (see ref 1, pp 293–296). Evidence that supports this assumption was obtained from studies of miscible poly(*n*-butyl methacrylate) (PBMA) blends with a series of STVPh polymers of different VPh compositions.[1]

Interassociation equilibrium constants are used to describe the hydrogen bonding association between two different functional groups (which could be located in different molecules or different segments).

$$B_h + A \overset{K_A}{\rightleftharpoons} B_hA \tag{3}$$

At equilibrium, in a simple mixture of phenol and ethyl isobutyrate (EIB), for example, there still exists the "free" and hydrogen bonded hydroxyl–hydroxyl dimers and multimers, mentioned before, but now there are additional species formed by the "capping" of hydrogen bonded hydroxyls by a hydrogen bond to the carbonyl group of an EIB molecule.[1,2] The precise distribution of all of these species will now be dependent upon the composition of the mixture, the temperature, and the equilibrium constants that describe both self-association and interassociation.

Interassociation equilibrium constants may be determined directly from infrared spectroscopic data obtained from mixtures of low or high molecular weight phenols with carbonyl containing compounds.[1,2] The carbonyl stretching frequency is split into two distinct bands assigned to "free" and hydrogen bonded carbonyl groups. The fraction of hydrogen bonded carbonyl groups, $f_{HB}^{C=O}$, is calculated from the relative intensities of these two bands (taking care to account for differences in absorption coefficients). From the stoichiometry of the system, equations relating $f_{HB}^{C=O}$ to the equilibrium constants, K_2, K_B (self-association), and K_A (interassociation), have been developed.[1,2] The value of K_A is usually determined from a least squares fit of these equations to experimental data acquired from mixtures of varying composition. It is important to recognize that the equilibrium constants describing self- and interassociation cannot be calculated independently from infrared spectral data obtained solely from the mixtures. Values of the former have to be known in order to determine the latter. [A wide range of values of K_2 and K_B will reproduce the data, providing that the ratios K_2/K_A and K_B/K_A (i.e., self-association/interassociation) are held constant.]

Of particular relevance to this present study is a comparison of the K_A values obtained for phenolic OH/ester carbonyl interactions in model compounds, random copolymers, and blends (all based upon a common reference molar volume of 100 cm^3/mol).[2,4] We found that low molecular weight analogs (EPh/EIB) had identical values of K_A to polymer solutions (PVPh/EIB), suggesting, but not proving, that our assumptions concerning the transferability of self-association equilibrium constants (K_2 and K_B) values were reasonable (i.e., that they are essentially the same value in EPh and PVPh). However, values of K_A for analogous random ethyl methacrylate-*stat*-vinylphenol (EMAVPh) copolymers and blends of PVPh and poly(ethyl methacrylate) (PEMA) were much lower than those obtained in the model systems and polymer solutions at 25 °C (67 and 37 versus 170 dimensionless units, respectively). In essence, we concluded that in the blend we are seeing an enhanced fraction of hydroxyl–hydroxyl contacts due to chain connectivity effects that results in fewer interchain (i.e., OH···ester) contacts than would normally be expected when compared to a comparable low molecular weight mixture.[2] A theoretical basis for this effect will be published elsewhere.[5] But, as we will see, the experimental results presented in this paper will serve to demonstrate that this issue is much more complex than we initially imagined.

Experimental Section

Tetrahydrofuran (THF), 1,4-dioxane, methyl ethyl ketone (MEK), toluene, 4-ethylphenol (EPh), 2,3-dimethyl-2-butene, 2,3-dimethylbutadiene (DMB), 4-acetoxystyrene (AcOSt), 4,4′-azobis(4-cyanovaleric acid) (ACVA), sodium dodecyl sulfate, t-dodecanethiol, and hydrazine hydrate were all purchased from Aldrich Chemical Co. and used without further purification. The poly(*n*-alkyl methacrylate)s (PAMA)—poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-butyl methacrylate) (PBMA), poly(*n*-hexyl methacrylate) (PHMA), poly(*n*-octyl methacrylate) (POMA), poly(*n*-decyl methacrylate) (PDMA), poly(*n*-lauryl methacrylate) (PLMA), poly(*n*-hexadecyl methacrylate) (PHDMA), and poly(*n*-octadecyl methacrylate) (PODMA)—ethylene-*co*-methyl methacrylate (EMMA) copolymers containing 47, 38, and 33 wt % MMA, denoted EMMA[47], etc., poly(vinyl acetate) (PVAc), and the ethylene-*co*-vinyl acetate (EVA) copolymers containing 70, 45, 25, and 18 wt % VAc, denoted EVA[70], etc., have been used and described in previous blend studies.[1,6]

The synthesis of diene copolymers containing 4-vinylphenol has been reported previously in the literature, with most examples requiring the use of a protective group.[7] It is necessary to choose the protective group with care to ensure that deprotection can be achieved quantitatively and without the occurrence of undesirable cyclization and/or cross-linking reactions. For our purposes the studies of Ledwith and coworkers[8] are germane as these authors have demonstrated that the acetyl protection group can be removed under mild conditions using hydrazine hydrate. Statistical copolymers of DMB and AcOSt were prepared by emulsion polymerization in a manner similar to that described by Grosso and Vogl.[7a] DMBVPh[24], a DMB copolymer containing ≈24 wt % VPh, was synthesized as follows. Degassed DMB (1 equiv) and AcOSt (0.33 equiv) were transferred under an argon atmosphere to a 250 mL round bottom flask containing the remainder of the emulsion reagents: ACVA initiator (0.0058 equiv), sodium dodecyl sulfate (0.0126 equiv), and distilled water (40 mL). In addition, a small amount of t-dodecanethiol (0.003 equiv) was added as a chain transfer agent. The flask was then placed in an oil bath at 65 °C, and the contents were vigorously stirred. A conversion of <20% was imposed to minimize compositional drift, branching, and cross-linking of the polymer. The polymer was then isolated by introducing 10 mL of an aqueous lithium chloride solution (10% w/v), followed by precipitation into a large amount of methanol, filtering, and drying at room temperature. Molecular weights of the copolymer (M_n = 29 000 and M_w = 65 000), based upon polystyrene standards, were determined by gel permeation chromatography (GPC), and the copolymer composition was determined by ^{1}H NMR.

Deprotection was performed in the following manner. In a 100 mL round bottom flask 1 g of the protected copolymer and 0.1 g of Ultranox 236 antioxidant were dissolved in 40 mL of degassed 1,4-dioxane. Hydrazine hydrate (2 equiv/mol of protective group) was added to the stirred solution and allowed to react for 4 h at room temperature. Removal of the protective group was monitored by infrared spectroscopy using the acetoxy carbonyl stretching mode (1758 cm^{-1}) as the diagnostic band. The completely deprotected DMBVPh[24] copolymer was then precipitated into a large excess of water and filtered. Further purification was performed by multiple reprecipitation from THF solution into methanol. Finally, the copolymer was reprecipitated into hexane, filtered, and dried at room temperature. A glass transition temperature (T_g) of 11 °C for DMBVPh[24] was determined by thermal analysis.

Polymer blend films for infrared analysis were cast on KBr windows from 1% solutions in a common solvent. After the majority of the solvent had evaporated, the films were placed under vacuum at room temperature for at least 24 h to completely remove residual solvent. Several different solvents

Table 1. Dimensionless Self-Association Equilibrium Constants at 25 °C

polymer	molar vol (cm^3/mol)	dimer formation K_2	multimer formation K_B
PVPh	100	21.0	66.8
DMBVPh[24]	525	4.0	12.7

(THF, MEK, and toluene) were employed, and the one chosen for a particular blend was predicated upon mutual solubility. The polarity of the different PAMA, EMMA, and EVA (co)-polymers changes significantly with copolymer composition (or side group size in the case of the homologous series of PAMA), and it was necessary to initially perform solubility studies to find "good" solvents in order to avoid the preferential precipitation of one of the (co)polymers during evaporation of the solvent. This is important because otherwise large scale phase separation can occur. For example, THF was used to prepare the films of DMBVPh[24] blends with EVA[70], but it was necessary to change to toluene for the analogous blends with EVA[18]. Significantly, the cloud point of a 1% solution of EVA[18] in THF is just above room temperature. We will be reporting on the details of such studies in the near future.[9]

All the polymer blends examined in this work were predicted to be miscible and indeed were optically transparent at 100 °C with infrared spectra that are typically characteristic of single phase materials. Where appropriate (i.e. where there was a distinct difference in the T_g's of the pure components), thermal analysis was used to confirm miscibility. For example, 50:50 blends by weight of DMBVPh[24] (T_g = 11 °C) with PMMA (T_g = 105 °C) and PODMA (T_g = −100 °C), which are the most important in that they represent the extremes of the homologous PAMA series studied, exhibited single intermediate T_g's of 62 and −47 °C, respectively. Thermograms of the analogous DMBVPh[24] blends with EVA or EMMA copolymers, especially the ethylene rich copolymers, were complicated by crystallization of ethylene sequences. For example, a single intermediate T_g of ≈−9 °C was observed for the 50:50 DMBVPh[24] blend with EVA[18] (pure T_g = −50 °C), but this is unlikely to be representative of the actual blend composition because a broad melting peak spanning a range from 0 to 90 °C was also in evidence.

Infrared spectroscopic measurements were recorded on a Digilab Model FTS60 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. Special attention was paid to ensure that all the samples examined were sufficiently thin to be within the absorption range where the Beer−Lambert law is obeyed. ^{1}H and ^{13}C NMR spectra were obtained on Bruker WP-200 and 300 MHz FT-NMR spectrometers using tetramethylsilane as an internal standard. Molecular weights and molecular weight distributions were determined by GPC using a Waters 150C GPC/AL equipped with a refractive index detector and four μStyragel columns−100 000, 10 000, 500, and 100−connected in series. Calibration was performed using polystyrene standards. Thermal analysis was conducted on a Seiko Instruments differential scanning calorimeter (DSC-220CU) coupled to a computerized data station. A heating rate of 20 °C/min was used, and the glass transition temperatures were recorded as the midpoint of the heat capacity change.

Results and Discussion

The DMBVPh[24]/EVA[18] Blend System. We commence with a discussion of the results obtained from blends of DMBVPh[24] with an EVA copolymer containing 18 wt % vinyl acetate (EVA[18]). Emphasis here is placed upon the methodology that is necessary to most accurately determine interassociation equilibrium constants and enthalpies of hydrogen bond formation. The molar volume (V_B) and values of the dimensionless self-association equilibrium constants (K_2 and K_B) of PVPh at 25 °C are well established[1,2] and are listed in Table 1. The corresponding enthalpies of hydrogen bond formation (h_2 = 5.6 and h_B = 5.2 kcal/mol) determined by Whetsel and Lady[3] permit the calculation of K_2 and K_B at any other temperature, assuming applicability of the van't Hoff relationship.[1] The self-association equilibrium constants for DMBVPh[24] at 25 °C, also listed in Table 1, are simply determined by scaling with respect to the "average specific repeat unit", defined so as to contain one phenolic hydroxyl group, which has an estimated molar volume from group contributions[1] of 525 cm^3/mol. Armed with values of the molar volume, self-association equilibrium constants, and enthalpies of hydrogen bond formation for DMBVPh[24], it is a relatively straightforward task to calculate the fraction of hydrogen bonded carbonyl groups, $f_{HB}^{C=O}$, that will be present at equilibrium in a miscible blend with EVA-[18] at a given temperature using the computer program that accompanies our monograph.[1] Additional input that is required is the molar volume of the EVA[18] average specific repeat unit consisting of one acetoxy group (531 cm^3/mol from group contributions) and selected values of the interassociation equilibrium constant, K_A.

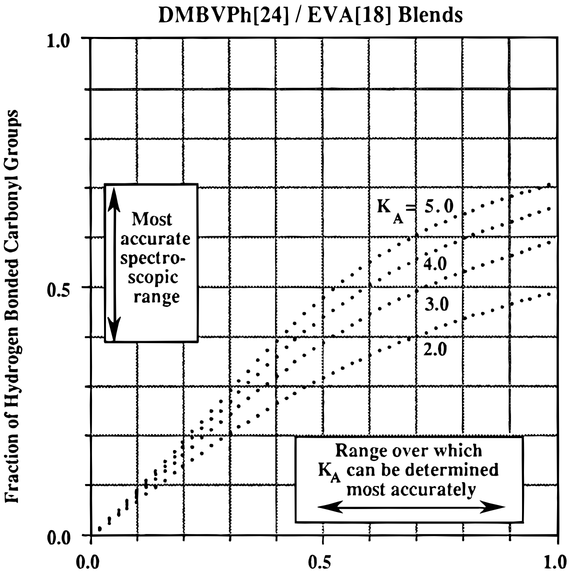


Figure 3. Simulation of the fraction of hydrogen bonded carbonyl groups as a function of composition for DMBVPh-[24] blends with EVA[18] at 100 °C. The self-association equilibrium constants were kept constant at K_2 = 0.59 and K_B = 2.16, and calculations were performed using K_A values of 2, 3, 4, and 5.

Such a simulation is shown in Figure 3 for DMBVPh-[24]/EVA[18] blends at 100 °C. [A temperature of 100 °C was chosen for this simulation, because it is the temperature at which we will perform most of our experimental studies. It is well above the T_g's of both the components of the blends, which facilitates attainment of equilibrium. It is also above the T_m of any residual EVA[18] crystallinity that could be formed in the blends, but below the point where oxidative degradation is a concern.] Here the values of K_2 and K_B are 0.59 and 2.16, respectively, and we employed arbitrary K_A values of 2.0, 3.0, 4.0, and 5.0 (the most probable range in which the "true" value of K_A might be anticipated to lie). The most accurate range for determining $f_{HB}^{C=O}$ spectroscopically is from ≈0.4 to 0.7, because this is where both the "free" and hydrogen bonded carbonyl bands are well separated and have significant absorbances. This is illustrated in Figure 4 which shows the infrared spectra of DMBVPh[24]/EVA[18] blends of

Table 2. Determination of K_A from DMBVPh[24]/EVA[18] Blends

temp and self-association equ const values	vol fraction DMBVPh[24]	exptl $f_{HB}^{C=O}$	least squares determination interassociation equ const	calcd $f_{HB}^{C=O}$	difference: calcd minus exptl
120 °C	0.800	0.600	$K_A = 3.57$	0.607	0.007
$K_2 = 0.40$	0.700	0.567		0.564	−0.003
$K_B = 1.51$	0.600	0.507		0.509	0.002
	0.500	0.447		0.440	−0.007
110 °C	0.800	0.613	$K_A = 4.02$	0.616	0.003
$K_2 = 0.49$	0.700	0.574		0.573	−0.001
$K_B = 1.80$	0.600	0.521		0.519	−0.002
	0.500	0.452		0.451	−0.001
100 °C	0.800	0.634	$K_A = 4.68$	0.631	−0.003
$K_2 = 0.59$	0.700	0.590		0.588	−0.002
$K_B = 2.16$	0.600	0.530		0.535	0.005
	0.500	0.466		0.466	0.000
90 °C	0.800	0.650	$K_A = 5.49$	0.643	−0.007
$K_2 = 0.73$	0.700	0.603		0.601	−0.002
$K_B = 2.63$	0.600	0.542		0.549	0.007
	0.500	0.477		0.480	0.003

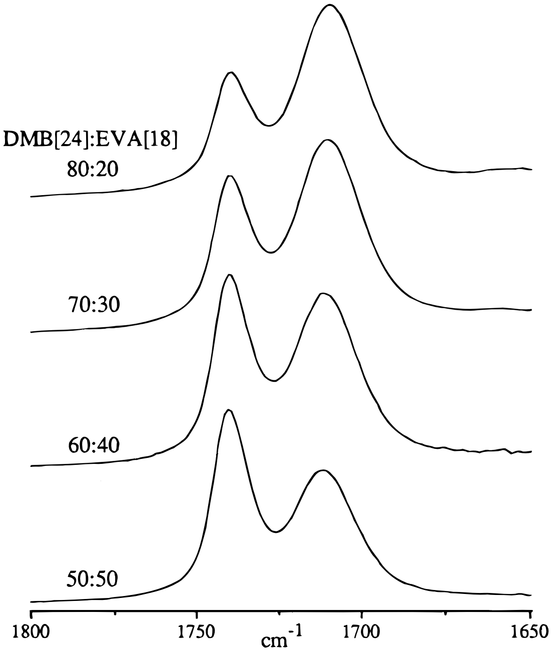


Figure 4. Infrared spectra of films of 80:20, 70:30, 60:40, and 50:50 wt % DMBVPh[24]/EVA[18] blends recorded at 100 °C in the carbonyl stretching region (1650−1800 cm^{-1}).

varying composition recorded at 100 °C. Outside this $f_{HB}^{C=O}$ range of ≈0.4−0.7, one or other of the bands is buried under the other and is observed as a rather ill defined shoulder. Curve fitting these types of spectra is subject to the greatest error. Moreover, it can be seen from Figure 3 that the value of $f_{HB}^{C=O}$ is most sensitive to the magnitude of K_A at DMBVPh[24] blend compositions of >50%. Below this composition the variation of $f_{HB}^{C=O}$ with K_A is quite insensitive and below our ability to accurately measure differences in $f_{HB}^{C=O}$. Hence, for the specific DMBVPh[24]/EVA[18] system the optimum blend composition for the quantitative analysis of the $f_{HB}^{C=O}$ is between 50 and 90 vol % DMBVPh[24].

It is important to stress that the optimum blend compositions for quantitative analysis varies enormously from system to system, and we strongly recommend simulations such as those illustrated in Figure 3 in order to minimize experimental errors and prevent the collection of inconsequential data (something we ourselves have been guilty of in previous work). One of the major factors to consider is the difference in the molar volume of the specific repeat units for the two (co)polymers. It was not simply coincidence that we chose to initially study blends of EVA[18] with DMBVPh[24]. These two copolymers have specific repeat units with very similar molar volumes (531 and 525 cm^3/mol), which enhances the compositional range over which K_A can be accurately determined when compared to analogous DMBVPh[24] blends with EVA copolymers containing a higher concentration of vinyl acetate (see later).

Having determined the optimum blend composition range for the quantitative analysis of DMBVPh[24]/EVA[18] blends, infrared spectra were recorded, similar to those shown in Figure 4, containing 80:20, 70:30, 60:40, and 50:50 vol % at temperatures of 90, 100, 110, and 120 °C. Using the curve fitting procedure described in detail elsewhere,[1,2,6,10] the "free" and hydrogen bonded carbonyl band areas were determined and an experimental $f_{HB}^{C=O}$ calculated using the appropriate absorptivity ratio ($a_R = 1.5$). These results are listed in the third column of Table 2. The interassociation equilibrium constant K_A can now be determined at a particular temperature by a least squares fit of the $f_{HB}^{C=O}$ data to the appropriate equation describing the stoichiometry.[1,2] To reiterate, the values of the self-association equilibrium constants (K_2 and K_B) were held constant in the least squares procedure. Values of K_A at 90, 100, 110, and 120 °C are listed in the fourth column of Table 2. In the fifth column of Table 2 are the calculated values of $f_{HB}^{C=O}$ for the different blend compositions, at the four different temperatures, using the K_A determined from the least squares procedure. The difference between the experimental and calculated $f_{HB}^{C=O}$ values is listed in the last column of Table 2. The maximum difference between the two sets of $f_{HB}^{C=O}$ data is <0.01, which translates to an error of <5% in the determination of K_A and probably represents the best that we can hope to achieve experimentally.

The enthalpy of hydrogen bond formation, h_A, may now be readily obtained from a van't Hoff plot of ln K_A versus inverse temperature. Using the four K_A values listed in Table 2, the following equation was determined by a linear least squares fit ($R^2 = 0.998$):

$$\ln K_A = -3.980 + \frac{2061}{T} \tag{4}$$

This corresponds to a h_A value of −4.1 kcal/mol, which is most encouraging as it is the same value obtained from recent experimental studies of PVPh/PEMA blends[4]

Table 3. Dimensionless Interassociation Equilibrium Constants for Vinyl Acetate (Co)polymers

polymer	molar vol (cm^3/mol)	$K_A^{100\ °C}$	$K_A^{25\ °C}$ ($h_A = -4.1$ kcal/mol)	K_A^{Std} ($V_B = 100$ cm^3/mol; $T = 25$ °C)	R (cm^3/mol)
PVAc	69.8	3.80	15.4	80.6	0
EVA[70]	113	4.37	17.7	92.9	43.4
EVA[45]	194	4.53	18.3	96.1	124
EVA[25]	374	4.82	19.5	102	304
EVA[18]	531	4.76	19.3	101	461

and very close to previous values obtained for similar PVPh blends[1] (3.8−4.0 kcal/mol).

From eq 4, K_A equals 18.8 at 25 °C ($V_B = 525$ cm^3/mol). If we now scale this value to our standard reference molar volume of $V_B = 100$ cm^3/mol (the molar volume of PVPh), we obtain a K_A value of 99 at 25 °C, which we will henceforth denote K_A^{Std}. Note that this is significantly different, almost a 2-fold increase, over that experimentally obtained from the analogous PVPh/EVA-[70] blends, where K_A^{Std} was determined previously[1] to be 58. This difference is real and way outside the range of experimental error. It also contradicts one of the fundamental assumptions we have used in the calculation of miscibility windows and maps, that interassociation equilibrium constants, based upon a common reference molar volume (V_B), which describe the specific interaction between the phenolic hydroxyl and acetoxy carbonyl group, are invariant with copolymer composition, as long as the comonomer under consideration is an inert diluent. In other words, it was tacitly assumed that the value of K_A^{Std} experimentally determined from a miscible blend of PVPh (or DMBVPh, STVPh, etc.) with any EVA copolymer should be identical [differences in the size of the interassociating specific repeat units are accounted for in the stoichiometric equations by the factor r defined as V_A/V_B—see ref 1, pp 214−220]. As they obviously are not, this has many ramifications and raises a number of important questions pertaining to chain connectivity and the accessibility of functional groups. We would also be remiss if we did not address the question of why the predicted miscibility maps calculated using constant K_A^{Std} values matched experimental observations so well for STVPh copolymer blends with EVA, ethylene-*stat*-methyl acrylate (EMA), styrene-*stat*-methyl acrylate (STMA) copolymers, and the homologous series of PAMA that are presented in our monograph.[1] But before we attempt to answer such questions, however, we will consider additional experimental results that have been obtained on DMBVPh-[24] blend systems.

DMBVPh[24] Blends with PVAc, EVA[70], EVA-[45], and EVA[25]. In the above section we stressed the importance of performing simulations to establish the optimum composition range for quantitative $f_{HB}^{C=O}$ measurements that are required for the accurate determination of the interassociation equilibrium constant, K_A. The need for this is immediately apparent if one compares the simulations of $f_{HB}^{C=O}$ versus blend composition at 100 °C for DMBVPh[24] blends with PVAc, EVA[70], EVA[45], and EVA[25] that are shown in Figure 5. Again the appropriate values of the self-association equilibrium constants $K_2 = 0.59$ and $K_B = 2.16$ at 100 °C were held constant. K_A values of 2.0 and 5.0 were selected for the simulations, as this represents the most probable range in which the actual value of K_A might be anticipated to lie. Molar volumes calculated from group contributions for the average specific repeats, V_A, of the EVA copolymers (i.e., those containing one acetoxy group) are given in the second column of Table 3.

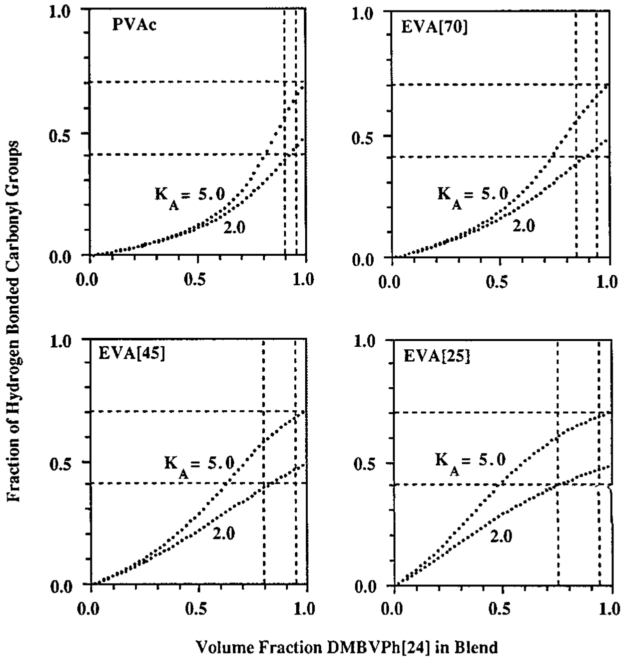


Figure 5. Simulation of the fraction of hydrogen bonded carbonyl groups as a function of composition at 100 °C for DMBVPh[24] blends with PVAc (top left), EVA[70] (top right), EVA[45] (bottom left), and EVA[25] (bottom right). The self-association equilibrium constants were kept constant at $K_2 = 0.59$ and $K_B = 2.16$, and calculations were performed using K_A values of 2 and 5.

The most accurate range for determining $f_{HB}^{C=O}$ spectroscopically remains from 0.4 to 0.7 for the reasons stated in the prior section and is delineated in Figure 5 by the dashed lines parallel to the x-axes. Note now, however, that the blend composition range over which the $f_{HB}^{C=O}$ can be measured accurately (the vertical dashed lines) is compressed as we progress from EVA-[25] to PVAc, a consequence of the increasing disparity of the molar volumes of the average specific repeats of the particular EVA copolymers and DMBVPh[24]. In other words, an 80:20 vol % blend of DMBVPh[24] with EVA[18] (which have similar segment molar volumes, i.e., 525 and 531 cm^3/mol, respectively) has approximately the same ratio of VPh:VAc (the remainder of the blend being "inert" diluent). On the other hand, an 80:20 vol % blend of DMBVPh[24] with PVAc (which have very different segment molar volumes, i.e., 525 and 69.8 cm^3/mol, respectively) has only a VPh:VAc ratio of about 35:65 and the $f_{HB}^{C=O}$ is correspondingly small in this case. This is, of course, understandable, as the fraction of hydrogen bonds formed is a function of the concentration of phenolic hydroxyl and acetoxy carbonyl groups in the blend (which includes the "inert" diluent). In any event, in the case of DMBVPh[24]/PVAc blends only compositions having ≥90 vol % can be used to determine K_A with any degree of accuracy.

Because the optimum blend composition range is so restricted in the case of the DMBVPh[24] blends with the EVA copolymers rich in VAc, we deemed it necessary to change our experimental procedure. Rather

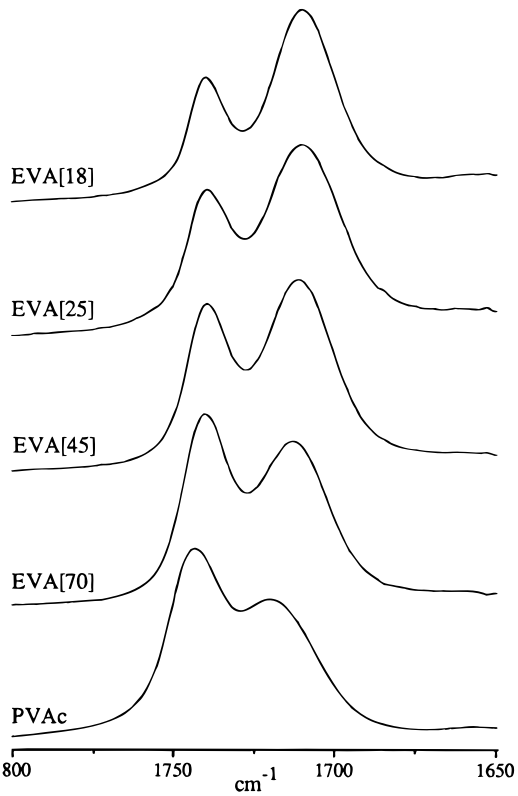


Figure 6. Infrared spectra of films of 80:20 wt % DMBVPh[24] blends with PVAc, EVA[70], EVA[45], EVA[25], and EVA[18] blends recorded at 100 °C in the carbonyl stretching region (1650−1800 cm^{-1}).

than employ several blend compositions and carry out a least squares fit to the stoichiometric equation as described above for the DMBVPh[24]/EVA[18] blends, we instead averaged single blend composition results of three completely separate $f_{HB}^{C=O}$ measurements performed at 100 °C on each of the different EVA blends containing 90% DMBVPh[24]. Accuracy should not be sacrificed, because as we demonstrated above for the DMBVPh[24]/EVA[18] blends, in the optimum composition range a single point determination resulted in less than a 5% error in the calculated value of K_A.

Typical infrared spectra of DMBVPh[24]/EVA blends recorded at 100 °C are illustrated in Figure 6. The curve fitting, determination of $f_{HB}^{C=O}$, and ultimate calculation of K_A is straightforward,[1,2] and the results are presented in the third column of Table 3. We estimate that the values of K_A determined in this manner are subject to a maximum error of ≈5%. The fourth and fifth columns of Table 3 list, respectively, the corresponding values of K_A at 25 °C calculated using an enthalpy of hydrogen bond formation, h_A, of −4.1 kcal/mol (see previous section) and those of K_A^{Std} after the scaling to our standard reference volume of $V_B = 100$ cm^3/mol.

Note that the value of K_A^{Std} is not constant, but gradually increases from 81 for PVAc to 96 for EVA[45], and then appears to level off at ≈100 as we approach EVA[25]. To reiterate, K_A is determined directly from the fraction of hydrogen bonded carbonyl groups formed. Accordingly, one plausible explanation for this trend, and one that makes intuitive sense, is that chain connectivity effects cause some of the acetoxy carbonyl groups in PVAc to be "shielded" to some extent (or just not as accessible) to the phenolic hydroxyl groups of DMBVPh[24], when compared to EVA[70], EVA[45], and EVA[25], where the carbonyl groups are progressively spaced apart in the copolymer chain by methylene groups. A saturation phenomenon would not be unexpected if this were indeed correct and could explain the observed "plateau" at K_A^{Std} ≈100 for the blends containing EVA[25] and EVA[18]. In a similar vein, we note that K_A^{Std} determined previously[1] from experimental studies of the miscible PVPh/EVA[70] system was 58. This is significantly different from the value obtained from the analogous DMBVPh[24]/EVA[70] blends studied here where K_A^{Std} was determined to be 93. Is this then a manifestation of similar "screening" effects, but in reverse in the sense that the phenolic hydroxyl groups in PVPh are not as accessible to the EVA[70] carbonyl groups relative to those in DMBVPh[24], which are spaced apart by DMB segments in the copolymer? We will return to this subject after we have presented additional results obtained from DMBVPh[24] blends with the homologous series of PAMA homopolymers and three ethylene-*stat*-methyl methacrylate (EMMA) copolymers.

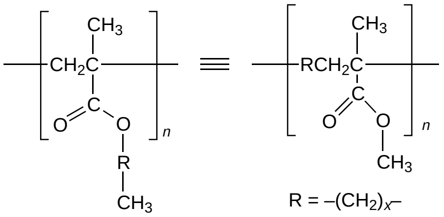
DMBVPh[24] Blends with PAMA, EMMA[47], EMMA[38], and EMMA[33]. As discussed in the Introduction, blends of DMBVPh[24] were predicted to be miscible with the homologous series of PAMA homopolymers from PMMA through to those containing well in excess of 20 methylenes in the side group (see Figure 1). The PAMA homopolymer with the longest side group that we have been able to acquire is poly(*n*-octadecyl methacrylate) (PODMA), one that contains 17 methylene groups in the side chain. Although we are unable to experimentally test the outer limit of the miscibility gap for DMBVPh[24]/PAMA blends, having available a range of potentially miscible DMBVPh[24] blends from PMMA to PODMA permits us to test several of the assumptions used in the calculation of miscibility maps. Previously, we had determined that the value of K_A at 150 °C ($V_B = 100$ cm^3/mol), obtained experimentally from miscible PVPh blends with PEMA and poly(*n*-propyl methacrylate) (PMMA), was 5.62 and 5.76, respectively, and had concluded that these results were probably within error the same.[1] However, these experiments could only be performed for PEMA and PPMA blends (a very restricted range of miscible blends), because PBMA and the higher homologues are immiscible with PVPh at 150 °C. In any event, the standard value of the interassociation equilibrium constant that describes the interaction of VPh hydroxyl groups with methacrylate carbonyl groups $K_A^{Std} = 37.1$ was used to calculate the PAMA miscibility maps with STVPh and DMBVPh shown in Figure 1.

Implicit in the calculation of such PAMA miscibility maps (Figure 1) is the assumption that a PAMA "homopolymer" is equivalent to an EMMA copolymer with an average specific repeat containing the same type and number of groups (see ref 1, pp 448−449). In other words, the methylene groups were simply considered "diluents", and it did not matter whether they were located in the main chain or the side chain. For example, PPMA (where R is two methylene groups in Scheme 1) was considered equivalent to a 1:1 molar EMMA copolymer. We cautioned that steric factors may complicate this simple hypothesis,[2] but the extraordinarily close agreement obtained between the predicted and experimental miscibility map for STVPh/PAMA blends gave us confidence that the interchangeability of homopolymer and isomorphically equivalent average segments of statistical copolymers was a good first

Table 4. Dimensionless Interassociation Equilibrium Constants for Methacrylate (Co)polymers

polymer	molar vol (cm^3/mol)	$K_A^{100\ °C}$	$K_A^{25\ °C}$ ($h_A = -4.1$ kcal/mol)	K_A^{Std} ($V_B = 100$ cm^3/mol; $T = 25$ °C)	R (cm^3/mol)
PMMA	84.9	2.57	10.4	54.6	0
PEMA	101	2.58	10.4	54.7	16.5
PBMA	134	2.17	8.78	46.1	49.5
PHMA	167	1.93	7.82	41.1	82.5
POMA	200	1.91	7.72	40.5	116
PDMA	233	1.79	7.25	38.1	149
PLMA	266	1.70	6.88	36.1	182
PHDMA	332	1.56	6.30	33.1	248
PODMA	365	1.30	5.26	27.6	281
EMMA[47]	218	3.65	14.8	77.4	133
EMMA[38]	277	3.98	16.1	84.5	192
EMMA[33]	324	4.09	16.6	86.9	239

Scheme 1



approximation.[1] However, the STVPh/PAMA blend system has a rather limited miscibility range and, as we will see below, was not really a definitive test of this hypothesis.

We will not dwell on the simulations performed to find the optimum blend compositions for quantitative $f_{HB}^{C=O}$ analysis and the determination of K_A in the case of the DMBVPh[24] blends with the homologous series of PAMA and the EMMA copolymers. As discussed above, the disparity in the molar volumes of the specific repeat units of the two (co)polymers in the blend (see the second column of Table 4) is the dominate factor, and the results are essentially the same as those obtained for the analogous EVA copolymer blends. Essentially, there is a very restricted range over which K_A can be accurately determined, especially in the case of the initial members of the homologous series of PAMA up to say PDMA. Accordingly, the procedure of averaging the results of three completely separate $f_{HB}^{C=O}$ measurements performed at 100 °C was employed on each of the different PAMA and EMMA blends containing 90% DMBVPh[24]. Figure 7 shows a comparison of the infrared spectra recorded at 100 °C in the carbonyl stretching region of DMBVPh[24] blend samples with POMA, PLMA, and PHDMA and the three EMMA copolymers. POMA and EMMA[47] have specific segments that have similar molar volumes ($V_A = 200$ versus 218 cm^3/mol—see Table 4), and if the equivalence depicted in Scheme 1 is valid, then the $f_{HB}^{C=O}$ of a miscible DMBVPh[24] blend with either (co)polymer of the same blend composition at the same temperature should be essentially identical. Simple inspection of the appropriate spectra in Figure 7 shows that this is

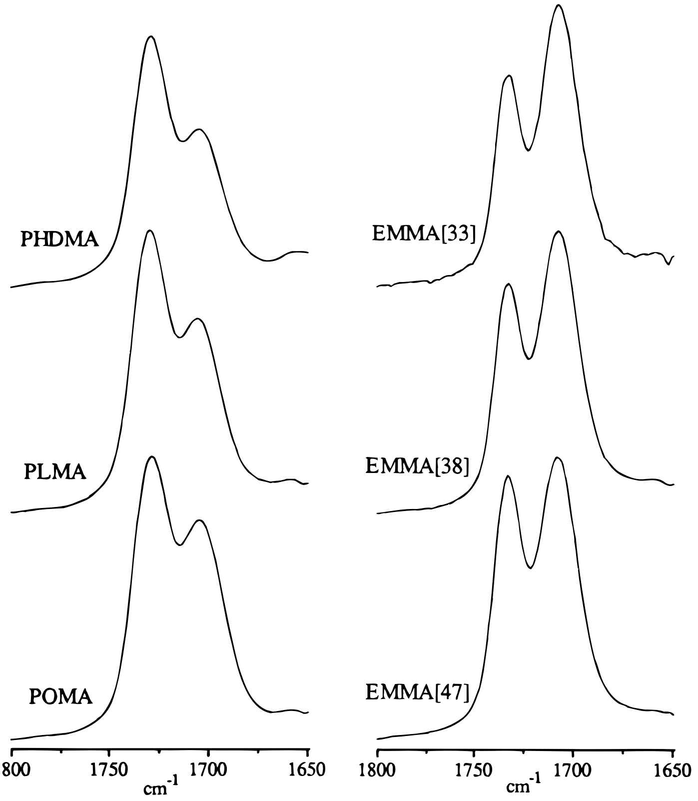


Figure 7. Infrared spectra of films of 80:20 wt % DMBVPh[24] blends with POMA, PLMA, PHDMA, EMMA[47], EMMA[38], and EMMA[33] blends recorded at 100 °C in the carbonyl stretching region (1650−1800 cm^{-1}).

obviously not the case. A similar conclusion is reached for PLMA/EMMA[38] (V_A = 266 versus 277 cm^3/mol) and PHDMA/EMMA[33] (V_A = 332 versus 324 cm^3/mol) blends.

Quantitative analyses were performed to determine the $f_{HB}^{C=O}$ of all the PAMA and EMMA blends and K_A was calculated at 100 °C as before. The results are presented in the third column of Table 4. A maximum error of approximately 5% was estimated in the values of K_A (most were within 2%). The fourth column of Table 4 lists the corresponding values of K_A at 25 °C calculated using an enthalpy of hydrogen bond formation, h_A, of −4.1 kcal/mol, while the fifth column lists K_A^{Std} at 25 °C after scaling to our standard reference volume of V_B = 100 cm^3/mol.

Let us focus initially on the results obtained from the EMMA copolymer blends, as they are analogous to the EVA copolymer blends previously discussed. In common with the EVA copolymer blends, the trend in the value of K_A^{Std} is very similar, with a significant increase from 55 for PMMA (i.e., EMMA[100]), to 77 for EMMA[47], to 85 for EMMA[38], and then it appears to reach a plateau near EMMA[33] at ≈87. The explanation advanced above for this phenomenon remains credible. In effect, we presume that some of the methacrylate carbonyl groups in PMMA are just not accessible to the phenolic hydroxyl groups of DMBVPh[24], due to the close proximity of the MMA segments to one another in the polymer chain, when compared to EMMA[47], EMMA[38], and EMMA[33], where the MMA carbonyl groups are progressively spaced apart in the copolymer chain by methylene groups. For completeness, it should also be mentioned that the value of K_A^{Std} determined previously[1] from experimental studies of the miscible PVPh/PEMA system was 37—a value significantly less than that obtained from the analogous DMBVPh[24] blend studied here, where K_A^{Std} was determined to be 55 (see Table 4). This we postulate is most probably caused by similar "screening" effects, but where in this case the phenolic hydroxyl groups in PVPh are not as accessible to the PEMA carbonyl groups when compared to those of DMBVPh[24], where the VPh segments are spaced apart by the DMB segments in the copolymer. All in all, the results and major trends observed for the DMBVPh[24] blends with EVA and EMMA copolymers are consistent and appear understandable.

Turning now to a comparison of K_A^{Std} values for the DMBVPh[24]/PAMA blends, we see that the value of K_A is not constant, but decreases systematically with increasing size of the side group, from 55 for PMMA to 28 for PODMA (Table 4). Given the above arguments, we should not find this surprising. Consider the schematic shown in Figure 8, which depicts a portion of a chain of PHMA (denoted A) and compares it to a part of an equivalent EMMA copolymer (B) chain containing the same average number of methylene groups in the specific repeat (i.e., R is five methylene groups in Scheme 1). Acknowledging that Figure 8 is a highly simplistic representation of the actual conformation of the respective (co)polymer chains, it nonetheless pictorially illustrates the apparent differences in steric accessibility of the methacrylate carbonyl groups. It is therefore reasonable to assume that there will be increased steric shielding of these carbonyl groups as the size of the side group becomes larger, resulting in a decrease in the measured $f_{HB}^{C=O}$ for comparable DMBVPh[24] blends with PAMA having larger values of R. This, of course, is reflected in the value of K_A^{Std} that is determined from the experimental $f_{HB}^{C=O}$ data.

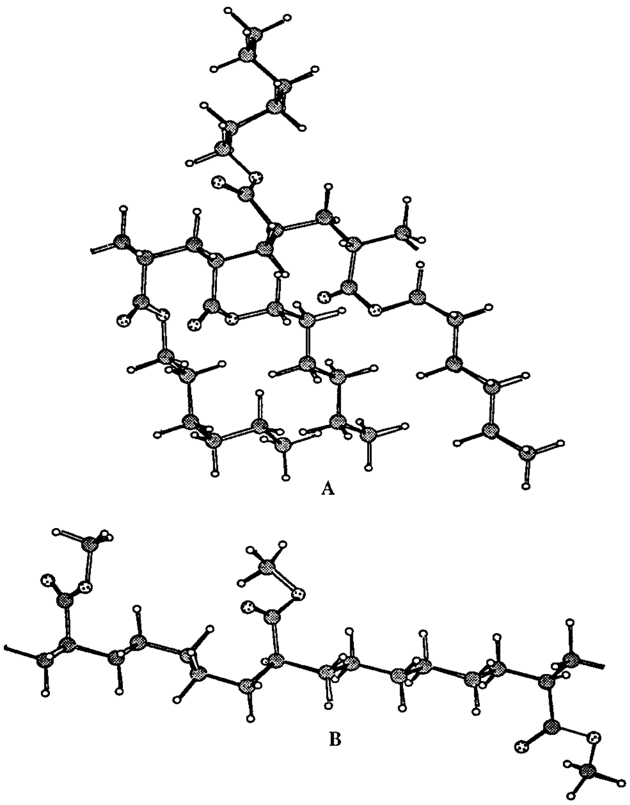


Figure 8. Model depicting a typical section of the polymer chain of (A) PHMA and (B) an equivalent EMMA copolymer containing the same average number of methylene groups in the specific repeat.

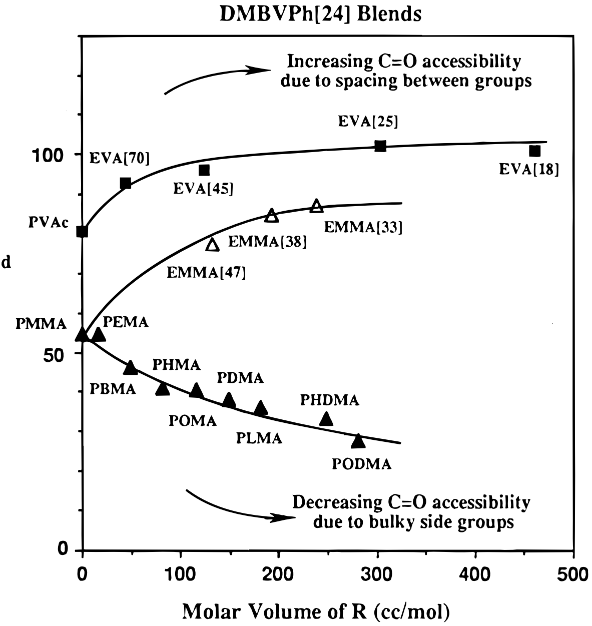


Figure 9. A plot of K_A^{Std} versus the molar volume of R for DMBVPh[24] blends with EVA and EMMA copolymers and the homologous series of PAMA from PMMA to PODMA.

Summary and Ramifications

Figure 9 summaries all the experimental results obtained in this study of the DMBVPh[24] blends. Values of K_A^{Std} calculated from the $f_{HB}^{C=O}$ data obtained at 100 °C are plotted against the molar volume of R (the number of methylene groups in the specific repeat of the PAMA side group or the ethylene portion of the equivalent EMMA or EVA copolymer—see Scheme 1). Thus, $R = 0$ for both PMMA and PVAc. Values of R for the other (co)polymers are listed in Tables 3 and 4. Two major trends are evident from an examination of Figure 9. First, as we increase R by increasing the length of the MMA side groups in the homologous series of PAMA blends with DMBVPh[24], there is a systematic decrease in the value of K_A^{Std}. This is consistent with the concept of a decreasing accessibility of MMA carbonyl groups due to steric shielding as a result of the bulky nature of the side groups. Second, as we increase R by spacing the acetoxy (or MMA) groups further apart in the EVA (or EMMA) copolymer chain, the value of K_A^{Std} initially increases and then reaches a plateau, which is consistent with the idea that the increased spacing of the acetoxy (or MMA) segments along the chain increases accessibility of the carbonyl groups in the blends with DMBVPh[24]. There is a saturation limit, however, above which further separation does not appear to enhance accessibility to any measurable extent.

Recall that we have assumed a constant value of K_A^{Std} in all our prior calculations of miscibility windows and maps which, if accurate, would result in a straight line parallel to the x-axis in Figure 9. Only at large values of R (≥ 200 cm^3/mol) for the EVA and EMMA copolymer blends does the relationship between K_A^{Std} and R appear to be reasonably linear, and it is plausible that values of K_A^{Std} determined from this linear region represent a limiting value of K_A^{Std}, i.e., one that reflects the "true" K_A^{Std} value in the absence of any problems of "screening" or functional group accessibility. Remember also that the K_A^{Std} values determined from miscible PVPh blends were significantly lower than those determined from comparable DMBVPh[24] blends (by a factor of about 2/3). However, barring unforeseen complications, it appears reasonable to assume that with an equivalent R value of ≈ 425 cm^3/mol the VPh segments are sufficiently spaced apart in DMBVPh[24] to eliminate accessibility problems. If this is correct, then the K_A^{Std} values, unperturbed by problems of functional group accessibility, are approximately 100 and 90, respectively, for the mixing of (co)polymers such as PVPh (or STVPh or DMBVPh, etc.) with acetoxy or methacrylate (co)polymers.

This is an important result, which has a number of ramifications. In a recent paper[4] we reported a value of $K_A^{Std} = 170$, for low molecular model compound mixtures of ethylphenol (EPh) and ethyl isobutyrate (EIB). An identical value, within error, was obtained for a polymer solution consisting of PVPh with EIB. In neither case would one expect any problems of "shielding" or functional group accessibility, and indeed this is reflected in the common value of K_A^{Std}. In the same paper we reported a value of $K_A^{Std} = 38.4$ for the analogous polymer blend of PVPh and PEMA, which we now know embraces a number of complicating factors, not the least being problems of "shielding" or functional group accessibility. As we have seen above, we would have obtained a value of $K_A^{Std} = 54.7$ (Table 4) had we used PEMA blends with DMBVPh[24] rather than PVPh, and a limiting value of $K_A^{Std} = 87$ had we determined it from EMMA[33] blends with DMBVPh[24]. The latter value, representing the limiting value of K_A^{Std}, unperturbed by problems of functional group accessibility, is still a factor of about 2 times less than that of the analogous EPh/EIB low molecular weight mixtures and PVPh/EIB polymer solution. This difference, we believe, is caused by further complications associated with chain connectivity that result in an excess of intramolecular contacts formed in the mixing of two polymers over that formed in an analogous low molecular weight mixture or polymer solution. A model that takes such factors into account has recently been developed and will be discussed in more detail elsewhere.[5]

Before finishing this topic we should briefly discuss the K_A^{Std} value obtained recently from a series of ethyl methacrylate-*stat*-4-vinylphenol (EMAVPh) copolymers. We reported a value of $K_A^{Std} = 67.4$, which is intermediate between that obtained from the PVPh/PEMA polymer blends and the EPh/EIB low molecular weight mixtures or PVPh/EIB polymer solutions. Problems of functional group accessibility are inescapable in EMAVPh copolymers and interpreting the significance of this result is fraught with difficulties. While single phase materials are the rule for such statistical methacrylate/VPh copolymers (something that is impossible in some analogous polymer blends), it will be necessary to synthesize statistical terpolymers of VPh, a methacrylate and an inert "diluent" or "spacer" such as DMB to determine unperturbed values of K_A^{Std}.

Finally, now that we know that K_A^{Std} is not a constant for hydrogen bonded (co)polymer blends, but varies significantly depending upon the accessibility of the functional groups, how is it that we were able to successfully predict[1] the miscibility windows and maps for the STVPh copolymer blends with EVA and PAMA (co)polymers using constant values of K_A^{Std} determined from the individual PVPh/EVA[70] ($K_A^{Std} = 58.0$) and PVPh/PEMA ($K_A^{Std} = 37.1$) miscible blend systems? Let us first consider the EVA blends. We have mentioned above that the values of K_A^{Std} determined from the DMBVPh[24] blends increase with increasing ethylene content of the EVA copolymers until a plateau value of $K_A^{Std} \approx 100$ (Table 3) is reached. Accordingly, when we used the value of $K_A^{Std} = 58.0$, determined from the PVPh/EVA[70] blends, we actually overestimated K_A^{Std} for the PVPh/PVAc blends and underestimated those applicable to the PVPh blends with the ethylene rich EVA copolymers. To make matters worse, the value of K_A^{Std} is a function of the STVPh copolymer composition, and is further underestimated for the analogous STVPh blends due to the enhanced accessibility of the VPh segments from spacing by the "inert" styrene segments. Notwithstanding these apparently insurmountable complications, if we recalculate the miscibility maps at 25 °C for EVA blends with STVPh and DMBVPh, but using the limiting value of $K_A^{Std} = 100$ (i.e., that unperturbed by functional group accessibility problems), we obtain a result that is shown in Figure 10. While there are subtle differences between these miscibility maps and their counterparts shown in Figure 1, the essential features are very similar. What this means is that although there is greater than a 40% difference in the magnitude of the K_A^{Std} values, the effect on the predicted area of miscibility is marginal. In this particular case the dominant factor is the difference in the solubility parameters of the respective

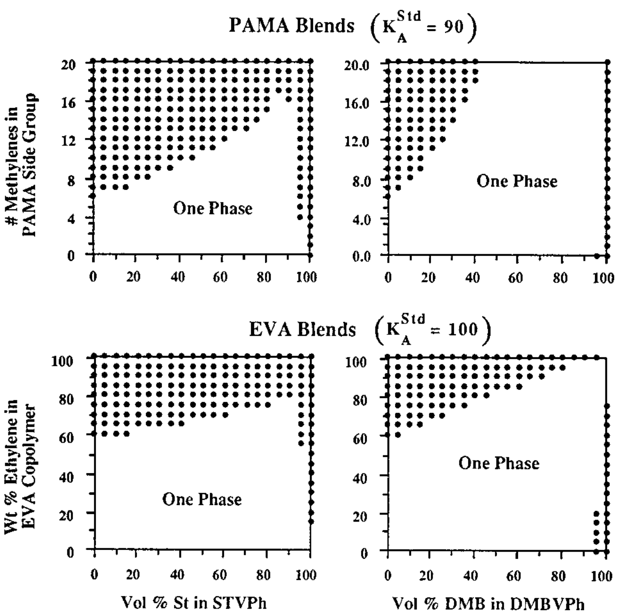


Figure 10. Theoretical miscibility maps calculated at room temperature. Top: PAMA blends with STVPh (left) and DMBVPh (right) using the limiting K_A^{Std} value of 90. Bottom: EVA blends with STVPh (left) and DMBVPh (right) using the limiting K_A^{Std} value of 100.

STVPh and DMBVPh copolymers as a function of the volume fraction of VPh (see discussion in the Introduction).

Turning now to the PAMA blends; we noted above that the values of K_A^{Std} determined from the DMBVPh-[24] blends decrease with increasing size of the PAMA side group (Table 4) and are considerably less than the limiting value of K_A^{Std} $\approx$90 determined from the EMMA copolymers (i.e., that unperturbed by functional group accessibility problems). If we employ this limiting value of K_A^{Std} to calculate miscibility maps for PAMA blends, similar to those mentioned above for the EVA copolymer blends PAMA, we overestimate the area of miscibility by a considerable amount (compare the appropriate miscibility maps in Figures 1 and 10). This is hardly surprising, as we have demonstrated that steric crowding affects the accessibility of the methacrylate carbonyl groups as the size of the side group increases (Figure 10). To reiterate, the value of K_A^{Std} = 37.1, determined previously from the PVPh/PEMA blends is less than that obtained from the DMBVPh[24]/PEMA blends (K_A^{Std} = 54.7; Table 4) and supposedly reflects the enhanced accessibility of the VPh segments in DMBVPh[24] as they are spaced apart. However, unlike the EMMA (or EVA) copolymers, where increasing the volume fraction of the methylene groups in the main chain increases the value of K_A^{Std} up to a limit, increasing the volume fraction of the methylene groups in the PAMA side groups decreases K_A^{Std}. Accordingly, in the absence of a theoretical function that describes the relationship between K_A^{Std} and the size of the PAMA side group, we can only use the experimental values of K_A^{Std} (Table 4) and compare the calculated miscibility windows for STVPh (or DMBVPh) copolymers with each separate PAMA homopolymer. Typical results are shown in Figure 11. If one compares these STVPh/PAMA miscibility windows with those displayed in our monograph calculated using a constant value of K_A^{Std} = 37.1 (ref 1, pp 460−466), the results are almost identical. Careful examination of the individual K_A^{Std} values listed in Table 4 reveals the reason for this peculiar result. For PMMA, PEMA, and PBMA, the values of K_A^{Std} (54.6, 54.7, and 46.1, respectively) are significantly higher than 37.1, but as these homopolymers are predicted to be miscible with all STVPh copolymers up to >95% ST, the additional contribution from $\Delta G_H/RT$ (eq 1) arising from the higher value of K_A^{Std} makes only a marginal difference. For PHMA, POMA, PDMA, and PLMA, the values of K_A^{Std} (41.1, 40.5, 38.1, and 36.1, respectively) are roughly the same as the original constant value of 37.1 and make little difference to the calculated miscibility windows.

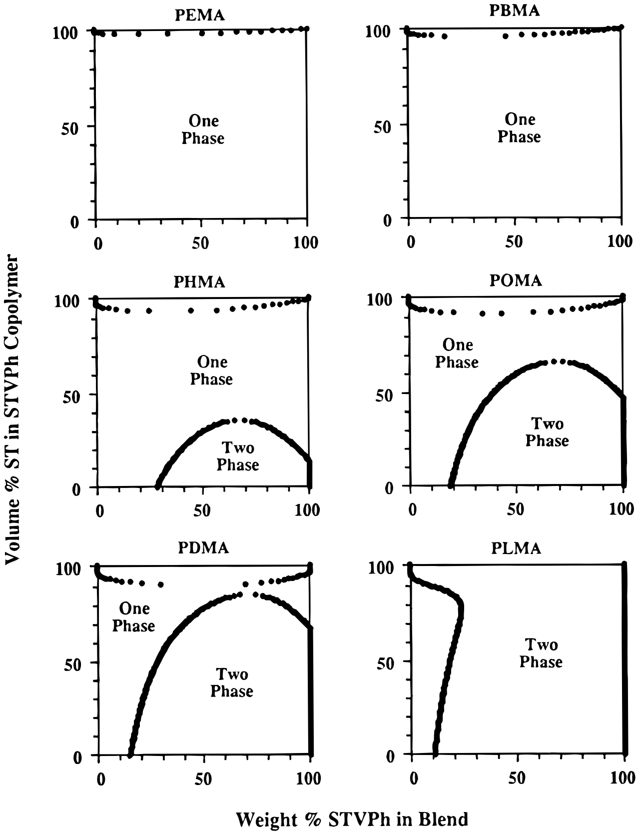


Figure 11. Theoretical miscibility windows calculated at room temperature using the K_A^{Std} values listed in Table 4 for STVPh blends with a PEMA, PBMA, PHMA, POMA, PDMA, and PLMA.

So what have we learned? Miscibility in hydrogen bonded polymer blends is governed by the interplay between the Flory interaction term $\Phi_A\Phi_B\chi$ and the hydrogen bonding term $\Delta G_H/RT$ in the free energy (eq 1). The number of hydrogen bonds is determined by the competition between self-associating BB bonds and interassociating BA bonds. If the magnitudes of the self-associating and interassociating equilibrium constants are similar, this competition is complicated, and the number of BB and BA hydrogen bonds depends upon the concentration in a rather subtle manner. However, the situation becomes much simpler if both equilibrium constants are large (in dimensionless units $K_B \gg 1$, $K_A \gg 1$) *and* the interassociation constant is much larger than that of self-association: $K_A \gg K_B$. The first condition implies that almost all the hydrogen bonds, that could be formed, are formed. The second condition implies that interassociation dominates and there are as many BA bonds as possible. In this case the number of hydrogen bonds formed is determined predominantly by the concentration of the corresponding groups present in the blend, and large errors in the absolute values of the hydrogen bonding equilibrium constants make very little difference. Accordingly, we arrive at the very interesting and encouraging conclusion that *quantitative* prediction of phase diagrams can be obtained for many systems even if there are uncertainties in the exact values of the equilibrium constants.

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References and Notes

(1) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing: Lancaster, PA, 1991.
(2) Coleman, M. M.; Painter, P. C. *Prog. Polym. Sci.* **1995**, *20*, 1.
(3) Whetsel, K. B.; Lady, J. H. In *Spectrometry of Fuels*; Friedle, H., Ed.; Plenum Press: London, 1970.
(4) Coleman, M. M.; Xu, Y.; Painter, P. C. *Macromolecules* **1994**, *27*, 127.
(5) Painter, P. C.; Veytsman, B.; Kumar, S.; Shenoy, S.; Graf, J. F.; Xu, Y.; Coleman, M. M. *Macromolecules*, submitted.
(6) (a) Yang, X.; Painter, P. C.; Coleman, M. M.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **1992**, *25*, 2156. (b) Coleman, M. M.; Yang, X.; Painter, P. C.; Graf, J. F. *Macromolecules*, **1992**, *25*, 4414. (c) Coleman, M. M.; Yang, X.; Zhang, H.; Painter, P. C.; Scherer, K. V., Jr. *J. Polym. Sci., Chem. Ed.* **1993**, *31*, 2039. (d) Xu, Y.; Graf, J. F.; Painter, P. C.; Coleman, M. M. *Polymer* **1991**, *32*, 3103. (e) Xu, Y.; Painter, P. C.; Coleman, M. M. *Makromol. Chem. Macromol. Symp.* **1991**, *51*, 61. (f) Xu, Y.; Painter, P. C.; Coleman, M. M. *Makromol. Chem. Macromol. Symp.* **1991**, *52*, 91. (g) Coleman, M. M.; Yang, X.; Painter, P. C.; Kim, Y. H. *J. Polym. Sci., Part A, Polym. Chem.* **1994**, *32*, 1817.
(7) (a) Grosso, P.; Vogl, O. *J. Macromol. Sci.—Chem.* **1986**, *A23*, 1299. (b) Long, T. E.; Teegarden, D. M. *Chem. Abstr.* **1991**, 117:8700h. (c) Bender, A.; Leicht, E.; Sattelmeyer, R. *Chem. Abstr.* **1989**, 114:145239s.
(8) (a) Arshady, R.; Kenner, G. W.; Ledwith, A. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2017. (b) Ledwith, A.; Rahnema, M.; Sen Gupta, P. K. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2239.
(9) Pehlert, G. J.; Painter, P. C.; Coleman, M. M. In preparation.
(10) (a) Coleman, M. M.; Pehlert, G. J.; Yang, X.; Stallman, J. B.; Painter, P. C. *Polymer*, accepted. (b) Pehlert, G. J.; Yang, X.; Painter, P. C.; Coleman, M. M. *Polymer*, accepted.

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