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# Solubility of Polystyrene in Supercritical Fluids

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ABSTRACT: The partitioning of polystyrene chains into supercritical fluids (primarily ethane and also $CO_2$ and an ethane–propane mixture) was measured to characterize the distribution of the different styrene oligomers between a coacervate phase and an SCF phase, as functions of pressure (8.5 MPa $\leq P \leq$ 34.5 MPa), temperature (313 K $\leq T \leq$ 333 K) and polymer chain length ($3 \leq X_i \leq 40$). In all cases studied, the ability of supercritical ethane to fractionate polystyrene chains could be varied continuously from a gaslike to a liquidlike character, with relatively small changes in operating conditions. A statistical-mechanics-based lattice equation of state, developed to model polymer–supercritical fluid systems, was employed in the correlation of the data on the solubility of polystyrene chains into SCF. This model can reproduce quantitatively all the experimental trends for the polystyrene–ethane system, across changes in state variables, with one (apparently constant) binary interaction parameter, $\delta_{12}$.

## Introduction

The fractionation of polymers on the basis of molecular weight with liquids or very dense gases has received considerable attention in the past few decades (see, for instance, ref 1–5 and literature cited therein). It has been demonstrated[6-8] that for the fractionation of polymers with liquidlike solvents, to a first approximation, a mass-based partition coefficient for each chain length between the two equilibrium phases depends only on the molecular mass of the chain in an exponential fashion

$$\ln (K^*_i) = \ln (w''_i/w'_i) = -\sigma X_i + \ln \xi \qquad (1)$$

where the single and double primes are used to denote the phases dilute and concentrated in polymer, respectively. $w_i$ represents the weight fraction of the polymer chain in the relevant phase, $K^*_i$ is a partition coefficient, $X_i$ is the degree of polymerization (DP), and $\xi$ is a constant. $\sigma$, also termed the "separation factor", determines the dependence of the partition coefficient on the molecular weight of the polymer chain and is a function of temperature, pressure, and concentration.

Brønsted[6] and Schulz[7] derived eq 1 through the use of empirical arguments; later, Flory[8] presented the first theoretical development. Since the fractionation occurs between a polymer-rich phase and a solvent-rich phase, polymer chains of each DP must be in thermodynamic equilibrium across the two phases. The mathematical criterion that expresses this situation is the equality of chemical potentials of the relevant species in both phases

$$\mu'_i = \mu''_i \qquad \text{(all components } i\text{)} \qquad (2)$$

Flory obtained expressions for the chemical potential of each constituent of the mixture through the use of the Flory–Huggins lattice model.[9,10] On substituting these formulae in eq 2, the functional form for the partition coefficient, $K^*_i$, represented in eq 1, can be recovered.[3,8] One finds that $\sigma$, the separation factor in eq 1, is independent of the chain length of the component $i$, to zeroth order.

To date, data reported in the literature for fractionation of polymers by liquid solvents are usually obtained from molecular weight averages on polymers of relatively narrow molecular weight distributions. Equation 1, which is the governing equation for this fractionation process, however, is valid strictly only for individual chain lengths. The calculation of $\sigma$ from eq 1, using average molecular mass data, will therefore not allow for an unequivocal determination of the molecular mass dependence of $\sigma$. Schulz and Jirgensons[2] suggested that $\sigma$ is a weak function of molecular mass based on average molecular mass data for the fractionation of polymers with liquid solvents. This observation has been subsequently verified by Okamoto and Sekikawa,[11] Breitenbach and Wolf,[12] Tsuyomoto et al.,[13] and Koningsveld and co-workers.[14] Tong et al.,[15] however, show that the separation factor may become dependent on the polymer's molecular mass when the sample is of a broad distribution.

The solubility and fractionation of polymers (specifically polyethylene) in very high-pressure ethylene (of the order of 200 MPa; where 1 MPa ≡ 10 bar) have been reported by Spahl and Luft.[5] For the polymers considered, mostly of molecular weight around 1000, they found an exponential dependence of the partition coefficient on the average DP of the polymer in consideration, implying that $\sigma$ has a constant value in the regime investigated.

Using liquid or liquidlike solvents to fractionate polymers has, however, the disadvantage that the fractionating ability of such solvents cannot be adjusted easily through changes in operating conditions. A remedy for this problem would be to use solvents with continuously adjustable solvent power such as supercritical fluids (SCF) or fluids near their critical point.

The region around the critical point is one of rapid changes in properties. The density of a substance in this regime is very sensitive to changes in state variables and can vary from gaslike to liquidlike with relatively small changes in pressure or temperature. In Figure 1 a plot of the reduced pressure vs. reduced density for a substance near its critical point is reproduced to illustrate this point.[16] The sensitivity of the density to state variables in the vicinity of the critical point is of importance since the solvent power of an SCF is related directly to its density.

Almost all of the published, quantitative data for solubility of solids or liquids in SCF are restricted to low molecular weight compounds with some skeletal data for undefined, relatively high molecular weight materials.[17] Little data exist to indicate the variation of solubility as a function of molecular weight in a homologous series of compounds. Of course, the solubilities of the members of a homologous series in an SCF decrease as the solute chain length increases, as has been inferred from chromatographic techniques.[18] Schröder and Arndt[19] observed qualitatively that the solubility of a polymer (PVC and polystyrene) in supercritical $CO_2$ decreases as one proceeds along a homologous series, and Krukonis and McHugh[20,21] have used the concept of preferential solubility of lower molecular weight compounds from a mixture into an SCF to fractionate a polydisperse polymer on the basis of molecular mass.

To date, however, little quantitative data exist on the fractionation of polymers with supercritical fluids.[22] It was

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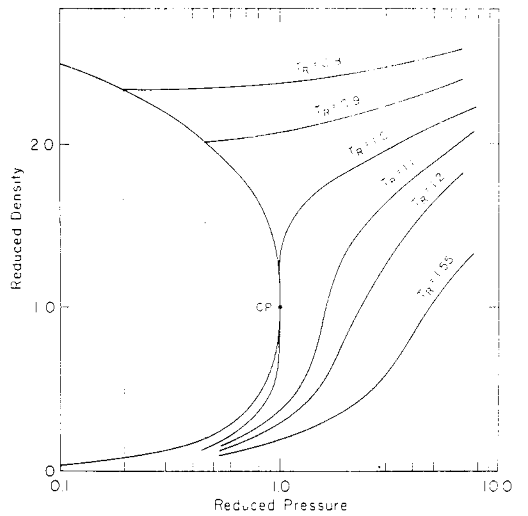

**Figure 1.** A reduced pressure vs. reduced density plot for $CO_2$ near its critical point ($T_c$ = 304.2 K, $P_c$ = 7.38 MPa). Several isotherms are shown.[16]

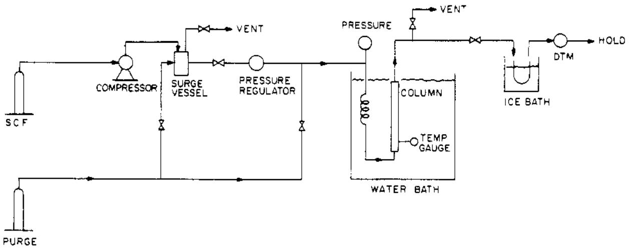

**Figure 2.** A schematic drawing of the experimental apparatus for the determination of solubility of polymer chains in SCF.

the aim of this work to measure partition coefficients for individual chain length polymers in SCF as functions of pressure and temperature and for several solvents. The fractionation data obtained with SCF solvents were also compared to corresponding values for a conventional liquid solvent to illustrate the efficacy of SCF as media with continuously adjustable solvent quality. A statistical-mechanics based lattice equation of state[23-25] was then used to model the data quantitatively across variations in polymer chain length, pressure, and temperature.

## Experimental Section

The experimental apparatus used for the measurement of solubility of polymers in SCF is shown schematically in Figure 2. It consisted of a flow-through system with polymer in a column (Autoclave Engineers) being contacted with the SCF. The whole system was maintained at a constant temperature (±0.1 K) in a water bath with a mixer–stirrer (Thermomix 1460) and at constant pressure (±0.01 MPa) with a pressure regulator (Matheson, Model 3064). Gas was removed from the top of the column (saturated with the polymer) and flashed to atmospheric pressure with a metering valve (Autoclave Engineers). This valve was maintained at a temperature at least 20 K above the glass-transition temperature of the pure polymer to prevent "plugging". To ensure that a thermodynamic equilibrium was established between the polymer and the SCF, the flow rate of the fluid was reduced until it was found that there was no measurable effect on the solubility; this was achieved for a SCF flow of ca. 1 standard L/min. The precipitated polymer was collected in U tubes and the integrated gas flow measured (±0.01 L) with a dry-test meter (Singer, DTM 115). The polymer in the U tube was subsequently dissolved in a measured amount of tetrahydrofuran (E.M. Sciences, TX0282-1, Omnisolv Grade) and analyzed by size exclusion chromatography (Hewlett-Packard liquid chromatograph Model 1090A with Waters' Ultrastyragel columns 10571, 10572, and 10573 in series) for total mass and DP distribution. Chains of DP up to 13 were resolved into individual peaks by this procedure; the universal calibration was employed for DP above this threshold.

High purity ethane (99.9%, Matheson Gas Products), carbon dioxide (99.9%, Matheson Gas Products), and a gas mixture (87% ethane, 13% propane by mole, Matheson Gas Products) were the SCF used in this study. Heptane (Mallinckrodt) was also employed as a solvent. Two narrowly distributed polystyrene standards ($M_n$ = 2060 g mol$^{-1}$, $M_w/M_n \approx 1.2$, and $M_n$ = 800 g mol$^{-1}$, $M_w/M_n \approx 1.25$, Pressure Chemicals) were the polymers used in the experiments. Details of the experimental technique have been presented elsewhere.[25]

## Modeling

Solubility data were modeled by a novel lattice model equation of state (EOS) that was developed to correlate data from such systems.[23-25] While we shall present a brief synopsis of the model here, a more detailed description has been presented elsewhere.[24] In this model, molecules are assumed to occupy cells in a three dimensional cubic lattice of coordination number $z$ (set to 10) and of cell size $v_H$ (set to $9.75 \times 10^{-6}$ m$^3$ mol$^{-1}$). Each molecule (≡ species 1) is assumed to occupy $r_1$ sites, and the lattice has empty sites termed "holes". Under these assumptions the EOS that defines a *pure* component is

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v} + (q_1/r_1) - 1}{\tilde{v}}\right) - \frac{\vartheta^2}{\tilde{T}} \quad (3)$$

where $\vartheta$ is the surface area fraction of sites in the lattice that are occupied by molecular segments. ($zq_1$) is the number of external contacts per molecule, $P$ the pressure, $T$ the temperature, and $v$ the specific volume. The tilde (~) denotes reduced variables, which are defined by the equations

$$\tilde{P} = (P/P^*) \qquad \tilde{v} = (v/v^*) \quad (4a)$$

$P^*$ and $T^*$, the quantities used in reducing $P$ and $T$ to nondimensional variables, are related by the equation

$$(z/2)\epsilon_{11} = P^* v_H = RT^* \quad (4b)$$

where $\epsilon_{11}$ is the interaction energy between segments of molecules. In the EOS for each pure component there are two unknown parameters, $\epsilon_{11}$ and $v^*$, the reducing parameter for volume.

We have shown elsewhere[24,25] that the EOS in eq 3 is a simple extension of well-known EOS, at the same time more rigorous but less adaptable for the empirical fitting to experimental data than other published EOS of the same genre (see, e.g., Kleintjens,[26] Kleintjens and Koningsveld,[27] Flory,[9] Sanchez and Lacombe,[28,29] Okada and Nose[30,31]). It reduces in some limits to well-known EOS both for polymer and small molecule EOS,[25] thus suggesting that it has the correct functional form for applications to the systems of interest. It also has the merit of requiring only two adjustable parameters per pure component. It was expected that this EOS would fit experimental data well and allow for reliable predictions with a minimum number of binary adjustable parameters when applied to mixtures of polymers and SCF.

Application of eq 3 requires determination of $\epsilon_{11}$ and $v^*$. For pure components below their critical points, the technique of Joffe et al.[32] was employed. This involved the matching of chemical potentials of the component across the liquid and vapor phases at the vapor pressure of the substance. Also the actual and predicted saturated liquid densities were matched

$$\mu_L = \mu_v \quad (5a)$$

$$v_L(\text{computed}) = v_L(\text{experiment}) \quad (5b)$$

This set of equations was solved by the use of a Newton's method to yield the pure component parameters.

**Table I**
**Pure Component Parameters Used**

| component | $T$, K | $T_c$, K | $P_c$, MPa | $\epsilon_{11}/R$, K | $v^*$, cm$^3$ g$^{-1}$ |
|---|---|---|---|---|---|
| ethane[a] | 310–360 | 305.4 | 4.98 | 73.732 | 1.70 |
| carbon dioxide[b] | 310–370 | 304.2 | 7.38 | 82.026 | 0.82 |
| propane[c] | 333 | 369.1 | 4.19 | 93.575 | 1.29 |
| polystyrene[d] | 310–340 | | | 121.363 | 0.88 |

[a] Data for the ethane system from Goodwin et al.[35] [b] $P$–$v$ data for carbon dioxide from Angus et al.[36] [c] Data for propane from Reid et al.[37] [d] Data for the polystyrene from Panayiotou and Vera.[33]

For substances above their critical point, the pure component parameters were obtained by fitting the EOS (eq 3) to isothermal $P$–$v$ data. For supercritical ethane and carbon dioxide in the temperature range of interest (310–360 K), the calculated parameters were found to be relatively constant, both with variations in temperature and pressure.

The parameters for polystyrene above its glass transition temperature (~380 K) have been determined by Panayiotous and Vera.[33] We employed these parameters in our modeling in the temperature range of interest, with the following two assumptions:

(i) We assumed that polystyrene at the experimental conditions ($313\ \mathrm{K} \leq T \leq 333\ \mathrm{K}$, $8.0\ \mathrm{MPa} \leq P \leq 34\ \mathrm{MPa}$) in the presence of the SCF used is in a thermodynamic equilibrium state. It is well-known that $T_g$ is strongly dependent on chain length, and for polystyrene this chain length dependence is available.[41] At 0.1 MPa, for instance, chains of molecular weight 3400 have a corresponding $T_g$ of ca. 340 K. In the presence of solvents the glass transition temperature of a polymer is further reduced. Studies with high molecular weight polystyrene in the presence of $CO_2$[34] have shown that the gas, even at low pressures (~0.5 MPa), causes a dramatic decrease in the glass transition temperature due to plasticization. Higher pressure increases the $T_g$ value due to the reduction of free volume, but in the pressure range $8.0\ \mathrm{MPa} \leq P \leq 25\ \mathrm{MPa}$ the $T_g$ value for such systems is of the order of 333 K. The combined effects of low DP and the SCF would depress $T_g$ sufficiently to ensure that the polymer in our experiments is nonglassy.

(ii) $\epsilon_{11}$ and $v^*$ (in units of m$^3$ kg$^{-1}$) were chosen to be independent of chain length, since no specific data on thermodynamic properties for oligomers of any chain length are available. The pure-component parameters used in this study are listed in Table I.

Extension of this model to binary and multicomponent mixtures requires mixing and combining rules. The coordination number ($z$) and the lattice size ($v_H$) are assumed constant, independent of composition. A linear mixing rule of the type

$$B_M = \sum B_i y_i \tag{6}$$

is used for the mixture parameters $v^*$, $q$, and $r$. In eq 6, $B$ represents some generalized property, while $y_i$ is the mole fraction of component $i$ in the relevant phase. The mixing rule for the energy parameter ($\epsilon$) is[24]

$$\epsilon_M = \sum\sum \vartheta_i \vartheta_j \epsilon_{ij} \Gamma_{ij} \tag{7}$$

where $\vartheta_i$ is the surface area fraction of the segments of $i$ molecules and $\Gamma_{ij}$ is a factor that corrects for the nonrandom distribution of segments of $j$ molecules about the segments of $i$ molecules. (This factor is obtained by the solution of the quasi-chemical equations.[23-25,38]) The combining rule for the mixture parameter $\epsilon_{ij}$ in eq 7 is

$$\epsilon_{ij} = \epsilon_{ii} \qquad (i = j) \tag{8}$$

$$\epsilon_{ij} = 0.5(\epsilon_{ii} + \epsilon_{jj})(1 - \delta_{ij}) \qquad (i \neq j)$$

$\delta_{ij}$ represents a single adjustable parameter (per binary) used in fitting the model to data.

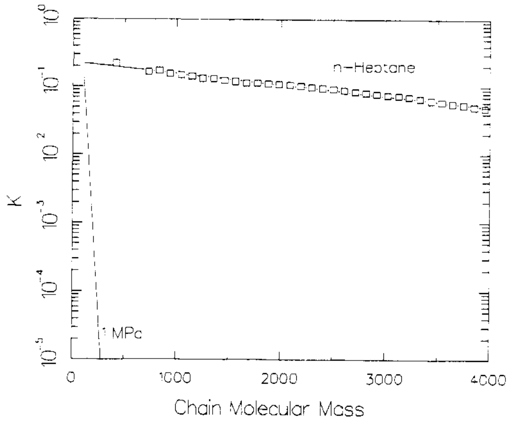

**Figure 3.** Comparison of the partitioning behavior of *n*-heptane (298 K) and ethane (at 1 MPa and 333 K) for polystyrene oligomers between a polymer-rich phase and a solvent-rich phase. (□) Experimental data; the line through the points is a best-fit straight line. Ethane results are calculated ideal solubilities.

## Results and Discussion

**Solubility in a Liquid and a Gas Solvent.** In Figure 3, we present a plot of the equilibrium solubility of polystyrene of number-average molecular weight 2060 in $n$-heptane. The plotted ordinate is a mass-based partition coefficient that is defined as

$$K_i = w_i^{\mathrm{v}} / w_i^{\mathrm{s}} \tag{9}$$

where $w_i^{\mathrm{v}}$ is the mass fraction of the chain with DP $i$ (the "$i$-mer") in the solvent phase (in units of g of $i$-mer/g of solvent) while $w_i^{\mathrm{s}}$ is the mass fraction of the same $i$-mer in the solid, polymer phase (in units of g of $i$-mer/g of *solvent-free solid*). This is in contrast to eq 1 where the mass fraction of the chain in both phases (with the solvent) was used to calculate the separation factor. ($K$ and $K^*$ are different, but under the conditions addressed in this paper they differ by an essentially constant factor.) The point to be emphasised in Figure 3 is the observed log–linear dependence of the partition coefficient on the molecular weight of the polymer chain between the polymer-rich and the heptane-rich phases. This relationship has already been summarized in eq 1 and is well-known in the literature. The data presented here are for *individual* chain lengths, while in the past average molecular weights have usually been reported. Results in Figure 3 show that the equation

$$\log K_i = C_0 - C_1 X_i \tag{10}$$

is strictly valid on an individual chain length basis for the system examined. Here $X_i$ is the DP of the relevant oligomer, and $C_0$ and $C_1$ are temperature-dependent constants. In Figure 3 we also show the fractionation expected if an ideal gas (ethane, in this case) at a pressure of 1 MPa and 333 K were used as a solvent.

Pronounced fractionation is obtained with the use of a gaseous solvent. However, the loading of the polymer in the gas phase is low. Liquid solvents, on the other hand, offer poor fractionation, as suggested by the small, absolute value of the slope of the line log $K_i$ vs. molecular mass, but afford higher loadings. The two lines shown in this figure thus represent the two cases of fractionation that can be achieved through the use of conventional solvents. Since the solvent power of conventional solvents cannot be altered easily, these also represent the fractionation that is normally achievable with such solvents. We examine

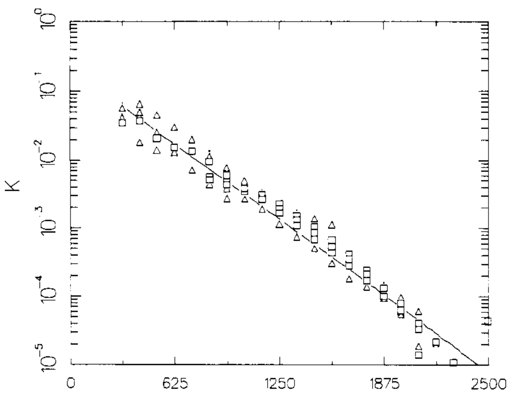

**Figure 4.** Experimental data for the partition coefficients of different styrene oligomers between a polymer-rich phase and an ethane-rich phase at 25 MPa and 333 K: (□) data obtained with a polymer of average molecular mass of 2060 and (△) from a polymer of molecular mass 800.

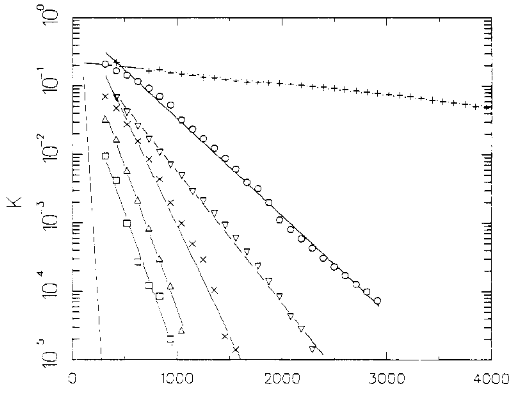

**Figure 5.** Experimental data for the solubility of polystyrene in various solvents. [The lines are best-fit straight lines.] (+) are data for partition coefficients in $n$-heptane at 298 K. All other data are at 333 K with ethane as solvent: (□) at 8.5 MPa, (△) 10 MPa, (×) 15 MPa, (▽) 25 MPa, and (○) 34 MPa. The line with no points corresponds to "ideal" ethane at 1 MPa.

SCF–polymer systems as a possible means to access the region in Figure 3 that cannot be achieved by the use of conventional solvents.

**Experimental Solubilities in Supercritical Ethane at 333 K.** The dependence of the partition coefficient of polystyrene chains in supercritical ethane ($T$ = 333 K) on molecular mass is presented in Figure 4 at a single pressure (25 MPa). Plotted data are those obtained from polystyrenes of number-average molar mass 800 and 2060 g mol$^{-1}$.[22] Results from several runs at 25 MPa are shown in Figure 4 to illustrate the accuracy and error inherent in all measurements. It is seen that the measured values of $K_i$ for the various oligomers from both the samples fall on the same line. This has important connotations. First, it demonstrates that the partition coefficient of any chain from the polymer-rich phase to the supercritical phase is *independent* of the composition of the parent polymer. Figure 4, therefore, suggests that the observed linearity represents a general, universal behavior for the solubility of polystyrene chains in supercritical ethane at these operating conditions. *In essence, therefore, we are dealing with a linear combination of independent quasi-binaries of SCF with the individual chain length polymers.* We shall use this important deduction as a starting point in our modeling.

**Table II**
**Variation of $C_0$ and $C_1$ with Pressure at 333 K**

| $P$, MPa | $C_0$ | $C_1$ | $P$, MPa | $C_0$ | $C_1$ |
|---|---|---|---|---|---|
| 8.5 | −0.74 | 0.423 | 25.0 | −0.34 | 0.192 |
| 10.0 | −0.08 | 0.417 | 34.0 | −0.16 | 0.137 |
| 15.0 | 0.16 | 0.319 | | | |

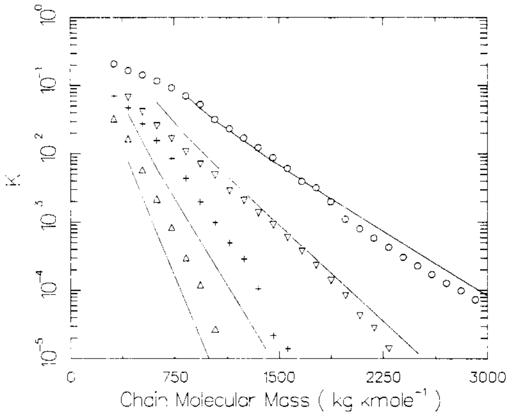

**Figure 6.** Comparison of the lattice model predictions with $\delta_{12}$ = 0.018 (—), with experimental partition coefficient data for the polystyrene–ethane system at 333 K and (△) 10 MPa, (+) 15 MPa, (▽) 25 MPa, and (○) 34 MPa.

In Figure 5, we present averaged data for partition coefficients as a function of DP at several pressures between 8.5 and 34 MPa at 333 K. (The lines through the points are best fit straight lines.) Again, these include data from both the 800 and 2060 g mol$^{-1}$ polymer samples. The partition coefficient data from Figure 3 ($n$-heptane and ethane at 1 MPa) are also shown for comparison. A log-linear dependence for $K_i$ on chain molecular mass is observed at all pressures. At the lowest pressure (8.5 MPa) the partition coefficient line is steep, indicating a pronounced fractionation. As one proceeds to higher pressures, the ethane density increases and consequently its solvent power becomes more "liquidlike". The loading of the SCF phase with chains of higher mass thus increases. However, the fractionation obtained becomes less pronounced. In summary, the partitioning behavior of the SCF can be varied easily from gaslike to liquidlike with relatively small changes in pressure. This is a direct consequence of the sensitivity of the density and hence the solvent power of such solvents in the vicinity of their critical points.

The data in Figure 5 were fitted to a line of the form of eq 10, and the "best fit" values of $C_0$ and $C_1$ are shown in Table II. The dependence of $C_1$ on pressure reflects the strong dependence of the selectivity of the solvent SCF on operating conditions. $C_0$, however, does not follow a trend explainable in a similarly simple fashion, and the observed variation may only be a manifestation of experimental error.

**Theoretical Results for Ethane at 333 K.** In modeling the experimental data, a statistical-mechanics based lattice model EOS[24] was employed along with the assumption that the polymer–SCF equilibrium could be treated as a linear combination of individual $n$-mer–SCF quasi-binaries. In Figure 6, the *averaged* experimental data presented in Figure 5 are compared to the results obtained from the lattice EOS for these two-phase quasi-binary systems. A single interaction parameter, $\delta_{ij}$ (= 0.018), independent of chain length and pressure was employed. The model results are in good agreement with the experimental data (within experimental error, see Figure 4) at all pressures beyond a molecular weight of ca. 1200. The reason for the disagreement between the model and experiment below this molecular mass is speculated to be due to two factors. First, we assume that segments of all chains interact with the same energy per contact area, $\epsilon_{11}$.

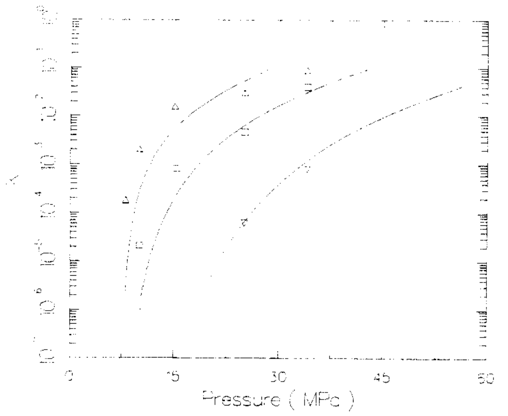

**Figure 7.** Experimental data and lattice model predictions (—) for the partition coefficients of individual polystyrene chain lengths in ethane at 333 K plotted as a function of pressure. Chains of molecular masses (△) 624, (□) 1040, and (▽) 2040 g mol$^{-1}$ are examined.

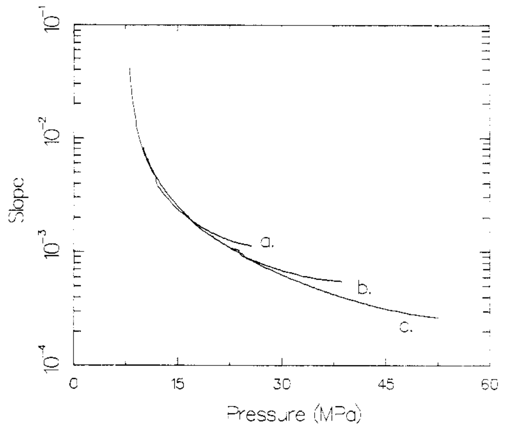

**Figure 8.** Lattice model predictions with $\delta_{12} = 0.018$ for the quantity $(1/X_i)[\partial \ln K_i/\partial P]_{T,\sigma}$ (in units of bar$^{-1}$) for the solubility of polystyrene chains (of molecular weights (a) 624, (b) 1040, and (c) 2080 g mol$^{-1}$) in ethane at 333 K.

Clearly, this assumption breaks down for shorter chains when end effects become important. Second, the results shown are valid only as long as there are two phases in equilibrium; the shortest chains are, however, believed to be completely miscible with ethane at the conditions employed; e.g., at pressures greater than 8 MPa at 333 K, *pure* styrene monomer is completely soluble in ethane. Results predicted with a two-phase, quasi-binary model are, therefore, unreliable for the smallest oligomers.

The data from Figure 6 were plotted vs. pressure in Figure 7 so that the variation of the partition coefficient with pressure for different chain lengths could be observed. The lattice model reproduces the experimental trends accurately for the chain lengths examined. For the lowest molecular mass examined (624 g mol$^{-1}$), the partition coefficient increases rapidly at a pressure around 8 MPa and begins to level off at higher pressures (ca. 10 MPa). This is consistent with observed trends for the solubility of small-molecule compounds in SCF (naphthalene or acridine in supercritical $CO_2$, for example[39]) where a sharp increase in solubility is observed in the region of rapidly increasing density of the SCF. As one proceeds to the higher molecular mass chains, this increase in solubility is more gradual and extends to higher pressures. For example, model predictions for the partition coefficient of the polymer chain of molecular mass 2040 g mol$^{-1}$ show that it is still increasing at a relatively high pressure of 40 MPa. The behavior of macromolecular compounds in SCF is thus seen to be different in character from that of small molecular materials.

The lattice model EOS quantitatively reproduces most of the relevant features of the partition coefficient diagrams. Clearly, the model must be used only outside the immediate vicinity of the critical point of the SCF ($|T - T_c|/T_c$, $|\rho - \rho_c|/\rho_c <$ ca. 0.05), since the EOS is a mean-field equation and, therefore, limited to use outside the critical region.

In Figure 7 it has been shown that $K_i$ for polystyrene chains increases with increasing ethane pressure. Also, we have shown that, as one proceeds to longer chain lengths, the region of rise in solubility (when plotted against pressure) becomes less pronounced and extends to higher pressures. At this point, we are interested in the theoretical reasons for the manifestation of these phenomena. From a straightforward mathematical procedure, one may show that[25]

$$\left.\frac{\partial \ln K_i}{\partial P}\right|_{T,\sigma} \approx X_i \frac{(V_1^{s} - \bar{V}_1)}{RT} \tag{11}$$

where $\sigma$ is a derivative taken when an equilibrium exists between the condensed and the SCF phases. $V_1^{s}$ is the chain's molar volume per monomeric unit, $\bar{V}_1$ the partial molar volume per monomeric unit in the dilute SCF solution, and $X_i$ is the DP. The pressure derivative of the partition coefficient of a polystyrene chain (into supercritical ethane), therefore, scales linearly with its chain length. So, although the isotherms for low molecular weight compounds (as the monomer and dimer) essentially level out at pressures greater than ~15 MPa, the isotherms for higher molecular weight polymers will continue to rise since their rate of increase with pressure is magnified by their chain lengths, as suggested by eq 11.

To examine the validity of eq 11 and the assumptions made in its derivation, in Figure 8 we present plots of the quantity $(1/X_i)[\partial \ln K_i/\partial P]_{T,\sigma}$ against pressure for three different polystyrene chain lengths (of molecular weight 624, 1040, and 2080 g mol$^{-1}$), as predicted from the lattice model. If eq 11 wer valid, we would obtain a single curve that is independent of polymer chain length. Results shown in Figure 8 illustrate that this result is valid near the critical density of ethane (at 333 K, $|T - T_c|/T_c$ is larger than 0.05). Discrepancies arise at higher pressures, but the point to be emphasised here is the remarkable agreement of the slopes for the different chain lengths in the vicinity of the sharp rise in density of the solvent SCF. The important deduction that may be made on the basis of Figure 8 is that the qualitative differences noted in the behavior of small and large molecular weight compounds when dissolved in SCF are a manifestation of the difference in chain lengths of the solutes. While eq 11 stresses the differences in behavior between a small and a macromolecular compound, the identical value of slopes noted in the pressure regime $P < 20$ MPa verifies the presence of a governing universality determining the solubility of different sized molecules in SCF.

**Solubilities in Ethane at Several Temperatures.** Partition coefficient curves for different temperatures at one pressure (25 MPa) were examined to understand the effect of the variation of temperature, another state variable, on the fractionation ability of supercritical ethane. In Figure 9, the $K_i$ values for polystyrene chains are plotted against chain molecular mass at 25 MPa and three different temperatures (313, 323, and 333 K, respectively). The first point demonstrated by this diagram is that the partition coefficient curves for this system are not very sensitive to temperature changes. This could be due to the fact that, at these conditions, ethane has an essentially liquidlike density (~300 kg m$^{-3}$) which varies little with

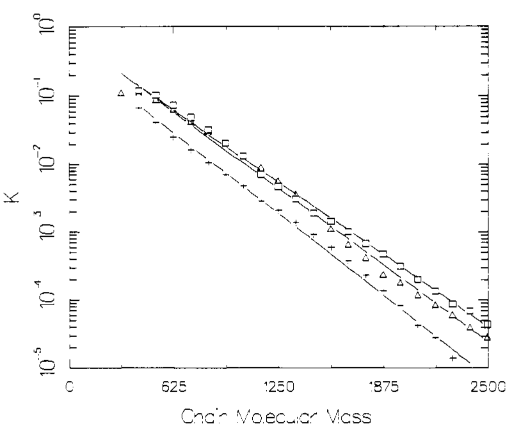

**Figure 9.** Experimental partition coefficient data for the polystyrene–ethane system at 25 MPa and (□) 313, (△) 323, and (+) 333 K. The lines represent best fit straight lines.

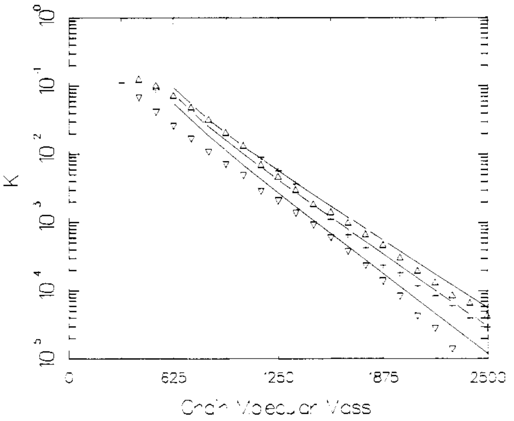

**Figure 10.** Comparison of the lattice model predictions [$\delta_{12}$ = 0.018 (—)] with experimental partition coefficient data for the polystyrene–ethane system at 25 MPa and (△) 313, (+) 323, and (▽) 333 K.

**Table III**
**Variation of $C_0$ and $C_1$ with Temperature at 25 MPa**

| $T$, K | $C_0$ | $C_1$ |
|---|---|---|
| 313 | −0.11 | 0.173 |
| 323 | −0.08 | 0.182 |
| 333 | −0.34 | 0.192 |

relatively small changes in temperature.

Data at different temperatures were fitted to an equation of the form presented in eq 10, and the results are reported in Table III.

The lattice model EOS was again used to fit the experimental data. It was found that the same value of $\delta_{ij}$ (0.018) that was used at 333 K could be used over the temperature range of interest. (The proximity to the solvent critical temperature makes this an unexpected result.) Data fits obtained with this value of the binary interaction parameter are demonstrated in Figure 10. The lattice model thus allows for the quantitative reproduction of experimental data (within experimental error, see Figure 4) for the polystyrene–ethane system across variations in chain length, pressure, and temperature with one apparently constant value of the interaction parameter, $\delta_{ij}$. The utility of the lattice model in the modeling of such systems is emphasized by its capability of predicting quantitative trends, in principle, by fitting it to a single datum point for the system of interest.

An interesting feature of Figures 9 and 10 is, that the curves corresponding to lower temperatures fall above the ones at higher temperatures. This would imply that a lower temperature affords a higher loading of the longer polystyrene chains than a higher temperature. This apparently anomalous result is a manifestation of the fact that at a lower temperature (at the same pressure) ethane has a higher density and hence solvent power for polystyrene, causing the polymer to have a higher solubility in the SCF phase. However, this result must be contrasted to corresponding results obtained for the solubility of a low molecular weight compound in an SCF; as an example, literature values for acridine[39] are reproduced in Figure 11. (In this diagram, the mole fraction of acridine in the gas phase plays a role analogous to $K$ in our figures.) In such cases there is a region in the diagram, called the retrograde region, where the lower temperature solubilities are higher than at higher temperatures; at higher pressures, this trend is reversed. This reversal has been attributed to the fact that at higher temperatures the solid has a higher vapor pressure, thus causing it to be more soluble than at a lower temperature. In the case of a macromolecular species, for which the vapor pressure is dramatically reduced, this effect is not seen, suggesting again that the behavior of macromolecular compounds in SCF is different from that of small molecule solutes.

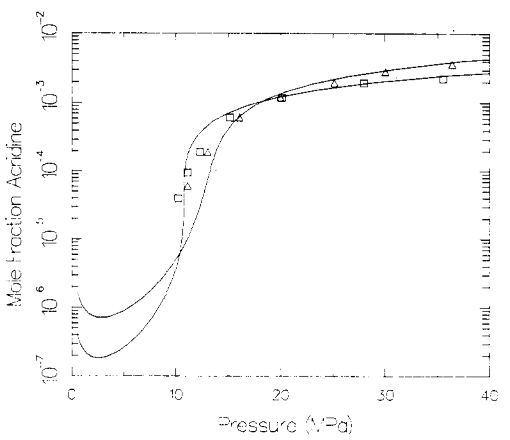

**Figure 11.** Comparison of the experimental data for the solubility of acridine in $CO_2$ at (□) 328 and (△) 343 K with lattice model predictions (—) with $\delta_{ij}$ = 0.135.

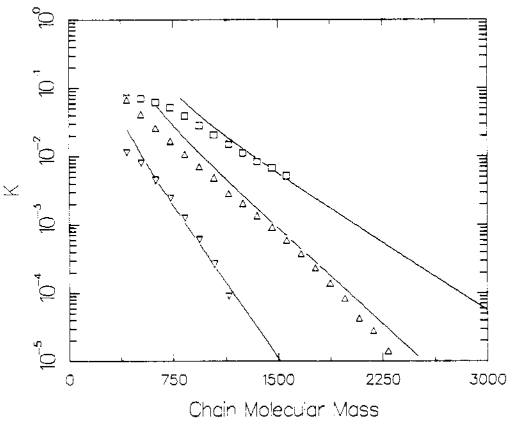

**Figure 12.** Comparison of lattice model fits (—) to experimental data for the fractionation of polystyrene chains with (△) ethane ($\delta_{12}$ = 0.018), (▽) $CO_2$ ($\delta_{12}$ = 0.08), and (□) ethane + 13% propane ($\delta_{12}$ = 0.03).

**Solubilities in Different Solvents.** The effect of the variation of solvent type on the partition coefficient curves was also examined. To this end, $CO_2$, a popular supercritical solvent, and a mixture of ethane and propane (ca. 87:13 by mole) were used. Propane is a liquid under the experimental conditions and is expected to behave in a manner similar to heptane; a mixture of ethane and propane was expected to behave in fractionation in a fashion intermediate between ethane and heptane. The averaged experimental data for the partition coefficient of chains of different molecular masses in the different gases at 333 K and 25 MPa is shown in Figure 12.

Carbon dioxide is the poorest solvent at these conditions. One could argue that at 25 MPa $CO_2$ is at a lower reduced pressure (and hence lower reduced density) than the other solvents; a comparison of ethane and $CO_2$ at the same reduced pressure shows, however, that $CO_2$ is still a poorer solvent than ethane. The mixture of ethane and propane, on the other hand, is a better solvent (and consequently a poorer fractionating medium) than pure ethane. This leads us to the important conclusion, in agreement with heuristic knowledge, that the solvent quality of an SCF can be made more liquidlike simply by adding a higher member of the same homologous series or, extrapolating, another less volatile compound to the SCF. As expected no "synergistic" effects were observed when solvent mixtures were used.

The experimental data in Figure 12 have been modeled by the lattice EOS. Again quantitative fits were obtained with the use of a single adjustable parameter per binary.

## Conclusions

In summary, regions of the partition coefficient diagram that could not be accessed with the use of conventional solvents can be reached with relative ease with the use of SCF. Experimental data on the solubility and fractionation ability of SCF/polystyrene systems show that the partitioning ability of ethane can be modified from gaslike to liquidlike with relatively small changes in pressure. However, temperature does not play as important a role in the ranges examined. The effect of changing pressure on the behavior of the partition coefficient curves can be duplicated easily either by the use of other solvents or by adding liquid "dopants" to the SCF.

Experimental data on these systems can be quantitatively reproduced with a lattice model EOS with the use of a single adjustable parameter per binary that apparently is independent of pressure, chain length (beyond a DP of 12), and temperature. Model results also show that, even qualitatively, the behavior of macromolecular systems in SCF is substantially different from the corresponding trends with small molecule solutes.

Experimental data and modeling results for the polystyrene–SCF system suggest that the observed log–linear dependence of the partition coefficient on the chain molecular mass is a general trend for this polymer system. If we examine the lattice model in the context of a two-phase, quasi-binary polymer–SCF equilibrium system, we may generalize the polystyrene results to the case of any polymer–SCF system. Using expressions for the chemical potentials presented elsewhere[24,25] and simplifying, we obtain eq 10, which is valid outside the immediate vicinity of the region of the sharpest change in properties of the SCF ($|T - T_c|/T_c$, $|\rho - \rho_c|/\rho_c <$ ca. 0.05); a detailed derivation has been provided elsewhere.[25] Under the assumption of independent quasi-binaries, therefore, the trends observed in the partition coefficient on chain molecular mass appear to represent general rules for the solubility of polymers into SCF.[40]

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## Notation

| | |
|---|---|
| $C_0$, $C_1$ | fitted parameters in eq 10 |
| $K$, $K^*$ | partition coefficient |
| $P$ | pressure ($N\ m^{-2}$) |
| $r$ | number of segments per molecule (eq 3) |
| $R$ | universal gas constant ($J\ mol^{-1}\ K^{-1}$) |
| $T$ | temperature (K) |
| $v$ | molar volume ($m^3\ mol^{-1}$) |
| $v^*$ | molecular hard core volume ($m^3\ mol^{-1}$) |
| $v_H$ | lattice cell volume ($m^3\ mol^{-1}$) |
| $\bar{V}_1$ | partial molar volume per monomeric unit in SCF ($m^3\ mol^{-1}$) |
| $w$ | weight fraction of relevant species |
| $X$ | degree of polymerization |
| $z$ | lattice coordination number |
| $zq$ | number of external contacts per molecule segment (eq 3) |

## Greek Symbols

| | |
|---|---|
| $\Gamma$ | nonrandomness correction (eq 7) |
| $\delta_{ij}$ | binary interaction parameter between segments of $i$ and $j$ molecules |
| $\epsilon_{11}$ | interaction energies between molecule segments ($J\ mol^{-1}$) |
| $\vartheta$ | surface area fraction of sites occupied by molecular segments |
| $\mu$ | chemical potential |
| $\xi$ | constant (eq 1) |
| $\rho$ | density ($mol\ m^{-3}$) |
| $\sigma$ | separation factor (eq 1) |
| $\sigma$ | derivative taken along the saturation curve (eq 11) |

## Subscripts

| | |
|---|---|
| $c$ | critical property |
| $g$ | glass transition property |
| $i$ | $i$-mer polymer chain |
| $j$ | property of mixture component $j$ |
| $L$ | liquid-phase property |
| $M$ | mixture property |
| $V$ | vapor-phase property |

## Superscripts

| | |
|---|---|
| $'$ | phase dilute in polymer |
| $''$ | phase concentrated in polymer |
| $\sim$ | reduced variable (eq 3) |
| $*$ | reducing variable |
| $s$ | condensed-phase property |
| $v$ | vapor-phase property |

**Registry No.** $CO_2$, 124-38-9; $H_3CCH_3$, 74-84-0; $H_3CCH_2CH_3$, 74-98-6; polystyrene, 9003-53-6.

## References and Notes

(1) Hashizume, J.; Teramoto, A.; Fujita, H. *J. Polym. Sci., Polym. Phy. Ed.* **1981**, *19*, 1405.
(2) Schulz, G. V.; Jirgensons, B. *Z. Phys. Chem.* **1940**, *B46*, 105.
(3) Kurata, M. *Thermodynamics of Polymer Solutions*; Harwood Academic Publishers: New York, 1982; Chapter 2.
(4) Kleintjens, L. A.; Koningsveld, R.; Stockmayer, W. H. *Br. Polym. J.* **1976**, *8*, 144.
(5) Spahl, R.; Luft, G. *Angew. Makromol. Chem.* **1982**, *115*, 87.
(6) Brönsted, J. N. *Z. Phys. Chem.* **1941**, *44*, 257.
(7) Schulz, G. V. *Z. Phys. Chem.* **1941**, *44*, 155.
(8) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(9) Flory, P. J. *J. Chem. Phys.* **1941**, *9*, 660; **1942**, *10*, 51.
(10) Huggins, M. L. *J. Chem. Phys.* **1941**, *9*, 440; *J. Phys. Chem.* **1942**, *46*, 151.
(11) Okamoto, H.; Sekikawa, K. *J. Polym. Sci.* **1961**, *55*, 597.
(12) Breitenbach, V. J. W.; Wolf, B. A. *Makromol. Chem.* **1967**, *108*, 263.
(13) Tsuyumoto, M.; Einaga, Y.; Fujita, H. *Polymn. J.* **1984**, *16* (3), 229.
(14) Koningsveld, R.; Stockmayer, W. H.; Kennedy, J. W.; Kleintjens, L. A. *Macromolecules* **1974**, *7* (1), 73.
(15) Tong, Z.; Einaga, Y.; Fujita, H. *Macromolecules* **1985**, *18*, 2264.
(16) Paulaitis, M. E.; Krukonis, V. J.; Kurnik, R. T.; Reid, R. C. *Rev. Chem. Eng.* **1983**, *1* (2), 179.

(17) Chrastil, J. *J. Phys. Chem.* **1982**, *86*, 3016.
(18) Schmitz, F. P.; Klesper, E. *Makromol. Chem., Rapid. Commun.* **1981**, *2*, 735.
(19) Schröder, E.; Arndt, K.-F. *Faserforschung und Textiltechnik* **1976**, *27* (3), 135; **1976**, *27* (3), 141; **1976**, *27* (3), 151.
(20) Krukonis, V. J. *Polym. News* **1985**, *11*, 7.
(21) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*; Butterworth: Stoneham, MA, 1986.
(22) Kumar, S. K.; Suter, U. W.; Reid, R. C. *Fluid Phase Equil.* **1986**, *29*, 373.
(23) Kumar, S. K.; Reid, R. C.; Suter, U. W. In *Supercritical Fluids: Chemical and Engineering Principles and Applications*; Squires, T. G., Paulaitis, M. E., Eds.; ACS Symposium Series 329, American Chemical Society: Washington, DC, 1987; pp 88-100.
(24) Kumar, S. K.; Suter, U. W.; Reid, R. C. *Ind. Eng. Chem.*, in press
(25) Kumar, S. K. Sc.D. Thesis, Massachusetts Institute of Technology, 1986.
(26) Kleintjens, L. A. *Fluid Phase Equil.* **1983**, *10*, 183.
(27) Kleintjens, L. A.; Koningsveld, R. *Sepn. Sci. Tech.* **1982**, *17* (1), 215.
(28) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80* (21), 2352.
(29) Sanchez, I. C.; Lacombe, R. H. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 71.
(30) Okada, M.; Nose, T. *Polymn. J.* **1981**, *13* (4), 399.
(31) Okada, M.; Nose, T. *Polymn. J.* **1981**, *13* (6), 591.
(32) Joffe, J.; Schroeder, G. M.; Zudkevitch, D. *AIChE J.* **1970**, *48*, 261.
(33) Panayiotou, C.; Vera, J. H. *Polym. J.* **1982**, *14* (9), 681.
(34) Wang, W. V.; Kramer, E. J.; Sachse, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1371.
(35) Goodwin, R. D.; Roder, H. M.; Straty, G. C. *Thermophysical Properties of Ethane from 90 to 600 K at Pressures to 700 Bar*; National Bureau of Standards: Boulder, CO, 1976.
(36) Angus, S.; Armstrong, B.; deReuck, K. M. *International Thermodynamic Tables of the Fluid State of Carbon Dioxide*; Pergamon: Oxford, 1976.
(37) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
(38) Guggenheim, E. A. *Mixtures*; Clarendon: Oxford, 1954.
(39) Schmitt, W. J. Ph.D Thesis, Massachusetts Institute of Technology, 1984.
(40) It must be emphasized that this result is contingent on the assumption that the interaction energies between segments of molecules are independent of the chain length of the molecule under consideration. A model that assumes this will, naturally, predict a linear dependence of $K$ on the molecular mass of the relevant chain. For example, Flory[9] has predicted this same functional dependence for the fractionation of polymers with liquid solvents.
(41) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.

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# Entropically Driven Miscibility in a Blend of High Molecular Weight Polymers

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ABSTRACT: Molecular miscibility between *cis*-1,4-polyisoprene and atactic poly(vinylethylene), as evidenced by their spontaneous interdiffusion, is reported. It is suggested that miscibility arises in this blend of nonpolar hydrocarbons, not from specific interactions between moieties on the respective chains, but merely from the small combinatorial entropy accompanying mixing. This is made possible by fortuitous near equivalence of the dispersive energy densities of the respective chain subunits. The customary single glass transition is observed in the mixtures, at a temperature whose composition dependence is quantitatively in accord with theory for random arrangement of the statistical segments. No UCST was observed in this system, even for the least stable compositions, at temperature down to the onset of glassy behavior (ca. −45 °C). Crystallization of the polyisopropene is inhibited by the presence of the poly(vinylethylene); the latter, moreover, is apparently unable to disentangle from the crystallizing chains of the polyisopropene.

## Introduction

The majority of polymer blends, notwithstanding any technological utility, are heterogeneous mixtures.[1] This is a consequence of the limited increase in positional disorder which accompanies their mixing, so that even a small positive mixing enthalpy will bring about phase separation. Specifically, for miscibility to occur over the entire composition range, the Flory interaction parameter, $\chi$, for the polymer repeat units must be less than a critical value that is a measure of the combinatorial entropy[2,3]

$$\chi^* = \frac{1}{2N_1}\left\{1 + \left(\frac{N_1\nu_1}{N_2\nu_2}\right)^{1/2}\right\}^2 \qquad (1)$$

where $\nu$ represents the volume of the chain statistical segment and $N$ is the number of statistical units per chain. In systems whose local interactions are dominated by van der Waals forces, $\chi$ will be positive; moreover, for the high molecular weights usually encountered (e.g., degrees of polymerization greater than 1000) it is observed that $\chi$ invariably is of sufficient magnitude to effect a multiphase blend structure.

When specific interactions are present (e.g., the ether complexes with phenyl groups in polystyrene–poly(vinyl methyl ether) blends[4] or hydrogen bonding in blends of novolac resins with certain carbonyl containing polymers[5]), a negative heat of mixing can result in miscibility. A net negative $\chi$ can also occur, in the absence of any specific interactions, when a copolymer is blended with a homopolymer whose subunits interact less unfavorably with the copolymer subunits than these copolymer segments interact among themselves.[6,7] Miscible systems exhibiting positive interaction parameters have been reported for 1,4-polybutadiene[8] and for polystyrene[9] when blended with their respective deuterated analogues. The small difference in molar volume accompanying replacement of the protons with deuterium causes a reduction in volume upon mixing with consequent positive $\chi$.[10] Its magnitude, however, is sufficiently low that such blends are most often found to be miscible.

In this paper a miscible blend is described whose components, atactic poly(vinylethylene) (PVE) and *cis*-1,4-polyisoprene (PIP), are essentially nonpolar aliphatic hydrocarbons in which the interactions are consequently of

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