the slow translational motions of larger particles (high molecular weight polymer fractions) are influenced by the very slight differences between the base line and the tail of the net intensity–intensity time correlation function, $\lim_{t\to\infty} b|g^{(1)}(K,t)|^2$, resulting in a larger than expected high molecular weight tail. A plot of $F_{w,cum}$ $[=\int_0^M F_w(M)\,dM]$ vs $M$ clearly shows that the high molecular weight tail is within the experimental error limits of $\sim$1–2%. The answer is that there could be very high molecular weight fractions ($M > \sim 3 \times 10^7$ g/mol); but these very high molecular weight fractions are within the experimental uncertainties; i.e., our light scattering measurements cannot confirm the existence of a high molecular weight tail. The sharp cutoff in the low molecular weight limits also represents a limitation of the light scattering technique since it cannot "see" small particles well because of their much lower scattering power. Our results put a weight-average emphasis on the MWD when compared with MWD determined by SEC. Nevertheless, we have been able to refine our characterization of PETFE which cannot be studied by more standard techniques and to provide reasonable macromolecular parameters for such an intractable polymer.

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**Registry No.** PETFE (alternating copolymer), 111939-51-6.

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# Group Contribution Methods for Predicting Polymer–Polymer Miscibility from Heats of Mixing of Liquids. 2. Polyester-Containing Binary Blends

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ABSTRACT: A modified Guggenheim quasi-chemical method is used to predict the heats of mixing and miscibility of polymer blend components from binary interactions between the various structural groups which comprise the polymer repeat units. The predictions are found to compare well with experimental observations for blends of aliphatic polyesters with bisphenol A polycarbonate (PC), with the poly(hydroxy ether) of bisphenol A, and with tetramethylbisphenol A polycarbonate. For these systems, the variation of miscibility with polyester structure is correctly predicted, although the magnitudes of the predicted interactions often disagree with experimental values. This method also successfully predicts the miscibility of PC with poly(methyl methacrylate) (PMMA) and the miscibility of PMMA with poly(ethylene oxide).

## Introduction

In the first paper of this series,[1] a modified Guggenheim quasi-chemical (MGQ) group contribution method was introduced and examined for its ability to predict heats of mixing of both liquids and polymer repeat units. The interest in so doing is related to experimental observations that polymer–polymer miscibility requires an exothermic heat of mixing between the polymer repeat units, to a first approximation, and that heats of mixing between repeat units are very similar to those between low molecular weight liquids with similar structures.[2-13] These observations suggest that a thermodynamic model, which can predict exothermic heats of mixing for liquid mixtures with a minimum number of structurally based parameters, could be useful for predicting polymer–polymer miscibility. The MGQ model has this capability, and it is found to correlate and to predict, to within 9% relative error, heats of mixing for a wide variety of ester, alkane, and chlorinated hydrocarbons.[1] The group interaction parameters obtained from these data for liquids are able to predict the heats of mixing of repeat units of various aliphatic polyesters with poly(vinyl chloride). Good agreement is observed in both magnitude and sign between the heat of mixing behavior predicted from the group interaction parameters and that observed through polyester melting point depression studies in the polymer blends.

This paper broadens the application of the MGQ model to miscibility predictions for more complex molecules, including aliphatic polyesters with bisphenol A polycarbonate (PC), with tetramethylbisphenol A polycarbonate; and with the poly(hydroxy ether) of bisphenol A (Phenoxy). Predictions of the phase behavior of blends containing poly(methyl methacrylate) (PMMA) with PC and with poly(ethylene oxide) (PEO) are also examined.

## Summary of the MGQ Method

**Thermodynamic Model.** The MGQ model used in this work has been developed in detail elsewhere[1] and will only be summarized here. The model assumes that each molecule can be divided into structural units, a $CH_2$ group, for example, so that even a pure material is a mixture of interacting structural groups. The observed heat of mixing of pure liquids is then the enthalpy change associated with all of the binary interactions between unlike groups in the mixture minus the enthalpy changes associated with the "self-interactions" of the pure components, a calculation

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which is conceptually identical with binary interaction models presented by others.[12-16] The MGQ model differs from the others by also taking into account the "nonrandomness" of the mixing process through use of the Guggenheim quasi-chemical assumption[17] and by considering the mixing to occur between the surface fractions of the structural groups instead of between volume fractions.

The expression for the heat of mixing is

$$\Delta H_{\text{mix}} = z\sum_{i}\sum_{j>i}[\sum_{m} n_m q_m]\Gamma_{ij}\Delta E_{ij}\Theta_i\Theta_j - z\sum_{k}\sum_{i}\sum_{j>i}[\sum_{m} q_m n_m^{(k)}]\Gamma_{ij}^{(k)}\Delta E_{ij}\Theta_i^{(k)}\Theta_j^{(k)} \quad (1)$$

In the above equation, $i$, $j$, and $m$ are counters for the structural groups in the system and $k$ is the counter for pure component molecules in the system; $\Delta E_{ij}$ is the exchange energy associated with the formation of an $i$–$j$ contact; $n_m$ and $n_m^{(k)}$ are the number of $m$ groups in the mixture and in molecule $k$, respectively; $\Theta_i$ and $\Theta_i^{(k)}$ are the surface fractions of group $i$ in the mixture and in molecule $k$, respectively; $q_m$ is the surface area of structural group $m$; and $z$ is the number of coordinating neighbors per unit surface area. Following the work of Abrams and Prausnitz,[18] $z$ is set equal to 10 and $q_m$ is estimated by the equation

$$q_m = A_{wm}/(2.5 \times 10^9) \quad (2)$$

where $A_{wm}$ is the van der Waals surface of group $m$ (in $cm^2/mol$) given by Bondi.[19]

The nonrandom factor in eq 1 is designated by $\Gamma_{ij}$ in the mixture and by $\Gamma_{ij}^{(k)}$ in molecule $k$. This parameter was introduced into the original Guggenheim quasi-chemical theory as a calculational convenience by Paniyiotou and Vera.[20] In a system containing $f$ different structural groups, calculation of the $\Gamma_{ij}$ parameters requires the simultaneous solution of $f(f-1)/2$ equations, each of the form

$$\frac{\Gamma_{ij}^2\Theta_i\Theta_j}{(1 - \sum_{j\neq i}\Theta_j\Gamma_{ij})(1 - \sum_{i\neq j}\Theta_i\Gamma_{ij})} = K_{ij} \quad (3)$$

where $\Gamma_{ij} = \Gamma_{ji}$ and where $K_{ij}$ is the quasi-chemical equilibrium constant for the interaction of $i$ groups with $j$ groups.

Using standard statistical mechanical arguments, Guggenheim[17] showed that

$$K_{ij} = \exp(-2\Delta E_{ij}/RT) \quad (4)$$

where $T$ is the absolute temperature and $R$ the gas constant. Our empirical modification to the Guggenheim theory, the MGQ model, considers $K_{ij}$ to be a "true" chemical equilibrium constant, which follows

$$K_{ij} = \exp(-2\Delta G_{ij}/RT) = \exp(2\Delta S_{ij}/R)\exp(-2\Delta E_{ij}/RT) = A_{ij}\exp(-2\Delta E_{ij}/RT) \quad (5)$$

where $\Delta G_{ij}$ is the change in Gibbs free energy and $\Delta S_{ij}$ the change in entropy associated with the $i$–$j$ interaction. The MGQ model thus requires two parameters, $A_{ij}$ and $\Delta E_{ij}$, to describe each binary interaction between structural groups. The additional parameter per interacting pair in the MGQ model, relative to Guggenheim's original theory, may be responsible for the MGQ model's superior ability to fit a wide range of heats of mixing with minimum error.[1]

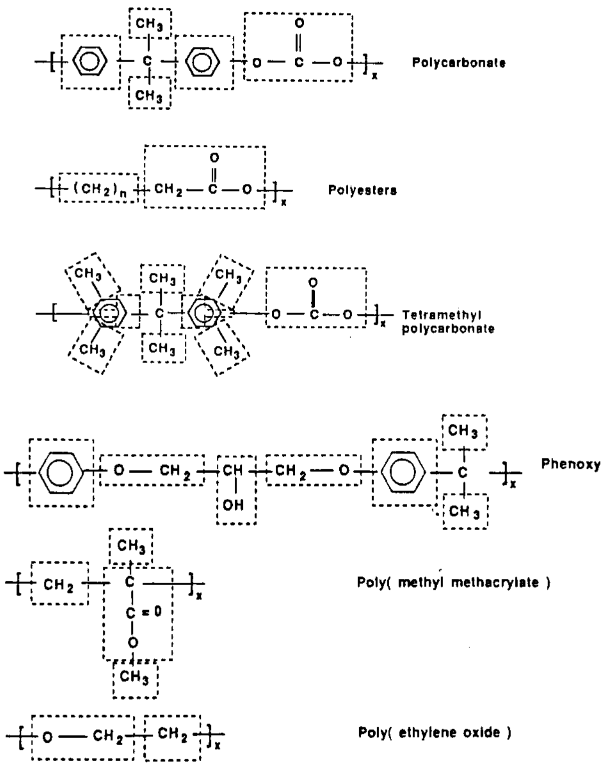

**Figure 1.** Polymer repeat units and structural groups.

**Table I**
**Surface Parameters**

| class | type | $q_m$ | class | type | $q_m$ |
|---|---|---|---|---|---|
| $CH_2$ | $CH_3$ | 0.848 | $CH_2OH$ | $CH_2OH$ | 1.124 |
| | $CH_2$ | 0.54 | | CHOH | 0.812 |
| | CH | 0.228 | $CH_2COO$ | $CH_2COO$ | 1.420 |
| | C | 0.0 | | CCOO | 0.880 |
| PhCH | PhCH | 0.400 | COOO | COOO | 1.120 |
| | PhC | 0.120 | $OCH_2$ | $OCH_2$ | 0.780 |

**Application.** Before one can estimate the enthalpic interactions between polymers, one must divide the repeat units of the polymers into structural groups. The parameters, $\Delta E_{ij}$ and $A_{ij}$, for each unlike binary pair of groups are then determined from correlation of heats of mixing data for solutions of liquids which contain the structural groups of interest.

The MGQ model follows UNIFAC[21] and UNIQUAC[18] in setting choices of structural groups, where possible. While these choices are not the only choices that could be used in a group contribution method, they are generally reasonable, and there is no compelling reason to choose otherwise. Figure 1 and Table II show these choices for the polymers of interest to this discussion. UNIFAC sorts structural groups into classes for the purpose of differentiating between types of groups while keeping the numbers of individual classes to be considered relatively low. Each member of a class is assumed to interact identically with groups outside the class, and the only difference between members in a class is their surface size, $q_m$. For example, structural groups of the type $CH_3$, $CH_2$, CH, and C are all considered to be members of class $CH_2$. Each of these units is assumed to have the same $A_{ij}$ and $\Delta E_{ij}$ for interaction with unlike group $j$, but their sizes vary considerably as noted in Table I. Since UNIFAC has not considered carbonate structures and offers no guidance, we have specified this group as COOO. The rest of the choices, however, are consistent with those in UNIFAC, with the possible exception of the CHOH group which occurs in the Phenoxy molecule, Figure 1. Due to the lack of a sufficient amount of experimental heats of mixing for branched alcohols with other materials, we have had to assume that the CHOH group is in the same general class as the same general class as the $CH_2OH$ group. We have also assumed

Table II
Summary of MGQ Parameters

| $i/j$ | systems studied | data pts | sources | $A_{ij}$ | $\Delta E_{ij}$, cal/mol | rms error, % |
|---|---|---|---|---|---|---|
| $CH_2/COOO$ | 2 | 8 | Table III | 0.916 | 282.2 | 2 |
| $PhCH/COOO$ | 1 | 6 | Table III | 2.033 | 111.9 | 3 |
| $PhCH/CH_2COO$ | 1 | 5 | Table III | 1.049 | 17.4 | 6 |
| $CH_2COO/COOO$ | 2 | 9 | Table III | 1.526 | 35.1 | 4 |
| $CH_2/OCH_2$ | 5 | 46 | ref 23, 24 | 0.612 | 70.3 | 14 |
| $CH_2/CH_2OH$ | 15 | 136 | ref 25, 26 | 14.17 | 3837 | 9 |
| $PhCH/OCH_2$ | 2 | 9 | Table III | 0.129 | 14.3 | 47 |
| $PhCH/CH_2OH$ | 6 | 53 | ref 27-29 | 9.643 | 3550 | 11 |
| $CH_2COO/OCH_2$ | 1 | 8 | ref 35 | 0.700 | −46.5 | 2 |
| $CH_2COO/CH_2OH$ | 8 | 130 | ref 31-33 | 0.546 | 163.4 | 5 |
| $OCH_2/CH_2OH$ | 4 | 73 | ref 34-36 | 0.583 | 143.9 | 9 |

Table III
Measured Heats of Mixing at 25 °C

| mol % A | $\Delta H_{mix}$, J/mol | mol % A | $\Delta H_{mix}$, J/mol |
|---|---|---|---|
| Diethyl Carbonate (A) + Ethyl Heptanoate | | Dodecane (A) + Diethyl Carbonate | |
| 67.88 | 178 | 32.93 | 1414 |
| 60.55 | 193 | 38.56 | 1494 |
| 54.41 | 194 | 44.89 | 1538 |
| 48.77 | 192 | 48.37 | 1552 |
| | | 56.88 | 1433 |
| Diethyl Carbonate (A) + Propyl Butyrate | | Benzene (A) + Ethyl Phenyl Ether | |
| 34.74 | 79.8 | 42.6 | 57.9 |
| 45.48 | 86.3 | 57.2 | 63.3 |
| 52.07 | 92.7 | 54.3 | 58.1 |
| 56.08 | 89.0 | 72.5 | 56.9 |
| 65.12 | 85.1 | 75.4 | 51.9 |
| Benzene (A) + Dimethyl Carbonate | | Benzene (A) + Butyl Phenyl Ether | |
| 67.60 | 307 | 55.6 | 76.0 |
| 61.62 | 336 | 63.8 | 78.5 |
| 52.37 | 354 | 73.8 | 65.2 |
| 50.67 | 364 | 81.5 | 62.5 |
| 36.35 | 378 | Benzene (A) + Propyl Butyrate | |
| 33.98 | 335 | 52.32 | −59.4 |
| Benzene (A) + Diethyl Carbonate | | 60.49 | −63.8 |
| 51.57 | 18.0 | 65.98 | −57.1 |
| 57.63 | 18.4 | 71.88 | −47.2 |
| 62.63 | 15.6 | 74.68 | −39.9 |
| 70.88 | 7.8 | | |
| Octane (A) + Dimethyl Carbonate | | | |
| 26.88 | 1442 | | |
| 30.06 | 1513 | | |
| 35.84 | 1579 | | |

that the $CH_2OH$ group is not in the same class as the $CH_2CH_2OH$ group.

The liquid heats of mixing data, needed to generate the MGQ parameters, were either obtained from the literature,[22] where possible, or measured to within 3% relative error with an LKB Model 2107 batch calorimeter at 25 °C. The primary sources of the data, the number of data points correlated, the root-mean squared deviation between the model and the data, and the MGQ parameters are displayed in Table II. As before,[1] only one set of parameters, $A_{ij}$ and $\Delta E_{ij}$, is evaluated per heat of mixing data set. That is, when more than two groups are involved in the analysis of a system, parameters previously generated from other data sources are used with eq 1, leaving only one pair of parameters to be correlated at a time.

## Results and Discussion

**Polycarbonate/Polyester Blends.** Cruz et al.[38] found that bisphenol A polycarbonate (PC) is miscible with aliphatic polyesters which have $CH_2/COO$ ratios in their repeat units between 2 and 5, partially miscible for ratios up to 7, and immiscible for ratios greater than 7. These authors also showed that the sign of the heat of mixing for solutions of aliphatic esters with diphenyl carbonate, a reasonable analogue for the polycarbonate repeat structure, could be used as an index for predicting polycarbonate/aliphatic polyester miscibility. Aliphatic esters, with $CH_2/COO$ ratios between 2 and 7, showed exothermic or negative heats of mixing with diphenyl carbonate (DPC), while aliphatic esters with ratios greater than 7 showed endothermic heats of mixing with DPC.

Prediction of the PC/polyester miscibility with variation in polyester structure by the MGQ model, eq 1, requires the independent evaluation of the $A_{ij}$ and $\Delta E_{ij}$ parameters for all of the unlike binary combinations of groups suggested by the assignments in Figure 1. Parameters for the $CH_2/PhCH$ and $CH_2/CH_2COO$ pairs were obtained earlier.[1] The parameters for the $CH_2COO/PhCH$, $COOO/CH_2$, $COOO/CH_2COO$, and $COOO/PhCH$ interacting pairs were determined from the measured heats of mixing of various materials; see Table III. Dodecane/diethyl carbonate and octane/dimethyl carbonate mixtures were analyzed to obtain the parameters for the $COOO/CH_2$ interaction, diethyl carbonate/ethyl heptanoate and diethyl carbonate/propyl butyrate were analyzed to obtain the parameters for the $COOO/CH_2COO$ interaction, and benzene/propyl butyrate mixtures were examined to obtain the $CH_2COO/PhCH$ interaction parameters. The parameters for the $COOO/PhCH$ interaction were obtained from analysis of benzene/dimethyl carbonate mixtures. The MGQ model, eq 1, fits these data quite well, and the root-mean-squared deviations of the model from the data are generally less than 6%; see Table II.

Figure 2 shows the "window of miscibility" for PC with aliphatic polyesters, predicted by using the parameters discussed above. The ordinate of this figure is the binary interaction density, $B_{AB}$, defined by

$$B_{AB} = (1/V)\Delta H_{mix}/\Phi_A\Phi_B \qquad (6)$$

where $\Phi_A$ is the volume fraction of polymer A, $V$ the volume of the mixture, and $\Delta H_{mix}$ the heat of mixing calculated by eq 1. $B_{AB}$ tracks the heat of mixing and serves to indicate its sign, and from the foregoing discussion, polymer–polymer miscibility can be expected for $B_{AB} < 0$. The MGQ model therefore predicts that PC is miscible with aliphatic polyesters whose $CH_2/COO$ ratios range between 2.0 and 7.4. This prediction agrees very well with the experimental observations of Cruz et al., discussed above, although there is no experimental evidence to verify or refute the prediction that aliphatic polyesters with $CH_2/COO$ ratios less than 2 are immiscible with PC. As

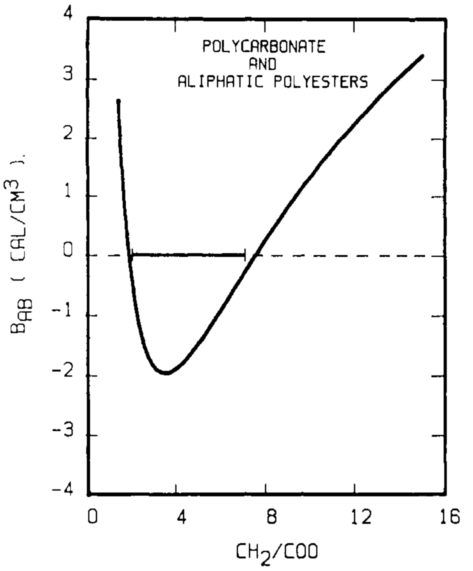

**Figure 2.** Predicted window of miscibility for PC blends with aliphatic polyesters.

discussed previously,[1] the MGQ model predicts $B_{AB}$ to be a weak function of both temperature and blend composition. For purposes of comparison with $B_{AB}$ values, obtained experimentally from polyester melting points in the blends, below, the curve in Figure 2 is predicted at 60 °C and a 0.9 volume fraction polyester in the blend, conditions that are close to those associated with the melting point depression measurements.

In principle, one could use observed curvature in plots of melting point depression versus amorphous volume fraction squared to verify the model or to evaluate MGQ model parameters. We have not attempted this because the precision in melting point depression measurements is usually too low to define a good curve and because the number of structural parameters involved is often too large to permit accurate determination of their magnitudes.

There is little consistent information with which to compare the predicted and observed magnitudes of $B_{AB}$ for miscible PC/aliphatic polyester blends. Miscible blends of PC with poly($\epsilon$-caprolactone) (PCL), a polyester with a CH$_2$/COO ratio of 5 in its repeat structure, have been most widely studied[37-39] and serve to indicate some of the difficulties in applying melting point depression analyses to PC/aliphatic polyester systems. Values of $B_{AB}$ have been found to range from nearly zero[37] to $-1.84$ cal/cm$^3$, calculated from ref 38; however, the value obtained appears to depend on the details of the sample preparation and annealing procedures employed. The most negative value results from ingredients which were melt mixed at 260 °C for 8 min, without extensive annealing[38] prior to measurement, and this result could indicate the presence of transesterification between PCL and PC.[40,41] The nearly athermal value[37] results from extensive procedures in which the PCL was carefully annealed following the Hoffman–Weeks protocol. Studies of the same system in which the polymers were blended by a solvent casting method a low temperature[39] without extensive annealing prior to measurement show $B_{AB} = -0.4$ cal/cm$^3$. The MGQ model predicts $B_{AB}$ to be $-1.46$ cal/cm$^3$ at 60 °C, the melting point of PCL, for a blend containing 90 wt % PCL. This value is in the range of experimentally determined values; however, it is probably somewhat too negative based on the experimental measurements in ref 37 and 39.

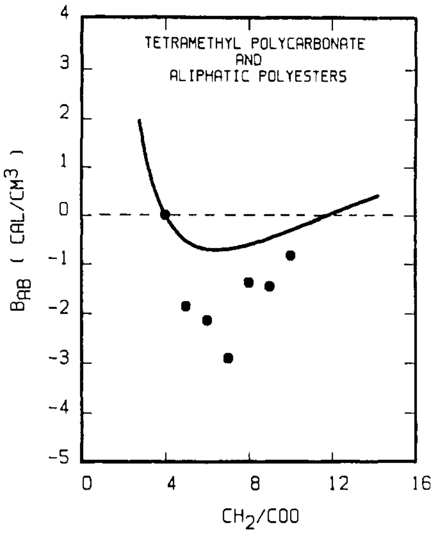

**Figure 3.** Comparison of predicted and observed binary interaction densities for tetramethylbisphenol A polycarbonate blends with aliphatic polyesters, at 60 °C, having various CH$_2$/COO ratios in their repeat units: (—) predicted by the MGQ model; (●) from melting point depression measurements.[45]

**Tetramethylbisphenol A Polycarbonate/Polyester Blends.** Tetramethylbisphenol A polycarbonate (MPC) is a variant of PC formed from tetramethylbisphenol A. It is known to be miscible with polystyrene and SAN copolymers which have acrylonitrile contents less than 10 mol %.[42-44] It is also found to be completely miscible with aliphatic polyesters which have CH$_2$/COO ratios between 5 and 10.[45] Partially miscible blends with MPC are seen when the polyester CH$_2$/COO ratio is 4. Comparison with Figure 2 shows that the higher CH$_2$/COO ratios are required for miscibility with MPC than for miscibility with PC. Such a trend is reasonable in view of the greater aliphatic hydrocarbon content of MPC relative to PC.

Figure 3 compares the interaction densities, $B_{AB}$, calculated by the MGQ model for the structural divisions shown in Figure 1, with those obtained experimentally from polyester melting point depression measurements.[45] The predicted miscibility range, CH$_2$/COO from 4.0 to 11.4, agrees quite well with experimental observation, however the predicted magnitudes of $B_{AB}$ differ from experimental values by a factor of nearly 3.

The reasons for the poor prediction are not clear at this time. Instead of simply considering the CH$_3$ group to be independent of the structure to which it is attached, some work has been done which considers methyl groups connected to aromatic carbon as a separate group classification. Consideration of aromatic methyl groups as a separate class does give an MGQ model prediction for $B_{AB}$ which matches the experimental magnitudes shown in Figure 3; however, the predicted miscibility window is then shifted to lower CH$_2$/COO ratios, between 1.4 and 7.4. Consequently, there appears to be no benefit, at this time, in creating this separate class of groups.

**Phenoxy/Polyester Blends.** The poly(hydroxy ether) of bisphenol A (Phenoxy) is known to be miscible[46] with aliphatic polyesters whose CH$_2$/COO ratios range from 3 to 5, and the $B_{AB}$ interaction parameters which describe the interactions of the polymer repeat units are found to be reasonably consistent, to within ±0.5 cal/cm$^3$, by both melting point depression and solvent probe methods.[5] Figure 4 shows a comparison between the observed variations of $B_{AB}$ with polyester structure and those predicted by using eq 1–6 with the parameters in Table II. Using the sign of $B_{AB}$ as an indication of miscibility, the MGQ model predicts that aliphatic polyesters whose CH$_2$/CH$_2$COO ratios range between 2 and 5.8 are miscible with

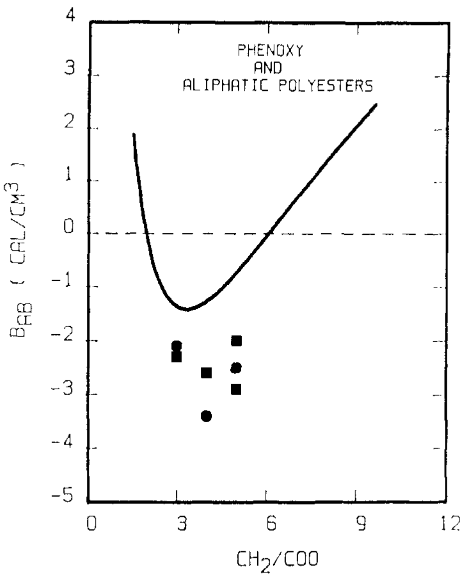

**Figure 4.** Comparison of predicted binary interaction densities for Phenoxy blends with aliphatic polyesters at 60 °C: (—) predicted by the MGQ model; (■) from solvent sorption; (●) from melting point depression.[5]

phenoxy. This compares reasonably well with the observed limits to the miscibility window; however, the predicted $B_{AB}$ values are less negative than those observed by a factor of nearly 2.

One possible reason for the poor agreement between predicted and observed $B_{AB}$ values is the uncertainty associated with evaluating the parameters which describe interactions of the ether group, $OCH_2$, and the hydroxyl group, CHOH, on the phenoxy repeat unit with other groups in the system, see Figure 1. First of all, the $\Delta E_{ij}$ and $A_{ij}$ parameters for the $CH_2/OCH_2$ interaction are evaluated from heats of mixing of aliphatic ethers with hydrocarbons, and one can question whether these parameters are really appropriate for describing the interaction of an aromatic ether with $CH_x$ units. These parameters are then specified in the analysis of the heats of mixing of benzene with ethyl phenyl ether and with butyl phenyl ether, see Table III, to obtain the parameters for $OCH_2$/PhCH binary interaction. This specification may not be appropriate, as suggested by the very poor fit, 47% RMS error, of the MGQ model to the experimental measurements, and the parameters associated with both the $CH_2/OCH_2$ and $OCH_2$/PhCH interactions may be quite uncertain.

The reason for the poor agreement can also be traced to the self-association by hydrogen bonding, known to occur between the OH groups in phenoxy. Coleman and Moskala[47] have conclusively shown, through Fourier transform infrared spectroscopy, that the OH groups in pure phenoxy are nearly completely self-associated at room temperature and that the fraction of unassociated, or free, OH groups increases rapidly with increasing temperature. The self-associated OH groups in the pure state are responsible for endothermic contributions to $\Delta H_{mix}$ by the phenoxy, and these contributions are observed, spectroscopically, to be larger per mole than the hydrogen bond formed between the free OH group and the aliphatic ester carbonyl. We can match the observed and calculated $B_{AB}$ values, Figure 4, by simply raising the temperature of our calculation from 60 to 120 °C to reduce the calculated fraction of associated OH in the MGQ model. From eq 5, this is essentially equivalent to saying that the $\Delta E_{ij}$ values for $CH_2/CH_2OH$ and $PhCH/CH_2OH$ should be 4528 cal/mol and 4189 cal/mol, respectively, instead of the Table II values, 3837 cal/mol and 3550 cal/mol. The $\Delta E_{ij}$ values could be uncertain by 10%, as judged by the RMS error in the correlations used in their evaluation, and this small uncertainty, is nearly sufficient to explain the poor agreement between experiment and prediction for the Phenoxy system.

**Blends Containing PMMA.** Poly(methyl methacrylate) (PMMA) has been recently found to form miscible blends with PC[48] and with poly(ethylene oxide) (PEO).[49-51] The MGQ model can predict the state of miscibility in these systems from the parameters in Table II and the structural groups in Figure 1, and it is interesting to compare these model predictions for $B_{AB}$ with experimentally observed values.

Experience with other blend systems[52,53] suggests that phase separation of a miscible mixture, caused by heating the mixture to relatively low temperatures, can indicate weak interactions between the blend components. Based on this experience, the interactions between the repeat units of PC and PMMA should be nearly athermal, as evidenced by the presence of a cloud point curve with a minimum temperature, corresponding to the lower critical solution temperature, LCST, near 185 °C. This temperature is far below that for normal melt processing of PC, and miscible PC/PMMA blends cannot be made by conventional melt blending methods. Miscible blends can be made, however, by a precipitation from solvent method,[48] and the resulting blends show the single $T_g$, characteristic of miscible systems, until they are heated above the cloud temperature.

By use of the parameters in Table II, the MGQ model predicts the interaction density for PC/PMMA to be $B_{AB} = +0.03$ cal/cm$^3$ at 25 °C, when equal volumes of both components are present. Strict interpretation of the requirement for miscibility suggests that this mixture should be immiscible; however, the uncertainty associated with the prediction is high enough to allow for the predicted possibility that PMMA/PC forms a miscible binary. This nearly athermal predicted interaction is qualitatively consistent with the observed presence of the low-temperature cloud point curve. It is also consistent, within an estimated uncertainty of ±0.2 cal/cm$^3$ in the prediction, with a recent report[54] which estimates $\chi_{AB} = +0.043$ from measurements of the phase compositions in the immiscible PC/PMMA mixture. From the well-known relationship, $B = \chi RT/V$, and with $V = 150$ cm$^3$/mol as an average molar volume of the repeat unit, the reported value of $\chi_{AB}$ is equivalent to $B_{AB} = +0.17$ cal/cm$^3$.

The potential advantage of a group contribution method is that the groups and associated parameters can be easily used to predict the behavior of new systems. The parameters in Table II, for example, can be used to predict the miscibility behavior of poly(ethylene oxide) (PEO) with PMMA, see Figure 1. The MGQ model predicts the blend interaction density, $B_{AB}$, to be equal to $-2.88$ cal/cm$^3$ at 74 °C and 10 vol % PMMA. This prediction compares well with $B_{AB} = -2.8$ cal/cm$^3$,[49,50] obtained from PEO melting point depression measurements in the blends. The prediction also compares reasonably well with the range of values, $B_{AB} = -3.5$ to $-0.7$ cal/cm$^3$, calculated from small-angle neutron scattering results,[51] for PMMA contents between 0.3 and 0.7 monomer fraction.

## Summary and Conclusions

This paper has expanded the application of the MGQ model toward prediction of polymer–polymer miscibility for systems where one blend component in an aliphatic polyester. By use of interaction parameters obtained from analysis of liquid heats of mixing data, the MGQ model is able to predict, with reasonable accuracy, the limits of miscibility for aliphatic polyesters with Phenoxy, with PC, or with MPC. Although the evidence is less clear, the MGQ model also seems to adequately predict the magnitude of the polymer–polymer interaction parameter, $B_{AB}$, for PC/PMMA and PMMA/PEO blends. The model fails, however, to adequately predict the magnitudes of $B_{AB}$ for the systems containing polymers based on bisphenol A.

Part of the reason for failure of the model to accurately predict $B_{AB}$ magnitudes is related to monomer complexity. As illustrated by the Phenoxy/polyester study, relatively small uncertainties in parameter values can result in large uncertainty in the net interaction. This problem undoubtedly grows worse as the polymer repeat unit becomes structurally more complex and more parameters are required to describe the interactions of its groups. One possible way to minimize this problem would be to define larger structural groups than those used in this study. Such an approach could prove useful for more accurately predicting the behavior of a narrow class of polymer repeat units, but it would probably require more carefully chosen liquid analogues for use in evaluating the binary interaction parameters. This is precisely the problem with the earlier, simpler binary interaction model[13] which we had hoped to solve by developing the MGQ group contribution method discussed here.

Despite the difficulties noted above, the MGQ model does show promise for predicting polymer–polymer miscibility from group contributions. This approach seems to be reasonably successful for predicting binary blend miscibility in cases where at least one component is a polyester. Part of this success is related to the availability in the literature of high-quality liquid heats of mixing data related to esters. Part of this success is also related to the generally good fit of the MGQ model to the data for purposes of determining parameters, although improvements are needed to more accurately determine net interactions between complex structures, as discussed above. Finally, part of this success is also related to the correctness of the group contribution assumption that group enthalpic interactions are independent of the size and nature of the molecules to which the groups are attached.

The group contribution assumption is obviously not always correct, as evidenced by the greater acidity shown by an OH group attached to an aromatic ring as compared to an OH attached to an aliphatic hydrocarbon, and care must be taken to recognize this problem by use of appropriate liquid analogues and group classes. The MGQ model also does not consider the important influences on blend miscibility caused by polymer tacticity,[55,56] by branches in repeat units,[46,57] and by other mechanisms, present in polymers but not low molecular weight liquids, which restrict complete mutual access of the groups attached to the polymers. With reasonable care, however, the MGQ model can be as useful predictive tool for finding new, potentially miscible polymer blends.

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**Registry No.** PMMA, 9011-14-7; (bisphenol A)(PC) (copolymer), 25037-45-0; (bisphenol A)(PC) (SRU), 24936-68-3; (bisphenol A)(epichlorohydrin) (copolymer), 25068-38-6; (tetramethylbisphenol A)(carbonic acid) (copolymer), 52684-16-9; (tetramethylbisphenol A)(carbonic acid) (SRU), 38797-88-5; poly(ethylene oxide), 25322-68-3; diethyl carbonate, 105-58-8; ethyl heptanoate, 106-30-9; benzene, 71-43-2; propyl butyrate, 105-66-8; dimethyl carbonate, 616-38-6; butyl phenyl ether, 1126-79-0; ethyl phenyl ether, 103-73-1; octane, 111-65-9; dodecane, 112-40-3.

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# Transition of Linear Polymer Dimension from Θ to Collapsed Regime. Intrinsic Viscosity

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ABSTRACT: Intrinsic viscosity $[\eta]$ of polystyrene in cyclohexane from the Θ temperature to the collapsed regime has been measured by using a novel precision capillary viscometer which has a time resolution of ±0.001 s. The temperature ($T$) dependence of $[\eta]$ can be represented by a master curve in a $\alpha_\eta^3|\tau|M_w^{1/2}$ ($g^{1/2}$ $mol^{-1/2}$) vs $|\tau|M_w^{1/2}$ ($g^{1/2}$ $mol^{-1/2}$) plot, where $\alpha_\eta$ $[\equiv([\eta(T)]/[\eta(\theta)])^{1/3}]$ is the expansion factor and $\tau$ $[\equiv(T-\Theta)/T]$ is the reduced temperature. A comparison of the plateau value for the scaled expansion factors $\alpha^3|\tau|M_w^{1/2}$ in the collapsed regime based on the radius of gyration $R_g$ with $\alpha_s = R_g(T)/R_g(\Theta)$, the hydrodynamic radius $R_h$ with $\alpha_h = R_h(T)/R_h(\Theta)$, and the intrinsic viscosity shows $\alpha_h^3{:}\alpha_\eta^3{:}\alpha_s^3 = 2.14 \pm 0.19{:}1.2 \pm 0.1{:}1$, in fairly good agreement with the blob theory prediction of 2.08:1.28:1 with $\alpha_\eta^3 = \alpha_s^2\alpha_h$ and a plateau value of 24.1 ± 3% for $\alpha_\eta^3|\tau|M_w^{1/2}$.

## I. Introduction

Recent light-scattering studies on the transition of linear polymer dimension from the Θ temperature to the collapsed regime have shown our successes in being able to reach the collapsed state: (1) based on the static radius of gyration $R_g$ by using high molecular weight fractions of polystyrene with (a) $M_w$ ranging from $4 \times 10^6$ to $20 \times 10^6$ g/mol in cyclohexane,[1] below the upper Θ temperature ($\Theta_U$ = 35 °C), and (b) $M_w$ ranging from $2 \times 10^6$ to $8.6 \times 10^6$ g/mol in methyl acetate,[2] both below the upper Θ temperature ($\Theta_U$ = 43 °C) and above the lower Θ temperature ($\Theta_L$ = 114 °C); (2) based on the hydrodynamic radius $R_h$ by using a specially fractionated high molecular weight polystyrene with $M_w = 4.83 \times 10^7$ g/mol and $M_w/M_n \lesssim 1.03$ at a concentration $C \approx 3 \times 10^{-8}$ g/mL in cyclohexane.[3] Results of polymer coil-to-globule transition have also been reviewed[4] and its relationship to critical phenomena reexamined[5] on the basis of an extended universal coexistence curve for polymer solutions[6] as originally proposed by Sanchez.[7] In this paper, we report intrinsic viscosity measurements of polystyrene in cyclohexane using a new precision capillary viscometer[8] which has a time resolution of ±0.001 s. The purpose of the present study is twofold. We want (1) to check the intrinsic viscosity results of Perzynski et al.[9] in the collapsed regime and (2) to compare the plateau value for the scaled expansion factor $\alpha^3|\tau|M_w^{1/2}$ in the collapsed regime based on the radius of gyration $R_g$ with $\alpha_s = R_g(T)/R_g(\Theta)$, the hydrodynamic radius $R_h$ with $\alpha_h = R_h(T)/R_h(\Theta)$, and the intrinsic viscosity $[\eta]$ with $\alpha_\eta^3 = [\eta(T)]/[\eta(\Theta)]$. Perzynski et al. have already observed that $[\eta]$ scaled with $|\tau|M_w^{1/2}$ where $M_w$ and $\tau$ $[\equiv(T-\Theta)/T]$ are the weight-average molecular weight and the reduced temperature, respectively. However, a plateau value of $\alpha_\eta^3|\tau|M_w^{1/2} \simeq 27$ $g^{1/2}$ $mol^{-1/2}$ starting at $|\tau|M_w^{1/2} \gtrsim 40$ $g^{1/2}$ $mol^{-1/2}$ appeared to show much larger than usual experimental error limits. With the higher time resolution of our viscometer, we could reduce the polymer concentration further and test possible phase separation effects in the very immediate neighborhood of the coexistence curve. As polydispersity has been shown to play a major role in our experiments[3-5,10] and the amount of specially fractionated polystyrene[3] ($M_w = 4.83 \times 10^7$; $M_w/M_n \leq 1.03$) was insufficient for viscosity studies, we selected the highest molecular weight fraction ($M_w = 8.6 \times 10^6$ g/mol; $M_w/M_n \simeq 1.26$) polystyrene which we used successfully to reach the collapsed regime based on the radius of gyration in two different solvents[1,2] as our polystyrene sample for the intrinsic viscosity experiment. It should be noted that a polydispersity index ($\equiv M_w/M_n$) of ≤1.03 for an ultrahigh molecular weight polystyrene sample represented a polymer fraction which could not be obtained by standard analytic means. It took us close to a year to finally obtain quantities of a few milligrams. Thus, we did not want to repeat the effort for the viscosity experiment. On the other hand, $M_w/M_n \simeq 1.26$ for the $8.6 \times 10^6$ g/mol polystyrene sample is somewhat broad. Then, we would expect phase separation before we reach the coexistence (COEX) curve based on more monodisperse polystyrene samples.

In the literature, only few experiments[1-3,5,9,11] have successfully reached the collapsed regime based on static and hydrodynamic properties of polymer solutions, exclusively using polystyrene as the polymer and mostly using cyclohexane as the solvent. The experimental difficulties encountered could mainly be attributed as due to polymer polydispersity for high molecular weight polystyrene samples. With the exception of the $8.6 \times 10^6$ g/mol polystyrene sample purchased from Toyo Soda, almost none exist with narrow enough molecular weight distributions commercially. Now as we have established an extended universal coexistence (COEX) curve for polystyrene in cyclohexane[6] with

$$\psi_C - \psi_D = (0.595 \pm 0.001)X^{0.327} - (0.425 \pm 0.001)X^{0.827} \quad (1)$$

$$\psi_{SD} - \psi_C = (0.595 \pm 0.001)X^{0.327} + (0.018 \pm 0.004)X^{0.827} \quad (2)$$

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