AD-A265 304

IMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 1993	Final Report 9/15/89 - 11/14/92

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
Polymer-Polymer Interactions	61102F 2303/CS

6. AUTHOR(S)

Isaac C. Sanchez, and Donald R. Paul

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Univ of Texas PO Box 7726 Austin, TX 78713-7726	AFOSR-TR- 9 0658

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR/NC Building 410, Bolling AFB DC 20332-6448	AFOSR-89-0479

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.	

13. ABSTRACT (Maximum 200 words)

See Attached

DTIC
ELECTE
JUN 01 1993
S A D

93 5 2 006

93-12236

14. SUBJECT TERMS			15. NUMBER OF PAGES
			14
			16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

13. Our approach for understanding polymer-polymer interactions is to measure heats of mixing of small molecule analogs. In particular, we have focused on small molecule analogs of polystyrene (PS) and Poly (2, 6 dimethyl phenylene oxide) (PPO). this well-known system is miscible, but the origin of its miscibility has perplexed investigators for over 25 years. Our measurements and associated molecular mechanics/Monte Carlo calculations have firmly established that the two methyl groups on PPO play a significant role in affecting miscibility.

We have developed two equation of state models for hydrogen bonding interactions. They represent a significant advance in our understanding of hydrogen bonding interactions in both polymeric and non-polymeric systems. The models have been successfully applied to a variety of systems that include supercritical fluids.

Solubility of gases in liquid polymers has been treated theoretically using the lattice-fluid model. Qualitatively, the model indicates that gas solubility should increase with molecular size as observed experimentally. In addition, the physical properties of the gas and polymer should dominate gas solubility with the gas-polymer interaction playing a secondary role. Using no adjustable parameters, gas solubilities can be quantitatively predicted for hydrocarbon and chlorinated hydrocarbon vapors in non-polar polymers. Good results are also obtained for polar gases in polar polymers. For polar/non-polar combinations, the addition of a simple correlation for the polymer-gas interaction parameter allows for the satisfactory treatment of these systems as well.

It has been demonstrated that the compression response of polymers, solvents, and polymer solutions to hydrostatic pressure satisfies a corresponding states principle. A dimensionless pressure variable is used to superpose compression data as a function of temperature into a universal curve. A rigorous thermodynamic analysis is developed to relate isothermal compression to the free energy. The curvature of the free energy as a function of density, in particular its anharmonicity around its minimum, governs the compression response. The apparent independence of the energy curvature to temperature, and in some cases composition, is responsible for the observed universality. The compression response is also relatively insensitive to chemical structure for many polymers. The observed temperature-pressure superposition requires that the free energy satisfy a universal functional form that is derived. Using Pade analysis, a new isothermal equation of state has been obtained. A theoretical bound is placed on the amount of isotropic tension (negative pressure) that a liquid or solid can sustain.

Final Report

Polymer-Polymer Interactions
AFOSR-89-0479

Principal Investigators:

Isaac C. Sanchez
Donald R. Paul

**Chemical Engineering Department
and
Center for Polymer Research
The University of Texas at Austin**

Abstract

Our approach for understanding polymer-polymer interactions is to measure heats of mixing of small molecule analogs. In particular, we have focused on small molecule analogs of polystyrene (PS) and poly (2, 6 dimethyl phenylene oxide) (PPO). This well-known system is miscible, but the origin of its miscibility has perplexed investigators for over 25 years. Our measurements and associated molecular mechanics/Monte Carlo calculations have firmly established that the two methyl groups on PPO play a significant role in affecting miscibility.

We have developed two equation of state models for hydrogen bonding interactions. They represent a significant advance in our understanding of hydrogen bonding interactions in both polymeric and non-polymeric systems. The models have been successfully applied to a variety of systems that include supercritical fluids.

Solubility of gases in liquid polymers has been treated theoretically using the lattice-fluid model. Qualitatively, the model indicates that gas solubility should increase with molecular size as observed experimentally. In addition, the physical properties of the gas and polymer should dominate gas solubility with the gas-polymer interaction playing a secondary role. Using no adjustable parameters, gas solubilities can be quantitatively predicted for hydrocarbon and chlorinated hydrocarbon vapors in non-polar polymers. Good results are also obtained for polar gases in polar polymers. For polar/non-polar combinations, the addition of a simple correlation for the polymer-gas interaction parameter allows for the satisfactory treatment of these systems as well.

It has been demonstrated that the compression response of polymers, solvents, and polymer solutions to hydrostatic pressure satisfies a corresponding states principle. A dimensionless pressure variable is used to superpose compression data as a function of temperature into a universal curve. A rigorous thermodynamic analysis is developed to relate isothermal compression to the free energy. The curvature of the free energy as a function of density, in particular its anharmonicity around its minimum, governs the compression response. The apparent independence of the energy curvature to temperature, and in some cases composition, is responsible for the observed universality. The compression response is also relatively insensitive to chemical structure for many polymers. The observed temperature-pressure superposition requires that the free energy satisfy a universal functional form that is derived. Using Padé analysis, a new isothermal equation of state has been obtained. A theoretical bound is placed on the amount of isotropic tension (negative pressure) that a liquid or solid can sustain.

Introduction

This project has been a combined experimental and theoretical investigation of polymer interactions with other polymers and small molecules. A significant amount of progress has been made in the following areas:

- Systematic calorimetric measurements of small molecule analogues of polystyrene (PS) and poly(2, 6 dimethyl phenylene oxide) (PPO).

- Molecular mechanics and Monte Carlo calculations of heats of mixing of small molecule analogues of PS and PPO.

- Development of *two* equation of state models of hydrogen bonding in polymer solutions.

- Development of a predictive model for gas solubility in polymers.

- Demonstration that the compression response of polymers, polymer solutions, and solvents satisfy a corresponding states principle.

Small Molecule Analogue Calorimetry

The energetic interactions between molecules is always an important issue in the phase behavior of mixtures; however, this becomes a dominant factor when the combinatorial entropy is small (e.g., polymer-solvent solutions) or nearly non-existent as in the case of polymer-polymer blends. Thus, there is a compelling need to understand the energetic interactions between polymer chains of different types. Unfortunately there is no simple way to determine these interactions since it is obviously not possible to directly measure the heat effects associated with mixing two high molecular weight polymers. However, the interactions between polymer segments are, in principle, basically the same as those between lower molecular weight compounds with similar molecular structures. When the latter are liquids of low enough viscosity, the heat of mixing can be measured by direct calorimetry. One objective of this research has been to gain fundamental insights about the role of molecular structure on polymer-polymer interactions from the experimental determination of heats of mixing of liquid analogs of polymer segments.

Our initial work has focused on the PPO/PS system which forms miscible mixtures. The interactions between these two polymers is obviously favorable (exothermic mixing). Numerous attempts have been made to quantify this interaction by small angle neutron

1

scattering and a variety of indirect measurements with results that are not in full agreement with one another. As analogs of PPO we have used available derivatives of anisols which are liquids at room temperature. For polystyrene we have used a wide variety of phenyialkanes as analogs including ethylbenzene and liquid oligomers of styrene. Figure 1 summarizes heat of mixing results for anisole and 2, 6-dimethylanisole with ethylbenzene.
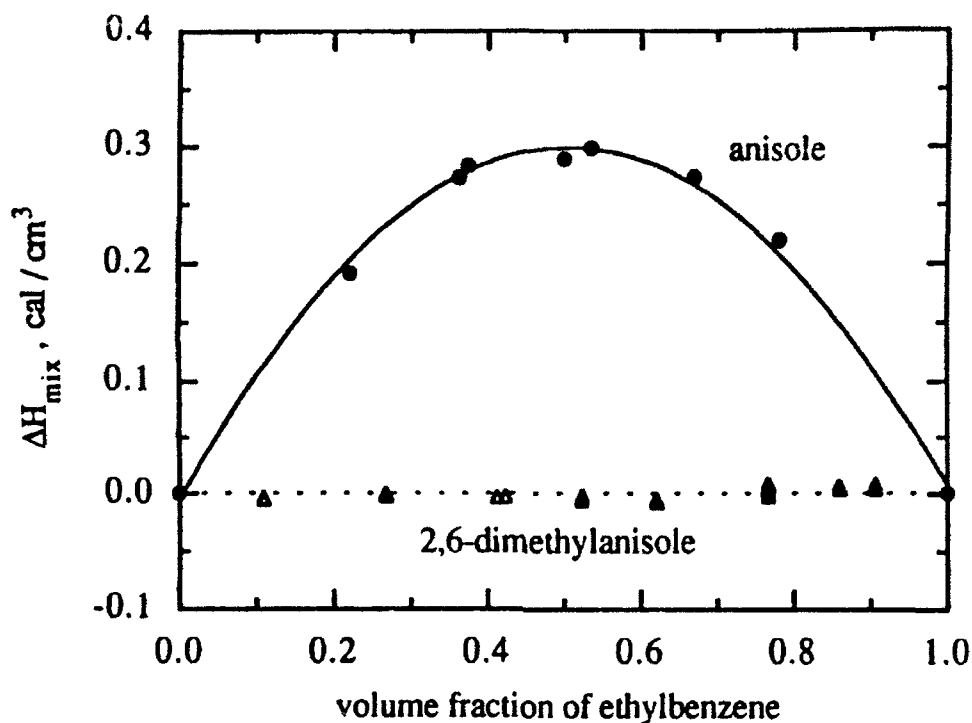

Figure 1 Heat of mixing of anisoles with ethylbenzene at 25^0 C.

The composition dependence of these data is adequately represented by the parabolic form of the van Laar expression

$$\Delta H_{mix} = B \, \Phi \, (1 - \Phi)$$

where Φ is the volume fraction of either component. This permits summarizing the results in terms of an interaction energy density, B.

It is interesting to note that the interaction of ethylbenzene (a close analog of PS) with 2,6-dimethyl anisole (similar to the repeat unit of PPO) is near zero, but weakly favorable, while that with anisol (no ring methyl groups) is strongly unfavorable. The latter is consistent with convincing indirect evidence that polystyrene is not miscible (unfavorable

2

interaction) with the unsubstituted (no methyl groups) PPO. This result suggests that the ring methyl groups play a pivotal role in the PPO-PS favorable interaction. A central question is whether this stems from a "physical" role due to the mere presence of such aliphatic hydrocarbon units anywhere in the repeat unit structure or a more "chemical" role which the methyl groups induce in the electronic character of the repeat unit. Table 1 directly answers this question by showing that the heat of mixing of ethylbenzene with dimethyl anisoles depends on where the two methyl groups are located on the ring. The interaction can switch from favorable to unfavorable depending on this location.
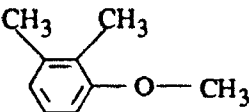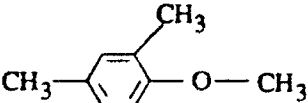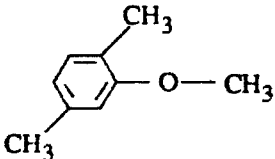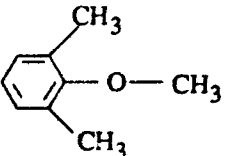
dimethylanisole isomer	B, cal/cm3
CH₃ CH₃ O — CH₃	0.312
CH₃ CH₃ — O — CH₃	0.302
CH₃ O — CH₃ CH₃	0.023
CH₃ O — CH₃ CH₃	-0.025

Table 1 Effect of methyl group placement on heat of mixing of dimethyl anisole with ethylbenzene at 25° C.

It would be very useful to be able to represent the interactions between molecules in terms of those between smaller groups within each molecule since the number of such groups could be significantly smaller than the number of molecules of potential interest. For example, such an approach may allow us to account for the fact that the liquid analogs are not exactly identical in structure to the polymers being modelled (e.g., 2,6-dimethylanisole has the methyl group attached to the oxygen that is not part of the PPO

3

structure). In principle, the same type of information that has been successfully used to account for interactions between copolymers and other polymers could be employed. For example, the molecules of interest here might be divided into groups as follows

anisole   2,6-dimethylanisole   phenylalkane
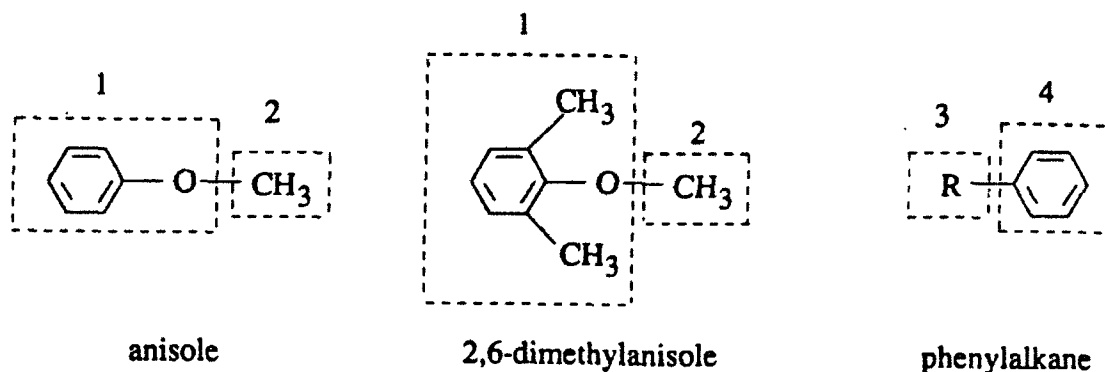
However, this division must be done with considerable care since as demonstrated in Table I, the ring methyl groups in dimethylanisole cannot be treated as separate entities from the aromatic ring. An important issue then is how can one obtain theoretical or *a priori* guidance about what groups can be successfully treated as separate entities and which cannot. Sandler[1] has proposed an interesting approach that we are pursuing. This idea is based on the premise that molecular interactions can be modeled in terms of the sum of contributions from non-polar, dispersion interactions between atoms and polar interactions represented by electrostatic partial charges on these atoms. The latter depend on the bonding to adjacent atoms (the former does not) and can be calculated using *ab initio* and semi-empirical molecular modelling software packages. The emerging premise is that division into sub-molecular groups will be appropriate when the net electronic charge distribution on any group is constant regardless of what other groups it may be bonded to. In this way, a group makes an identical contribution to a molecule in a mixture. Our preliminary results with this approach look very promising.

Heats of Mixing From Molecular Mechanics

As Fig. 1 illustrates, the interaction of ethylbenzene with is unfavorable with anisole, but much more favorable with 2, 6-dimethylanisole. Our goal in this study is to use molecular mechanics to study interactions in the small molecule analogs to see if the heat of mixing can be calculated.

Our initial attempts focused on dimer interactions; i.e., interactions of the type A-A, B-B, and A-B. These attempts were not successful. It was found that larger clusters of molecules were required to obtain realistic estimates of interaction energies. Our current

methodology consists of doing Monte Carlo simulations using a constant pressure-temperature ensemble (NPT) on large molecular clusters of up to 125 molecules[2]. It is important to use the NPT ensemble because our intermolecular force field must not only yield the correct interaction energies, but also the correct liquid densities at atmospheric pressure. These calculations typically take about 1 to 5 hours of CPU supercomputer time. These calculations successfully predict liquid densities with less than 2 % error and energies of vaporization to within 5 % error for pure anisole, 2, 6-dimethylanisole, and ethylbenzene. Although the absolute heats of mixing are not predicted very well, the trend is recovered; anisole/ethylbenzene mixtures are energetically less favorable than 2-6 dimethylanisole/ethylbenzene mixtures. The results are summarized in Tables II and III.

	Liquid density (g/cm^3)			Energy of vaporization (kJ/mol)		
	simulation	expt.	% error	simulation	expt.	% error
anisole	0.973	0.989	-1.6	42.63	44.31	-3.8
2, 6-dimethylanisole	0.936	0.950	-1.5	49.89	52.38	-4.8
ethylbenzene	0.871	0.864	+0.8	40.46	39.79	+1.7

Table II   Calculated and experimental densities and interaction energies at 25^0 C and 1 atm pressure.

	Heat of Mixing (kJ/mol)	
	simulation	experiment
anisole/ethylbenzene	0.75	0.12
2, 6-dimethyl anisole/ethylbenzene	0.46	-0.04

Table III   Calculated and experimental heats of mixing at 25^0 C and 1 atm pressure for 50/50 mole mixtures.

As can be seen in Table II, density and intermolecular energy values are highly correlated; a force field that yields a correct liquid density will also yield a good value of the energy. Current studies are directed at refining the force field used in these calculations and extending the calculations to other model systems shown in Table I.

Hydrogen Bonding Models

We have developed two alternative approaches for the treatment of hydrogen bonding in fluids and their mixtures[3,4]. We believe this to be a significant advance in understanding hydrogen bonding interactions in polymer and non-polymeric systems. Both approaches arise from well-founded lattice-fluid model partition functions. These models are called the lattice-fluid association (LFAS) and lattice-fluid hydrogen bonding (LFHB) models. The key approximation in both approaches is that the hydrogen-bonding interactions are considered separable from the physical or van der Waals interactions. The latter are taken into account through the lattice-fluid (LF) theory. The equation of state character of the LF theory allows both approaches to be valid at any fluid state, liquid, gaseous, or super-critical. Associated with this is the capability of both approaches to describe in a most natural manner the density dependence of the degree of hydrogen bonding. This capability appears to be equivalent in both qualitative and quantitative terms. In both approaches the hydrogen-bonding correction has led to LF scaling constants for the associated fluids which are now close to the corresponding constants of the normal hydrocarbons.

There is however, an important advantage of LFHB model over the LFAS model: its applicability to polymer mixtures and, in general, to systems forming multi-dimensional physical networks through hydrogen-bond association. Extension of the LFAS model to these systems remains a formidable combinatorial problem and has resisted our attempts at solution. The LFHB model, on the contrary, leads to remarkably simple analytical expressions for the basic thermodynamic quantities in these highly complex systems. An interesting class of systems which can now be treated over extended ranges of external conditions is aqueous polymer solutions. This model has already been applied to hydrogen bonding in supercritical fluids[5].

It is important to point out that both approaches are approximate in character and their drawbacks stem from both the physical or LF model and the chemical or hydrogen bonding model. Since the two parts are separable, one can substitute for one or both of them the models of his/her choice along the lines of the present framework for its improvement. Both of these approaches will be reviewed in forthcoming book on thermodynamic modeling[6].

Gas Solubility in Polymers

Solubility of gases in liquid polymers has been treated theoretically using the lattice-fluid (LF) model[7]. Qualitatively, the model indicates that gas solubility should increase

with molecular size as observed experimentally. In addition, the physical properties of the gas and polymer should dominate gas solubility with the *gas-polymer interaction* playing a secondary role. Using no adjustable parameters, gas solubilities can be quantitatively predicted for hydrocarbon and chlorinated hydrocarbon vapors in non-polar polymers. An example is shown in Fig. 2.
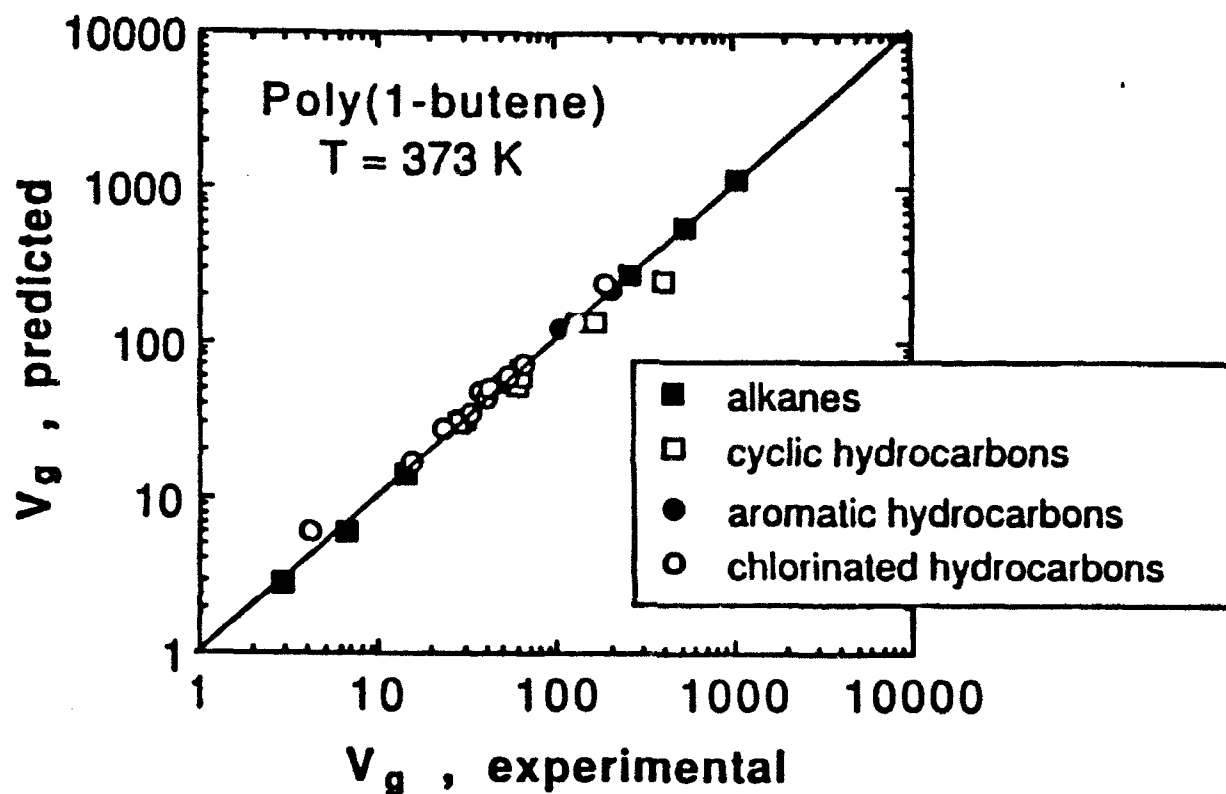

Figure II Comparison of calculated (no adjustable parameters) and experimental values of IGC specific retention volumes (direct measure of gas solubility) for 27 hydrocarbons in poly(1-butene) @ 373 K. Average error 13%.

Good results are also obtained for polar gases (excluding alcohols) in polar polymers. However, polar/non-polar combinations are not correlated as well. For the latter case, the addition of a simple correlation for the polymer-gas interaction parameter base on three-dimensional solubilities parameters allows for the satisfactory treatment of these systems as well[8].

Universal Compression

Since the early theoretical and experimental work of Simha and co-workers in the 1960's, it has been known that polymer PVT data satisfy a corresponding states principle. Other theoretical equation of state models have also suggested corresponding states behavior. All models predict that density is a function of a dimensionless temperature, $\tilde{T} = T / T^*$, and pressure, $\tilde{P} = P / P^*$. The scale parameters T^* and P^* are constants for a given polymer. These parameters are different for each model. Our statement of the corresponding states behavior or universality differs from any known theoretical model; a single dimensionless pressure variable, independent of any model, is used to describe the compression of a liquid or solid. This variable is $(P - P_0)/B_0$ where B_0 is the isothermal bulk modulus evaluated at some convenient reference pressure P_0. It arises in a natural way from a thermodynamic analysis of compression.

The compressional strain ε is defined as

$$\varepsilon \equiv \int_{V_0}^{V} \frac{dV'}{V'} = \ln(V / V_0) = \int_{P_0}^{P} \frac{\partial \ln V}{\partial P} dP \equiv - \int_{P_0}^{P} B^{-1} dP$$

$$= \int_{P_0}^{P} \frac{dP}{B_0 + B_1(P - P_0) + \frac{1}{2} B_2(P - P_0)^2 + ...}$$

$$= -\Delta p + \frac{1}{2!} B_1 (\Delta p)^2 - \frac{1}{3!}(2B_1^2 - B_0 B_2)(\Delta p)^3 + ...$$

where V is the volume at pressure P, V_0 is the volume at the reference pressure P_0, B is a bulk modulus, and Δp is a dimensionless pressure variable

$$\Delta p \equiv (P - P_0) / B_0$$

where B_0 is the bulk modulus evaluated at the reference pressure P_0. This dimensionless pressure variable plays a key role in all that follows.

A typical example of the isothermal compression behavior of a polymer at several temperatures is shown in Fig. III. Note that these data for poly(dimethylsiloxane) (PDMS) cover a wide temperature range (nearly $300°$). The same data shown in Fig. III are plotted in Fig. IV as a function of the dimensionless pressure Δp defined in eq. (2) using a

reference pressure of 10 MPa (100 bar). Note that all data fall onto a single non-linear curve. This result illustrates temperature-pressure (T-P) superposition and implies that compression is a function of Δp only. In turn this requires that the first few coefficients in the expansion for the compressive strain be *temperature independent*; all of the temperature dependence has been absorbed in B_0.
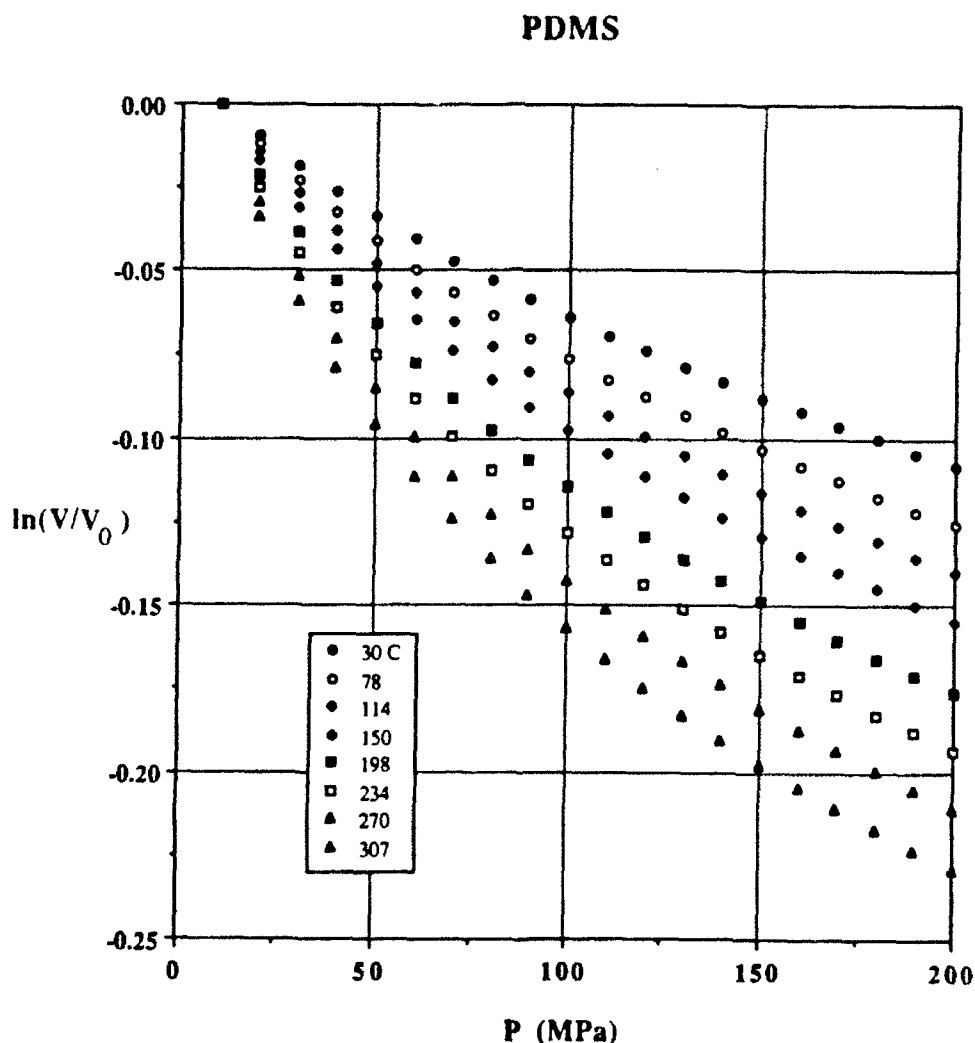
PDMS

Figure III: Isothermal compression data for a poly(dimethylsiloxane) ($M_w = 1.9 \times 10^5$) at the temperatures indicated. The reference volume V_0 at each temperature was determined at a reference pressure P_0 of 10 MPa.
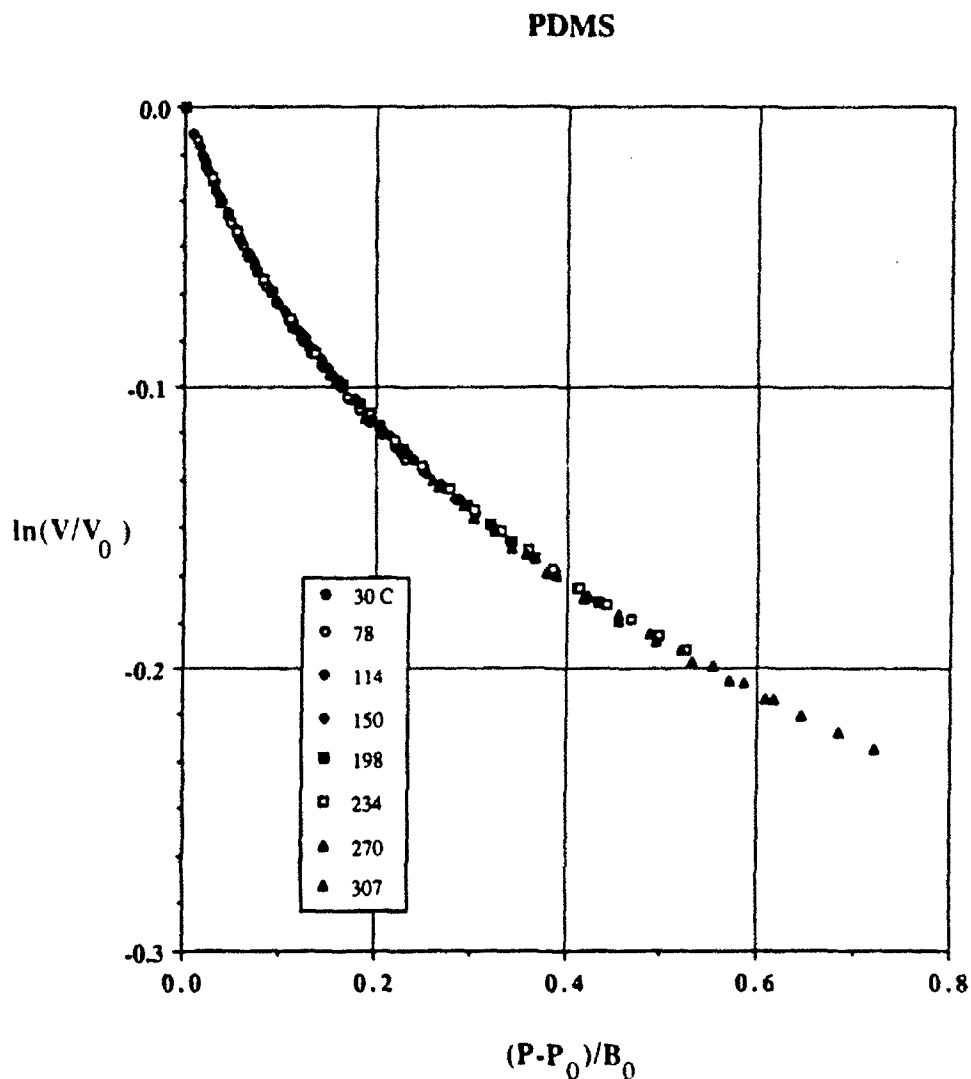
9

PDMS

Figure IV: The compression data in Fig. III are replotted against the reduced pressure variable $(P - P_0)/B_0$ where $P_0 = 10$ MPa and B_0 is the isothermal bulk modulus at 10 MPa for each isotherm

A summary of the important results from this work is given below:

• Polymers and organic solvents (possibly all liquids and isotropic solids?) satisfy T-P superposition; i.e., compression data for a given polymer or solvent over a range of temperatures can be superposed into a universal curve by plotting the data as a function of the dimensionless pressure variable, $\Delta p \equiv (P - P_0)/B_0$.

10

- If polymer and solvent have similar compression behavior, as say measured by the pressure coefficient of the bulk modulus, B_1, then the compression of their solutions should satisfy T-P-C superposition. This has been illustrated for toluene solutions of polystyrene.

- Although we have focused on PDMS, we have observed T-P superposition in all polymers (29) and solvents (5) that we have studied. Even water, which has an anomalous modulus that passes through a maximum with temperature, satisfies T-P superposition. The compression behavior of many polymers, widely varying in chemical structure, is very similar. For 29 polymers that we have examined, $B_1 = 11.0 \pm 1.5$.

- T-P superposition implies that the free energy satisfies a universal functional form. In particular, the curvature properties of the free energy are temperature independent. This further implies that the reduced pressure derivatives of the modulus are temperature independent. These universal functional relations will provide future guidance for theoretical model development.

- Two approximations have been derived for universal compression. The first assumes the bulk modulus varies linearly with pressure. It is a one parameter equation (B_1). The second approximation assumes that the modulus diverges with pressure as P^ω where ω is a positive constant less than unity. A Padé analysis of this behavior yields a new isothermal equation of state. The Padé approximation involves two parameters, the first and second pressure derivatives of the bulk modulus (B_1 and B_2). The Padé approximation is only necessary for systems that exhibit significant negative curvature in the modulus. For the polymers that we have studied, including PDMS, the linear modulus approximation affords an excellent approximation to compression data. The Padé approximation may prove useful in extrapolating low pressure data to higher pressures.

- A liquid or solid under isotropic tension, (negative pressure) will fail prior to the pressure reaching a negative value of $-B_0 / B_1$. This is a bound on the amount of negative pressure a substance can sustain. At a given temperature, B_0 / B_1 is a measure of the strength of attractive forces.

- It is speculated that the failure of a solid polymer under uniaxial tension may be related to the attendant dilation.

References

1. H. S. Wu, and S. I. Sandler, Ind. Eng. Chem. Res., 30, 881 and 889 (1991).
2. W-C Hu and I. C. Sanchez, *Polymer Preprints*, **33**, 515 (1992).
3. C. Panayiotou and I.C. Sanchez, *Macromolecules* **24**, 6231 (1991).
4. C. Panayiotou and I.C. Sanchez, *J. Phys. Chem.* **95**, 10090 (1991).
5. R.B. Gupta, C. Panayiotou, I.C. Sanchez, and K.P. Johnston, *AIChE J*, **38**, 1243 (1992)
6. I.C. Sanchez and C. Panayiotou, "Equation of State Thermodynamics of Polymer and Related Solutions", in *Thermodynamic Modeling*, S.I. Sandler, ed., Marcel Dekker, NY (in press).
7. I.C. Sanchez and P. A. Rodgers, *Pure & Appl. Chem.*, **62**, 2107 (1990).
8. P. A. Rodgers and I. C. Sanchez, *J. Poly. Sci., Phys. Ed.*, **31**, 273 (1992).