Light Scattering Characterization of an Alternating Copolymer of Ethylene and Tetrafluoroethylene. 3. Temperature Behavior of Polymer Size

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ABSTRACT: Laser light scattering, including intensity and line-width measurements, has been used to characterize a high molecular weight alternating copolymer of ethylene and tetrafluoroethylene (PETFE; $M_w = 3.21 \times 10^6$ g/mol) in diisobutyl adipate at 240 °C and to determine the temperature dependence of the static properties such as the second virial coefficient A_2 and the radius of gyration R_g. The results show that, over the molecular weight range of 5×10^5 to 3.2×10^6, our copolymer samples in diisobutyl adipate at 240 °C obey the scaling relations R_g (nm) $= 2.04 \times 10^{-2} M_w^{-0.58}$ and D_0^0 (cm^2/s) $= 8.89 \times 10^{-4} M_w^{-0.58}$ with M_w and D_0^0 being the weight-average molecular weight (g/mol) and the translational diffusion coefficient at infinite dilution, respectively. An exponent ($\alpha_D = \alpha_R$) value of 0.58 is more reasonable than the previously reported value of 0.60. For the high molecular weight PETFE, we obtained a broader molecular weight distribution with $M_w/M_n \approx 2$ and a Θ temperature of 231.0 ± 0.5 °C. Variation of the scaled expansion factor $\alpha^3|\tau|M_w^{1/2}$ as a function of scaled reduced temperature $|\tau|M_w^{1/2}$ shows that PETFE in diisobutyl adipate follows the usual crossover behavior in polymer coil concentration from the Θ point to the collapsed regime. The expansion factor α and the reduced temperature τ are defined as $R_g(T)/R_g(\Theta)$ and $|T - \Theta|/\Theta$.

I. Introduction

By combining static and dynamic properties (M_w, A_2, k_d, R_g, and D_0^0) of an alternating copolymer of ethylene and tetrafluoroethylene (PETFE), $(-CF_2CF_2CH_2CH_2)_x-$, in diisobutyl adipate at three different molecular weights and 240 °C with a detailed analysis of the intensity–intensity time correlation function, we succeeded in determining the molecular weight distribution (MWD) of PETFE.[1-3] A variety of Laplace inversion techniques, including multiexponential singular value decomposition[4,5] (MSVD), a method of regularization[5,6] (RILIE), and CONTIN,[7,8] showed essentially the same estimated normalized characteristic linewidth distribution function $G(\Gamma)$ which could be converted to MWD by using $G(\Gamma)$ measured at small scattering angles ($KR_g < 1$) where the particle scattering factor $P(K) \simeq 1$ and the relation

$$D_0^0 \propto M_w^{-0.60} \tag{1}$$

with M_w (g/mol), A_2, k_d, R_g, D_0^0 (cm^2/s), and K being the weight-average molecular weight, the intensity second virial coefficient, the diffusion second virial coefficient, the z-average root-mean-square radius of gyration, the translational diffusion coefficient extrapolated to zero scattering angle and zero concentration, and the scattering vector, respectively. Thus, we have demonstrated our light scattering characterization of PETFE to be independent of the Laplace inversion method of data analysis. Furthermore, our analytical approach has taken into account effects due to intermolecular and intramolecular interferences. On closer examination, we note that the magnitude of polydispersity in the MWD depends on the empirically determined scaling exponent ($\alpha_D \sim 0.60$) in eq 1. A α_D value of 0.60 represents the upper limit for the PETFE coil if it were in a good solvent. Yet, PETFE is soluble in diisobutyl adipate only near the solvent boiling point. With A_2 values of 1.97×10^{-4} and 1.02×10^{-4} mol mL g^{-2} for $M_w = 5.4 \times 10^5$ and 1.16×10^6 g/mol, respectively, the solvent quality could not be considered as really good. As indicated previously,[3] we should qualify the value of 0.6 especially when the experiments[2,3] covered a molecular weight range of PETFE by a factor of only ($11.6/5.4 \simeq$) 2. In this paper we present a further study of the light scattering characterization of PETFE using a specially synthesized high molecular weight PETFE, in order to secure a more precise α_D value and to investigate the temperature dependence of the static and dynamic properties of PETFE in diisobutyl adipate from near the solvent boiling point to below the Θ temperature; i.e., until phase separation occurs at finite but dilute PETFE concentrations. With knowledge of the solvent viscosity, we can then determine the hydrodynamic radius R_h by using the Stokes-Einstein relation and the R_g/R_h ratio as a function of temperature.

II. Experimental Methods

Materials, preparation of solutions, and methods of measurements have been described in detail elsewhere.[2] The high molecular weight PETFE was specially prepared at Du Pont (courtesy of W. Buck, Polymer Products Department, Du Pont Experimental Station, Wilmington, DE). It is not one of those commercial samples of Tefzel (a registered trademark of Du Pont).

III. Results and Discussion

1. Light Scattering Intensity Measurements. The excess absolute integrated intensity of light scattered at scattering vector K from a dilute polymer solution has the form

$$\frac{HC}{R_{vv}(K)} \simeq \frac{1}{M_w}\left(1 + \frac{K^2R_g^2}{3}\right) + 2A_2C \tag{2}$$

where H is an optical constant; $K = (4\pi/\lambda) \sin(\theta/2)$ with λ ($=\lambda_0/n$) and θ being the incident wavelength of light in the scattering medium of refractive index n and the scattering angle, respectively. The subscripts vv denote vertically polarized incident and scattered light. Figure 1 shows a Zimm plot for the high molecular weight PETFE in diisobutyl adipate at 240 °C using $\lambda_0 = 488$ nm. Least-squares fitting and extrapolation to infinite dilution and zero scattering angle yield $M_w = (3.21 \pm 0.29) \times 10^6$

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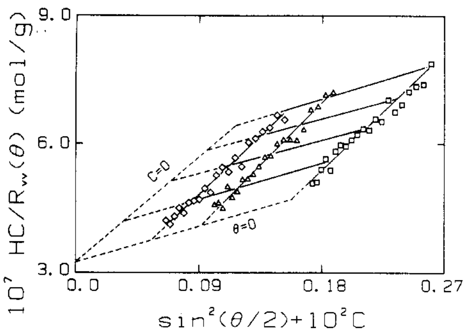

Figure 1. Zimm plot of high molecular weight PETFE in diisobutyl adipate at 240 °C using $\lambda_0 = 488$ nm, $M_w \simeq (3.21 \pm 0.29) \times 10^6$ g/mol, $R_g \simeq (1.30 \pm 0.21) \times 10^2$ nm, and $A_2 \simeq (5.11 \pm 0.54) \times 10^{-5}$ mol mL g^{-2}. Hollow diamonds, triangles, and squares denote $C = 3.57 \times 10^{-4}$, 7.11×10^{-4}, and 1.43×10^{-3} g/mL, respectively.

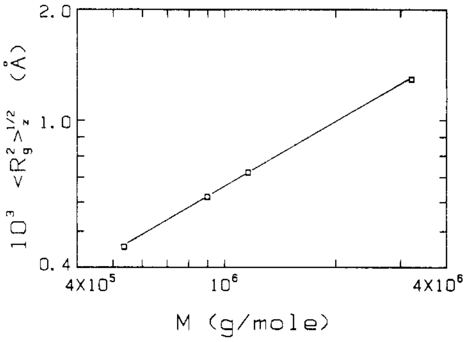

Figure 2. log–log plot of R_g vs M_w for PETFE in diisobutyl adipate at 240 °C. Solid line denotes $R_g = 2.04 \times 10^{-2} M_w^{0.58}$ with R_g and M_w expressed in nm and daltons, respectively.

g/mol, a factor of close to 3 times higher than the highest molecular weight sample ($M_w = 1.16 \times 10^6$) in our previous studies. With the high molecular weight PETFE sample, we also determined R_g ($\equiv + \langle R_g^2\rangle_z^{1/2}$) = $(1.30 \pm 0.21) \times 10^2$ nm and $A_2 = (5.11 \pm 0.54) \times 10^{-5}$ mol mL g^{-2}. In a log–log plot of R_g vs M_w, as shown in Figure 2, we obtained a new scaling relation for PETFE in diisobutyl adipate at 240 °C

$$R_g = 2.04 \times 10^{-2} M_w^{0.58} \qquad (3)$$

where R_g and M_w are expressed in nm and daltons, respectively. An α_R value of 0.58 did become more reasonable than the previous estimate in eq 5 of ref 2 with $R_g = 1.68 \times 10^{-2} M_w^{0.60}$. Equation 3, covering a molecular weight range of close to 6, instead of ~2 for eq 5 of ref 2, should produce a more reliable value of α_R ($\simeq$0.58). It again confirms that PETFE polymer molecules in diisobutyl adipate at 240 °C behave like polymer coils, not extended wormlike chains.

In our light scattering studies of dilute solutions of PETFE in diisobutyl adipate, we noted phase separation of PETFE in the neighborhood of 225 °C, suggesting a strong temperature dependence of the solvent quality; i.e., diisobutyl adipate changes from a fairly good solvent with a positive A_2 and $\alpha_R \sim 0.58$ at 240 °C to phase separation behavior in less than 20°. Thus, we can learn about the PETFE polymer solution behavior by investigating the temperature dependence of the second virial coefficient A_2 and of the radius of gyration R_g. Figure 3 shows the temperature dependence of A_2 for the high molecular weight PETFE polymer sample, yielding a Θ temperature of 231.0 ± 0.5 °C. With A_2 of $\sim 10^{-5}$ mol mL g^{-2} for $M_w \sim 3.2 \times 10^6$ g/mol, it appears that an α_R value of 0.58 at 240 °C could still be somewhat high. Figure 4 shows the temperature dependence of R_g for the same high molecular weight PETFE polymer sample. Although the curve looks smooth, there are two crossover regions of interest, i.e., from Θ to the fairly good solvent regime ($T > \Theta$) and from Θ to the collapsed regime ($\Theta > T$). The transition from random-coil behavior in the Θ state to a globule coil in the collapsed state has been the focus of interest of many theoreticians and experimentalists for a couple of decades,[9] including a renormalization group description of polymer contraction below the Θ point.[10] An interesting feature of the temperature dependence on the crossover behavior from the theta point to the globule state can be presented by a plot of the scaled expansion factor $\alpha^3|\tau|M_w^{1/2}$ of static size versus the scaled reduced temperature $|\tau|M_w^{1/2}$ where the expansion factor of static size is defined as $R_g(T)/R_g(\Theta)$ and $|\tau| = |T - \Theta|/\Theta$. Figure 5 shows variation of the scaled expansion factor $\alpha^3|\tau|M_w^{1/2}$ of static size as a function of scaled reduced temperature $|\tau|M_w^{1/2}$ for PETFE ($M_w = 3.21 \times 10^6$ g/mol) in diisobutyl adipate. The emphasis of

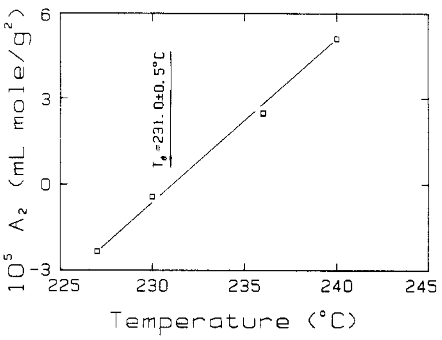

Figure 3. Temperature dependence of the second virial coefficient A_2 for PETFE ($M_w = 3.21 \times 10^6$ g/mol) in diisobutyl adipate. At $A_2 = 0$, a Θ temperature of 231.0 ± 0.5 °C was interpolated.

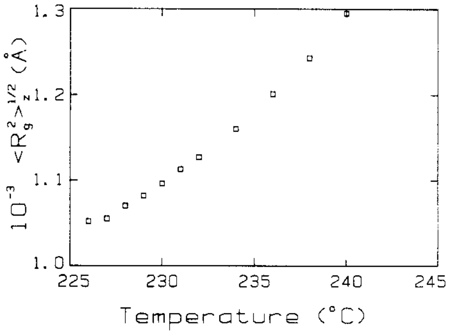

Figure 4. Temperature dependence of the radius of gyration R_g for PETFE ($M_w = 3.21 \times 10^6$ g/mol) in diisobutyl adipate (Θ = 231.0 ± 0.5 °C).

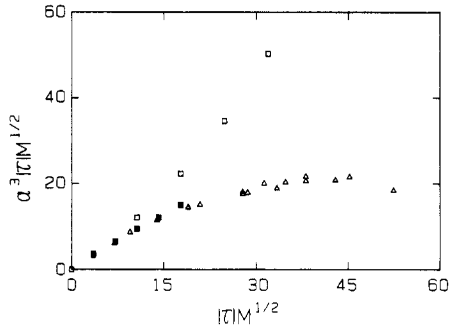

Figure 5. Variation of the scaled expansion factor $\alpha^3|\tau|M_w^{1/2}$ of static size as a function of scaled reduced temperature $|\tau|M_w^{1/2}$ for PETFE in diisobutyl adipate using the 3.21×10^6 g/mol PETFE polymer sample. Hollow squares denote data measured at $T > \Theta$; filled squares denote data measured at $T < \Theta$. For comparison, we have included the data for polystyrene in cyclohexane with a Θ temperature of 35 °C.

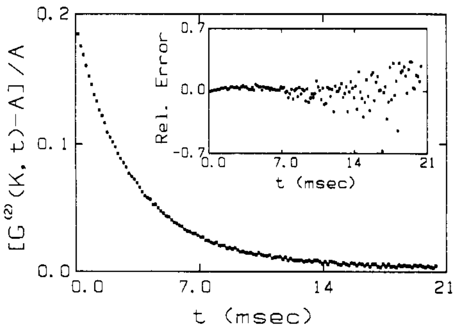

Figure 6. Typical unnormalized net intensity–intensity autocorrelation function for 3.57 × 10^{-4} g/mL PETFE (M_w = 3.21 × 10^6 g/mol) in diisobutyl adipate measured at θ = 20° and 240 °C. Inset denotes a relative deviation plot of the measured and computed time correlation function using the MSVD technique. Relative deviation = $[(b|g^{(1)}|^2)_{\text{measd}} - (b|g^{(1)}(t)|^2)_{\text{calcd}}]/(b|g^{(1)}(t)|^2)_{\text{measd}}$.

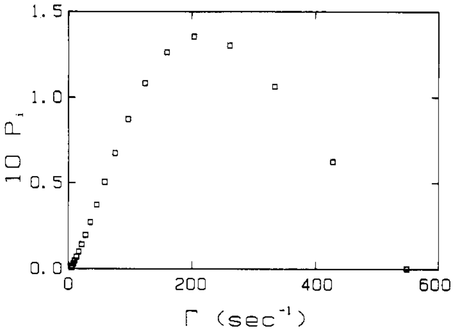

Figure 7. Normalized characteristic line-width distribution for Figure 6 using the MSVD technique. We have already demonstrated that the approximate form of $G(\Gamma)$ is relatively independent of the Laplace inversion technique.[3]

this plot is in making a comparison of the crossover regime for the coil-to-globule transition between PETFE in diisobutyl adipate (denoted by filled squares) and polystyrene in cyclohexane[9] which shows a plateau region of $\alpha^3|\tau|M_w^{1/2} \sim 20$ g$^{1/2}$ mol$^{-1/2}$. The PETFE has not yet reached the collapsed state at $|\tau|M_w^{1/2} \sim 40$. The temperature dependence of the expansion factor for PETFE in diisobutyl adipate above the theta temperature (denoted by hollow squares) differs from that below the Θ temperature (filled squares). The purpose of presenting a figure such as shown in Figure 5 is not to investigate the coil-to-globule transition or the coil expansion from Θ to good solvent; it is intended to demonstrate that PETFE in diisobutyl adipate, like other polymer coils, exhibits fairly standard behavior.

2. Light Scattering Line-Width Measurements. The intensity–intensity time correlation function $G^{(2)}(K,\tau)$ has the form

$$G^{(2)}(K,t) = A(1 + b|g^{(1)}(K,t)|^2) \tag{4}$$

where A, b, and $|g^{(1)}(K,t)|$ are respectively the base line, a coherence factor, and the normalized field correlation function. Figure 6 shows a typical net intensity–intensity time correlation function $[G^{(2)}(K,t) - A]/A$ ($\equiv b|g^{(1)}(K,t)|^2$) for PETFE (M_w = 3.21 × 10^6 g/mol) in diisobutyl adipate at C = 3.57 × 10^{-4} g/mL, and Θ = 20 and 240°C. A Laplace inversion of the measured intensity–intensity time correlation function in Figure 1 yields a normalized characteristic line-width distribution function $G(\Gamma) = \sum_j P_j \delta(\Gamma - \Gamma_j)$, as shown in Figure 7. The relative deviation between measured and computed $G^{(2)}(K,t)$ is shown in the inset of Figure 6. We used the MSVD[4] technique for the Laplace inversion. Figure 8 shows a log–log plot of D_0^0 versus M_w where $D^0 = \lim_{K\to 0} \Gamma/K^2 = D_0^0(1 + k_dC)$. A least-squares fitting of the data over the more extended molecular weight range (by a factor of ~6 instead of ~2) yields

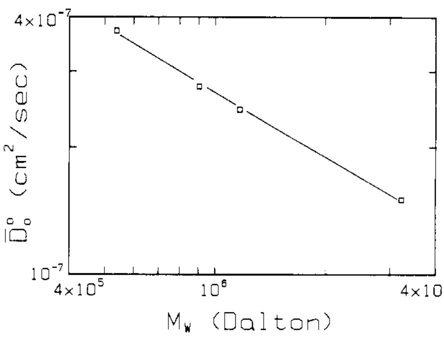

Figure 8. log–log plot of D_0^0 vs M_w for PETFE in diisobutyl adipate at 240 °C. Solid line denotes $D_0^0 = 8.89 \times 10^{-4} M_w^{-0.58}$ with D_0^0 and M_w expressed in cm^2/s and g/mol, respectively.

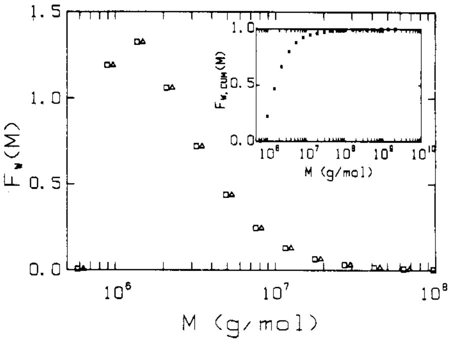

Figure 9. Molecular weight distribution of the high molecular weight PETFE polymer sample based on the MSVD technique of data analysis on Figure 1 and conversion of $G(\Gamma)$ from Figure 7 using eq 5. Hollow squares denote $M_z{:}M_w{:}M_n$ = 7.93:2.01:1.00 with $D_0^0 = 8.52 \times 10^{-4} M_w^{-0.58}$ and $M_{w,\text{calcd}}$ = 3.21 × 10^6 g/mol. Hollow triangles denote $M_z{:}M_w{:}M_n$ = 7.93:2.01:1.00 with $D_0^0 = 8.89 \times 10^{-4} M_w^{-0.58}$ and $M_{w,\text{calcd}}$ = 3.45 × 10^6 g/mol. Inset denotes a plot of $F_{w,\text{cum}} = \int_0^M F_w(M)\,dM$. Note the high molecular weight tail resulting in a larger than expected M_z value. From the plot $F_{w,\text{cum}}$ vs M, we emphasize that the small amount of the high molecular weight tail could result from uncertainties in the Laplace transform because of noise associated with the base-line subtraction.

$$D_0^0 = 8.89 \times 10^{-4} M_w^{-0.58} \tag{5}$$

with $\alpha_D = 0.58 = \alpha_R$ of eq 3 and D_0^0 and M_w expressed in cm^2/s and g/mol, respectively. In previous publications on the Tefzel work,[2,3] the prefactor was miscalculated by a factor of ~3. With the more precise value of α_D (=0.58), we could again make a transform of $G(\Gamma)$ in Figure 7 to MWD as shown in Figure 9. By combining eq 5 with $G(\Gamma)$ of Figure 7, we can compute the MWD in terms of the weight distribution $F_w(M)$ yielding a calculated weight-average molecular weight $M_{w,\text{calcd}}$ of 3.45 × 10^6 g/mol and $M_z{:}M_w{:}M_n \simeq$ 7.93:2.01:1.00. If we take $D_0^0 = 8.52 \times 10^{-4} M^{-0.58}$, $M_{w,\text{calcd}}$ = 3.21 × 10^6 g/mol, in agreement with the value determined directly by absolute light scattering intensity measurements. The polydispersity factor in terms of $M_z{:}M_w{:}M_n$ remains unchanged since we have set $\alpha_D = 0.58$. It should be noted that a light scattering determination of PETFE in diisobutyl adipate, like other light scattering characterizations, emphasizes on the high molecular weight fractions since the scattering power is proportional to MC ($\sim M^2$). Furthermore, the approximate $G(\Gamma)$ as determined by Laplace inversion of $G^{(2)}(K,t)$ using the MSVD technique (or other similar approaches) represents a truncated form of $G(\Gamma)$. Thus, the polydispersity index in terms of M_w/M_n may tend to be smaller than that determined by size exclusion chromatography (SEC). Yet

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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 $F_{w,\mathrm{cum}}$ [$=\int_0^M F_w(M)\,\mathrm{d}M$] vs M clearly shows that the high molecular weight tail is within the experimental error limits of ~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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