Equilibrium Constants and the Prediction of Phase Behavior for Phenoxy Blends with Aliphatic Polyesters

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ABSTRACT: An association model is applied to blends where one component contains secondary alkyl hydroxyl groups. The use of this model requires a knowledge of parameters (equilibrium constants) describing the self-association of the pure component, and the determination of these parameters from infrared studies of model compounds is described. Included is the complication that the self-associating species also contains ether groups, so that we can apply the model to the poly(hydroxy ether of Bisphenol A) (Phenoxy). Interassociation parameters describing the interaction between the Phenoxy hydroxyl and ester type carbonyl groups were obtained from infrared studies of miscible Phenoxy-poly(ε-caprolactone) blends. Using these parameters we have calculated a number of theoretical phase diagrams and miscibility windows for Phenoxy blends with aliphatic polyesters and polymethacrylates. The results are in very good agreement with experimental results reported in the literature.

Introduction

Through the efforts of a number of groups it is becoming clear that a wide range of polymers that hydrogen bond to one another are capable of forming miscible polymer blends. In this laboratory we have focused on the development and experimental testing of an association model that is capable of describing the free energy changes that occur as a result of such interactions.[1,2] This approach has the major advantage that the parameters describing hydrogen bonding (equilibrium constants) can, in principle, be determined by infrared spectroscopy. In certain systems, particularly those involving hydroxyl groups, there are various experimental difficulties that complicate these measurements, however. As a result, much of our experimental work has involved blends where one component is poly(vinylphenol) (PVPh) or its copolymers[1-9] as carefully determined equilibrium constants describing the self-association of phenolic OH groups are available in the literature. We are now turning our attention to blends where one component contains an alkyl OH group, but here we could not find appropriate equilibrium constants (most studies have used CCl_4 as a solvent, which affects the degree of association relative to a hydrocarbon solvent). Accordingly, we have set out to determine these ourselves and recently, in collaboration with Eli Pearce and T. K. Kwei, characterized systems involving the hexafluoro-2-propanol group.[10]

In this paper we examine the self-association of secondary OH groups, but throw in an additional complication. We let the self-associating molecule also contain an ether oxygen, so that hydrogen bonds in the pure state exist not only between OH groups but also between hydroxyl and ether oxygens. This is because we wish to examine blends where one component is the poly(hydroxy ether of Bisphenol A) (Phenoxy). Here we will describe the measurement of fundamental parameters which are then applied to a calculation of the phase behavior of Phenoxy/polyester blends and compared to experimental measurements.

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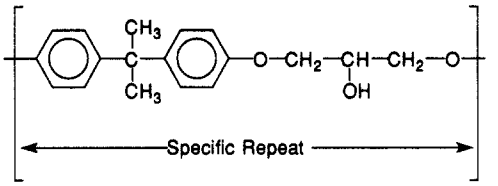
In calculating the stoichiometry of hydrogen bonding, phase behavior, etc., we have found it useful as a computational convenience (it has no more significance than this) to define something we label a *specific repeat unit*. This is simply the average unit which contains just one group that is capable of forming a hydrogen bond. If we now examine the specific repeat unit of Phenoxy, now

PHENOXY



defined so that it contains one hydroxyl group, we see this corresponds to the repeating segment of the polymer chain, but in addition to one strongly self-associating interacting site (the hydroxyl group), it also contains two ether oxygens. This complicates matters, as significant specific interactions (hydrogen bonds) between the hydroxyl and ether groups are also likely to be present, as mentioned above. The usual hydroxyl-hydroxyl interactions characteristic of the self-association of simple alcohols, phenols, etc. already require a minimum of two equilibrium constants, K_2 and K_B, to account for the formation of hydrogen-bonded dimers and "chainlike" multimers, respectively.[1] For the Phenoxy polymer we will require a third self-association equilibrium constant, K_E, to account for hydroxyl-ether interactions. Although this leads to stoichiometric and free energy equations that are algebraically more complex, the problem is conceptually straightforward, and the principle problem is the accurate determination of these constants from infrared measurements.

Equilibrium constants describing the self-association of polymers containing hydroxyl groups may be obtained from infrared studies of chemically analogous low molecular weight model compounds (e.g., phenol in the case of PVPh) as long as the chain is perfectly flexible (see below). Having determined the equilibrium constants for the model compound, the corresponding values for the

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polymer are simply scaled with respect to differences in molar volume.[1] It is perhaps worthwhile to initially summarize the general approach we take in these studies and discuss important assumptions made in determining the equilibrium constants describing the self-association for the Phenoxy polymer. First, we employ the method of Coggeshall and Saier[10,11] to determine equilibrium constants for the model compound 2-propanol (K_{c_2} and K_c, in units of liter/mole, describing the formation of hydrogen-bonded dimers and "chainlike" multimers, respectively). Next, we employ their method to determine K_e, the equilibrium constant (in units of liter/mole) describing the interaction between the hydroxyl and ether groups, from 2-propanol–phenyl methyl ether (PME) mixtures in dilute solutions. These equilibrium constants are then converted to their dimensionless counterparts, K_2, K_B, and K_E (as defined by Flory and discussed in ref 1), and used in the appropriate stoichiometric equations to calculate the theoretical fraction of free monomers as a function of dilution for the model compound 1,3-diphenoxy-2-propanol (DPP), a close relative of the Phenoxy specific repeat. These calculated values were then compared to experimental infrared data. As we will see, excellent agreement is observed, confirming the transferability of the individual equilibrium constants. Along the way we found that direct least-squares fitting of the infrared data to the stoichiometric equations is a faster, more convenient and accurate method of obtaining the necessary dimensionless equilibrium constants than the graphical methods previously utilized, and we will also describe this procedure.

To predict phase diagrams, miscibility windows, and maps for polymer blends using our association model,[1] it is now necessary to determine the corresponding constants (K_A and h_A) that describe the interassociation of the Phenoxy hydroxyl groups with other functional groups, such as the carbonyl groups of esters, acrylates, etc. For this we need to perform quantitative infrared studies on an appropriate miscible blend. Fortunately, the Phenoxy–poly(ϵ-caprolactone) (PCL) blend system is miscible in the amorphorus state.[16-18] Armed with these necessary parameters, we then draw upon the systematic experimental studies of Phenoxy–polyester blends by Harris et al.[19] and the recent reports of Espi and Iruin[20] and Chiou and Paul[21] to test our theoretical predictions.

Experimental Section

Cyclohexane, toluene, 2-propanol, phenyl methyl ether (PME), and 1,3-diphenoxy-2-propanol (DPP) were purchased from Aldrich Chemical Co. and used without further purification. The poly(hydroxy ether of Bisphenol A) (Phenoxy) used in these studies was purchased from Scientific Polymer Products Inc. and has a reported weight-average molecular weight of 67 000. Poly(ϵ-caprolactone) (PCL) was obtained from Aldrich.[18] Blends of various compositions were prepared by codissolving appropriate amounts of the components in tetrahydrofuran to yield 2% (w/v) solutions. Thin films for FTIR studies were obtained by casting the blend solutions onto potassium bromide windows at room temperature. The solvent was removed slowly under ambient conditions for a minimum of 24 h. The samples were then dried in a vacuum desiccator for an additional day before being placed in a vacuum oven at 110 °C for 4 h to completely remove the residual solvent. To minimize water absorption, samples were stored under vacuum desiccation while awaiting study.

Infrared spectroscopic measurements were recorded on a Digilab Model FTS60 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. For the solution infrared studies, liquid mixtures were contained in a standard 1-mm KBr liquid cell, and a total of 64 interferograms were signal averaged. Spectra recorded at elevated temperatures were obtained using a heating cell mounted inside the sample chamber. Temperature was regulated by a Micristar 828D digital process controller which has a reported accuracy of ±0.1 °C. All films were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed.

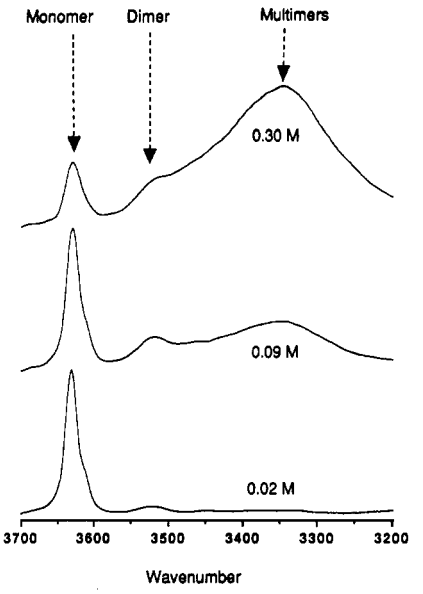


Figure 1. Infrared spectra in the hydroxyl stretching region recorded at 25 °C of three different concentrations of 2-propanol in cyclohexane.

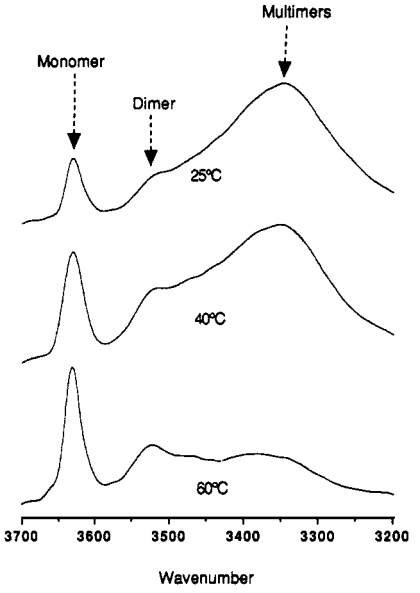


Figure 2. Infrared spectra in the hydroxyl stretching region of a 0.3 M solution of 2-propanol in cyclohexane recorded at three different temperatures.

Results and Discussion

Figure 1 shows representative infrared spectra in the hydroxyl stretching region of three different concentrations of 2-propanol in cyclohexane at 25 °C, while Figure 2 illustrates the effect of temperature for one particular concentration. Cyclohexane is essentially an "inert" diluent (i.e., non-hydrogen-bonding), and as its concentration is increased in the mixture the fraction of hydrogen-bonded hydroxyls decreases. A similar effect is observed as temperature is increased. The band at 3630 cm^{-1}, which we emphasize is the only one that we use in our forthcoming quantitative measurements, has been assigned to non-hydrogen-bonded hydroxyl groups, and its absolute intensity is assumed to be a measure of the amount of free "monomers" in the mixture.[11,12] The absorption at ap-

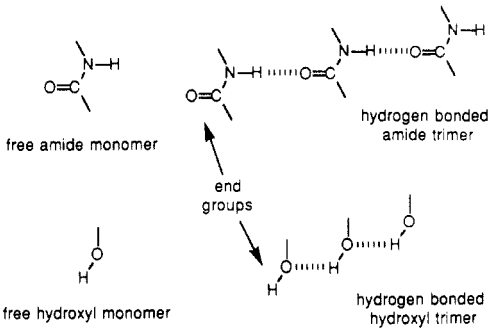


Figure 3. Schematic diagram depicting free monomers, end groups, and hydrogen-bonded amide and hydroxyl groups.

proximately 3530 cm^{-1} is attributed to hydrogen-bonded OH dimers, whereas the very broad band centered at approximately 3350 cm^{-1} corresponds to the distribution of hydrogen-bonded multimers.

It is important to recognize that there is a profound distinction between free "monomers" and free end groups. In previous work we have shown that the carbonyl band corresponding to free (non-hydrogen-bonded) carbonyl groups is a measure of not only free isolated monomers but also the terminal groups of hydrogen-bonded multimers. This is schematically illustrated for amides in Figure 3. Although the terminal carbonyl group of a hydrogen-bonded multimer is attached to an NH group that is, in turn, hydrogen bonded to another amide group, it is not *directly* hydrogen bonded (there is a covalent bond separating the C=O and NH groups), and we are unable to differentiate between carbonyl groups associated with terminal ends of hydrogen-bonded multimers and those due to isolated free "monomers". Accordingly, the self-association equilibrium constants obtained directly from quantitative measurements of the fraction of free carbonyl groups in polyamides and polyurethanes were calculated from equations that take into account the fact that the free (non-hydrogen-bonded) carbonyl band reflects both isolated and terminal carbonyl groups.[1]

The case of hydroxyl-containing molecules is not so clear-cut. Here we are considering the OH stretching vibration and (in contrast to the carbonyl stretching vibration discussed above) the terminal hydroxyl end group of a hydrogen-bonded multimer is perturbed directly by the hydrogen bond from the oxygen atom to the adjacent hydroxyl proton (Figure 3). While there is no ambiguity in the position of the band corresponding to the isolated free "monomer", an important question is, do the hydroxyl end groups of hydrogen-bonded multimers contribute to the absorbance at the same frequency? In developing equations to calculate self-association equilibrium constants for simple alcohols, Coggeshall and Saier[11] assumed that the band at 3630 cm^{-1} was solely due to isolated free "monomers". An identical assumption was made by Whestel and Lady[12] in their studies of phenol, and we have implicitly carried this assumption forward in our own work on PVPh and related copolymers[1] by scaling equilibrium constants derived from the infrared studies of phenol. Evidence does exist, however, that suggests some error might be introduced in the estimation of equilibrium constants by assuming the 3630-cm^{-1} band is assigned simply to isolated free "monomers".[13] This is primarily due to minor contributions to the absorption at 3630 cm^{-1} from the overlap of bands associated with terminal end groups and, at higher concentrations, with the broad hydrogen-bonded OH band. It is important to stress that while there may be some errors introduced by assuming that the 3630-cm^{-1} band is simply due to isolated "monomers", at the other extreme, assuming that the band is due to isolated monomers *plus* terminal end groups is definitely erroneous and would lead to major errors. For the purposes of the work described in this paper we will remain internally self-consistent and continue in the footsteps of Coggeshall and Saier[11] and Whestel and Lady[12] by assuming that the 3630-cm^{-1} band is due simply to isolated "monomers".

Table I
Absorbance Data Pertaining to 2-Propanol–Cyclohexane Mixtures

	intensity (absorbance)				
c (M)	25 °C	40 °C	50 °C	60 °C	70 °C
0.025	0.109	0.108	0.106	0.103	0.101
0.030	0.128	0.128	0.125	0.122	0.120
0.035	0.145	0.146	0.144	0.140	0.139
0.040	0.162	0.164	0.162	0.158	0.157
0.045	0.179	0.180	0.179	0.176	0.175
0.050	0.195	0.197	0.196	0.193	0.192
0.055	0.210	0.213	0.212	0.209	0.209
0.060	0.224	0.228	0.228	0.225	0.225
0.065	0.235	0.243	0.243	0.241	0.241
0.070	0.248	0.255	0.259	0.257	0.258
0.075	0.261	0.269	0.273	0.271	0.273
0.080	0.269	0.285	0.287	0.287	0.288
0.085	0.280	0.298	0.299	0.299	0.303
0.090	0.297	0.310	0.314	0.312	0.317
0.095	0.306	0.323	0.326	0.329	0.330
0.15	0.385	0.425	0.444	0.458	0.470
0.20	0.442	0.506	0.523	0.550	0.572
0.25	0.502	0.571	0.601	0.632	0.663
0.30	0.556	0.613	0.621	0.700	0.743
0.35	0.587	0.650	0.700	0.765	0.801
0.40	0.614	0.690	0.730	0.800	0.887
0.45	0.655	0.730	0.754	0.847	0.901
0.50	0.675	0.730	0.785	0.901	0.956

[We intend to address this subject and that of the general transferability of self-association equilibrium constants from low molecular weight model compounds to polymers in a forthcoming paper, but it should be noted in passing that in determining a *set* of equilibrium constants to describe both self-association and interassociation for polymer blends, we experimentally determine the interassociation equilibrium constant, K_A, from a least-squares fit of infrared data acquired from a miscible polymer blend to equations describing the stoichiometry of the system, using *constant values* of K_2 and K_B. The equilibrium constants describing self-association and interassociation are therefore not independent. Accordingly, reasonable errors in the absolute values of the self-association equilibrium constants tend to be compensated by the method used to obtain the complementary interassociation equilibrium constants. Factors such as chain stiffness in the polymer are also absorbed into this experimentally determined quantity. For the prediction of phase diagrams, miscibility windows, and maps, the important consideration is the ratio between the self-association and interassociation equilibrium constants, not their absolute values.]

2-Propanol. Quantitative measurements of the absorbance of the isolated free hydroxyl band at 3630 cm^{-1} as a function of concentration in 2-propanol–cyclohexane mixtures at 25, 40, 50, 60, and 70 °C are listed in Table I. The intensity (absorbance) of the isolated hydroxyl band, I, is related to the absorptivity coefficient, ϵ, the concentration, c, and the path length, l, by the well-known Beer–Lambert law, $I = \epsilon lc$. Accordingly, from a plot of

Table II
Fraction of Free Monomer Data for 2-Propanol–Cyclohexane Mixtures

	fraction of isolated hydroxyl groups				
c (M)	25 °C	40 °C	50 °C	60 °C	70 °C
0.025	0.883	0.906	0.924	0.932	0.942
0.030	0.864	0.894	0.908	0.920	0.932
0.035	0.839	0.875	0.896	0.905	0.926
0.040	0.820	0.860	0.882	0.894	0.915
0.045	0.805	0.839	0.867	0.885	0.907
0.050	0.789	0.826	0.854	0.873	0.895
0.055	0.773	0.812	0.840	0.860	0.886
0.060	0.756	0.797	0.828	0.848	0.874
0.065	0.732	0.784	0.814	0.839	0.864
0.070	0.717	0.764	0.806	0.831	0.859
0.075	0.704	0.752	0.793	0.817	0.848
0.080	0.681	0.747	0.782	0.812	0.839
0.085	0.667	0.735	0.766	0.796	0.831
0.090	0.668	0.722	0.760	0.784	0.821
0.095	0.652	0.713	0.748	0.784	0.810
0.15	0.520	0.594	0.645	0.691	0.730
0.20	0.447	0.530	0.570	0.622	0.667
0.25	0.406	0.479	0.524	0.572	0.618
0.30	0.375	0.428	0.451	0.528	0.577
0.35	0.340	0.389	0.436	0.495	0.533
0.40	0.311	0.362	0.398	0.452	0.517
0.45	0.295	0.340	0.365	0.426	0.467
0.50	0.273	0.306	0.342	0.408	0.446

Table III
Self-Association Equilibrium Constants for 2-Propanol

temp (°C)	25	40	50	60	70
molar vol (cm^3/mol)	76.56	78.22	79.15	80.14	81.19
Method of Coggeshall and Saier[a]					
K_{c_2} (L/mol)	2.56	2.00	1.61	1.45	1.18
K_c (L/mol)	4.64	3.51	3.14	2.20	1.77
K_2 (dimensionless)	33.4	25.6	20.3	18.1	14.5
K_B (dimensionless)	60.6	44.9	39.6	27.5	21.8
Direct Least-Squares Method					
K_2 (dimensionless)	34.8	26.4	21.1	19.1	15.3
K_B (dimensionless)	57.6	46.1	41.8	28.9	24.7

[a] Reference 11.

(I/lc) versus c we can determine ϵ from the limit

$$\left|\frac{I}{cl}\right|_{\text{limit } c\to 0} = \epsilon \tag{1}$$

The experimental fraction of isolated hydroxyl groups, f_m^{OH}, at any given concentration is then simply

$$f_m^{OH} = I/I_0 \tag{2}$$

where $I_0 = c\epsilon l$. Table II lists the calculated fraction of isolated hydroxyl groups in 2-propanol–cyclohexane mixtures as a function of concentration and temperature.

As we have described in some detail elsewhere,[10] the infrared spectroscopic method of Coggeshall and Saier[11] that was used to determine the equilibrium constants describing the formation of dimers (K_{c_2}) and higher multimers or "chainlike" complexes (K_c) in 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol, we will only present a terse summary of this methodology here. In essence, using the data presented in Tables I and II, K_{c_2} is obtained by plotting $[2c(f_m^{OH})^2]/(1 - f_m^{OH})$ versus c and extrapolating to zero concentration. K_c is then calculated from an expression relating the *disassociation* of hydrogen-bonded multimers to that of the *disassociation* of dimers, the fraction of nonassociated or free molecules, and the concentration (see eq 3 in ref 10). The results of such an exercise are given in Table III.

For our purposes it is convenient to convert the above equilibrium constants, K_{c_2} and K_c, in units of liter/mole

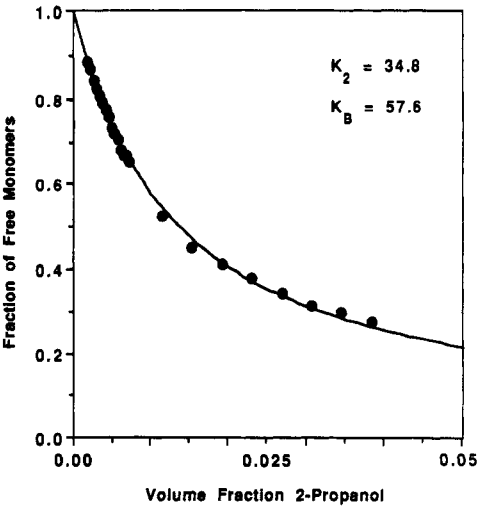


Figure 4. Graph showing the results of a least-squares fit of eq 4 (solid line) to the experimental fraction of free monomers versus concentration (●) for 2-propanol in cyclohexane at 25 °C.

to the *dimensionless* equilibrium constants, K_2 and K_B, values that we employ in our association model. This we have described before[1] and the two sets of equilibrium constants are simply related by

$$K_2 = K_{c_2}\frac{1000}{V_B}$$

and

$$K_B = K_c\frac{1000}{V_B} \tag{3}$$

where V_B is the molar volume of 2-propanol calculated from the density at the temperature of interest. The density of 2-propanol at 25 °C is reported to be 0.7850 g/cm^3, and values of 0.7683, 0.7593, 0.7499, and 0.7402 g/cm^3 at 40, 50, 60, and 70 °C, respectively, were calculated from the Francis equation using the appropriate constants as determined by Wilhoit and Zwolinski.[14] Calculated values of K_2 and K_B for 2-propanol at five temperatures are included in Table III.

An alternative to the Coggeshall and Saier[11] method for determining the two self-association equilibrium constants of 2-propanol is to use the data presented in Table II and employ an iterative least-squares fitting procedure to directly obtain the best fit to eq 4 (see ref 1, pp 191–196), which relates the fraction of free monomers, f_m^{OH}, to the dimensionless equilibrium constants, K_2 and K_B.

$$f_m^{OH} = \frac{\Phi_{B_1}}{\Phi_B} = \left[\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{(1 - K_B\Phi_{B_1})^2}\right)\right]^{-1} \tag{4}$$

A typical example is illustrated in Figure 4 for the 2-propanol–cyclohexane mixtures at 25 °C, and the calculated equilibrium constants at the five temperatures[23] are also included in Table III. The good agreement between the equilibrium constant values obtained from both methods is encouraging, and in view of the fact that the least-squares fitting procedure is more accurate and remarkably simple, it will be our method of choice for future studies.

Having obtained equilibrium constants at five different temperatures, we may calculate the enthalpies of hydrogen bond formation, h_2 and h_B, from the slope of a plot of ln K versus T^{-1} as illustrated in Figure 5. Values of −3.6 and −3.9 kcal/mol were obtained for h_2 and h_B, respectively.

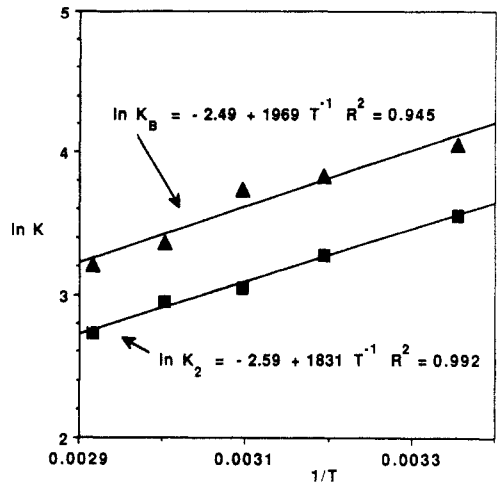


Figure 5. Van't Hoff plot of ln K versus $1/T$ for 2-propanol.

Table IV
Data for 2-Propanol–PME Mixtures in Cyclohexane

concn of PME (M)	intensity (absorbance)	f_m^{OH}	K_e (L/mol)
T = 25 °C			
0.303	0.082	0.830	0.71
0.604	0.071	0.719	0.66
0.905	0.065	0.658	0.58
1.207	0.055	0.557	0.67
1.506	0.050	0.506	0.65
T' = 60 °C			
0.303	0.079	0.894	0.41
0.604	0.073	0.826	0.35
0.905	0.069	0.781	0.31
1.207	0.062	0.701	0.35
1.506	0.054	0.611	0.42

2-Propanol–Phenyl Methyl Ether Mixtures. As we mentioned above, the Phenoxy specific repeat contains two aromatic aliphatic ether groups capable of forming hydrogen bonds with hydroxyl groups. From the dilute solution studies of 2-propanol in cyclohexane, we have obtained equilibrium constants that describe the self-association of secondary aliphatic hydroxy–hydroxyl groups. We now require an equilibrium constant that describes hydroxyl–ether interactions, and we can also obtain this parameter using the methodology of Coggeshall and Saier.[11] Using a constant dilute concentration (0.02 mol/L) of 2-propanol in cyclohexane, where initially the fraction of free monomers approaches unity, known molar concentrations of phenyl methyl ether (PME) are added. PME, a good model for the aromatic aliphatic ether groups in the Phenoxy polymer, hydrogen bonds to a fraction of the OH groups, and as a result the fraction of free monomers decreases with increasing concentration of PME, as dictated by the equilibrium constants describing hydroxyl–hydroxyl (K_{c_2} and K_c) and hydroxyl–ether (K_e) interactions. The appropriate equation after Coggeshall and Saier[11] is

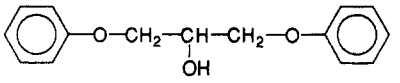
$$K_e = \frac{1 - f_m^{OH}}{f_m^{OH}[c_E - (1 - f_m^{OH})c_B]} \quad (5)$$

where c_E and c_B are the concentrations in moles/liter of PME and 2-propanol, respectively.

Table IV lists the data obtained for 2-propanol–PME mixtures in cyclohexane. Values for K_e obtained at 25 and 60 °C were determined to be 0.65 ± 0.07 and 0.37 ± 0.06 L/mol. This is equivalent to dimensionless equilibrium constants, K_E (equation 3), of 8.5 and 4.8, respectively (using the molar volume of 2-propanol as a reference volume). Note that the magnitude of K_E is considerably less than that of the equilibrium constants describing hydroxyl–hydroxyl interactions in 2-propanol (K_E = 8.5 versus K_2 = 33.4 or K_B = 60.6 at 25 °C). Using the equilibrium constant values at the two different temperatures, an estimate for the enthalpy of hydrogen bond formation between secondary aliphatic hydroxyl and aromatic/aliphatic ether groups was determined at h_E = −3.2 kcal/mol.

1,3-Diphenoxy-2-propanol. As it is not possible to dissolve Phenoxy in an inert diluent such as cyclohexane, we are unable to perform direct infrared experiments similar to those described directly on the polymer. However, an excellent model for the Phenoxy specific repeat, 1,3-diphenoxy-2-propanol (DPP), shown schematically below, is soluble in toluene, and our next task is to transfer the three equilibrium constants obtained above to DPP and determine whether or not they satisfactorily describe the self-association of this molecule by predicting the correct concentration dependence of the fraction of free monomers.

DPP



In past work[1,10] we have shown how we determine self-association equilibrium constants for polymers from the experimental values obtained from appropriate model compounds after adjusting for differences in the molar volumes of the model and the polymer *specific repeat*. For example, K_2 and K_B values for poly(vinylphenol) were simply scaled from the dimensionless equilibrium constants obtained for the model compound phenol using the relationship

$$K_B^* = K_B^{model}(V_B^{model}/V_B^*) \quad (6)$$

Implicit in this methodology is the assumption that the specific interaction sites are identical in both cases and that differences in molar volume between the model compound and the polymer specific repeat can be simply considered in terms of a change in concentration of the number of hydrogen-bonding groups per unit volume (i.e., a "dilution" effect).

The molar volume of DPP at 25 °C was estimated from group contributions in the following manner. As mentioned above, the molar volume of 2-propanol, 76.56 cm^3/mol, was obtained from density measurements. Using group molar volume constants,[1] the contribution from the CH(OH) group was estimated by subtracting two methyl group contributions from 2-propanol, to yield a value of 76.6 − 63.6 = 13.0 cm^3/mol. The molar volume of the DPP was then calculated from contributions of two CH_2, two ether, two monosubstituted phenyl, and one CH(OH) group molar constants to give a total of 207.2 cm^3/mol. Accordingly, values of K_2, K_B, and K_E for DPP are calculated (eq 6) to be 12.9, 21.3, and 3.1, respectively.

Although the algebra becomes more unwieldy, it is nonetheless a relatively straightforward task to extend the stoichiometric equations to include the three self-association equilibrium constants, K_2, K_B, and K_E, which describe, respectively, the formation of hydroxyl–hydroxyl dimers, hydroxyl–hydroxyl "chainlike" multimers, and hydroxyl–ether specific interactions; i.e.

$$B_1 + B_1 \overset{K_2}{\rightleftharpoons} B_2$$

$$B_h + B_1 \overset{K_B}{\rightleftharpoons} B_{h+1} \quad (h \geq 2)$$

$$B_h + E_1 \overset{K_E}{\rightleftharpoons} B_hE$$

The equations relating the fraction of free monomers to the three equilibrium constants are very similar to those derived previously (ref 1, pp 191–196), and it can be shown that (see Appendix)

$$f_m^{OH} = \Phi_{B_1}/\Phi_B \tag{7}$$

and

$$\Phi_B = \Phi_{B_1}\Gamma_2\left[1 + \frac{K_E\Phi_B X_E}{1 + K_E\Phi_{B_1}\Gamma_1}\right] \tag{8}$$

where

$$\Gamma_1 = \left(1 + \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{1 + K_B\Phi_{B_1}}\right) \tag{9}$$

$$\Gamma_2 = \left(1 + \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{(1 + K_B\Phi_{B_1})^2}\right) \tag{10}$$

and Φ_B and Φ_{B_1} are the volume fractions of B (DPP in this case) and isolated (non-hydrogen-bonded) B monomers, respectively. X_E is defined as the number of E functional groups located in B (2 in the case of DPP).[24] Equation 8 may be solved analytically, and we have added an option to our existing computer software package[1] that calculates the fraction of free monomers as a function of the volume fraction of B given values of K_2, K_B, K_E, and X_E. Alternatively, a least-squares fit of experimental f_m^{OH} data to eq 8 may be performed.

For the sake of argument let us initially ignore the potential hydroxyl–ether specific interaction and assume that hydroxyl–hydroxyl interactions dominate in describing the self-association of DPP. If this were true we should be able to directly calculate K_2 and K_B for DPP from the values obtained experimentally for 2-propanol and there should be good agreement between the theoretical predictions (eq 4) and the experimental fraction of free monomers, f_m^{OH}, determined in DPP–toluene mixtures of varying concentrations. Table V summarizes the data obtained from infrared studies of DPP–toluene mixtures, and Figure 6 shows the fraction of free monomers plotted as a function of the volume fraction of DPP compared to the theoretical curve calculated from eq 4 using the above values of K_2 = 12.9 and K_B = 21.3 for DPP derived from 2-propanol. There is a systematic deviation of the experimental values of f_m^{OH} from the theoretical curve, which is due to the fact that we have ignored the contribution from hydroxyl–ether interactions.

Figure 7 shows the result of a least-squares fit of the f_m^{OH} data for DPP–toluene mixtures (Table V) to eq 8. The values of K_2 and K_B were held constant at 12.9 and 21.3 (the values scaled previously from 2-propanol), respectively, while the value of K_E was allowed to vary so as to produce a best fit to the experimental data. Employing this methodology K_E was determined to be 3.1. This is precisely the same value that we obtained from the 2-propanol–PME mixtures in cyclohexane using Coggeshall and Saier's method. This is very encouraging as it demonstrates self-consistency, transferability of equilibrium constants, and the validity of a much simpler least-squares fitting method to obtain K_E.

Table V
Data for DPP–Toluene Mixtures at 25 °C

concn (M)	vol frac	f_m^{OH}	concn (M)	vol frac	f_m^{OH}
0.0114	0.00237	0.935	0.0694	0.01438	0.687
0.0162	0.00335	0.911	0.0765	0.01586	0.662
0.0213	0.00441	0.877	0.0973	0.02016	0.596
0.0272	0.00563	0.845	0.1245	0.02580	0.533
0.0310	0.00642	0.825	0.1382	0.02864	0.501
0.0391	0.00810	0.800	0.1611	0.03337	0.458
0.0423	0.00877	0.789	0.1743	0.03611	0.438
0.0489	0.01013	0.760	0.1948	0.04037	0.416
0.0580	0.01202	0.727			

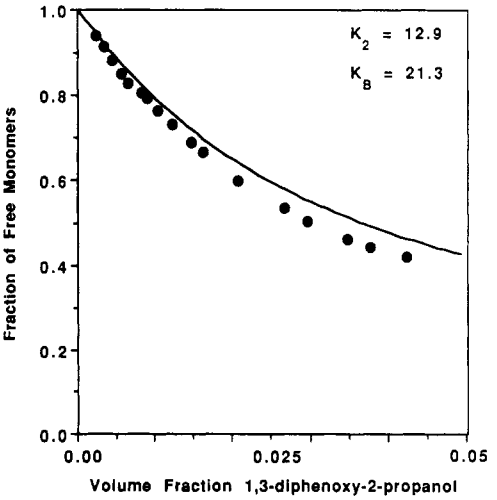


Figure 6. Graph showing a comparison of the theoretical curve (solid line) obtained using values of K_2 = 12.9 and K_B = 21.3 in eq 4 to the experimental fraction of free monomers versus concentration (●) for 1,3-diphenoxy-2-propanol in toluene at 25 °C.

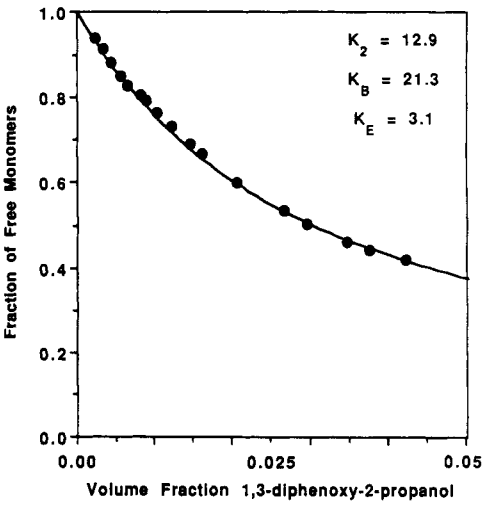


Figure 7. Graph showing the results of a least-squares fit of eq 8 (solid line) to the experimental fraction of free monomers versus concentration (●) for 1,3-diphenoxy-2-propanol in toluene at 25 °C. Values for K_2 = 12.9 and K_B = 21.3 were held constant and only K_E was permitted to vary.

Phenoxy Self-Association Equilibrium Constants. The molar volume of the specific repeat of the poly(hydroxy ether of Bisphenol A) calculated from group molar constants is 222.6 cm³/mol and the self-association equilibrium constants at 25 °C are now simply calculated from eq 6, yielding values of K_2 = 12.0, K_B = 19.8, and K_E = 2.9. The corresponding enthalpies of hydrogen bond formation are h_2 = −3.6, h_B = −3.9, and h_E = −3.2 kcal/mol, and values of the equilibrium constants at different temperatures may be calculated from the van't Hoff relationship.

Table VI
Curve Fitting Results for Phenoxy–PCL Blends at 75 °C

Phenoxy:PCL blend comp (wt %)	free C=O band ν (cm^{-1})	free C=O band $w_{1/2}$ (cm^{-1})	free C=O band area	HB C=O band ν (cm^{-1})	HB C=O band $w_{1/2}$ (cm^{-1})	HB C=O band area	$f_F^{C=O}$
90:10	1733	21.0	5.70	1715	30.1	3.01	0.706
80:20	1734	20.6	8.93	1715	30.1	3.88	0.745
70:30	1734	19.6	7.54	1715	29.2	2.61	0.786
60:40	1734	19.6	12.1	1715	28.6	3.41	0.819
50:50	1734	19.6	15.2	1715	28.5	3.58	0.844
40:60	1735	20.4	17.7	1715	28.0	3.22	0.875
30:70	1734	19.7	12.3	1715	28.0	1.73	0.901
20:80	1734	21.0	12.6	1715	28.0	1.37	0.921

Infrared Spectroscopic Studies of Phenoxy–PCL Blends. Typical infrared spectra of Phenoxy blends with PCL as a function of blend composition recorded in both the carbonyl and hydroxyl stretching regions at 75 °C (above the T_m of PCL) have been previously published.[18] For our purposes here we will be focusing attention on the carbonyl stretching region, where the infrared band attributed to the interaction involving the PCL carbonyl group and the hydroxyl group of Phenoxy is well separated (~20 cm^{-1}) from that of the free (non-hydrogen-bonded) PCL carbonyl group. The bands still overlap, however, and, in contrast to the spectra obtained from the analogous poly(vinylphenol) blends,[1] are not well resolved. This makes quantitative analysis of the fraction of free or hydrogen-bonded carbonyl groups from the infrared spectra more difficult, but with intelligent use of modern curve fitting methods reliable measurements can be obtained.

Table VI lists typical curve fitting results from infrared spectra of Phenoxy–PCL blends recorded at 75 °C that we obtained using a curve fitting program developed in our laboratory. Initially, we recorded the spectrum of pure PCL in the carbonyl stretching region at 75 °C using 12 different samples from which we determined the position (ν = 1734 ± 1 cm^{-1}), shape (s = 0.5 Gaussian—see ref 1, p 238), and width at half-height ($w_{1/2}$ = 20.2 ± 1.3 cm^{-1}) for the free carbonyl band. Next, after carefully setting the baseline, we curve resolved the experimental spectra of the blends of different compositions recorded at 75 °C using two bands between the limits of 1700 and 1750 cm^{-1}. The first, that of the free (non-hydrogen-bonded) carbonyl band, was initially set at ν = 1734 cm^{-1}, s = 0.54, and $w_{1/2}$ = 20.2, and during the least-squares fitting procedure the frequency and width at half-height were permitted to vary only within the strictly narrow limits of ±1 cm^{-1}, while the shape was not permitted to vary. Following comprehensive preliminary curve fitting studies, the second band, attributed to hydrogen-bonded carbonyls, was fixed at a Gaussian band shape and was permitted to vary in the least-squares fitting procedure between the limits of ν = 1715 ± 1 cm^{-1} and $w_{1/2}$ = 29 ± 2 cm^{-1}. An excellent fit of the experimental spectra data was observed using this procedure, and the results are summarized in Table VI.

From the areas of the two bands we can readily obtain the fraction of free carbonyl groups, $f_F^{C=O}$, if we have a knowledge of the absorptivity ratio reflecting the difference in the absolute absorptivities of the free and hydrogen-bonded carbonyl bands.[1] Garton[22] had previously determined the absorptivity ratio in Phenoxy–ester blends to be 1.23, and in the present study we obtained a similar value of 1.27 ± 0.06. Table VI also includes the $f_F^{C=O}$ calculated employing this value of the absorptivity ratio. Using the methodology described above, the $f_F^{C=O}$ was determined for the Phenoxy–PCL blends at 75, 105, 135, 165, and 195 °C, and these results are presented in Table VII.

Table VII
Fraction of Free Carbonyls for Phenoxy–PCL Blends

vol frac of Phenoxy	fraction of free carbonyl groups 75 °C	105 °C	135 °C	165 °C	195 °C
0.889	0.706	0.756	0.776	0.790	0.813
0.780	0.745	0.783	0.811	0.833	0.847
0.674	0.786	0.807	0.830	0.847	0.861
0.571	0.819	0.840	0.842	0.853	0.869
0.470	0.844	0.856	0.870	0.874	0.882
0.372	0.874	0.876	0.885	0.892	0.897
0.276	0.901	0.909	0.911	0.910	0.914

Table VIII
Equilibrium Constants and Enthalpy of Hydrogen Bond Formation for Phenoxy–Polyester Blends

temp (°C)	Phenoxy self-association equilibrium constants K_2	K_B	K_E	interassociation K_A
25	12.0	19.8	2.9	7.9
75	5.0	7.7	1.3	3.0
105	3.3	4.9	0.92	1.8
135	2.3	3.4	0.68	1.2
165	1.7	2.4	0.52	0.92
195	1.3	1.8	0.41	0.69
	h_2^a = −3.6	h_B^a = −3.9	h_E^a = −3.2	h_A^a = −3.9

[a] In kcal/mol.

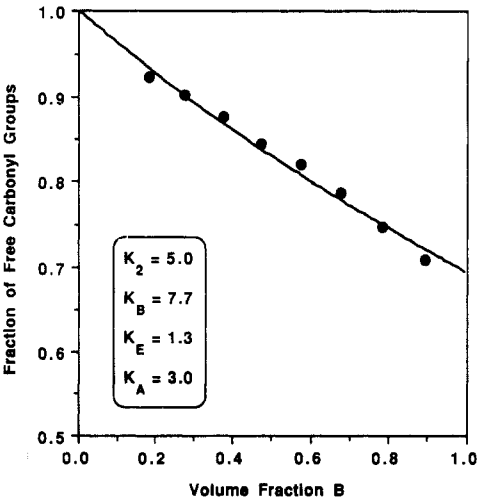


Figure 8. Graph showing the least-squares fitting of the stoichiometric equations to experimental results for the determination of K_A for Phenoxy–PCL blends at 75 °C.

Determination of Interassociation Equilibrium Constants. We now consider the determination of the interassociation equilibrium constant, K_A, between polymer mixtures containing the Phenoxy hydroxyl group and aliphatic ester type functionalities. The method employed here was identical to the method we have previously used to determine K_A values for PVPh blends with polymers containing methacrylate, acrylate, ester, and acetoxy groups,[1] except that in this case we have to use three equilibrium constants, K_2, K_B, and K_E, to describe the self-association of Phenoxy. K_A is determined from a least-squares fitting of the stoichiometric equations (see Appendix) to the $f_F^{C=O}$ data as a function of volume fraction of Phenoxy in the blends. The enthalpies of hydrogen bond formation and the three equilibrium constants for the self-association of Phenoxy at various temperatures are listed in Table VIII, and Figure 8 shows the result of the least-squares fit for the Phenoxy–PCL blends at 75 °C, which yields a value of K_A = 3.0. From

Table IX
Molar Volume and Solubility Parameters Employed

segment	molar vol (cm^3/mol)	solubility param $(cal\ cm^{-3})^{0.5}$
Phenoxy	222.6	10.2
PCL	102.1	9.4
$(CH_2)_6COO$	118.6	9.2
$(CH_2)_7COO$	135.1	9.1
$(CH_2)_8COO$	151.6	8.9
DMP	60.5	9.9
CDM	76.7	10.1
PPL	84.9	9.1
PMMA	84.9	9.1
PEMA	101.4	8.9
CH_2	16.5	8.0

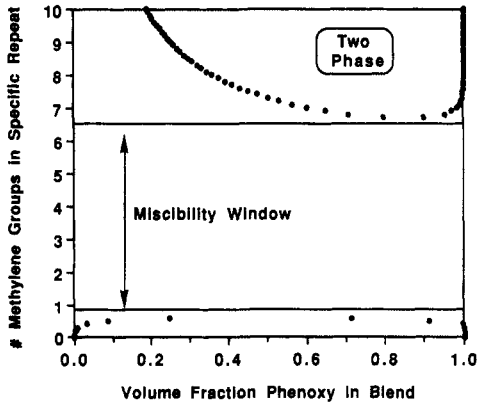


Figure 9. Miscibility window calculated at 25 °C for Phenoxy blends with a homologous series of aliphatic polyesters.

a similar plots, values of K_A = 1.8, 1.2, 0.92, and 0.69 were determined at 105, 135, 165, and 195 °C. A van't Hoff plot of ln K_A versus T^{-1} yields an enthalpy of hydrogen bond formation h_A = −3.9 kcal/mol. Accordingly, the equivalent equilibrium constant at our reference temperature of 25 °C is K_A = 7.9. A complete summary is included in Table VIII.

Calculation of Phase Diagrams and Miscibility Windows. Armed with equilibrium constants describing self-association and interassociation and the corresponding enthalpies of hydrogen bond formation, we are now in a position to calculate theoretical phase diagrams and miscibility windows and compare the predictions to experimental observations that are in the published literature. We have recently presented a general discussion of the calculation of phase diagrams, miscibility windows, and maps for polymer blend systems involving hydrogen bonds.[1] Computer software is available to calculate these diagrams,[1] but we have had to modify the program to accommodate the particular case of the Phenoxy self-association that requires three equilibrium constants. The necessary equations describing the free energy for this particular case are included in the Appendix. Note that we use carefully defined solubility parameters to determine non-hydrogen-bonding or "physical" interactions, which we calculate using group contributions determined in our laboratories.[1] Table IX summarizes the values of the parameters employed.

We commence by presenting in Figure 9 the theoretical predictions of the miscibility window calculated at 25 °C for Phenoxy blends with aliphatic polyesters. It is important to recognize that in our methodology we make no distinction between the specific repeat of say a homopolylactone containing n methylene groups and the average specific repeat of a copolymer containing the same number of methylenes per ester group. For example, the specific repeats of poly(γ-butyrolactone) and poly(ethylene adipate) both contain one ester and three methylene (n = 3) groups:

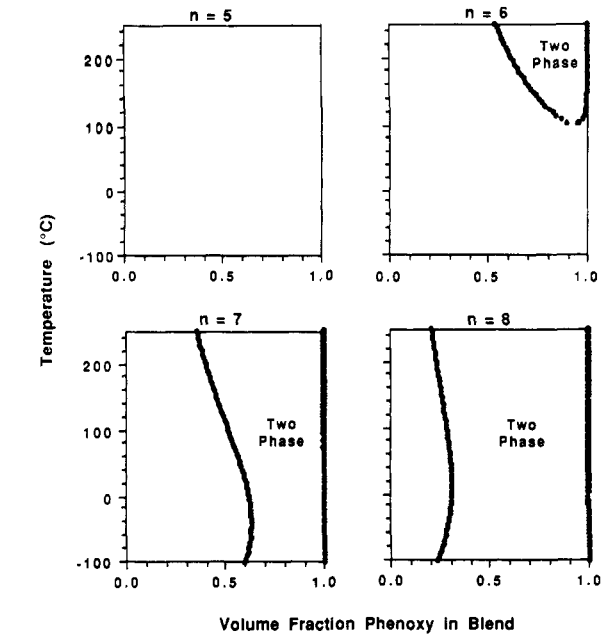
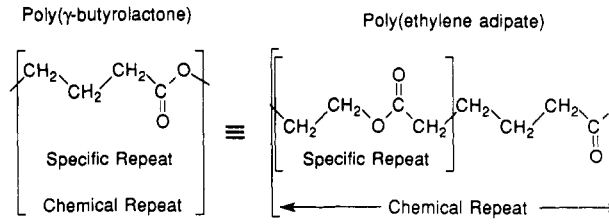


Figure 10. Calculated binodal phase diagrams for Phenoxy–aliphatic polyester blends (n = number of methylenes in specific repeat).



In the model we have employed it is the number of hydrogen-bonding groups per unit volume that is the crucial factor. Returning to Figure 9, on the x-axis is the volume fraction of Phenoxy in the blend, while on the y-axis is the number of methylene groups in the polyester specific repeat unit. The Phenoxy polymer is predicted to be miscible in the amorphous state with aliphatic polyesters containing from 2 to 6 methylenes in the specific repeat (a polyester containing 1 methylene per specific repeat is predicted to be "on the edge of miscibility"). This is in reasonable agreement with the experimental results of Harris et al.,[19] where poly(ethylene adipate) (n = 3), poly(1,4-butylene adipate) (n = 4), and poly(ε-caprolactone) (n = 5) were reported to be miscible, but poly(hexamethylene sebacate) (n = 7) was not. Only for poly(ethylene succinate) (PES) (n = 2) is there any discrepancy between theoretical prediction and experimental observations, but this system was not studied in any detail by Harris et al.,[19] who described it as immiscible solely on the basis of physical appearance above the melting point of PES.

Figure 10 shows theoretical binodal phase diagrams over the temperature range of −100 to +250 °C for four Phenoxy blends with aliphatic polyesters containing from 5 to 8 methylenes in the specific repeat unit. The first, n = 5, which corresponds to PCL (or its average ester-reversed analogue), is predicted to be completely miscible over the entire temperature range. One more methylene group in the specific repeat, n = 6, leads to the presence of a two-phase region in blends rich in Phenoxy at temperatures above 100 °C. Further addition of methylenes, n = 7 and n = 8, yields phase diagrams characteristic of

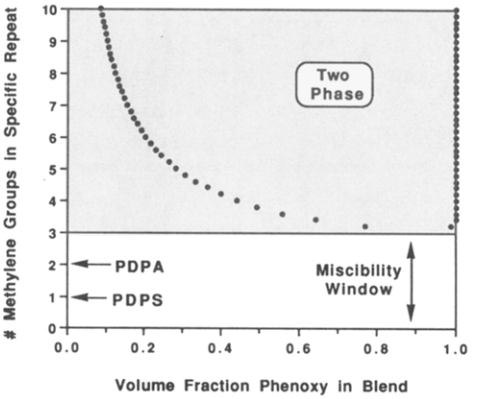


Figure 11. Miscibility window calculated at 25 °C for Phenoxy blends with a homologous series of DMP copolymers (see text).

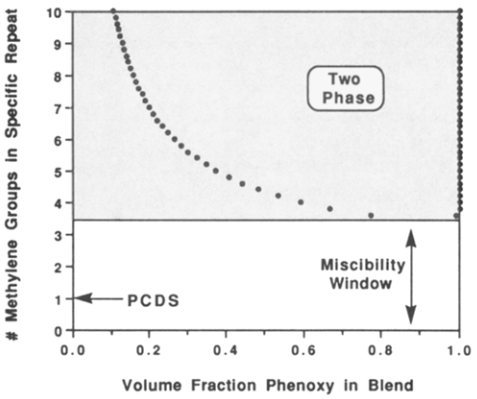
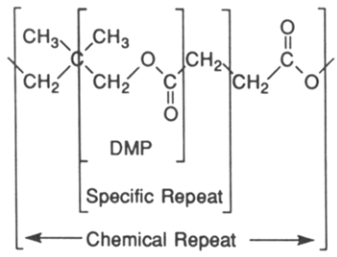


Figure 12. Miscibility window calculated at 25 °C for Phenoxy blends with a homologous series of CDM copolymers (see text).

immiscible systems, where a two-phase region extends throughout the entire temperature range. The most striking feature of this series of phase diagrams is the enormous effect that just one additional methylene group in the specific repeat unit of the polymer can have upon phase behavior.

In their paper Harris et al.[19] also considered Phenoxy blends with other, more chemically complicated, aliphatic polyesters. These can be readily handled using our methodology because we have all the equilibrium constants and group contribution data necessary to calculate phase diagrams and miscibility windows. Two of the polyesters, poly(2,2-dimethyl-1,3-propylene succinate) (PDPS) and poly(2,2-dimethyl-1,3-propylene adipate) (PDPA), can be considered to be the first two polymers of a homologous series, and it is convenient to calculate and view the miscibility behavior of such polymers in blends with Phenoxy in terms of a theoretical miscibility window. The chemical repeat of PDPS, shown below, contains 2 CH_3, 4 CH_2, 2 ester, and 1 >C< groups. The specific repeat unit, which is defined in terms of the average unit containing one ester group, is thus half that of the chemical repeat.

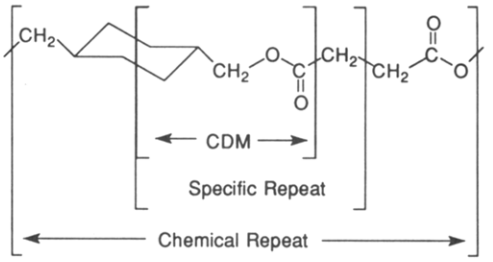
Poly(2,2-dimethyl-1,3-propylene succinate)



For convenience we will calculate a miscibility window at 25 °C by systematically adding methylene groups to the segment DMP (see above) which consists of 1 CH_3, 1 CH_2, 1 ester, and 0.5 >C< groups. Accordingly, if we add 1 CH_2 to DMP, we obtain the specific repeat of PDPS, 2 CH_2's that of PDPA, etc. The parameters used are given in Table IX, and the theoretical miscibility window is presented in Figure 11. The predicted range of miscibility extends from 0 to 3 methylene groups, and both PDPS (n = 1) and PDPA (n = 2) are predicted to be miscible, which is in agreement with the experimental observations of Harris et al.[19]

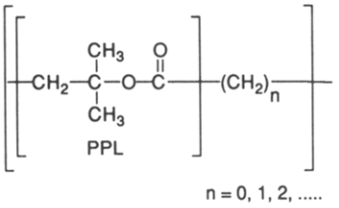
In a similar fashion poly(1,4-cyclohexanedimethanol succinate) (PCDS) can be viewed as the first in a homologous series of polymers defined in terms of systematically adding methylene groups to the segment CDM (see below) that is composed of 1 CH_2, 1 ester, and 0.5 disubstituted cyclohexane groups. Again, the parameters required for our calculations are listed in Tables VIII and IX, and the theoretical miscibility window is shown in Figure 12. The predicted range of miscibility extends from 0 to approximately 3.5 methylene groups and PCDS (n = 1) is predicted to be miscible, which is also in agreement with experiment.[19]

Poly(1,4-cyclohexane-dimethanol succinate)



Harris and co-workers[19] also considered Phenoxy blends with one final aliphatic polyester, polypivalolactone (PPL), and it was concluded that the system was immiscible based primarily upon the observations that in the melt the blend remained opaque and that no melting point depression of PPL (T_m = 234 °C) was detected. Important trends in the phase behavior of polymer blends are best visualized using miscibility windows, as we will illustrate here. Consider the hypothetical copolymer poly(pivalolactone-*co*-methylene) shown schematically below:

Poly(pivalolactone-co-methylene)



Naturally, when n = 0, we have the PPL polymer. For n = 1, we now have a specific repeat that is composed of 2 CH_3, 2 CH_2, 1 ester, and 1 >C< groups. How these groups are arranged, within the bounds of chemical reason, is unimportant in our methodology. For example, this specific repeat contains the same number and type of groups as poly(ethyl methacrylate) (PEMA). Similarly, the specific repeat of PPL is the same as that of PMMA. Figure 13 shows the theoretical miscibility window for Phenoxy–poly(pivalolactone-*co*-methylene) blends (n = 0–10) calculated at 240 °C (above the T_m of PPL). At this

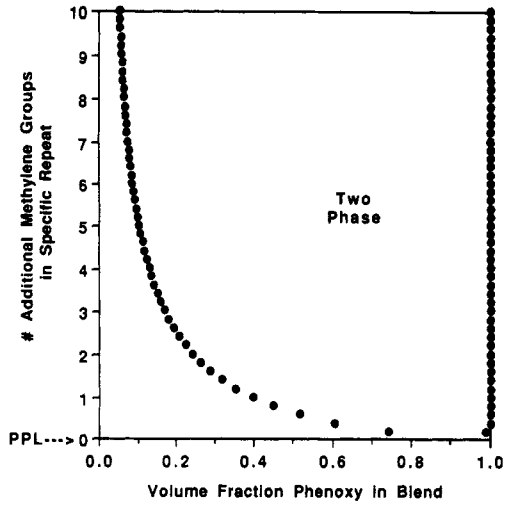


Figure 13. Miscibility window calculated at 240 °C for Phenoxy blends with a homologous series of PPL copolymers (see text).

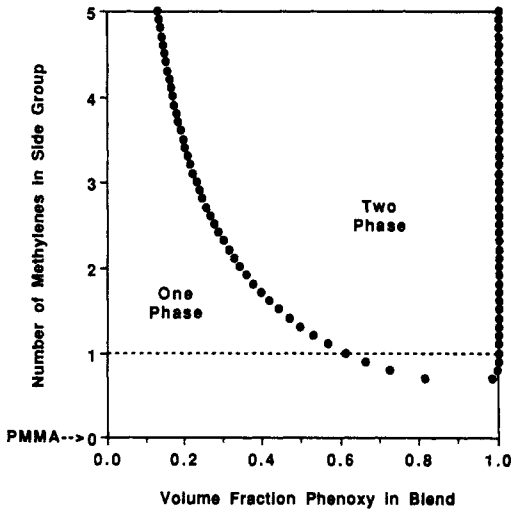


Figure 14. Miscibility window calculated at 100 °C for Phenoxy blends with a homologous series of poly(*n*-alkyl methacrylates).

temperature, for all intent and purposes, Phenoxy–PPL blends and all the other blend systems considered are predicted to be immiscible.

This leads conveniently to the more recent studies pertaining to Phenoxy–PMMA blends. Chiou and Paul[21] report that Phenoxy–PMMA blends are miscible and exhibit cloud points at temperatures in the range 280–330 °C, although they correctly caution that chemical reactions may complicate matters at these high temperatures. The miscibility of the Phenoxy–PMMA blend system has been confirmed by Espi and Iruin.[20] Using the values of the parameters listed in Tables VIII and IX, we can readily calculate a theoretical miscibility window for a series of poly(*n*-alkyl methacrylates)[1] by simply incrementally adding methylene groups to PMMA, as shown in Figure 14. [Note we have assumed values of K_A and h_A for Phenoxy–methacrylate interactions that are the same as those for Phenoxy–ester interactions, but we do not anticipate that this will introduce serious errors.[1]] This miscibility window, calculated at 100 °C, above the T_g of the blends, successfully predicts the miscibility of Phenoxy–PMMA blends. It also predicts a very narrow range of miscibility and indicates that PEMA and the higher homologues should be immiscible. This latter prediction has not yet been experimentally tested and would provide an additional test of the validity of our approach.

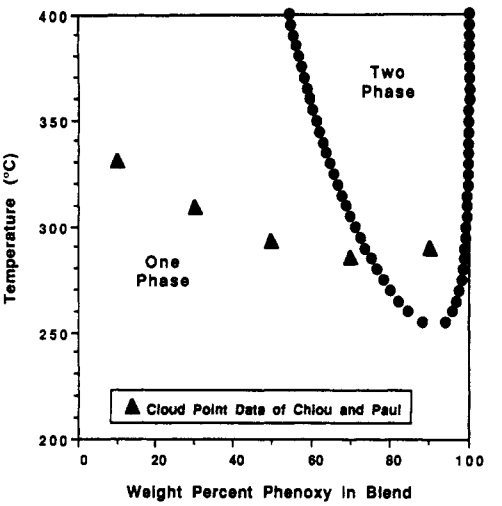


Figure 15. Comparison of cloud point data to the calculated binodal phase diagram for Phenoxy–PMMA blends between 200 and 400 °C.

Finally, we show in Figure 15 the theoretical binodal phase diagram of Phenoxy–PMMA blends calculated over the temperature range 200–400 °C. Our calculations predict a critical point occurring at approximately 240 °C at a composition rich in Phenoxy. Superimposed are the cloud point observations of Chiou and Paul.[21] In truth, given the assumptions of the association model and the errors inherent in the determination of equilibrium constants, enthalpies of hydrogen bond formation, and solubility parameters, we have to believe that the fine agreement between the calculated LCST and experimental cloud point observation is to some degree fortuitous. We now anticipate being able to predict which system has an LCST in the accessible range of temperature and to get within 100 °C or so of the experimental LCST, but the above observed agreement seems just too good to be true. Nevertheless, we could not resist the temptation to include this figure.

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Appendix

We adopt here the nomenclature listed in our preceding publications, to which the interested reader is referred.[1] Certain new quantities are introduced and will be defined here. Essentially, our equations need to be modified to account for hydrogen bonding between OH and ether groups in one of the pure components. We will let K_E be the equilibrium constant describing this interaction. Then in pure Phenoxy the equations describing the stoichiometry of the system are

$$\Phi^\circ_B = \Phi^\circ_{B_1}\Gamma^\circ_2\left[1 + \frac{K_E\Phi^\circ_{E_1}}{r_E}\right] \quad \text{(A1)}$$

$$\Phi^\circ_E = \Phi^\circ_{E_1}[1 + K_E\Phi^\circ_{B_1}\Gamma^\circ_1] \quad \text{(A2)}$$

where Φ°_E is the volume fraction of ether oxygen containing segments in the molecule or polymer specific repeat unit under consideration and $\Phi^\circ_{E_1}$ is the volume fraction of the ether groups that are not hydrogen bonded. This suggests that one approach is to somehow divide the molecule into segments such that each segment contains just one hydroxyl group or one ether oxygen. This is not necessary, however, because it is possible to demonstrate a relationship between Φ_B and Φ_E as follows. If X_E is the number

of ether functional groups in one B molecule or specific repeat unit, then

$$\Phi_E = \frac{n_E V_E}{V_T} = \frac{n_B X_E V_E}{V_T} = \frac{n_B V_B X_B r_E}{V_T} = \Phi_B X_E r_E \quad \text{(A3)}$$

where

$$r_E = V_E/V_B \quad \text{(A4)}$$

It follows that

$$\frac{\Phi^\circ_{E_1}}{r_E} = \frac{\Phi^\circ_B X_E}{1 + K_E \Phi_{B_1} \Gamma^\circ_1} \quad \text{(A5)}$$

In a mixture with molecules of A that can also hydrogen bond to the B unit (e.g., esters), we then have

$$\Phi_B = \Phi_{B_1} \Gamma_2 [1 + X_1 + X_2] \quad \text{(A6)}$$

$$\Phi_E = \Phi_{E_1} [1 + K_E \Phi_{B_1} \Gamma_1] \quad \text{(A7)}$$

$$\Phi_A = \Phi_{A_1} [1 + K_A \Phi_{B_1} \Gamma_1] \quad \text{(A8)}$$

where

$$X_1 = K_E \Phi_{E_1}/r_E \quad \text{(A9)}$$

$$X_2 = K_A \Phi_{A_1}/r_A \quad \text{(A10)}$$

The contribution of hydrogen bonding to the free energy of mixing is now given by

$$\frac{\Delta G_H}{RT} = \Phi_B \ln\left(\frac{\Phi_{B_1}}{\Phi^\circ_{B_1}}\right) + \frac{\Phi_E}{r_E} \ln\left(\frac{\Phi_{E_1}}{\Phi^\circ_{E_1}}\right) + \frac{\Phi_A}{r_A} \ln \Phi_{A_1} + \Phi_B \left[\left[\frac{\Gamma^\circ_1}{\Gamma^\circ_2} - \frac{\Gamma_1}{\Gamma_2} \right] + \frac{\Gamma_1}{\Gamma_2} \left(\frac{X_1 + X_2}{1 + X_1 + X_2} \right) - \frac{\Gamma^\circ_1}{\Gamma^\circ_2} \left(\frac{X^\circ_1}{1 + X^\circ_1} \right) \right] - \left[\frac{\Phi_B}{n^\circ_{B_h}} \ln \Phi_B + \frac{\Phi_A}{r_A} \ln \Phi_A \right] \quad \text{(A11)}$$

The chemical potentials and spinodal can be obtained from this equation by numerical calculation or by analytical solutions, derived in the same manner as in previous work.[1]

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(23) Although the effect is marginal, minor corrections to the volume fraction of 2-propanol in cyclohexane as a function of temperature were made to reflect the difference in the temperature dependence of the densities of the two molecules.[14,15]
(24) For polymers, such as Phenoxy, B is defined here in terms of the specific repeat containing one hydroxyl group (see Introduction) and X_E is again 2.

Registry No. PCL (homopolymer), 24980-41-4; PCL (SRU), 25248-42-4; DPP, 622-04-8; PDPS (copolymer), 28257-92-3; PDPS (SRU), 28776-65-0; PDPA (copolymer), 27925-07-1; PDPA (SRU), 28039-87-4; PCDS (copolymer), 60836-39-7; PCDS (SRU), 60806-40-8; PPL (homopolymer), 24969-13-9; PPL (SRU), 24937-51-7; PMMA, 9011-14-7; PEMA, 9003-42-3; PME, 100-66-3; $HO(CH_2)_6CO_2H$ (homopolymer), 28574-36-9; $HO(CH_2)_6CO_2H$ (SRU), 28576-62-7; $HO(CH_2)_7CO_2H$ (homopolymer), 142189-46-6; $HO(CH_2)_7CO_2H$ (SRU), 28212-16-0; $HO(CH_2)_8CO_2H$ (homopolymer), 142189-47-7; $HO(CH_2)_8CO_2H$ (SRU), 32201-85-7; 2-propanol, 67-63-0; cyclohexane, 110-82-7; toluene, 108-88-3; phenoxy, 25068-38-6.