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Polymer Compatibility by Gas-Liquid Chromatography¹

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ABSTRACT: Reliable methods for identifying soluble polymer pairs have long been limited to the solid state even though the possibility exists that a pair of polymers which is immiscible in the solid is miscible in the melt. Inverse chromatographic procedure has been used to study polymer-polymer miscibility in the molten state. Results for poly(ϵ -caprolactone)-poly(vinyl chloride) blends indicate that complementary dissimilarity is the rule of polymer compatibility when specific interacting forces are involved. Such forces in PCL-PVC blends are of the same order of magnitude as those between PVC and its usual plasticizers. When these results are combined with earlier treatments of Flory equation of state, it turns out that variation of mixture parameters leads to bimodality of the phase diagram as well as asymmetry of the critical concentration.

In the study of polymer compatibility, reliable methods for the identification of soluble polymer pairs are applicable in the solid state;^{2,46} those applicable in the melt are generally limited by experimental difficulties. Microscopic methods are applicable only where there are substantial differences in refractive indices and light scattering techniques, including the recently developed pulse-induced critical scattering,³ are applicable for polymer-solvent systems only. Yet, it is conceivable that two polymers would be miscible in the melt but not in the solid on account of morphological differences, thermodynamic or kinetic changes accompanying crystallization, or vitrification or mere temperature effects on solubility. It is of interest to identify these systems; furthermore, it may be possible to induce miscibility down to the solid state via chemical or physical means.

Gas-liquid chromatography (GLC) has received general recognition as an effective simple technique for rapid measurement of polymer-solvent interaction and solvent activity coefficient in molten homopolymers.⁴⁻¹² It has also been used in determining such properties¹⁰ as the glass transition phenomena and the glassy state, crystallinity, adsorption isotherms, heats of adsorption, surface area, interfacial phenomena, diffusion coefficients, and complex equilibria in solution as well as curing processes in nonvolatile thermoset systems. For these type applications, Guillet has suggested^{11,12} the name "inverse gas chromatography" based on the fact that conventional usage of GLC determines the property of an unknown sample in the moving phase with a known stationary phase whereas inverse chromatography determines the properties of an unknown stationary phase with the aid of a known vaporizable solute in the moving phase. He considers the latter as a "molecular probe" experiment where the vaporizable molecules are designated "probe" molecules. In this paper, we describe an inverse chromatographic procedure whereby studies of two homopolymers and their blends, analyzed in terms of Scott's ternary solution treatment¹³ of the Flory-Huggins theory,¹⁴ yield the polymer-polymer interaction parameter. Relative measures of various contributions such as polar, complexing and noncomplexing interactions are obtained based on the most significant strength of selected probe molecules. Four types of polymer interactions investigated are: (i) proton accepting strength, probed with chloroform and ethanol; (ii) proton donor strength with methyl ethyl ketone and pyridine; (iii) polar strength with acetonitrile and fluorobenzene; (iv) nonpolar strength with hexane and carbon tetrachloride. The division and choice of solutes are based on the relative magnitude of dipole moments, polarizabilities, and hydrogen bonding capabilities. It is recognized, though, that no such clear-cut division exists and that association complexes stabilized by electronic and/or

electrostatic interactions are possible¹⁵ with all the probe molecules chosen. What is proposed is a scale of interaction by which the relative strength of different polymers could be measured. Plausible indices of interaction are the Flory-Huggins interaction parameter,¹⁴ χ_{ij} , its counterpart based on conditions of an hypothetical liquid at 0°K, χ_{ij}^* , or the exchange energy parameter of Flory equation of state,¹⁶⁻²¹ X_{ij} . The usual sign convention is assumed; i.e., a large positive value indicates unfavorable interaction, a low value indicates favorable interaction, while a negative value indicates a rather strong specific interaction. A nonpolar probe would generally yield positive quantities representative of noncomplexing contributions whereas specific interacting probes could yield negative values. The total specific interactions of such probes with a stationary solvent comprise⁵⁴ at least four different kinds: π electrons, dipolar, n electron, proton donor-acceptor interactions. These are, therefore, the basic interpretative concepts that will be applied in the discussion.

The above procedure has been applied to poly(vinyl chloride) (PVC), poly(ϵ -caprolactone) (PCL), and their blends. The results indicate that complementary dissimilarity is the rule of polymer miscibility when specific interacting forces are involved. Such forces in PCL-PVC blends are of the same order of magnitude as those between PVC and its usual plasticizers. When these results are combined with McMaster's application²² of Flory equation of state¹⁶⁻²¹ to polymer-polymer phase relations, asymmetry of the critical concentration as well as bimodal lower critical solution temperature (lcst) behavior are predicted.

Experimental Section

Apparatus. A Micro-Tek 2500R gas chromatograph equipped with thermal-conductivity detector was used for this study. Temperatures of the injection block, column outlet block, and detector cell were monitored by pyrometer but the column temperature was doubly checked with a Digitec Model 551-4 plug-in platinum resistance thermometer. The average error in column temperature is $\pm 0.5^\circ$. Flow rate of the helium carrier gas, controlled by a Micro-Tek regulator valve, is measured by a soap-bubble flowmeter. Column pressure was measured differentially against the atmospheric outlet pressure with a U-tube manometer filled with mercury. The elution profiles were recorded by a Honeywell Electronik 19 chart recorder.

Column Preparation. All stationary phases were coated onto Fluoropak-80, 60-80 mesh, by dissolution in appropriate solvent and slow evaporation in a Breeze-Away Packing Dryer (Chemical Research Services, Inc.) which is essentially a fluidized bed. The coated support was packed by a gentle tapping procedure into a 5 ft \times 0.25 in. o.d. stainless steel silanized tubing, the ends of which were loosely plugged with glass wool. The tubing was then coiled to fit the oven chamber. After each experiment, the weight of polymer used was determined by 1-week extraction with refluxing solvent in a Soxhlet extractor equipped with ceramic thimble.

Table I
Polymer Coating Analysis

	Polymer			
	Poly- styrene	Poly (ϵ -ca- prolac- tone	Poly (vinyl chlo- ride)	PCL- PVC (50:50)
Wt of polymer on support, g	2.80	3.90	1.65	2.40
Coverage ratio, % (g polymer/ g support)	13.50	14.50	8.52	10.55

Stationary Phase and Probe Molecules. Polystyrene (PS) ($\bar{M}_n = 110,000$; $\bar{M}_w/\bar{M}_n < 1.06$) is obtained from Pressure Chemical Co.; poly(ϵ -caprolactone) (PCL) is PCL-700 (Union Carbide Corporation, reduced viscosity = 0.7, 0.2 g/100 ml of benzene at 30°, $\bar{M}_n = 15,500$, $\bar{M}_w/\bar{M}_n = 2.61$); poly(vinyl chloride) (PVC) is QYSA (Union Carbide Corporation, inherent viscosity = 0.63 as per ASTM-D-1243 Method A, $\bar{M}_n = 13,500$, $\bar{M}_w/\bar{M}_n = 2.19$). The PVC and PVC-PCL blends contained 1% liquid stabilizer TM-181, based on PVC weight, for thermal stabilization. The molecular weights and their distributions were obtained with GPC and light scattering using tetrahydrofuran at 25°. The probe solutes were reagent grades and were used without further purification.

Measured retention time is made up of four contributions: from polymer sorption, from support sorption (nonexistent in most practical operations), from gas-solid interfacial adsorption, and from gas-liquid interfacial adsorption. Only the contribution due to polymer sorption is important, all others are essentially eliminated by use of high polymer loading and very small solute sample size. Summers et al.⁷ have shown that accurate results are obtained at the polymer-support ratio of >6.5% and Prausnitz et al.⁸ found that the situation is all the more improved by use of nonpolar support such as Fluoropak-80 made from poly(tetrafluoroethylene). Alternatively, complete elimination of surface adsorption terms would entail obtaining retention data on a series of columns having different loadings each with a varying amount of solute sample followed by an extrapolation procedure to extract the infinite dilution bulk sorption. The former approach was adopted in this work.

Results from polymer coating analysis appear in Table I. As for the mixed stationary phases, the relative concentrations are assumed to be identical to those in the original solution prior to deposition on the inert support. During operation, checks on the dependence of peak maximum on probe sample size showed no perceptible variation over the range of 0.001 to 0.1 μ l; elution profiles were symmetric over the same range. Hence, all tests were performed with sample sizes of about 0.01 μ l.

At a given temperature, five flow rates were employed and triplicate runs were made at each flow rate. To ensure operation at equilibrium, the retention-volume data were extrapolated to zero flow rate. These were used for subsequent calculations.

Data Reduction. The use of GLC in measuring polymer-solvent interaction has been adequately described^{4-8,12} and its use in measuring polymer-polymer interactions was recently elaborated on by Deshpande et al.⁵⁸ The work reported here, completed^{46b} before Deshpande's project⁵⁸ came to our attention, differs from his in certain aspects.

For a mixed stationary phase consisting of two high polymers, the solute probe, used essentially at zero concentration, is a third component and its infinite dilution weight fraction activity coefficient is

$$\ln \Omega_1^\infty = \ln \left[\frac{v_1}{w_2 v_2 + w_3 v_3} \right] + (1.0 + \chi_{12} \phi_2 + \chi_{13} \phi_3) - \chi_{23}' \phi_2 \phi_3 \quad (1)$$

where subscript 1 refers to the probe and subscripts 2 and 3 refer to the two polymers; w is the weight fraction; v is the specific volume; and ϕ is the volume fraction.

The Ω_1^∞ is calculated in the usual way^{4-8,12,58} from the specific retention volume of the probe, χ_{12} and χ_{13} are obtained separately for polymers 2 and 3, and χ_{23}' is unambiguously determined. Note that χ_{23}' is the traditional Flory-Huggins interaction parameter normalized to a single segment of component 2. If the hard-core

Table II
Characteristic Parameters for Solvents and Polymers

Material	P^* , atm	V^* , g/cm ³	T^* , °K
Ethanol	5400.0	0.9955	4845.0
Chloroform	3168.0	0.5460	5280.0
Methyl ethyl ketone (MEK)	5655.0	0.9580	4590.0
Pyridine	6366.0	0.8129	5124.0
Acetonitrile	6797.0	0.9583	4283.0
Fluorobenzene	5027.0	0.7636	4742.0
Toluene	5606.0	0.9115	5025.0
Carbon tetrachloride	5586.0	0.4870	4700.0
Octane	4330.0	1.1204	4850.0
Heptane	4317.0	1.1334	4641.0
Hexane	4238.0	1.1553	4440.0
Cyclohexane	4320.0	1.0012	4720.0
Pentane	4065.0	1.1723	4158.0
Polystyrene (PS)	5270.0	0.8170	7970.0
Poly(vinyl chloride) (PVC)	8645.0	0.6240	7960.0
Poly(ϵ -caprolactone) (PCL)	5905.0	0.7690	6363.0

Table III
Thermodynamic Quantities of Interaction in
Molten Polystyrene (cal/cm³)^{1/2} ($T = 150^\circ$)

Probe Molecules	Ω^*	χ	χ^*	X_{12} , cal/ cm ³	δ_2 , (cal/ cm ³) ^{1/2}
Ethanol	17.5	1.56	1.68	30.6	5.8
MEK	10.5 (9.44)	1.06	1.21	8.62	4.3
Acetonitrile	18.6 (19.8)	1.61	1.78	31.7	4.4
Toluene	5.3 (5.22)	0.46	0.58	0.9	5.9
Carbon tetrachloride	4.2	0.84	0.98	5.2	9.8
Hexane	11.5	0.96	1.12	3.59	8.9
Octane	7.9	0.64	0.77	5.6	9.2
Cyclohexane	11.0 (12.2)	1.07	1.21	8.47	9.4

volumes are utilized, χ_{23}^{*} is obtained and it is from this normalized quantity that the exchange energy parameter, X_{23} , is calculated.

In calculating the various quantities, virial coefficients were obtained from the correlation of O'Connell and Prausnitz²⁴ with the critical constants obtained from Dreisbach.²⁵ Antoine constants, solute densities and other physicochemical constants were obtained from Timmermans²⁶ or from internal sources. The hard-core characteristic volume (v^*), pressure (P^*), and temperature (T^*) of Flory's equation of state were either obtained from literature^{7,55} or calculated from internal experimental data. Polymer densities and thermal expansion coefficients (α) were obtained from literature,^{21,56,57} the thermal pressure coefficient (γ) was calculated from Flory's expression for P^* and data in Table II, while the segmental surface area per unit volume was estimated from the correlation of Bondi.²⁷ Probe solubility parameters and their temperature coefficients were taken from Scigliano's thesis.⁵⁹

Results and Discussion

(I) Interaction Indices for Homopolymers. Because of the abundant literature data available on polystyrene, a narrow molecular weight sample was studied in order to guide the development of our GLC technique. Table III illustrates the calculated thermodynamic quantities at 150°. Numbers in parentheses in the second column are the data of Newmann and Prausnitz⁸ on polystyrene ($\bar{M}_n = 97,000$; $\bar{M}_w/\bar{M}_n < 1.06$). In the cases compared, the discrepancies can be blamed on experimental uncertainties and, for our purposes, are acceptable.

The large Ω^∞ , χ , χ^* , and X_{12} for ethanol are not unexpected on account of its self-associating tendencies as explained by Prausnitz et al.²⁸ The high values for acetoni-

trile have been ascribed to the differences in dipolar interactions between pure and diluted acetonitrile.⁸ Methyl ethyl ketone yields lower X_{12} values relative to ethanol and acetonitrile. This may well be a reflection of a slight but measurable donor-acceptor complexation involving the oxygen of MEK with the styrene units; small negative partial enthalpy of dilution has been observed²⁹⁻³¹ before at low concentration of PS in MEK. The low across-the-board values for toluene reflect its similarity with the styrene unit. The PS-toluene system is known⁶⁰ to be athermal and the near zero value of X_{12} here lends credence to our GLC technique. Concerning the solubility parameter³²

$$\delta_2 = [\delta_1 - (RTX_{12}/V_1)^{1/2}]$$

one notes that all nonpolar probes give the same order of magnitude which is at least close to the generally accepted value for polystyrene (9.1); polar and/or specific interacting probes yield much lower values. This discrepancy reflects the inadequacy of the assumption inherent in the solubility parameter approach that the entropy of the components in a mixture is that of an ideal solution. Our results indicate that each type of interaction does not have an equal opportunity to exert itself and a different component of forces does contribute a different unknown proportion to the total interaction. Hence, one cannot proceed by subtracting out nonpolar and/or polar effects since the different probes do not necessarily pick up the same "amount" of nonpolar and/or polar contributions. The "homomorph" concept may not be the answer here as one still has to contend with the problem of ascertaining the different proportions and the relative effectiveness of the individual interacting components present in individual stationary phases. Another difficulty concerns the fact that the solubility parameter theory applies only for cases with $\chi \geq 0$ and as is well-known, and as will be seen shortly, negative χ do exist. Hence for our purposes, the polymer-probe interaction parameters for polar, nonpolar, proton-donor, and proton-acceptor probes are more acceptable as characterizing indices.

Table IV illustrates the derived data for PCL at 120°. Considering chloroform and fluorobenzene, the sign of the various interaction indices could be interpreted on the basis of: (i) hydrogen bonding of the C-H proton of chloroform to the ester group of PCL; (ii) charge transfer ($n \rightarrow \sigma^*$ type) between the ester group of PCL and the halogens of the two probes coupled with electrostatic interactions. Stabilization of the complex would also involve the π electrons in the case of fluorobenzene.

These type interactions have been found to be responsible for molecular association of a series of haloalkanes to electron donors such as simple high molecular weight ketones, ethers, esters, tertiary amines, and tertiary amides.³³⁻³⁶ For chloroform, the enthalpy of complex formation was as much as -2.5 kcal/mol, in accord with our results estimated from the relation χRT . Charge-transfer interactions are generally weaker as evidenced by the relatively smaller values obtained for fluorobenzene as compared to chloroform. Booth and Devoy³⁷ postulated a donor-acceptor complex formation between benzene and ether oxygen of poly(ethylene oxide) and poly(propylene oxide) on the basis of the exchange energy parameters obtained for these systems (-4 cal/cm³, -2 cal/cm³, respectively). A similar charge-transfer interaction between the benzene of the fluorobenzene and the ester oxygen of PCL is possible and the exchange energy value obtained (ca. -1.6 cal/cm³) may well represent fractions of molecules which exist as distinct charge-transfer complexes stabilized by electronic (n electrons, π electrons) and electrostatic

Table IV
Thermodynamic Quantities of Interaction in
Molten Poly(ϵ -caprolactone) ($T = 120^\circ$)

Probe molecule	Ω^*	χ	χ^*	X_{12} , cal/cm ³
Ethanol	11.1	1.08	1.15	21.4
Chloroform	1.57	-0.30	-0.20	-4.20
MEK	5.73	0.422	0.533	2.75
Pyridine	3.40	0.114	0.175	0.239
Acetonitrile	10.20	0.979	1.11	19.3
Fluorobenzene	3.04	0.0385	0.127	-1.61
Carbon tetrachloride	2.53	0.293	0.391	1.06
Hexane	14.0	1.12	1.24	7.89

(dipole-dipole, induced dipole-dipole) interactions.

The high values of the thermodynamic quantities for PCL-acetonitrile reflect the well-known fact⁹ that the order of proton-acceptor strength is different from the order of dipole moment. PCL does contain polar oxygen, but the dipolar segments are not necessarily oriented in the right direction to effect any directional force with acetonitrile. Stockmayer et al.³⁸ recently showed that $1/3$ of the polarity of PCL is oriented parallel to the chain backbone and is, therefore, unavailable for dipolar interaction. The other $2/3$ is localized but depends strongly on the conformational rearrangement of the molecule. Hence, "wrong" orientation is highly probable and may be responsible for the poor showing of PCL. The relative magnitude of the results for hexane and carbon tetrachloride shows the statistical effects due to their molecular size differences. The smaller probe has a lot more sites available to it than the much larger hexane, especially since the methylene segments of PCL consist of a five-carbon backbone. The X_{12} values for these systems reflect the noncomplexing unlike contact energy. The value for CCl₄ (~1 cal/cm³) is similar to what has been suggested³⁷ for the noncomplexing contact energy for poly(ethylene oxide) in benzene.

The data for PCL-ethanol show the effects of consecutive association and solvation. Solvation, by itself, yields a negative contribution to the heat of mixing, e.g., PCL-chloroform system. When preceded by self-association, as in the case of ethanol, the fraction of eventual 1:1 complexes is reduced. Since association makes a positive contribution, the total sum may indeed be positive. Similar deductions are made by Newmann and Prausnitz²⁸ on the specific retention data of alcohols on poly(methyl methacrylate), alkyd resin, poly(*n*-butyl methacrylate), thermoplastic epoxy resin, an unspecified polyamide, poly(vinyl acetate), and polyurethane.

The magnitude of the various thermodynamic quantities for PCL-MEK and PCL-pyridine is moderate and represents a combination of electronic and/or electrostatic interactions plus noncomplexing contribution to the total unlike contact energy.

The results for PVC with the corresponding probe molecules are illustrated in Table V. The high values reflect the generally known fact that PVC is an unusually insoluble polymer. Fortunately, we are concerned here with relative strength and when the data are considered in this light, one notes that n -electron donors or proton acceptors such as MEK and pyridine are preferred by PVC. The X_{12} values for proton-donating chloroform are relatively high (~16.5 cal/cm³) considering the fact that PCL-chloroform yields negative values (ca. -4.5 cal/cm³). That is PCL and PVC which form miscible blends⁴⁰ behave in opposite manner toward a probe capable of forming a molecular complex stabilized by both H bonding and charge-transfer interac-

Table V
Thermodynamic Quantities of Interaction in
Molten Poly(vinyl chloride) ($T = 120^\circ$)

Probe molecule	Ω^∞	χ	χ^*	X_{12} , cal/cm ³
Ethanol	45.5	2.23	2.35	40.6
Chloroform	9.39	1.23	1.38	16.6
MEK	11.3	0.85	1.00	4.41
Pyridine	8.99	0.831	0.939	7.34
Acetonitrile	26.4	1.67	1.85	29.3
Fluorobenzene	11.5	1.11	1.25	8.82
Carbon tetrachloride	9.4	1.35	1.49	10.2
Hexane	28.9	1.59	1.76	8.6

tion. The consequence of this observation is that polymer-polymer solubility should be looked at in terms of *complementary dissimilarity* rather than complementary similarity as the solubility parameter approach⁵¹ would stipulate. When the comparison concerns nonpolar and some nonspecific polar interactions, complementary similarity would be the rule in line with the solubility parameter approach. However, studies of polymer compatibility to date^{2,52} reveal that miscibility almost always occurs when some strong specific interaction exists; hence, *complementary dissimilarity controls polymer-polymer solubility*. Earlier recognition of this "acid-base" interaction principle led to the development of compatible blends³⁹ of PVC with polyethylene-*N*-vinyl-*N*-methylacetamide, polyethylene-*N,N*-dimethylacrylamide, and polyethylene-carbon monoxide copolymers.

For charge-transfer interacting fluorobenzene, the values of the various quantities are moderate, an indication of possible polarization between the π electrons of the probe and the chlorine atoms of PVC. Except for the exchange energy parameter, polar acetonitrile and nonpolar hexane behave similarly toward PVC. The very high X_{12} values for acetonitrile are due to the difference in the dipolar interactions between pure and dilute acetonitrile as explained before. For hexane and carbon tetrachloride, the magnitude of this parameter reflects the relative noncomplexing unlike contact energy for PVC.

(II) Polymer-Polymer Interaction. From the viewpoint of equilibrium thermodynamics compatibility implies miscibility on a molecular scale and incompatibility implies immiscibility on a molecular scale. Actual polymeric blends do not conform to this dictate. At best, a polyblend can be described as microheterogeneous, the size of the different phases and their interpenetration being limited by a host of factors among which are the extent of mixing, compatibility, molecular weight, clustering behavior of each polymer, rheological, and surface and interfacial properties. This notwithstanding, it is worthwhile to apply the results of thermodynamics at least in the equilibrium liquid state (melt). Such application yields a scale of relative miscibility and/or a set of selection rules, the reliability of which is admittedly limited by factors mentioned above.

As for the various interaction indices for PCL-PVC in Tables VI and VII, the relative magnitude and sign of χ_{23}' and χ_{23}^{*} illustrate the significant positive contribution of the equation-of-state effect.¹⁶⁻²¹ Since PCL and PVC form stable binary mixtures,⁴⁰ negative interaction index would be expected. This is a sufficient though not a necessary condition for stability⁴¹ and the fact that χ_{23}' registers positive values when chloroform is a probe may imply that χ_{23}^{*} and X_{23} are better indices of interaction. Nonpolar hexane and carbon tetrachloride probes yield positive

Table VI
Polymer-Polymer Interaction Indices for
Poly(ϵ -caprolactone)-Poly(vinyl chloride)
(50/50) ($T = 120^\circ$)

Probe molecules	χ_{23}'	χ_{23}^{*}	X_{23} , cal/cm ³
Ethanol	0.21	-0.13	-2.8
Chloroform	0.33	-0.09	-2.4
Methyl ethyl ketone	-0.10	-0.61	-6.4
Pyridine	-0.17	-0.47	-5.4
Acetonitrile	-0.40	-0.98	-9.3
Fluorobenzene	0.24	-0.15	-2.9
Carbon tetrachloride	1.07	0.63	3.0
Hexane	1.16	0.60	2.8

Table VII
Polymer-Polymer Interaction Indices for
Poly(ϵ -caprolactone)-Poly(vinyl chloride)
(70/30) ($T = 120^\circ$)

Probe molecules	χ_{23}'	χ_{23}^{*}	X_{23} , cal/cm ³
Ethanol	0.10	-0.32	-5.0
Chloroform	0.45	-0.07	-3.4
Methyl ethyl ketone	-0.15	-0.77	-8.1
Pyridine	-0.43	-0.77	-8.1
Acetonitrile	-0.46	-1.17	-10.7
Fluorobenzene	0.25	-0.23	-4.5
Carbon tetrachloride	1.31	0.76	2.2
Hexane	1.41	0.70	1.8

quantities reflective of noncomplexing unlike contact interaction. In general, one expects specific interacting probes to yield results which reflect the specificity and magnitude of a particular interaction. A case in point is the proton-donating power of PVC. When the infrared absorptions of two typical PVC plasticizers (dibutyl phthalate and tricresyl phosphate) are examined⁴² in the presence of carbon tetrachloride, chloroform, and PVC, the absorption maxima due to the ester carbonyl C=O and the phosphate P=O groups shift. The data (Table III; ref 42) show that PVC possesses approximately half as much proton-donating power as chloroform under the stated experimental conditions. Considering Tables IV and VI, the relative (χ_{ij}^{*} , X_{ij}) results for PCL-chloroform and PCL-PVC are surprisingly in agreement with the above observation. Another spectroscopic supporting evidence is provided by Shaw⁴³ who observed frequency shift of ~ 6 cm⁻¹ (25°) in the carbonyl band position for PCL-PVC (50:50) blend. On account of experimental difficulties, he observed no shift at much higher temperatures ($T > 100^\circ$). Using the correspondence noted above, a shift of 6 cm⁻¹ would correspond to $X_{23} \sim -2.9$ cal/cm³, which is within the range of values obtained here. Hence, the probe technique as a means of studying characteristics of miscible blends should be considered valid. It should be cautioned, though, that the information obtained is only as reliable as the model from which it is deduced and results obtained would depend strongly on the effectiveness of each probe molecule in revealing the different contributions to the polymer-polymer interaction energy. Thermodynamic methods generally yield a weighted average of a wide range of "many-body" interactions involving not only polar, nonpolar, and hydrogen-bonding interactions, but also a variety of electronic and electrostatic interactions. If knowledge of a particular complex is desired, spectroscopic and/or dipole measurement is used when simple molecules are concerned. But, for

Table VIII
Pure Component Properties^b

	\bar{M}_w/\bar{M}_n	$\alpha \times 10^3$, °K ⁻¹	γ , atm/°K	\bar{M}_w , g/mol	ρ , ^a g/cm ³	V^* , cm ³ /g	T^* , °K	P^* , cal/cm ³
PCL	2.61	0.72	14.04	40,400	1.0953	0.769	6364	143
PVC	2.19	0.518	22.37	29,500	1.4059	0.624	7961	210

^a Density of a hypothetical liquid at 25°. ^b Mixture properties: $S_2/S_3 = 2.39$ (also varied arbitrarily), $C_{12} = 0.0$, $Q_{12} = 0.0$, $n = 1.0$, $X_{12} = -0.1$ to -0.7 cal/cm³.

polymer-polymer systems, poor resolution and other experimental difficulties reduce the efficacy of spectroscopic technique to nothing more than qualitative, and thermodynamic methods still remain premier.

The variation of X_{23} with probe can be justified on the basis of the above argument which, in essence, states that the total polymer-probe interactions may not be correctly accounted for by the theory. For instance, the 0–5% residual crystallinity in PVC at the experimental temperature would modify the various probe quantities to a different extent even though the crystalline phase takes no active part in the solute sorption. Another rationalization is as follows: when a probe enters either 2 or 3, certain sites available to it for specific interactions would not be available in a blend of the two polymers. For H bonding, less carbonyl oxygen would be available to chloroform in a blend of PCL–PVC, so also for other electronic and/or electrostatic interactions. These effects lead to high Ω_1^∞ in the blend and, according to eq 1, more negative χ_{23}' . For MEK, pyridine, and acetonitrile, such effects are more pronounced, but the maximum χ_{23}' value obtained is still less than that obtained for polystyrene–poly(vinyl methyl ether) blends via a static vapor sorption method.⁴⁴ Kwei and coworkers obtained χ_{23}' of as much as -0.8 for bulk sorption of as much as 20% benzene. While the two systems under consideration may not necessarily possess similar interaction characteristics, the lower values observed for our systems may be related to the discrepancies between the results of bulk versus film measurements recently discussed by Prausnitz et al.⁴⁵

Concerning the concentration dependence, as the amount of PCL increases, the interaction indices decrease, i.e., become more favorable in terms of miscibility. A system with a large negative index would have a high “demixing” temperature and vice versa. Our data indicate that mixtures with high concentrations of PCL would have high “demixing” temperatures and those with high PVC content would have lower “demixing” temperatures. That is, lcst behavior is suggested; the minimum of the miscibility curve is closer to the region of high PVC concentration in agreement with the prediction ($\phi_{PCL} = 0.435$) of the Flory–Huggins lattice theory¹⁴ with a composition-independent interaction parameter. It turns out though that the predicted phase behavior is highly sensitive to variations in mixture parameters based on the Flory equation of state. This is the subject of the next section.

Measurements were also made at 110° with insignificant difference from values at 120°. Much higher temperatures could not be investigated on account of the thermal instability of PVC and we are limited by nonequilibrium effects much below $T_g + 50^\circ$.

(III) Polymer–Polymer Phase Behavior. Thermodynamic phase behavior of multicomponent polymer systems has been successfully treated by introduction of a Van Laar type parameter in the Flory–Huggins lattice theory⁴⁶ and by Flory’s equation of state.²² For the latter approach, the excess properties of such blends depend on the characteristic parameters V^* , T^* , and P^* for each pure component

and also on the exchange energy (X_{ij}) and the exchange entropy (Q_{ij}) parameters, these accounting for the intermolecular changes associated with the exchange of neighboring species. Literature reports exist for the characteristic parameters of a host of polymers but methods for evaluating the exchange quantities for binary systems have been, up to now, limited to what amounts to superposition of excess volume³⁷ or osmotic pressure²¹ data onto theoretical curves, a tedious approach generally applicable to polymer-solvent systems. As shown in the previous section, the inverse GLC provides means of calculating the parameter for polymer-polymer systems.

For a binary mixture, stability is determined by the curvature of the free energy curve $\Delta G(\phi_2)$ and the stability limit or the spinodal curve is given by⁴¹

$$\left(\frac{\partial^2 \Delta G^m}{\partial \phi_2^2} \right)_{P,T} = 0 \quad (2)$$

Recent analysis by McMaster²² in these laboratories utilized Flory’s free energy function^{16,18} to describe the phase relationship of binary systems. Here, the phase behavior of PCL–PVC will be analyzed in terms of McMaster’s approach²² using the exchange energy quantities obtained from the inverse GLC. For complete detail of “equation of state” approach, interested readers should consult McMaster’s paper.²²

The pure component data used are presented in Table VIII. Initial estimate of segmental surface area ratio, S_2/S_3 , was computed from the group contribution format of Bondi,²⁷ but arbitrary variation is introduced in what follows, since Bondi’s approach is not entirely satisfactory. If the segment is taken as a monomer unit, S_2/S_3 equals 2.39. The value would be 0.712 if the backbone unit were taken as a segment. It would also be of interest to see the effect on the phase diagram if the surface area ratio were smaller still, say ~60% of a backbone unit corresponding to S_2/S_3 of 1/2.39. As for X_{23} , results obtained from specific interacting probe molecules range from -1.0 to -10.0 cal/cm³. Values used in what follows are -1.0 , -2.0 , and -7.0 cal/cm³.

Some important features are evident from Figure 1 which shows the simulated spinodals for PCL–PVC blends. First, the blends exhibit lcst behavior in agreement with earlier deduction from the composition dependence of X_{23} . Second, the minimum temperatures and the general nature of the curves are strong functions of the exchange energy parameter and the segment surface area ratio.

With S_2/S_3 kept at 2.39 (curves 1–3), variation of X_{23} from -1.0 to -2.0 cal/cm³ leads to a shift in the T_{\min} from -67 to $+65^\circ$ and ϕ_{\min} essentially unchanged at 0.9, i.e., at high concentration of PCL whose chains are relatively longer than those of PVC. This phenomenon, referred to as asymmetry of the critical concentration, has been observed in the experimental cloud point curves of Allen, Gee, and Nicholson⁴⁷ for low molecular weight mixtures of poly(isobutylene) and poly(dimethylsiloxane). Such behavior can be described not by the concentration independent interaction parameter but by the Van Laar type interaction pa-

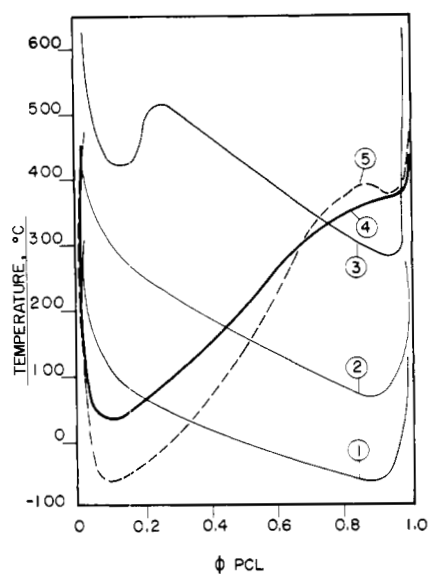


Figure 1. Simulated Spinodals for PCL-PVC mixtures.

Curve no.	X_{23} , cal/cm ³	S_2/S_3
1	-1.0	2.39
2	-2.0	2.39
3	-7.0	2.39
4	-2.0	0.712
5	-2.0	0.418

rameter using the Flory-Huggins lattice theory.⁴⁶ Decreasing X_{23} to -7 cal/cm³ leads to bimodality of the phase diagram with T_{\min} 's at 280 and 420°. Again, bimodality has been demonstrated for a low molecular weight polystyrene-polyisoprene system⁴⁸ and for a low molecular weight α -methylstyrene-covinyltoluene polymer when mixed with a low molecular weight polybutene.⁵⁰ Welygan and Burns⁴⁹ have observed a similar phenomenon when high molecular weight polystyrene and polybutadiene are comixed with tetralin at 29°. The general observation for the latter two of these systems is that the phenomenon becomes more obvious when the two polymers are monodisperse; Koningsveld et al.,⁴⁶ who were able to describe the phenomenon after the fact with the improved lattice theory, also concluded that it is not caused by the system polydispersity. All the experimental observation cited exhibit upper critical solution temperature (ucst) behavior and neither the asymmetry nor the bimodality have been observed for high molecular weight systems exhibiting lcst behavior. The reason may lie in the fact that very little effort has been expended so far on trying to observe the phenomena or it may be due to the deleterious effect of polydispersity. All the spinodals displayed in Figure 1 are generated for the polydisperse PCL-PVC systems (Table VIII), but then a quasi-binary spinodal curve is fixed for a fixed weight-average chain length. However, the binodal and the location of the consolute state depend on the ratio of the Z average to weight-average chain length of each component, hence the shape of the binodals would be more reflective of polydispersity.

When X_{23} is kept constant at -2.0 cal/cm³ and S_2/S_3 is changed from 2.39 to 0.712, a complete reversion of the spinodal is produced. As the ratio is decreased further to 1/2.39 the bimodality which starts from the previous curve now becomes obvious. These results suggest an importance to this mixture parameter which up to now has been unsuspected.

The question now is: what are the correct values of X_{23} and S_2/S_3 for use in predicting the phase behavior of PCL-PVC? Since direct comparison of the predicted miscibility curves with the cloud-point curve is rendered impossible on account of the thermal instability of PVC, one

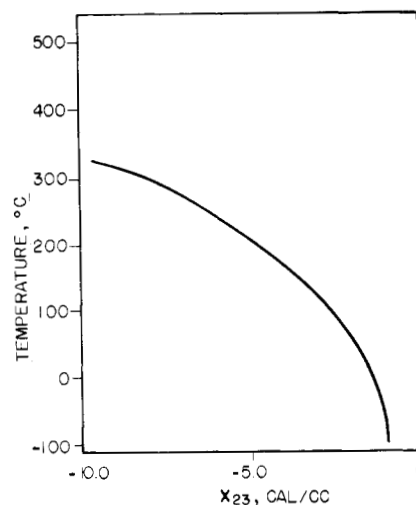


Figure 2. Dependence of the major T_{\min} on X_{23} for PCL-PVC mixtures, $S_2/S_3 = 2.39$.

can only speculate. The composition dependence of the interaction indices suggests that the lcst minimum must lie closer to the PVC axis implying that $S_2/S_3 \lesssim 1.0$ and Figure 2 shows that PCL-PVC would be predicted to be immiscible if $X_{23} > 0$.

Conclusion

Gas-liquid chromatographic data have been analyzed in terms of Scott's ternary solution treatment¹³ of Flory-Huggins theory in an attempt to study polymer-polymer miscibility in the molten state. Relative measures of various contributions such as polar, complexing, and noncomplexing interactions are obtained based on the most significant strength of certain selected probe molecules. The method holds promise in the systematic study of group contribution since a variation of the molecular structure of one member of a miscible polymer pair would result in systematic changes in their interaction indices.⁵³

Studies of PCL, PVC, and PCL-PVC blends indicate that complementary dissimilarity is the rule of polymer-polymer solubility when directional forces are involved. The hydrogen bonding strength in PCL-PVC blends is of the same order of magnitude as that between PVC and its usual plasticizers. When these results are combined with McMaster's earlier treatment²² of polymer-polymer thermodynamics, it turns out that variations in the exchange energy parameter or the surface area ratio lead to irregular asymmetry of the critical concentration as well as bimodality of the phase diagram. Both asymmetry and bimodality have been observed experimentally for other systems but direct comparison of the predicted spinodal with the cloud-point curve for PVC-PCL blends is rendered impossible on account of the thermal instability of PVC.

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The Cellulose Microfibril as an Imperfect Array of Elementary Fibrils

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ABSTRACT: Cellulose microfibrils are viewed as an imperfect array of elementary fibrils. We have investigated the possible defects in *Valonia* cellulose microfibrils, which are such that the microfibrils can be broken into elementary fibrils by deformation, but are not sufficient to allow for a small angle maximum corresponding to the elementary fibril dimension. The microfibril has been constructed by convolution of the elementary fibril with a two dimensional point lattice. Defects have been incorporated in the microfibril, first by introduction of gaps between the elementary fibrils. These regular gaps were then replaced by a statistical distribution of the elementary fibrils about the lattice points, modeled by Hosemann distortions of the first type. The cylindrically averaged transforms of such structures show that significant distortions can be incorporated within the microfibril without producing large scale changes in the equatorial intensity distribution. Larger distortions are necessary before a small angle maximum corresponding to the 35 Å elementary fibril is predicted, by which stage the wide angle X-ray pattern is unacceptable.

High resolution electron micrographs of negatively stained specimens of native cellulose¹⁻⁹ show that the microfibrils are comprised of regular subfibrils, termed "elementary" fibrils, which have a width of 35 Å. The major differences between celluloses from different sources occur in the packing of the elementary fibrils within the microfibril; this packing is expected to be dictated by the synthesis conditions. As an example, the microfibrils of *Valonia*

(algal) cellulose have cross-sectional dimensions of ~200 × 100 Å. X-Ray line broadening measurements indicate that the microfibrils are essentially single crystals,^{10,11} and thus the elementary fibrils must be arranged in a regular manner to give the larger crystallite width. If the elementary fibrils have cross sections 35 × 35 Å, the microfibril would correspond to a regular 6 × 3 array. In contrast, cotton microfibrils vary in width from ~100 to ~500 Å, with ~250 Å