A Pseudo Equation-of-State Approach for the Estimation of Solubility Parameters of Polyethylene by Inverse Gas Chromatography

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ABSTRACT: Hildebrand solubility parameters (δ) of a series of linear low-density polyethylenes (LLDPE) were measured at several elevated temperatures by the inverse gas chromatography (IGC) method of DiPaola-Baranyi and Guillet [*Macromolecules* **1978**, *11*, 228−235] with the incorporation of a compressible regular solution model, recently proposed by Ruzette and Mayes [*Macromolecules* **2001**, *34*, 1894−1907], for data analysis. It was found that, with the inclusion of the pressure−volume−temperature (PVT) properties of the pure components in the data analysis, the measured δ agreed well with those obtained from PVT measurements on similar systems. This suggests that the model of Ruzette and Mayes, even though it is mathematically less sophisticated than the conventional equation-of-state (EOS) theories, it is useful for deriving solubility properties of polymers. The results were consistent with the prediction of conventional EOS theories that, in addition to the type and strength of intermolecular interaction, PVT properties of the individual components comprising polymer solutions and blends also play a significant role in determining their phase behavior, especially at elevated temperatures.

Introduction

Owing to its simplicity, the concept of Hildebrand solubility parameter (δ) is frequently employed for miscibility prediction of polymer solutions and blends. Since polymers cannot be vaporized, various indirect methods have been developed to estimate their δ. Among the indirect methods available, the solvent swelling experiment has been the most frequently used one. A less known method is inverse gas chromatography (IGC). The essence of the technique involves the measurement of the Flory−Huggins interaction parameter (χ_{12}) between a solvent with known solubility parameter (δ_1) and a polymer whose solubility parameter (δ_2) is to be determined. δ_2 is calculated using the following well-known expression:[1−3]

$$\chi_{12} = \left(\frac{V_0}{RT}\right)(\delta_1 - \delta_2)^2 \tag{1}$$

Here, V_0 is the reference volume based upon which χ_{12} is calculated. In general, the molar volume of the solvent at the experimental temperature T is taken as V_0. R is the universal gas constant.

In practice, eq 1 is seldom used directly. Rather, it is converted into the following form and used to determine δ_2 because a set of solvents with known solubility parameters rather than a single solvent are used in IGC.[4]

$$\frac{{\delta_1}^2}{RT} - \frac{{\chi_{12}}^\infty}{V_0} = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \frac{{\delta_2}^2}{RT} \tag{2}$$

It should be emphasized that, mathematically speaking, eqs 2 and 1 are essentially the same equation but in different algebraic forms. Therefore, eq 2 suffers from the same drawbacks that eq 1 suffers except that negative χ_{12}^∞ values can be used. When eq 2 is used, the left-hand side (i.e., ${\delta_1}^2/RT - \chi_{12}^\infty/V_0$) is usually plotted against δ_1 for a set of solvents, and δ_2 is simply determined from the slope of the resultant linear line. Obviously, such an approach jeopardizes the reliability of the resultant δ_2 since the experimenter deliberately includes solvent−polymer pairs that exhibit negative χ_{12}^∞ (i.e., pairs do not follow the well-known geometric mean assumption (i.e., $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$) in the data analysis process. In our view, when negative χ_{12}^∞ is obtained, it should be disregarded. Nonetheless, for many weakly interacting solvent−polymer systems, the magnitude of the second term of the left-hand side of eq 2 (i.e., χ_{12}^∞/V_0) is generally about 1−2 orders of magnitude smaller than that of the first term (i.e., ${\delta_1}^2/RT$). As a result, the χ_{12}^∞/V_0 term cannot have any significant influence to the slope of the resultant line (i.e., δ_2). In other words, δ_2 measured in this manner is insensitive to the measured χ_{12}^∞ but predominately determined by the values of δ_1 of the set of solvents used at the experimental temperature. Consequently, the resultant δ_2 corresponds essentially to the average value of the solubility parameters of the solvents exhibiting favorable (i.e., small and positive) χ_{12}^∞ values with the polymer. In a sense, this method is another version of solvent swelling experiment except that a more quantitative indicator χ_{12}^∞ instead of the degree of swelling is used. This explains why δ_2 obtained from IGC, even with the solvents at infinite dilution, are always comparable to those obtained from the solvent swelling experiments.

Although the above-mentioned drawbacks can lead to inaccurate estimation of δ_2, the most serious deficiency of using either eq 1 or 2 is that the temperature dependence of δ_1 of the solvents is implicitly passed on to the resultant δ_2. In our view, this deficiency leads to the situation that the resultant δ_2 are seriously underestimated, especially at elevated temperatures. For example, in the present work, δ_2 of polyethylene obtained from the use of eq 2 in the temperature range of

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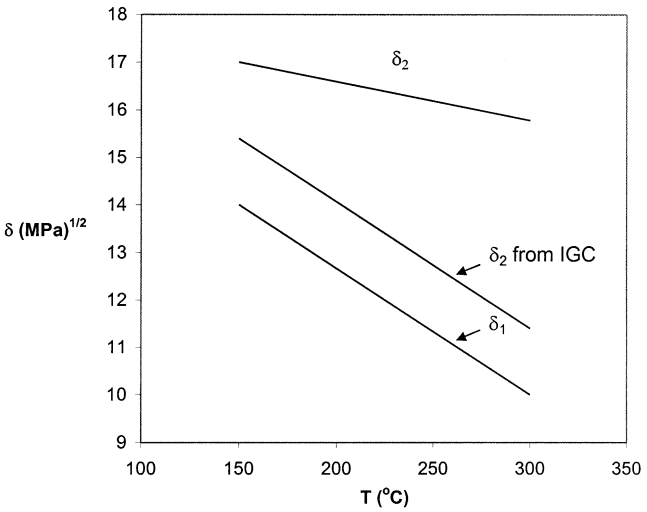

Figure 1. Schematic representation of the solubility parameters obtained from inverse gas chromatography.

170−230 °C are in the range 12.2−9.5 $(MPa)^{1/2}$, while much higher values are obtained from pressure−volume−temperature (PVT) measurements on similar polymer systems in the melt state at comparable temperatures (18−16 $(MPa)^{1/2}$).[5] This is because δ_1 used in IGC calculations are usually obtained from the corresponding heats of vaporization of the solvents at the experimental temperatures. And since the resultant δ_2 is mainly controlled by the δ_1 of the solvents used, not χ_{12}^{∞}, and solvents tend to have much higher free volumes or degrees of thermal expansion than those of the polymer, the above-described data analysis procedure inevitably yields δ_2 that is lower than their actual values. This idea is schematically illustrated in Figure 1.

Since the discrepancy between the δ_2 values obtained from IGC and PVT experiments is mainly attributed to the exclusion of PVT properties in the current IGC approach, we propose a new IGC data analysis approach in which a compressible regular solution model (i.e., with the inclusion of the PVT properties of the pure components in the data analysis), recently developed by Ruzette and Mayes, is incorporated.[6] The method is illustrated with the use of a series of linear low-density polyethylenes (LLDPE), but it is believed that such an approach should also be applicable to other high molecular weight polymers. This procedure is simple to use and only requires δ, thermal expansion coefficients (α), and hard-core volumes (V^*) of the solvents and polymers of interest as the input parameters. Since such information is generally available in the literature, PVT experiments are not required.

Theory

In the following, the detailed derivation of the equations that are used to determine δ_2 with the use of IGC data and the compressible regular solution model is presented. However, only the relevant expressions of the compressible regular solution model are shown here; interested readers should refer to the original article for the details and assumptions made in the derivation of those expressions.[6] To account for the differences in the PVT properties of the solvent and polymer, Ruzette and Mayes modified the original incompressible regular solution expression for $\Delta E_{mix}/V_T$ and obtained the following expression:

$$\frac{\Delta E_{mix}}{V_T} = \phi_1\phi_2(\tilde{\rho}_1\delta_{1,0} - \tilde{\rho}_2\delta_{2,0})^2 \tag{3}$$

where V_T is the total volume of the polymer solution, ϕ_1 and ϕ_2 are the volume fractions of the solvent and polymer, respectively, $\delta_{i,0}$ is the hard-core solubility parameter of component i, and $\tilde{\rho}_i$ is the reduced density defined as follows:[7]

$$\tilde{\rho} = \rho/\rho^* \tag{4}$$

Here, ρ is the density of the liquid at a given temperature while ρ^* is the hard-core density.

The reduced density is related to the reduced volume ($\tilde{V}$) by the following expression:[7]

$$\tilde{V} = V/V^* = \rho^*/\rho = 1/\tilde{\rho} \tag{5}$$

where V is the molar volume of the pure material at any temperature T and pressure P while V^* is the corresponding hard-core volume (zero kelvin, zero pressure). Here, the solubility parameter, hard-core solubility parameter, and reduced volume are related by the following equation:

$$\delta_i^{\,2} = \tilde{\rho}_i\delta_{i,0}^{\,2} = \frac{1}{\tilde{V}}\delta_{i,0}^{\,2} \tag{6}$$

To obtain the reduced volume or reduced density, an equation-of-state theory must be used. In this work, the one developed by Flory et al., as shown below, was used to determine $\tilde{V}$ for both the solvents and polymers.[8]

$$\tilde{V}^{1/3} - 1 = \frac{\alpha T}{3(1 + \alpha T)} \tag{7}$$

Here, α is the thermal expansion coefficient of the material of interest, which is essentially a manifestation of the PVT properties of a material. On the other hand, according to the Flory−Huggins lattice theory, $\Delta E_{mix}/V_T$ is given by the following equation:[1,2]

$$\frac{\Delta E_{mix}}{V_T} = RT\chi_{12}\phi_1\phi_2/V_0 \tag{8}$$

By combining the above equation with eq 3, one obtains the following expression:

$$\chi_{12} = \frac{V_0}{RT}(\tilde{\rho}_1\delta_{1,0} - \tilde{\rho}_2\delta_{2,0})^2 \tag{9}$$

By expanding the right-hand side of the above expression, Ruzette and Mayes showed that eq 9 could be separated into the compressible and incompressible contributions to the measured χ_{12}. The first term of the such expanded equation basically represents the relation between the hard-core Flory−Huggins interaction parameter, χ_{12}^*, and the hard-core solubility parameters of the solvent, $\delta_{1,0}$, and the polymer, $\delta_{2,0}$, and is as follows:

$$\chi_{12}^* = \left(\frac{V_0^*}{RT}\right)(\delta_{1,0} - \delta_{2,0})^2 \tag{10}$$

Here, V_0^* is the hard-core molar volume of the solvent or any arbitrary chosen reference volume. In this work, we used the hard-core molar volume of a repeat unit of the polymer of interest as V_0^* instead of those of the

Table 1. Molecular Weight Averages, Polydispersity, Melt Index, and Branch Content of the LLDPE Used

polymer	M_n	M_w	polydispersity	melt index	branch content
A-1	20 500	102 500	5.0	1.02	12.9
A-2	17 300	105 530	6.1	1.02	35.0
A-3	18 800	122 200	6.5	0.40	11.9
A-4	26 400	116 160	4.4	0.65	12.7
A-5	20 800	116 480	5.6	0.60	15.6
A-6	25 500	112 200	4.4	0.70	15.3
M-1	38 700	77 400	2.0	2.6	11.4
M-2	25 700	69 390	2.7	3.2	30.4
M-3	15 300	47 430	3.1	14.7	27.7
M-4	10 500	99 750	9.5	0.72	19.6
M-5	34 800	104 400	3.0	0.68	11.3
M-6	33 200	92 960	2.8	0.92	10.6

solvents used based upon the rationale given in ref 9. To obtain χ_{12}^*, Guillet and co-workers[10] showed that the following equation could be used

$$\chi_{12}^* = \ln\left(\frac{273.2RV_0^*}{V_g^0 P_1^0 V_1^*}\right) - 1 - \frac{P_1^0(B_{11} - V_1)}{RT} \qquad (11)$$

where V_1^* is the hard-core molar volume of the solvent and P_1^0 is the vapor pressure of the solvent, all at temperatures T. B_{11} is the second virial coefficient of the solvent while V_g^0 is the specific retention volume.

To obtain δ_2 with the use of the above equations and IGC, the following procedure has been developed. The first step is to measure χ_{12}^* (eq 11) and to calculate $\delta_{1,0}$ using δ_1 (from literature) and their corresponding thermal expansion coefficients (eqs 6 and 7). $\delta_{2,0}$ is then determined on the basis of the method of DiPaola-Baranyi and Guillet with the use of the expanded form of eq 10 instead of eq 2 and the measured χ_{12}^* and calculated $\delta_{1,0}$. Finally, δ_2 is calculated using the resultant $\delta_{2,0}$ and its corresponding thermal expansion coefficient (once again eqs 6 and 7).

Experimental Section

Materials. Twelve LLDPE samples were obtained from NOVA Chemicals Corp. in Calgary, Canada. The A-series LLDPEs were prepared by Ziegler−Natta while the M-series by single site catalysts. Owing to the differences in the catalyst and polymerization conditions used in the sample preparation processes, the samples vary in their branch content, molecular weight averages, and molecular weight distribution. Such characteristics of the samples are listed in Table 1. The solvents used were purchased from Fisher Scientific and used without further purification. They included both aliphatic and aromatic hydrocarbons such as 1-hexene, 1-octene, benzene, cyclohexane, *n*-hexane, *n*-dodecane, *n*-heptane, *n*-nonane, *n*-pentadecane, *n*-pentane, *n*-octane, toluene, and xylene. Methane was used as a marker for the determination of the net retention time of the other solvents. Thermophysical properties of the solvents used in the vapor phase (e.g., B_{11} and P_1^0) were obtained from refs 11−13, and thermal expansion coefficients of the solvents and polymers were estimated on the basis of correlations depicted in refs 14 and 15 while the specific volumes of the polymers were obtained from ref 16.

Preparation of Coated Solid Support. Each polymer was first dissolved in xylene in the temperature range 100−110 °C. An inert solid support chromosorb W (60/80) was then added to the polymer solution at a polymer to solid support mass ratio of approximately 10%. This was to ensure that the polymer would cover all the inner surfaces of the support. It should be noted that a lower ratio would not have enough polymer to coat all internal surfaces of the chromosorb, which would lead to long retention times. On the other hand, for ratios above 10%, the polymer coated on the solid support would form thick layers, and it would be difficult for the solvents to reach equilibrium promptly. Xylene was then slowly evaporated by gentle heating the slurry at about 100 °C with constant stirring using a rotary evaporator. The dried coated support was then transferred to a vacuum oven and conditioned at 80 °C for 4 h in order to remove the residual solvent. The percent loading of the polymer on the support was determined by calcinations of 1−1.5 g of the coated solid support in a furnace operated at a temperature of 850 °C for 12 h.

Table 2. Numerical Values of δ_1^2/RT and χ_{12}^∞/V_0 Terms for A-1 and M-1 at 170 °C

	A-1		M-1	
solvents/PE	δ_1^2/RT	χ_{12}^∞/V_0	δ_1^2/RT	χ_{12}^∞/V_0
1-hexene	0.0309	0.0036	0.0309	0.0029
1-octene	0.0408	0.0030	0.0408	0.0025
benzene	0.0585	0.0058	0.0585	0.0053
cyclohexane	0.0464	0.0036	0.0464	0.0031
hexane	0.0308	0.0034	0.0308	0.0028
n-dodecane	0.0489	0.0017	0.0489	0.0016
n-heptane	0.0365	0.0031	0.0365	0.0026
n-nonane	0.0424	0.0024	0.0424	0.0022
n-pentadecane	0.0543	0.0014	0.0543	0.0013
n-pentane	0.0222	0.0032	0.0222	0.0020
octane	0.0395	0.0027	0.0395	0.0024
toluene	0.0586	0.0044	0.0586	0.0040
xylenes	0.0561	0.0042	0.0561	0.0033

Column Preparation. Columns were prepared with the use of stainless steel tubes (100 cm length and approximately 0.18 cm i.d.) that were acetone washed in the lab and then plugged at one end by inert glass wool and filled with the coated solid support. To achieve even packing, each column was constantly vibrated during filling. After the column was filled, the other end was also plugged with the same type of glass wool. Columns were conditioned with prepurified helium for 2 days at 60 °C in a gas chromatograph in order to further eliminate any residual solvent before data collection. Helium was also used as a carrier gas in the actual experiments when various solvents were injected into the column, and its flow rates were measured at the corresponding experimental temperatures with the use of a soap bubble flowmeter. In general, the flow rates ranged from 18 to 20 mL/min, as recommended by the GC manual [HP 4890D Gas Chromatogragh Operating Manual, Hewlett-Packard Co. (1997)].

Instrumentation. All IGC measurements were carried out on a Hewlett-Packard 4890 gas chromatogragh equipped with a flame ionization detector (FID). Very small volumes (~1 μL) of the vapor of the selected solvents were injected manually with 10 μL Hamilton syringes with removable needle and Bevel tip #2 in order to satisfy the infinite dilution conditions for the solvents. For each solvent, three injections were carried out, and their differences were usually within 3% and the average retention times were used for subsequent calculations. Experiments were repeated at 170, 190, 210, and 230 °C for each column. The inlet and outlet pressures of the column were measured with the manometers and standard IGC procedures were followed for the measurement of χ_{12}^∞ values.[17]

Results and Discussion

Table 2 summarizes the numerical values of both the δ_1^2/RT and χ_{12}^∞/V_0 terms at 170 °C for A-1 and M-1 used in the present work. Results for the other LLDPEs at other temperatures are omitted here. As can be seen from the table, the δ_1^2/RT terms are significantly larger than the χ_{12}^∞/V_0 terms for these polymers. As a result, the method of DiPaola-Baranyi and Guillet yielded essentially identical Hildebrand solubility parameters at each temperature (see Table 3). It is worth noting that even though the technique is sensitive enough to yield χ_{12}^∞ for different polyethylenes with minor differ-

Table 3. Measured Hildebrand Solubility Parameters ((MPa)$^{1/2}$) of the LLDPE Used at Four Elevated Temperatures Using the Method of DiPaola-Baranyi and Guillet

polymer	T = 170 °C	T = 190 °C	T = 210 °C	T = 230 °C
A-1	12.2	11.2	11.1	9.5
A-2	12.2	11.1	11.1	9.6
A-3	12.2	11.1	11.1	9.6
A-4	12.2	11.2	11.1	9.6
A-5	12.2	11.1	11.1	9.5
A-6	12.2	11.1	11.1	9.6
M-1	12.2	11.2	11.1	9.6
M-2	12.2	11.1	11.1	9.6
M-3	12.2	11.1	11.1	9.5
M-4	12.2	11.2	11.1	9.6
M-5	12.2	11.1	11.1	9.6
M-6	12.2	11.1	11.1	9.6

Table 4. Thermal Expansion Coefficients and Hard-Core Volumes of the Solvents and Polyethylenes Used

solvents/PE	T (°C)	α (10^{-4} K^{-1})	V^* (cm^3/mol)	$\tilde{V}$
1-hexene	25	11.4	97.06	1.28
1-octene	25	11.6	121.80	1.28
benzene	25	11.4	69.21	1.28
cyclohexane	20	11.5	84.61	1.27
hexane	25	14.1	99.65	1.33
n-dodecane	25	9.3	184.30	1.23
n-heptane	25	12.6	113.70	1.30
n-nonane	25	10.8	141.41	1.26
n-pentadecane	25			
n-pentane	25	16.4	85.34	1.37
octane	25	11.6	127.87	1.28
toluene	25	10.5	84.58	1.26
xylenes	25	10.0	98.33	1.25
polyethylene	170	2.0	26.4[a]	1.08

[a] Hard-core volume of an ethylene repeat unit.

ences in their molecular structures, the χ_{12}^{∞}/V_0 term is still rather small compared to the δ_1^2/RT term. In other words, the characteristics of the polymers cannot really influence the slopes of the resultant lines (i.e., δ_2), and the δ_2 obtained from this approach were basically controlled by the magnitudes of the solubility parameters of the solvents used at the experimental temperatures. As a result, the temperature dependence of δ_1 was also passed on to the polymers. Since solubility parameters of the solvents used at the experimental temperatures are in the range 9.5−12.2 (MPa)$^{1/2}$, which were obtained using the following empirical correlation,[13] the resultant δ_2 felt into the same range.

$$\left(\frac{\delta_{1,T_2}}{\delta_{1,T_1}}\right)^2 = \left(\frac{V_{1,T_1}}{V_{1,T_2}}\right)^{2.27} \tag{12}$$

This explains why the measured δ_2 were considerably lower than those obtained from PVT measurements on the melts of similar LLDPE systems at comparable temperatures as mentioned before (e.g., PVT measurements show that a LLDPE similar to LLDPE-A2 has a δ_2 value of 18.1 (MPa)$^{1/2}$ at 170 °C).

To eliminate this problem, we incorporated the PVT properties of both the solvents and polymers in the data analysis process as described in the Theory section. Table 4 lists all the thermal expansion coefficients obtained from refs 14 and 15 and reduced volumes calculated on the basis of eq 7, which were required for the data analysis process. Thermal expansion coefficients of the solvents and the polymers were assumed to be temperature-independent. Obviously, if the temperature dependence of the thermal expansion coefficients were known, this would have made the estimation of δ_2 more accurate. It should be noted that polyethylene is characterized by a fairly small value of $\tilde{V}^{1/3}$ (i.e., 1.03) compared to those of the solvents (ca. 1.12) at 170 °C. According to eq 7, when $\alpha = 0$, $\tilde{V}^{1/3} = 1$ whereas as $\alpha \to \infty$, $\tilde{V}^{1/3} \sim {}^4/_3$. Therefore, for the solvents that are near their critical points, they will have very large $\tilde{V}^{1/3}$ values, $\sim{}^4/_3$. In such cases, the differences in the reduced volumes between the solvents and polymers are large, and ignoring such differences in the data analysis would lead to large errors in the estimation of the solubility parameters of the polymers.

Table 5. Measured Hildebrand Solubility Parameters ((MPa)$^{1/2}$) of the LLDPE Listed in Table 1 at Four Elevated Temperatures with the Incorporation of a Compressible Regular Solution Model for Data Analysis

polymer	170 °C	190 °C	210 °C	230 °C
A-1	16.2	16.2	16.2	16.0
A-2	15.9	16.2	15.4	15.3
A-3	16.1	15.9	15.3	15.3
A-4	16.1	16.2	15.4	15.1
A-5	16.1	16.2	15.6	15.6
A-6	16.1	15.9	15.4	15.4
M-1	15.7	16.2	15.3	15.3
M-2	15.7	15.9	15.3	15.3
M-3	16.1	16.0	15.4	15.3
M-4	16.1	16.0	15.4	15.4
M-5	16.1	16.0	15.4	15.3
M-6	15.9	15.9	15.4	15.4

With the incorporation of the PVT properties of the materials listed in Table 4 into the method of DiPaola-Baranyi and Guillet, a new set of δ_2 values were obtained and are listed in Table 5. It can be seen that the resultant Hildebrand solubility parameters for the LLDPEs fell into the range 15.1−16.2 (MPa)$^{1/2}$, which are much closer to those obtained from PVT measurements at comparable temperatures, indicating that the simple incompressible regular solution model succeeded in predicting the solubility parameters of the polymers at elevated temperatures. However, the values are still about 1−2 (MPa)$^{1/2}$ lower than those values obtained from PVT measurements. The following may explain the differences.

It is well-known that χ_{12} is a concentration-dependent parameter; therefore, the resultant δ_2 depends on the concentration of the solvent used in a particular IGC experiment. Since most of the IGC experiments are carried out under the condition that the solvent concentration is at infinite dilution in the polymer, δ_2 obtained in this manner inevitably deviates from the true value. Another possible explanation for the discrepancies is related to the well-known geometric mean assumption that comes from the regular solution theory. In theory, only one solvent is needed to obtain δ_2 provided that the pair interaction energy between the solvent and the polymer follows the geometric mean assumption. Within experimental errors, different solvents should yield comparable δ_2 if they all obey the assumption. Since this is not necessarily the case for all the solvents used, δ_2 obtained will be different for different sets of solvents. Unfortunately, there exists no mechanism to determine whether a particular set of solvent−polymer pairs follows the geometric mean rule or not simply on the basis of the measured χ_{12}^{∞} values unless they are negative. It is worth pointing out that solvent−polymer pairs that follow the geometric mean rule should yield positive χ_{12}, but systems exhibiting positive χ_{12} do not necessarily follow the assumption.

As a result, it is uncertain which solvents should be included in the calculation of δ_2 when eq 2 is used. In consideration of these factors, the agreement between the present results and those of the PVT measurements is actually fairly reasonable. Obviously, if the amount of inaccuracy due to the above factors could be estimated, this would have given better results.

Finally, it should be noted that the temperature dependence of the polymer solubility parameter obtained from the proposed approach was much weaker than that of the values obtained from the original method. This is reasonable because polymers tend to have small thermal expansion coefficients than those of the solvents. However, the increase in δ from 170 to 190 °C observed in some systems is merely due to the variability of the data. It should be noted that the accuracy of the measured δ is about 1−3% depending on the temperature (i.e., 0.1−0.4 $(MPa)^{1/2}$ in the absolute term). Since δ_2 is not very sensitive to temperature over a narrow temperature range, the decreasing trend can only be observed over a wider temperature range, as seen in the present work. Another noteworthy point is that δ_2 has also been found to be not very sensitive to the variation of characteristics such as branch content and molecular weight distribution of the polymers used. This is consistent with the results obtained by other researchers.[5] Considering the variation (within 1 order of magnitude) in the branch content and molecular weight distribution of the polymers used in the present work and the accuracy of the technique, their effects on the measured solubility parameter could not detected.

Conclusion

A new IGC data analysis procedure based upon a compressible regular solution model has been developed. With the new approach, the differences in the thermal expansion coefficients of the pure components were accounted for. The solubility parameters obtained using the above-mentioned method were in reasonable agreement with those obtained from PVT measurements on similar systems at comparable temperatures. In fact, the current results reinforced the prediction of conventional equation-of-state theories that, in addition to intermolecular interaction, PVT properties of the pure components comprising polymer solutions also play a significant role in determining their solubility characteristics, especially at elevated temperatures.

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