Liquid–Liquid Demixing from Solutions of Polystyrene. 1. A Review. 2. Improved Correlation with Solvent Properties

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Low pressure liquid–liquid demixing data for polystyrene dissolved in 76 different one-component solvent systems are reviewed and correlated. The phase diagrams are discussed. With only one exception the molecular weight of each solvent is less than that of two polystyrene monomer units. A new relation is developed which quantitatively correlates the area of solubility lying between the UCS and LCS demixing curves in the $(T_c, M_w^{-1/2})$ projection with solvent solubility parameters. © *1996 American Institute of Physics and American Chemical Society.*

Key words: Cloudpoint, consolute temperature, demixing, Hansen parameters, molecular weight dependence, phase equilibria, polymer solubility, polystyrene, scaling law, solubility parameters.

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1. Introduction

1.1. Comments on Polymer Solubility

Over the last fifty or more years the solubility of polymers in low molecular weight solvents has been investigated from both theoretical and experimental points of view. In spite of the large quantity of data which has accumulated, theories of demixing have usually been tested using data for just a few solvent systems, often choosing linear atactic polystyrene (PS) as the polymer of interest. Opportunities to compare theory to all (or at least most) of the experimental data have been hampered by the lack of comprehensive reviews of extant data, although recently Grulke (89GRU) and Barton (90BAR) have reviewed Θ-temperatures of selected PS solutions, and Kamide (90KAM) in his thorough text on polymer solution thermodynamics has discussed critical demixing temperatures for a number of PS/solvent systems. In the present paper our aim is to collect available data on liquid–liquid demixing from solutions of PS dissolved in various one-component solvents, compare them with theoretical predictions, and correlate the results solvent-to-solvent when possible. We have chosen not to include studies on the demixing of polymer blends in this review, and do not discuss PS/supercritical fluid mixtures.

Polymer solubility depends on concentration, temperature, pressure, molecular weight, isotope substitution, solvent quality (i.e., chemical nature of the solvent), polydispersity , shear, and perhaps other variables. Our examination of the literature showed the widest range of data, solvent-to-solvent, are available for polystyrene in the (MW,T_c) field, and in this review we focus attention there. T_c denotes the demixing temperature at the critical concentration, which to a good enough approximation corresponds to extrema in UCS or LCS cloudpoint vs concentration diagrams at low enough polydispersity: UCS=Upper Consolute Solubility branch, LCS=Lower Consolute Solubility branch. We use MW to refer to molecular weight in general. More specifically, M_w=weight average molecular weight, and M_n =number average molecular weight. Although data which define the concentration dependence of solubility in some solvents exist, they are not so common as are data in the (MW, T_c) plane (i.e., at a single concentration or just a few scattered concentrations). Investigations of the effects of other variables (shear, polydispersity, pressure, isotope label, etc.) are even less common. One of the most thoroughly studied PS/solvent systems is PS/methylcyclohexane (MCH) and we have recently reviewed the dependence of demixing in PS/MCH on pressure, MW, and other variables (95IMR/VAN).

1.2. Polymer/Solvent Phase Diagrams

A schematic phase diagram of the type which interests us is shown in Fig. 1. Throughout this paper we restrict attention to liquid–liquid demixing and do not show those parts of phase diagrams which depict liquid/solid transitions of one kind or another (93ARN/BER). In Fig. 1 the two phase (shaded) regions are found at the top and bottom centers. Figure 1(a) shows temperature, T, plotted against concentration, ψ, in the plane of the paper. It is often convenient to choose segment fraction polymer as the concentration variable, ψ. The third variable, which extends into the page, might be molecular weight, pressure, or another variable of

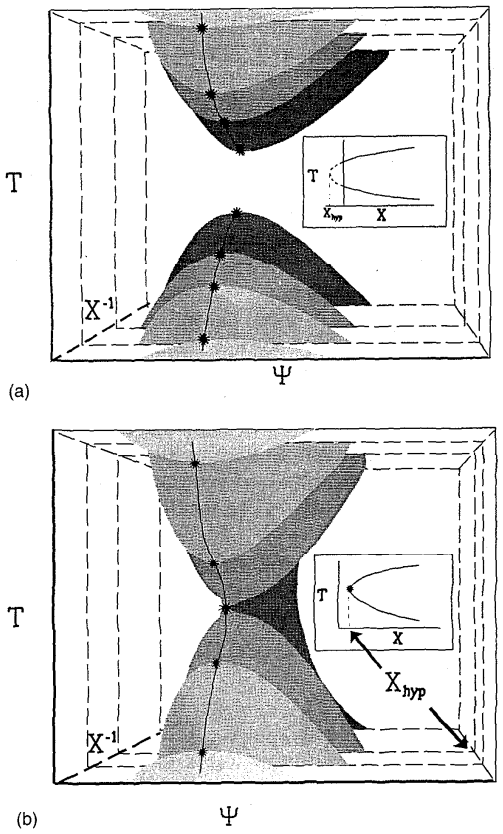


FIG. 1. Schematics for UCST/LCST demixing in (T,ψ,X^{-1}) space; $X = MW^{-1/2}$ including projections onto several (T_c,ψ) planes at different X. ψ denotes polymer concentration. The upper and lower branches of the two phase regions are shaded. Skewing in the (T,ψ) plane is understood in terms of Flory–Huggins theory. (a) For solutions in good (theta) solvents (like methylcyclohexane/ polystyrene). The inset shows the projection of the critical lines onto the (T_c,X) plane. The intercepts mark upper and lower Θ temperatures. The "*'s" represent critical concentrations for the various values of X. (b) For solutions in poor (nontheta) solvents (like acetone/ polystyrene or propionitrile/polystyrene). The upper and lower branches merge at the hypercritical temperature which in this diagram is found at finite MW. The inset shows the projection of the critical lines onto the (T_c,X) plane. The "*'s" represent critical concentrations for the various values of X and the large "*" represents the hypercritical point.

TABLE 1. A list of those solvents and their CAS registry numbers for which phase equilibrium data have been observed in the respective PS/solvent system. See later tables for references to original literature.

Acetates
—methyl acetate [79-20-9], ethyl acetate [141-78-6], ethyl acetoacetate [141-97-9], ethyl-chloroacetate [105-39-5], *n*-propyl acetate [109-60-4], isopropyl acetate [108-21-4], *n*-butyl acetate [123-86-4], *sec*-butyl acetate [105-46-4], *tert*-butyl acetate [540-88-5], isobutyl acetate [110-19-0], *n*-pentyl acetate [628-63-7], isoamyl acetate [123-92-2], *n*-hexyl acetate [142-92-7], vinyl acetate [108-05-4].

Alcohols
—*n*-butanol [71-36-3], *n*-hexanol, hexanol-3 [623-37-0], cyclohexanol [108-93-0], 3-methylcyclohexanol [591-23-1], octadecanol [112-92-5], isoamyl alcohol [123-51-3]

Alkanes and their derivatives
—*normal alkanes*: *n*-pentane [109-66-0], *n*-hexane [110-54-3], *n*-heptane [142-82-5], *n*-octane [111-65-9], octadecane [593-45-3]
—*derivatives of n-alkanes*: 1-chloro-*n*-decane [1002-69-3], 1-chloro-*n*-undecane [2473-03-2], 1-chloro-*n*-dodecane [112-52-7], dichloroethane [75-34-3 or 107-06-2 ?, 1,1 or 1,2 dichloro?], 1-phenyl-decane [104-72-3], nitroethane [79-24-3], 1-nitropropane[108-03-2]
—*cycloalkanes*: cyclopentane [287-92-3], cyclohexane [110-82-7], deutero-cyclohexane [1735-17-7], cycloheptane [291-64-5], cyclooctane [292-64-8], cyclodecane [293-96-9]
—*cycloalkane derivatives*: methylcyclopentane [96-37-7], deuterated methylcyclopentane [??], methylcyclohexane [108-87-2],1,4-dimethylcyclohexane (1:1 mixture of *cis* and *trans*) [589-90-2], ethylcyclohexane [1678-91-7]
—*bicyclic alkanes*: *trans*-decalin [493-02-7]

Alkenes
—octene [111-66-0 ? location of double bond unspecified]

Benzene and its derivatives
—*alkane derivatives*: benzene [71-43-2], toluene [108-88-3], ethylbenzene [100-41-4], hexyl-*m*-xylene [??]
—*halogen-derivatives*: bromobenzene [108-86-1], *o*-dichlorobenzene [95-50-1]

Esters (other than formates and acetates)
—dimethyl malonate [108-59-8], dimethyl succinate [106 65 0], dimethyl oxalate [553-90-2], diethyl malonate [105-53-3], diethyl oxalate [95-92-1], butyl stearate [123-95-5], ethyl-*n*-butyrate [105-54-4]

Ethers
—diethyl ether [60-29-7], 1,4-dioxane [123-91-1], dioctyl phtalate [117-81-7]

Formates
—*n*-butyl formate [592-84-7], ethyl formate [109-94-4]

Heterocyclics
—pyridine [110-86-1], 2,5-dimethylfuran [625-86-5]

Ketones
—acetone [67-64-1], deutero-acetone [666-52-4], methyl-amyl ketone [110-43-0 ?, 2-heptanone?], methyl ethyl ketone [78-93-3], cyclohexanone [108-94-1]

Terpenes
—dl-menthol [15356-70-4], dl-terpineol [98-55-5 ?, mixed isomers?]

Others
—dimethoxymethane [109-87-5], propionitrile [107-12-0], capronic (capric or caproic?) acid [334-48-5 or 142-62-1?]

interest. For the moment, and for reasons which will later become apparent, we choose $X = M_w^{-1/2}$ as that variable. It is useful, although not completely accurate, to represent the $(T, \psi, M_w^{-1/2})$ diagram as a series of coexistence curves (T vs ψ at constant $M_w^{-1/2}$). Four such projections (variously shaded) are sketched. As one moves into the page towards larger and larger MW the two phase regions increase in area. At high enough molecular weight, and if the solvent quality is poor enough, the two branches may eventually merge as shown in Fig. 1(b) (these conditions we loosely label as the hypercritical molecular weight, X_{hyp}), and the system collapses into the hour glass configuration. The heavy black curves in Figs. 1(a) and 1(b) (and the inserts) show the loci of critical concentrations along the UCS and LCS branches. At the hypercritical molecular weight one finds $(\partial M_w^{-1/2}/\partial T)_{Thyp} = 0$ and $(\partial^2 M_w^{-1/2}/\partial T^2)_{Thyp} > 0$ [see insert, Fig. 1(b)]. In Fig. 1(a), however, no such hypercritical point ex-

ists. The homogeneous one phase central region persists to infinite M_w where $M_w^{-1/2}=0$ and the intercepts, T_c^{ucs} and T_c^{lcs}, define upper and lower Θ temperatures, $\Theta^{lcs}=T_c^{lcs}(M_W^{-1/2}=0)$ and $\Theta^{ucs}=T_c^{ucs}$ $(M_w^{-1/2}=0)$. Traditionally Θ temperatures have been determined in one of two ways, the first by extrapolating critical temperatures, T_c, measured at finite molecular weight, to infinite molecular weight, most often using the Schultz–Flory equations, the second by extrapolating second virial coefficients gathered from viscosity, light scattering, or other measurements to zero. It is not certain that Θ temperatures obtained from these two different approaches are identical (91NAK/NOR, 94YAM/ABE, 95MUN/TIA), although there is certainly at least fair agreement. Because of this uncertainty we have used the term "possibly infinite" in Table 1 in referring to the M_w (max) in cases where the Θ temperature is only available from second virial coefficients.

It is interesting to consider the effect of pressure on the phase diagrams. Commonly, but not necessarily, an increase in pressure improves solvent quality and decreases the volume of the two phase regions in diagrams like Figs. 1(a) and 1(b). The effect of pressure on the phase diagram is shown schematically in Fig. 2. Here we diagram a set of (T_c,X) loci, like the ones shown in the inserts of Figs. 1(a) and 1(b), at increasing pressures $(p_1<p_2=p^*<p_3<p_4)$. In nontheta solvents like acetone or propionitrile the behavior is like that shown in the bottom-most curve of Fig. 2; a hypercritical point is observed at finite molecular weight and $p_1>0$. Since an increase in pressure usually betters solvent quality, it may happen as pressure increases that a solvent, poor enough to show a hypercritical temperature at some finite MW, may improve to the point where it transforms to a theta solvent (illustrated in Fig. 2 at $P_2=P^*$) and is able to dissolve a polymer of infinitely large MW. If pressure is increased further the solvent may continue to improve, now showing upper and lower Θ-temperatures (marked with stars "*" in Fig. 2) which continue to separate as pressure is increased (the middle and upper curves labelled P_3 and P_4, Fig. 2). Of course there is no reason to expect solvent quality to increase indefinitely with pressure. In some cases the effect may go through a maximum as shown by the dashed and dashed-dot lines and thereafter deteriorate (see the later discussion).

We see no reason to limit the discussion of pressure effects to the positive region only. One can place solutions under tension in order to examine the effect of negative pressure on phase separation. (Turning again to Fig. 2, it might be, for example, that $P^*=P_2=0$, and P_3 and $P_4>0$, while $P_1<0$.) Imre and Van Hook (94IMR/VAN) have experimentally confirmed continuity of the equation of state for demixing of PS/propionitrile solutions in the negative pressure region. The (T_c,P) demixing locus continues smoothly to negative pressures (where the solutions are under tension), and where cloudpoints were directly observed. The observation led us to generalize the standard formalism by introducing a molecular weight parameter X, $X=(1/M_w^{1/2})$ for $(1/M_w^{1/2})>0$, thus permitting analogous treatments in the (T,X), (T,P), and (P,X) projections. The assumption is that X extends smoothly into the negative region as diagrammed in the part of Fig. 2 which lies to the left of the (T,P) plane of origin for the projections labelled p_3 and p_4, i.e., we assume the equation of state is continuous in the $(T_c,-X)$ quadrant, just as it is in the $(T_c,-P)$ quadrant. Strictly speaking, of course, solutions can actually be placed in tension and $P<0$ is physically realizable. On the other hand $MW<0$ cannot be physically realized; the extension of the diagrams to $X=MW^{-1/2}<0$ must be interpreted as a convenient parametrization which leads toward the development of more rational empirical, semi-empirical, or theoretical descriptions of polymer phase equilibria.

Analysis of phase diagrams like the ones shown in Figs. 1 and 2 is complicated by polymer polydispersity. Coexisting phases, while at identical temperature and pressure, are fractionated with respect to molecular weight, polydispersity, and concentration. As a result cloud and shadow curves no longer coincide (as they do for monodisperse systems), and the locus of upper and lower critical points is displaced from the locus of maxima and minima for UCST and LCST cloudpoint curves. If polydispersity is not too high, however, the two curves may be (and often are) approximated as the same (95LUS/REB, 95LUS/VAN), and it is this approach which will be employed here.

2. Literature Surveyed

We have collected (T_c,MW) data for liquid-liquid demixing of PS in 76 solvent systems, in every case restricting attention to samples of linear atactic polystyrenes dissolved in single (i.e., unmixed) solvents. We have not considered demixing for polymer blends (one component PS), for ternary polystyrene/solvent systems [i.e., PS(MW_1)/PS(MW_2)/solvent], or in supercritical solvents. For most of the solutions in this review the polydispersity is specified and lies in the range $(1.03<M_w/M_n<2)$. Most data have been reported at 0.1 MPa or under the vapor pressure of the solutions, nominally small except at the highest experimental temperatures. Whenever possible the pressure is specified in the tables. In developing the correlations discussed later in the paper, corrections to a set of consistent pressures have been made when possible. Even so, for the bulk of the data, the corrections of experimentally observed T_c's to nominal pressures of 0 or 0.1 MPa are negligible compared to experimental precision (except for LCSTs near hypercritical points).

Table 1 lists the 76 solvents (with CAS numbers) for which demixing data are available. Table 2 compares upper and lower Θ temperatures in good-solvent/PS solvents as reported by the original authors, with those extracted from the present fourth order fitting procedure [*vide infra*, Eq. (2)], and also gives maximum solubilities. Tables 3–42 review the original experimental information for various classes of solvents. These Tables report UCS and LCS demixing temperatures at specified molecular weights, polydispersities, and pressures (when available). Table 43 reports parameters of polynomial fits [Eq. (2), *vide infra*], and Table 44 reports loci of hypercritical temperatures observed at the system vapor pressure [i.e., $(T_c,M_W)_{hyp}$] as obtained from

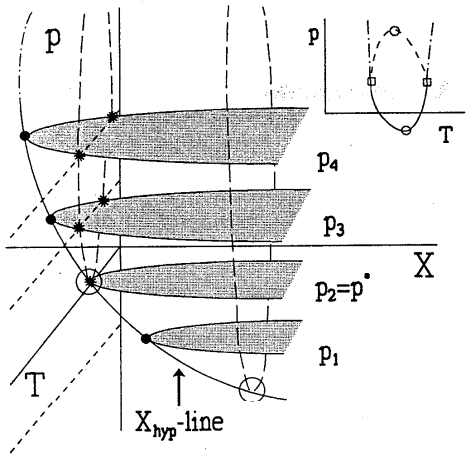


FIG. 2. Schematics for UCST/LCST demixing in (T_c, X, P) space, $X = M_w^{-1/2}$. The diagrams examine the dependence of demixing for solutions of critical concentrations on polymer molecular weight, temperature, and pressure. Depending on the precise strength of the polymer/solvent interaction the system can make a transition from a theta to a nontheta solvent at a positive pressure, a reachable negative pressure (tension), as shown, or at a negative pressure too low to be experimentally observed. The dotted lines show several isopleths, (T,P) projections, at finite MW, and the inset shows one such projection. It is not clear whether the diagram is open or closed at high pressure. The two alternatives are shown in the inset as the heavy dashed and the dotted lines respectively. * = theta temperature ; ○= lower or upper hypercritical temperatures, $T_{hyp,X,l}$ or $T_{hyp,X,u}$; ● hypercritical values of X ; □ upper or lower hypercritical pressures.

least squares fits to a scaling relation [*vide infra*, Eq. (3)]. Finally Table 45 lists solubility parameters which were employed in fits to the correlating equations developed in a later section.

3. The Fitting of Polymer/Solvent Demixing Data

3.1. Phase Behavior in (T,P,X) Space

Traditionally the dependence of the critical demixing temperature, T_c, on molecular weight has been described for good solvents using separate modified Schultz–Flory equations (86FLO) for UCS and LCS branches [Eqs. (1a) and (1b)], $X = M_w^{-1/2}$. This equation was originally introduced to describe UCST loci only, but later became widely used for fitting LCSTs as well,

$$1/T_c^{ucs} = (1/\Theta^{ucs})(1 + b^{ucs}X), \tag{1a}$$

$$1/T_c^{lcs} = (1/\Theta^{lcs})(1 + b^{lcs}X)^a. \tag{1b}$$

Five parameters, Θ^{lcs}, Θ^{ucs}, b^{lcs}, b^{ucs}, and a, are required to fit the data for any given system and the theory is strictly applicable only for Θ solvents ["a" is usually taken as 1, but is sometimes set to 3/4 (75KON/SAE)]. First order SF theory fails to account for the curvature in $1/T_c, M_w^{-1/2}$ plots which is often observed in Θ solvents (75KON/SAE, 86SAE/KUW), and invariably observed in poor (nontheta) solvents. About 25 years ago Paterson and co-workers introduced a modification to Schultz–Flory theory based on the Prigogine lattice model of solutions and formulated a reduced description of the demixing phenomenon (70DEL/PAT, 72SIO/DEL, 84COW/MCE). The method requires fewer adjustable parameters than the original theory and is applicable to solutions in both Θ and non-Θ solvents. In spite of the many positive features and the general qualitative success of the Patterson approach, its application very often results in unsatisfactorily large errors in predicted (T_c, X) loci (70DEL/PAT, 72SIO/DEL, 84COW/MCE). Recently Freed (89FRE/BAW, 89PES/FRE, 91DUD/FRE), Sanchez (91SAN), and Panayiotou (87PAN, 89KAR/DAF), and their co-workers, among others (88DEE/WAL, 93SCH, 95SCH/SIN), have developed sophisticated mean field theories of compressible polymer solutions which considerably improve on earlier modifications of the Flory–Huggins lattice model. Luszczyk and Van Hook (95LUS/REB, 95LUS/VAN), and Prausnitz and co-workers (93HU/YIN, 94HU/YIN, 95HU/YIN) have introduced computer programs to make realistic calculations of cloud and spinodal temperatures as functions of temperature, concentration, pressure, isotope substitution and other variables based on the Flory–Huggins (95LUS/REB, 95LUS/VAN) and Duduwicz–Freed (93HU/YIN, 94HU/YIN, 95HU/YIN, 91DUD/FRE) models respectively, but the calculations are tedious and have only been applied to a very few systems.

In considering the state of affairs outlined above it seemed reasonable to apply less tedious, and more efficient and rapid empirical or semi-empirical descriptions of polymer demixing to organize demixing data in order to define their general features. With semi-empirical descriptions in hand, one can more easily determine when to employ lengthy and tedious high precision calculations to make more detailed tests of theories of polymer solution. That is the approach chosen in the present paper. We focus on the qualitative or semiquantitative ordering of the molecular weight dependence of critical demixing on temperature and solvent quality at nominally low pressure.

In this paper we develop two separate descriptions of the MW dependence of T_c at nominally low pressure. The equations recognize that the UCS and LCS branches are manifestations of a single phenomenon and should behave similarly in both Θ and non-Θ solvents. Let us return to Fig. 2 which schematizes the effects of pressure, temperature, and molecular weight on solubility. First consider sections in the (T,X) plane at various pressures as shown by the shaded areas in the figure. In the most common case an increase in pressure widens the solubility gap ($\Theta^{lcs} - \Theta^{ucs}$) for Θ solvents (see Fig. 2 where $p_4 > p_3 > p_2 > p_1$), and displaces X_{hyp} toward more negative values. In Fig. 2 values of X_{hyp} at different pressures are marked with black dots which thus define the $X_{hyp\text{-}p}$ line. It is well known that Θ temperatures are pressure sensitive (76SAE/KUW, 72LEC/SCH). This suggests that for some polymer/solvent systems lowering the pressure, maybe even into the negative region [i.e., putting the solution under tension (87TRE)], might decrease the solubility gap to the point where the Θ temperatures merge

(in Fig. 2 this occurs at $p^* = p_2$). Actual demixing experiments take place at positive (and finite) molecular weights. Examples of isopleths at two values of X are plotted as the dotted lines in the figure. The minima in the curves (marked as "o's" on the diagram, which, remember, refers to solutions at the critical concentration) define the lower hypercritical temperatures, $T_{hyp,X,l}$, for that particular value of X. At $T_{hyp,X,l}$ $(\partial P/\partial T) = 0$, $(\partial^2 P/\partial T^2) > 0$. Notice that for each value of X there exists a pressure (which may be negative) where the (P,T,X) coordinates of $T_{hyp,X,l}$ and X_{hyp} coincide.

It is interesting to inquire whether isopleths like the dashed lines in Fig. 2 remain open and constantly broaden as pressure increases toward arbitrarily high values (see the insert to the figure), or show extrema and tend toward closure. The two possibilities are sketched in as the lightly dashed and the dashed-dotted projections in the insert to the figure. In the event that the isopleths are closed we will label the extrema of the isopleth for molecular weight parameter X the upper and lower hypercritical temperatures, $T_{hyp,X,u}$ and $T_{hyp,X,l}$ (marked as open circles), and the upper and lower hypercritical pressures, $P_{hcr,X,u}$ and $P_{hcr,X,l}$ (marked as the open squares in the insert), respectively. At $T_{hyp,X,u}$ $(\partial P/\partial T) = 0$, $(\partial^2 P/\partial T^2) < 0$, while at $P_{hyp,X,l}$ $(\partial T/\partial P) = 0$, $(\partial^2 T/\partial P^2) > 0$, and at $P_{hyp,X,u}$ $(\partial T/\partial P) = 0$, and $(\partial^2 T/\partial P^2) < 0$. The bulk of this analysis is speculative. To our knowledge no closed isopleths have been reported, or are there any known examples of upper hypercritical temperatures or pressures in polymer solutions. [However some small molecule solutions do show upper hypercritical points, one example is 2-butoxyethanol/ water (95WEL/LOO).] On the other hand there are many known solutions which show lower hypercritical temperatures (*vide infra*), and there are a number of other PS/solutions with high pressure demixing isopleths which unquestionably show an extrema in the (T,P) demixing locus along the UCS branch (i.e., a lower hypercritical pressure). These examples include demixing data for PS/cyclohexane (75SAE/KUW,81WOL/GEE), PS/methylcyclohexane(93HOS/NAK, 93WEL/LOO, 94VAN/KIE), PS/diethyloxalate (86SAE/KUW), and PS/1-phenyldecane (81WOL/GEE) solutions. Thus a closed loop in the (P,T_c) plane is possible (although not yet observed) as illustrated in the insert of Fig. 2, and to some extent one has the opportunity to control solvent quality by varying P. We continue to label the pressure at which $(\Theta^{lcs} - \Theta^{ucs}) = 0$ as P^*. The three kinds of behavior expected in PS/ solvent systems are: (1) The (Θ/poor-solvent) transition is found at a moderate and reachable positive pressure, $P^* > 0$. For $P < P^*$ the solvent is designated "poor." Above $P = P^*$ the system is a Θ-solution, and unless a hypercritical pressure, P_{hyp}(UCS) exists along the UCS branch will remain so to an arbitrarily high pressure. Should, however, P_{hyp}(UCS) exist, the solubility gap decreases for $P > P_{hyp}$. It may eventually shrink to zero and define an upper hypercritical temperature. (2) The Θ/non-Θ transition, if it occurs at all, is found below $P = 0$, $P^* < 0$. The high pressure behavior is analogous to case (1). This is the case normally designated "good solvent." (3) The Θ/non-Θ transition occurs, if at all, at unreachably high pressure and $P^* >> 0$. The solvent is poor and will not dissolve high molecular weight polymer.

3.2. Least-Squares Representation in the (T_c,X) Projection

To describe the data in Tables 3 to 42 we developed fourth order least squares polynomial representations of the experimentally observed T_c's at the system vapor pressure,

$$X = \Sigma A_j T^j; \quad 4 \geq j \geq 0; \quad X = M_w^{-1/2} \text{ for } M_w^{-1/2} > 0. \tag{2}$$

Least squares parameters of fit to Eq. (2) are reported in Table 43. In some cases, and these are noted in the table, a polynomial of lower order was employed, usually because too few data points were available to meaningfully define five parameters (very often one or the other demixing branch was not studied). Theta temperatures obtained from fits to Eq. (2) are reported in Table 2 and are compared there with the ones obtained from Eq. (1). The agreement is satisfactory.

We have also fit demixing data to a mean field scaling relation, Eq. (3), where the expansion is about the hypercritical locus (T_c^*, X^*). Here X^*refers to that particular molecular weight which locates the critical double point (hypercritical point) at the pressure of the measurement. [$MW^* = (X^*)^{-1/2}$ is the largest MW which is soluble at the critical concentration, which for polymers of low polydispersity can be approximated as the extremum in the solubility curve measured in the temperature-concentration plane, see Fig. 1(b)],

$$|(T_c - T_c^*)/T_c^*| = A|(X - X^*)/X^*|^{1/2};$$
$$X = M_w^{-1/2} \text{ for } M_w^{-1/2} > 0. \tag{3}$$

Fitting parameters and residuals are reported in Table 44. The quality of these three parameter fits compares favorably with that of the five parameter fits to Eq. (2).

Equation (3) presumes symmetrical behavior about T_c^*, which according to the best data in Tables 3–42 is not exactly true, but the asymmetry is only a few Kelvin, even in the worst cases. The drift is likely caused by inconsistencies in the pressures along the two branches, UCS data almost always refer to pressures of a few tenths MPa or less, but LCS data extend to a few MPa's or more, and corrections to $P = 0$ can be as much as a few K. To determine whether or not higher order terms are required in Eq. (3) [i.e., terms like $B|(X - X^*)/X^*|^{(n+1/2)}$, $n \geq 1/2$] we observed whether demixing data far from the critical origin require an extended description or not. Consider, for example, the data from Table 25 for PS/methylcyclohexane, which extend over an unusually wide range, $2 \times 10^7 \geq M_w \geq 761$. Figure 3 compares one term fits of Eq. (3) extending over that whole range with ones restricted to $M_w \geq 10\,000$. The differences are minimal, never more than 5 K, and indicate that within present experimental precision the one term scaling description is adequate.

TABLE 2. PS in different solvents: An alphabetical listing of solvents, the Θ-temperatures of their PS solutions (nominally at the vapor pressures of the solutions, except as marked), and the limiting molecular weight of the PS solute (when appropriate). Solutions marked with (+) and labelled "possibly infinite" have Θ-temperatures obtained by extrapolating second virial coefficients from light scattering, viscosity, or other techniques to zero, and interpreting that temperature as the Θ temperature. (?)—Small number of data points does not permit an accurate estimation.

Solvent	Θ-temperature from the literature (K)		Θ-temperature from this review (K), [Eq. (2)]		Solubility limit (hypercritical M_w(at vapor pressure (amu)) from fourth-degree fitting [Eq. (2)]/from scaling [Eq. (3)]
	UCST	LCST	UCST	LCST	
acetone	poor solvent	not Θ solv.	poor solvent	not Θ solv.	18000/25000 [a]
acetone (deuterated)	poor solvent	not Θ solv.	poor solvent	not Θ solv.	14000/15500 [a]
benzene	100	523	···	523.6[b]	infinite
bromobenzene	115	···	···	···	possibly infinite +
n-butanol	···	···	···	···	> 62600
n-butyl acetate	···	···	···	480.7 (?)	infinite (?)
sec-butyl acetate	210	442	···	···	possibly infinite +
tert-butyl acetate	288–296 [b]	327–331 [b]	292.1 [c]	372.4 [c]	infinite
n-butyl formate	264	···	···	···	possibly infinite +
butyl stearate	···	···	···	···	> 62600
capronic acid	···	···	···	···	> 62600
1-chloro-*n*-decane	279.7	···	···	···	possibly infinite +
1-chloro-*n*-dodecane	331.7	···	···	···	possibly infinite +
1-chloro-*n*-undecane	305.9	···	···	···	possibly infinite +
cyclodecane	289	···	289 [c]	···	infinite
cycloheptane	290	···	290 [c]	···	infinite
cyclohexane	307–308 [b]	486	306.7 [c]	486.4 [c]	infinite
cyclohexane (deuterated)	313.3	···	313 [c]	···	possibly infinite +
cyclohexanol	352–357 [b]	···	358.3 [d]/357.8 [c]	···	infinite
cyclohexanone	170	···	···	···	possibly infinite +
cyclooctane	285	···	286 [c]	···	infinite
cyclopentane	292–293 [b]	427	293.4 [d]/295.0 [c]	427.2 [d]/426.2 [c]	infinite
trans-decalin	288–295 [b]	>630	293.4 [c]	···	infinite
o-dichlorobenzene	220	···	···	···	possibly infinite +
dichloroethane	190	···	···	···	possibly infinite +
diethyl ether	poor solvent	not Θ solv.	poor solvent	not Θ solv.	30800/24300 [a]
diethyl malonate	304–309 [b]	578	304 [c]	570 [c]	infinite
diethyl oxalate	325–333 [b]	···	319.1 [d]/326.7 [c]	···	infinite
1,4 dimethylcyclohexane	poor solvent	not Θ solv.	poor solvent	not Θ solv.	4.1×10^6/4.8×10^6 [a]
2,5-dimethylfuran	145	···	···	···	possibly infinite +
dimethyl malonate	···	···	···	···	> 62600
dimethyl oxalate	···	···	···	···	> 62600
dimethyl succinate	···	···	···	···	> 62600
dimethoxymethane	···	···	···	385.2 [d]/379.1 [c]	infinite
dioctyl phtalate	···	···	278.5[d]/288.5 [c]	···	infinite
1,4-dioxane	198	···	···	···	possibly infinite +
ethyl acetate	222–229 [b]	412	229.2 [d]/230.2 [c]	411.9 [d]/410.0 [c]	infinite
ethyl acetoacetate	381.6	···	···	···	possibly infinite +
ethylbenzene	156	···	···	···	possibly infinite +
ethyl *n*-butyrate	···	471	180 [c]	470 [c]	infinite
ethyl chloroacetate	255	···	···	···	possibly infinite +
ethylcyclohexane	343	···	343.5 [d]/340.7 [c]	···	*infinite*
ethyl formate	poor solvent	not Θ solv.	poor solvent	not Θ solv.	57000/129000 [a]
n-heptane	poor solvent	not Θ solv.	poor solvent	not Θ solv.	< 9000
n-hexane	poor solvent	not Θ solv.	poor solvent	not Θ solv.	~ 3700
n-hexanol	···	···	···	···	> 62600
hexanol-3	···	···	···	···	> 62600
n-hexyl acetate	···	···	···	531.4 [c]	infinite
hexyl-*m*-xylene	285.6	···	···	···	possibly infinite +
isoamyl acetate	224	493	224.2 [c]	492.1 [c]	infinite
isoamyl alcohol	···	···	···	···	> 62600
isobutyl acetate	227	445	227.0 [d]/227.6 [c]	444.7 [d]/444.0 [c]	infinite
isopropyl acetate	246	380	245.3 [d]/246.4 [c]	388.0 [d]/379.9 [c]	infinite
dl-menthol	388.1	···	···	···	possibly infinite +
methyl acetate	316–322 [b]	382–387 [b]	312.3 [d]/318.6 [c]	387.7 [d]/386.1 [c]	infinite

TABLE 2. (*Continued.*)

Solvent	Θ-temperature from the literature (K)		Θ-temperature from this review (K), [Eq. (2)]		Solubility limit (hypercritical M_w (at vapor pressure (amu)) from fourth-degree fitting [Eq. (2)]/from scaling [Eq. (3)]
	UCST	LCST	UCST	LCST	
methyl *n*-amyl ketone	210	···	···	···	possibly infinite [+]
methylcyclohexane	333–344 [b]	480	345 [c]	464.5 (p=0)[c]	infinite
3-methylcyclohexanol	371.1	···	···	···	possibly infinite [+]
methylcyclopentane	348	417	342.1 [d]/349.4 [c]	428.9 [d]/419.9 [c]	infinite
methylcyclopentane (deuterated)	poor solvent	not Θ solv. ?	poor solvent	not Θ solv. ?	> 100000
methyl ethyl ketone	0 (estimated)	418-422 [b]	···	420.7 [d]/418.7 [c]	infinite
nitroethane	···	···	···	···	> 48000
1-nitropropane	272	···	···	···	possibly infinite [+]
octadecyl alcohol	···	···	···	···	> 62600
n-octane	poor solvent	not Θ solv.	poor solvent	not Θ solv.	< 14500
octadecane	···	···	···	···	> 4000
octene	···	···	···	···	> 62600
n-pentane	···	···	···	···	> 1100
n-pentyl acetate	···	···	···	500.7 (?)	infinite
1-phenyldecane	301–304 [b]	···	···	···	possibly infinite[+]
propionitrile	poor solvent	not Θ solv.	poor solvent	not Θ solv.	22900/23000 [a]
n-propyl acetate	193	451	193.3 [c]	450.6 [c]	infinite
pyridine	161	···	···	···	possibly infinite [+]
dl-terpineol	351.6	···	···	···	possibly infinite [+]
toluene	160	550	···	550.0 [d]/549.6 [c]	infinite
vinyl acetate	···	···	···	···	>62600

[a]First entry is M_w obtained from the fourth order polynomial fit, Eq. (2)/second is M_w as obtained from the scaling fit, Eq. (3).
[b]Range of reported Θ-temperatures.
[c]Obtained from fit of cloud point data to polynomial expression [Eq. (2)].
[d]Obtained from fit of cloud point data to Schultz-Flory expression [Eq. (1)]. Only when the difference between the fits to Eqs. (1) and (2) exceed 1 K are both values reported.

Figure 4 shows Schultz–Flory plots comparing SF [Eq. (1)] and Imre–Van Hook (IVH) [Eq. (3)] fits of UCS data in cyclohexane and methylcyclopentane. The example is typical. There is little or no advantage to one or the other equation when applied to demixing data in good solvents (like cyclohexane), a slight advantage for Eq. (3) in describing systems with more curvature in SF plots (say methylcyclopentane). Of course in the poor solvent limit Eq. (1) cannot be employed at all.

4. Solvent Groups: Remarks

We have divided the solutions in the tables into twelve groups containing chemically similar solvents in order to facilitate discussion. By "better solvent" we mean one with a more negative X^* and or larger width parameter, A. Thus deeper and/or wider scaling refers to better solvents. The experimental data are compared with polynomial or scaling fits in Tables 3–42 and Figs. 5–13. Comparison with the scaling fits are represented by dotted, dashed, or dash-dotted lines in the figures, and with polynomial representations by solid lines.

4.1. Acetates

Data from 14 PS/acetate systems are reviewed in Tables 3–12 and 42 and shown in Fig. 5. It is interesting to consider the series n-C_1 to n-C_6, or to compare *n*-propyl and *i*-propyl acetates, or *i*-propyl, *i*-butyl, and *i*-amyl acetates. The series of PS/(straight chain acetate) solutions shows a clear increase in solvent quality with chain length. The solubility curve for PS/(methyl acetate) is close to that for non-Θ solvents (shallow and narrow), the PS/(ethyl acetate) deepens further, and PS/(propyl acetate) has almost the deepest and widest solubility curve, at least for those cases where a complete data set is available. The other three solvents in the series PS/(n-C_4, n-C_5, n-C_6 acetates) have not been thoroughly studied, the available data are limited to the LCS branch only. However on the strength of that LCS data it is clear that solvent quality continues to increase with solvent chain length, at least so far as it correlates with the width of the scaling expressions. A comparison of the PS/(*i*-propyl acetate), PS/(isobutyl acetate), and PS/(*i*-amyl acetate) systems also shows that additional methylene increases solvent quality. In contrast the comparison of normal and branched chain acetates, PS/(*n*-propyl or *i*-propyl acetate) and PS/(*n*-butyl, *i*-butyl, and *t*-butyl acetate) shows the iso solvents to be poorer than the normal ones. Only one data point is available for PS/(vinyl acetate) demixing and we consider it unreliable because data for other solutions, published in that same paper (50JEN/KEL), are consistently different from other lit-

erature values by tens of degrees. Reasons for the difference are unknown, but are likely connected to poorly characterized PSs.

4.2. Alcohols

Most alcohols are considered to be nonsolvents for PS (89FUC), although UCS Θ temperatures have been reported for cyclohexanol, and single data points, presumably on the LCS branch, have been reported for a number of other alcohol solutions of PS of low *MW*. As for the acetates, the less highly branched alcohols are apparently the better solvents. (See Tables 13 and 42; Fig. 6.)

4.3. Alkanes and Some Derivatives

Normal alkanes are not very good solvents for PS [see Fig. 7(a)]. For lower members of the series (n-C_5 to n-C_8) solvent quality increases with chain length, but apparently the effect goes through a maximum because the quality has apparently dropped off again by n-C_{18}, but the data are scarce, and conclusions necessarily tenuous. We recommend a more thorough study of the chain length dependence of this important series of model solutions. Halogen derivatives of n-alkanes are definitely better solvents than the parent compounds. Dichloroethane, 1-chloro-n-decane, 1-chloro-n-undecane, and 1-chloro-n-dodecane are Θ solvents, as are other n-alkane derivatives (1-nitropropane, 1-phenyldecane, and, apparently, nitroethane).

Cycloalkanes are much better solvents than their straight chain parents [Fig. 7(b)]. Every reported cycloalkane between cyclopentane and cyclododecane is a theta solvent. There is no clear connection between the number of carbon atoms and solvent quality, partly because only two solvents as yet have had both UCS and LCS branches reported. Of the two, cyclohexane has a deeper and wider solubility curve (i.e., is a better solvent) than cyclopentane. Deuteration tends to decrease solvent quality, as does alkyl substitution on the ring. Thus methylcyclopentane, methylcyclohexane, and dimethylcyclohexane are worse solvents than their parent compounds. Each successive methyl group decreases solvent quality.

Solubility studies are available for only one bicyclic alkane, *trans*-decalin. That compound is a very good solvent, but only the UCS branch and its Θ temperature have been reported. The LCS branch very likely lies well above the liquid-vapor critical temperature of this solvent. At high *MW* solutions of PS/decalin are shear sensitive (85KRÄ/WOL). Shear raises the UCS precipitation temperature markedly. {Note added in proof: Additional data for PS/alkanes, PS/chloroalkane, and PS/n-alcohol solutions are found in 91 VAN/KON [van Opstal, L., Koningsveld, R., and Kleintjens, L. A., Macromolecules **24**, 161 (1991)]}. [See Tables 14–28 and 42; Figs. 7(a), 7(b), and 7(c).]

4.4. Alkenes

PS solubility has been reported in only one alkene, octene (Table 42, position of double bond unspecified). Alkenes are expected to be poor or limited solvents for PS, i.e., roughly similar to the parent alkanes.

4.5. Benzene and its Derivatives

Both benzene and toluene are traditionally considered to be good solvents, which is to say they show Θ^{ucs} well below the solvent freezing point together with rather high Θ^{lcs}. Direct observation of UCS solubilities in such cases is impossible and figures in the table have been obtained by extrapolating the temperature dependence of McMillan–Mayer second virial coefficients to zero. The derivatives show higher Θ^{ucs} than does benzene and are most likely worse solvents. (See Tables 29, 30, and 42; Fig. 8.)

4.6. Esters (other than formates and acetates)

Good solubility data for the UCS branch exists for diethyl oxalate, ethyl n-butyrate, and diethyl malonate although the data for the first compound does not extend to a high enough molecular weight to unequivocally establish the existence of a UCS Θ temperature. Diethyl malonate and ethyl n-butyrate are very good theta solvents. Scattered points are reported for other esters. (See Tables 31, 32, 33, and 42; Fig. 9.)

4.7. Ethers

Diethyl ether is a poor solvent with a hypercritical temperature reported around 275 K. Dioctylphthalate is a good solvent showing Θ_{UCS} around 285 K but without any reported LCS solubilities. PS/dioctylphthalate solutions are very shear sensitive (84RAN/MET), shearing can cause precipitation even above room temperature. 1,4-dioxane is most likely a good solvent, at least the UCS branch has been reported about a hundred degrees below room temperature. (See Tables 34, 35, and 42; Fig. 10.)

4.8. Formates

Solubilities have been reported for two formates. Ethyl formate is a poor solvent for PS showing a hypercritical temperature around 360 K and $M_w = 1.5\times10^5$, in comparison with its homologous sister, ethyl acetate, which is a theta solvent with a wide gap. n-Butyl formate is also a theta solvent, although data exist only for the UCS branch. (See Tables 36 and 42; Fig. 11.)

4.9. Heterocyclics

We have been able to find data for only two heterocyclic solvents (pyridine and 2,6-dimethylfurane). Both are good solvents with low values for Θ^{ucs}. (See Table 42.)

4.10. Ketones

Acetone is usually considered to be a poor solvent. Its hypercritical temperature is found at rather low M_w and T_c and deuterated acetone is an even poorer solvent. An additional CH_2 group, however, increases solvent quality markedly. Methyl ethyl ketone is one of the best solvents for PS showing $\Theta^{lcs}\sim$ 420 K and Θ^{ucs} near zero. Other larger ketones (cyclohexanone, methyl-n-amyl ketone) are also Θ solvents. The shape of the

Explanation of footnote symbols consistently used in Tables 3–41.

[a] Data obtained not at critical concentration, but close to it (the difference amounts to at most several K in T_c).

[b] M_n or $M_{viscosity}$ is tabulated rather than M_w.

[c] Graphical estimation, accuracy poor.

[d] Temperature of the maximum of cp-curve (difference between the real and reported T_v is larger than 1 K).

[e] Excluded from least squares fit to scaling equation, Eq. (3).

x Excluded from least squares fits to both polynomial and scaling equations [Eqs. (2) and (3)].

xx Estimated from the maximum in the spinodal curves

? Not reported in citation and unavailable.

v Measured at vapor pressure of solution.

TABLE 3. PS in methyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
2200	213.9		1.1	v	75KON/SAE
4000	218.8	484.5	1.1	v	75KON/SAE
10000	242.4	459.2	1.06	v	75KON/SAE
20400	254.6	445.4	1.06	v	75KON/SAE
37000	266.6	434.0	<1.06	v	74SAE/KON
48000		428	1	v	65MYR/ROW
51000		423.3	<1.2	0	72ZEM/PAT
59000		427	1	v	65MYR/ROW
64900		423	1.18	v	65MYR/ROW
97200	275.1	415.1	<1.2	0	72ZEM/PAT
99100		406 x	1.04	v	65MYR/ROW
105000		420[c] x	<1.15	?	70DEL/PAT
110000	284.2	415.7	<1.06	v	74SAE/KON
160000	281.4	409.0	<1.2	0	72ZEM/PAT
195000		409	1.1	v	65MYR/ROW
200000	289.7	409.9	<1.06	v	74SAE/KON
260000		415[c]x	<1.15	?	70DEL/PAT
270000		405	1.1	v	65MYR/ROW
390000		401	13	v	65MYR/ROW
498000	294.1	400.5	<1.2	0	72ZEM/PAT
530000	290[c]x	403[c]x	<1.15	?	70DEL/PAT
670000	301.5	398.4	<1.15	v	74SAE/KON
670000	296.4	397.8	<1.2	0	72ZEM/PAT
770000	300[c]x	400[c]x	1.04	v	93WAK/DIJ
770000	305.4	397.6	1.04	v	91BAE/LAM
860000	299.2	396.1	<1.2	0	72ZEM/PAT
1050000	295[c]x	395[c]x	<1.15	?	70DEL/PAT
1800000	303.1	392.7	<1.2	0	72ZEM/PAT
2600000	303[c]x	370[c]x	<1.15	?	70DEL/PAT
2700000	311.0	389.2	<1.1	v	74SAE/KON
infinite*	316	387		v	74SAE/KON
infinite*	320	382		0	72ZEM/PAT
infinite*		412		?	75KON/SAE
infinite*		399		?	75KON/SAE
infinite*	326			?	50JEN/KEL
infinite*	322[c]	370[c]		?	70DEL/PAT
infinite*	316	387		?	89ELI

TABLE 4. PS in ethyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000	204.1	451.0	<1.06	v	74SAE/KON
100000		437.5	1.06	v	91BAE/LAM
110000	213.9	435.4	<1.06	v	74SAE/KON
200000	216.5	430.6	<1.06	v	74SAE/KON
233000		424.9	1.06	v	91BAE/LAM
600000		420.3	1.1	v	91BAE/LAM
670000	222.9	421.4	<1.15	v	74SAE/KON
2700000	226.5	415.7	<1.1	v	74SAE/KON
infinite*	242.6		?	?	50JEN/KEL
infinite*	229	411		?	89ELI
infinite*	222			?	90BAR

TABLE 5. PS in *n*-propyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000		481.4	<1.06	v	74SAE/KON
110000	183.7	469.0	<1.06	v	74SAE/KON
200000	185.5	464.8	<1.06	v	74SAE/KON
670000	189.6	458.2	<1.15	v	74SAE/KON
2700000	191.0	454.2	<1.1	v	74SAE/KON
infinite*	193	451		?	74SAE/KON
infinite*	193	451		?	89ELI

TABLE 6. PS in iso-propyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
10000		468.5	<1.06	v	74SAE/KON
37000	206.6	436.7	<1.06	v	74SAE/KON
110000	220.9	414.2	<1.06	v	74SAE/KON
200000	225.6	407.7	<1.06	v	74SAE/KON
670000	235.5	395.2	<1.15	v	74SAE/KON
2700000	240.3	385.9	<1.1	v	74SAE/KON
infinite*	246	380		v	74SAE/KON

TABLE 7. PS in *n*-butyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
233000		494	1.06	v	95PFO/HIN
600000		489	1.1	v	95PFO/HIN

TABLE 8. PS in isobutyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000	197.9 x	487.4 x	<1.06	v	74SAE/KON
110000	210.4	468.5	<1.06	v	74SAE/KON
200000	212.9	463.3	<1.06	v	74SAE/KON
670000	220.9	453.9	<1.15	v	74SAE/KON
2700000	223.1	449.0	<1.1	v	74SAE/KON
infinite*	227	445		v	74SAE/KON

TABLE 9. PS in *t*-butyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000	230.6	443.7	1.06	v	75KON/SEA
100000	253.6[e]	422.0[e]	1.06	v	91BAE/LAM
110000	250.0	417.9	1.06	v	75KON/SEA
200000	256.2	410.1	1.06	v	75KON/SEA
233000	270.5[e]	403.3[e]	1.06	v	91BAE/LAM
600000	278.6[e]	391.0[e]	1.1	v	91BAE/LAM
670000	269		<1.1	0.1 ?	79SCH/WOL
670000	270.8	394.6	1.1	v	75KON/SEA
670000	270.8	393.7	<1.15	0	76SAE/KUW
1450000	276.7	387.1	<1.1	0	76SAE/KUW
2700000	280.7	382.5	<1.1	0	76SAE/KUW
3450000	281.8	380.3	?	v	75KON/SEA
3450000	281.8	381.2	<1.1	0	76SAE/KUW
infinite*	296.1	359.3		0	76SAE/KUW
infinite*	288	374		v	75KON/SEA
infinite*	296	357		v	75KON/SEA

TABLE 10. PS in *n*-pentyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
233000		519	1.06	v	95PFO/HIN
600000		512	1.1	v	95PFO/HIN
1971000		507	1.26	v	195PFO/HIN

TABLE 11. PS in *n*-hexyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
233000		542	1.06	v	95PFO/HIN
600000		538	1.1	v	95PFO/HIN

TABLE 12. PS in isoamyl acetate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000	199.4	526.2	<1.06	v	74SAE/KON
110000	210.1	510.1	<1.06	v	74SAE/KON
200000	212.3	505.1	<1.06	v	74SAE/KON
670000	218.2	499.2	<1.15	v	74SAE/KON
2700000	220.8	497.0	<1.1	v	74SAE/KON
infinite*	224	493		v	74SAE/KON

TABLE 13. PS in cyclohexanol.

M_n	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
84000 [b]	350		?	?	53SHU/FLO
236000 [b]	353.5		?	?	53SHU/FLO
881000 [b]	356		?	?	53SHU/FLO
5500000 [b]	357.5		?	?	53SHU/FLO
infinite*	356.6		?	?	89ELI

TABLE 14. PS in *n*-hexane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
900	296[c]	490[c]	<1.06	v	83COW/MCE
2030	318[c]	470[c]	<1.06	v	83COW/MCE
4800	no T_c at $p=v$				83COW/MCE

TABLE 15. PS in *n*-heptane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
2030	311[c]	515[c]	<1.06	v	83COW/MCE
4800	359[c]	477[c]	<1.06	v	83COW/MCE

TABLE 16. PS in *n*-octane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
2030	309[c]		<1.06	v	83COW/MCE
4800	353[c]	527[c]	<1.06	v	83COW/MCE
10300	no T_c at $P=v$		<1.06	v	83COW/MCE

TABLE 17. PS in cyclopentane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
5900		475 x	?	v	65ALL/BAK
13800		467 x	?	v	65ALL/BAK
33100		443 x	?	v	65ALL/BAK
37000	267.0	455.3	1.06	v	73SAE/KUW2
43000		455	1.01	v	93IWA/SHI
97200	275.2	445.5	1.06	v	73SAE/KUW
98900		445.5	1.02	v	93IWA/SHI
171900		441	1.03	v	93IWA/SHI
209000	280.9	440.0	1.06	v	73SAE/KUW
354000		436	1.02	v	93IWA/SHI
400000	284.7	435.4	1.06	v	73SAE/KUW2
600000		420 x	?	v	65ALL/BAK
600000	286.3		1.1	0.1	81WOL/GEE
600000	289.2		1.1	0.1	81WOL/GEE
670000	285.9	433.8	1.06	v	73SAE/KUW2
670000	286.0		<1.15	0.1	78ISH/KUW
791000		434	1.01	v	93IWA/SHI
2000000	291.0		<1.3	0.1	78ISH/KUW
2700000	289.9	429.5	1.06	v	73SAE/KUW2
infinite*	293	427		v	73SAE/KUW2
infinite*	292.8	427.4		?	74KUW/SAE
infinite*	292–293	427.3		?	89ELI

TABLE 18. PS in cyclohexane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
20400	279.6		1.06	v	91BAE/LAM
35400	284.6		1.31	?	70KON/KLE
37000	285.6	510.9	<1.06	v	73SAE/KUW
37000	285.4		<1.06	0.1	75SAE/KUW
42800	287		1.01	0.1	81HAS/TER
43600 [b]	292.6 x		?	?	52SHU/FLO
43600 [b]	293 x		?	?	51FOX/FLO
45300	287		1.01	0.1	84TSU/EIN
48000	288		1.06	?	91KAW/IMA
51000	288.85		1.04	?	70KON/KLE
51000	288		1.08	?	71SCH
51000	288		1.04	?	74DER/GOL
51000	289 xx		1.04	?	80IRV/GOR
51000	288.5 xx		1.04	?	80IRV/GOR
61500	290.45		1.12	?	70KON/KLE
80000	292.3		1.16	?	60DEB/COL
82000	292.1		1.05	0.1	62HAM/BOL
87000 [b]	297 x		?	?	51FOX/FLO
89000 [b]	297.1 x		?	?	52SHU/FLO
92000 [b]	298 x		?	?	51FOX/FLO
93000	293.65		1.02	?	70KON/KLE
97200	293.5	502.1	<1.06	v	73SAE/KUW
100000	294		1.06	v	91BAE/LAM
100000	292		1.43	?	72SCH
100000	292.5		2.63	?	72SCH
100000	293		4.62	?	72SCH
107000	294		1.01	0.1	81HAS/TER
110000	294		1.06	v	75KOJ/KUW
110000	294.3		<1.06	0.1	75SAE/KUW
111000	294		1.0	?	74DER/GOL
120000	294.5 xx		1.08	?	80IRV/GOR
124000	294.9		1.05	?	60DEB/COL
124000	295.7		1.05	?	62DEB/WOE
131000[c]	294.1[c]		?	?	75STR/BEN
150000	301 x		?	?	56JEN/SCH
153000	296.2		1.04	?	60DEB/COL, 60DEB/COL2
153000	297.0		1.04	?	62DEB/WOE
154000	293.4		1.465	?	90RÄT/KRÜ
163000	296		1.06	?	71SCH
163000	296.5 xx		1.06	?	80IRV/GOR
166000	296.60		1.08	?	70KON/KLE
166000	296		1.08	?	74DER/GOL
166000	296.5 xx		1.08	?	80IRV/GOR
180000 [b]	301 x		?	?	65REH/MÖL
186000	297		1.07	0.1	81HAS/TER
200000	296.78		<1.02	?	73KUW/NAK
200000	297.0	496.9	<1.06	v	73SAE/KUW
200000	297		1.04	?	74DER/GOL
200000	297 xx		1.04	?	80IRV/GOR
206000	296.94		<1.03	?	73KUW/NAK
215000	300		<1.1	?	77RIG/WOL
239000	298.0		1.08	?	60DEB/COL2
239000	298.5		1.08	?	62DEB/WOE
250000 [b]	301.1 x		?	?	52SHU/FLO
253000	298.1		1.02	?	60DEB/COL2
253000	298.5		1.02	?	62DEB/WOE
267000	298.1		1.08	0.1	62HAM/BOL
274000	299		1.02	?	95IKI/KLE
282000	298.7		1.43	?	70KON/KLE
310000[c]	298.8[c]		?	?	75STR/BEN
346000	301		1.65	?	65REH/MÖL, 67REH/MÖL
346000	300.1		1.65	?	68KON/STA
346000	300		1.65	?	67SCH

TABLE 18. (*Continued.*)

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
360000 [b]	300 x		?	?	51FOX/FLO
390000	300		1.06	0.1	77WOL/SEZ
394000	300.7		1.05	?	70KON/KLE
400000	300.3	494.7	<1.06	v	73SAE/KUW
400000	299.6		1.03	0.1	90GOE/ZIE
411000	300 xx		1.05	?	80IRV/GOR
415000	299.98		<1.06	?	73KUW/NAK
415000	300		<1.06	?	71KUW/FEN, 72LEE/TSC
415000	300.1		<1.06	v	69CHU/KUW
415000	300.1		<1.06	?	72TSC/LEE
424000	298.6		1.407	?	90RÄT/KRÜ
434000	300		3.24	?	90RÄT/KRÜ
450000	299.89		1.44	?	73KUW/NAK
470000	301.1		1.07	?	67REH/MÖL
470000	300.8		1.07	?	71BOR/REH, 72BOR
470000	300.6		1.07	?	68REH/WEF, 68REH/KON
498000	301		1.05	0.1	84TSU/EIN
500000	300.5 xx		1.02	?	80IRV/GOR
520000	300		1.20	?	71SCH
520000	301 xx		1.20	?	80IRV/GOR
527000	301.15		1.08	?	70KON/KLE
527000	300		1.08	?	74DER/GOL
540000 [b]	303 x		?	?	51FOX/FLO
569000	300.8		1.09	?	60DEB/COL2
569000	301.0		1.09	?	62DEB/WOE
600000	301.5		1.1	0.1	81WOL/GEE
610000	301		1.07	v	91BAE/LAM
625000[c]	301.2[c]		?	?	75STR/BEN
670000	301.1	491.7	<1.10	v	73SAE/KUW
670000	300.9		<1.1	0.1	75SAE/KUW
680000	301.03		<1.02	?	73KUW/NAK
860000	302 xx		1.00	?	80IRV/GOR
1190000	302.1		1.09	?	60DEB/COL2
1270000 [b]	304.6 x		?	?	52SHU/FLO
1270000 [b]	305 x		?	?	51FOX/FLO
1450000	303.6		<1.1	0.1	75SAE/KUW
1500000	303.2		1.2	?	70KON/KLE
1560000	303.6		<1.03	v (?)	78NAK/DOB
2610000	304.5 xx		1.31	?	80IRV/GOR
2700000	304.2	488.6	<1.10	v	73SAE/KUW
3500000	303		1.24	?	62DEB/CHU
infinite*	307	486		v	73SAE/KUW
infinite*	307.2–307.9			?	59KRI/GEY
infinite*	307			?	51FOX/FLO. 90BAR
infinite*	309			0	72LEC/SCH
infinite*	307.2[c]			?	75STR/BEN
infinite*	304.9–308.6			?	95MUN/TIA
infinite*	306–308			?	91NAK/NOR
unknown	302 x		?	?	73BRE/RIG

TABLE 19. PS in deuterated cyclohexane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
131000 [c]	297.5 [c]		?	?	75STR/BEN
310000 [c]	302.2 [c]		?	?	75STR/BEN
400000	303.6		?	?	90GOE/ZIE
625000 [c]	304.8 [c]		?	?	75STR/BEN
infinite*	313.3			?	89ELI
infinite*	312			?	75STR/BEN

TABLE 20. PS in cycloheptane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
51000	276.2		<1.1	?	86COW/MCE
153000	282.2		<1.1	?	86COW/MCE
267000	283.9		<1.1	?	86COW/MCE
860000	286.9		<1.1	?	86COW/MCE
10000000	288.7		<1.1	?	86COW/MCE
infinite*	290			?	86COW/MCE

TABLE 21. PS in cyclooctane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
51000	275.2		<1.1	?	86COW/MCE
153000	279.5		<1.1	?	86COW/MCE
267000	281.2		<1.1	?	86COW/MCE
860000	284.4		<1.1	?	86COW/MCE
10000000	285.5		<1.1	?	86COW/MCE
infinite*	285			?	86COW/MCE

TABLE 22. PS in cyclodecane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
51000	278.9		<1.1	?	86COW/MCE
153000	282.5		<1.1	?	86COW/MCE
267000	284.1		<1.1	?	86COW/MCE
860000	286.6		<1.1	?	86COW/MCE
10000000	287.8		<1.1	?	86COW/MCE
infinite*	289			?	86COW/MCE

TABLE 23. PS in methyl cyclopentane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
2510	255	507 x	<1.1	v	91SZY/VAN
4136	259.69		<1.06	0	95LUS/REB
5770	269	500	<1.05	v	91SZY/VAN
7820	270	491	1.19	v	91SZY/VAN
11500	295	480	1.07	v	91SZY/VAN
13502	291.93		<1.06	0	95LUS/REB
22091	300.94		1.03	0	95LUS/REB
25000	303.65		<1.06	0	95LUS/REB
106280	327.52		<1.06	0	95LUS/REB
110000	322	445	<1.1	v	84COW/MCE
239000	329	438	<1.1	v	84COW/MCE
860000	338	428	<1.1	v	84COW/MCE
2000000	342	422	<1.1	v	84COW/MCE
infinite*	348	417		v	91SZY/VAN

TABLE 24. PS in deuterated methylcyclopentane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
106280	339.41		1.06	0	95LUS/REB
25000	310.07		1.06	0	95LUS/REB

TABLE 25. PS in methylcyclohexane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
761	189		1.14	v	95IMR/VAN
1241	214		1.07	v	95IMR/VAN
1681	230		1.06	v	95IMR/VAN
2500	246		1.09	0	95IMR/VAN
4000	261		1.06	0	95IMR/VAN
5780	271		1.05	0	95IMR/VAN
9000	279		1.06	0	94VAN/KIE
9000	281		1.06	?	82SHI/VAN
10200	285.7		1.06	0	93HOS/NAK
10200	285.71		1.06	?	80DOB/NAK, 80DOB/NAK2
13000	291.3		1.06	v	91SHE/SMI
16100	296		1.06	0	93HOS/NAK
16100	295.98		1.06	?	80DOB/NAK, 80DOB/NAK2
17200	296.7		<1.06	?	84DOB/NAK
17300	296.13		1.06	?	80DOB/NAK, 80DOB/NAK2
17500	297		1.06	0	94VAN/KIE
17500	296.32		1.06	?	82SHI/VAN
20200	298.95		1.06	?	80DOB/NAK, 80DOB/NAK2
20400	299 [c] x	531 [c] x	?	v	74COW/MCE2
22000	301		1.03	0	93WEL/LOO
23000	302.2		1.06	v	91SHE/SMI
28500	305		1.1	0	94VAN/KIE
29000	306.1		1.06	v	91SHE/SMI
30000	302	497	1.03	0	95IMR/VAN
34900	309		1.06	0	93HOS/NAK
34900	309		1.06	?	80DOB/NAK, 80DOB/NAK2
37000	309.65		1.06	?	82SHI/VAN
37000	309.7	515.8 x	1.06	v	73SAE/KUW
37000	307 [c] x	523 [c] x	?	v	74COW/MCE2
46400	312.61		1.06	?	80DOB/NAK, 80DOB/NAK2
50000	313		1.06	0	94VAN/KIE
90000		490	1.04	0	95IMR/VAN
97200	321.8	505.9 x	1.06	v	73SAE/KUW
97200	318.1 x		1.1	?	71KAG/BAB
109000	322.71		1.06	?	80DOB/NAK, 80DOB/NAK2
110000	323.34		1.06	?	82SHI/VAN
156000	326 [c] x	505 [c] x	?	v	74COW/MCE2
181000	327.0		1.06	?	80DOB/NAK, 80DOB/NAK2
200000	327.4	499.9 x	1.06	v	73SAE/KUW
233000	329.92		1.06	?	82SHI/VAN
233000	330		1.06	v	91CHU/LIN
400000	332.7	496.4 x	1.06	v	73SAE/KUW
411000	344.0 x		1.1	?	71KAG/BAB
670000	334.5	492.3 x	1.1	v	73SAE/KUW
670000	336 [c] x	494 [c] x	?	v	74COW/MCE2
719000	334.8		<1.06	?	91SHE/SMI
719000	334.82		1.06	?	80DOB/NAK, 80DOB/NAK2
860000	346.3 x		1.1	?	71KAG/BAB
900000	336		1.1	v	91CHU/LIN
1260000	336.97 x		1.05	?	82SHI/VAN
1800000	348		1.1	?	71KAG/BAB
1860000	339		1.12	v	91CHU/LIN
1971000	336	476	1.26	0	95IMR/VAN
2700000	339.6	488.4 x	1.1	v	73SAE/KUW
20000000	343	470	1.2	0	95IMR/VAN
infinite*	343.7	484		v	80DOB/NAK2
infinite*	344.6	470		0	95IMR/VAN
infinite*	345	464.5		0	95IMR/VAN
infinite*	345	486		v	74COW/MCE2
infinite*	343.5			0	95IMR/VAN

TABLE 26. PS in 1,4-dimethyl cyclohexane (1:1 mixture of *cis* and *trans* isomers).

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
110000	374	494	<1.1	v	84COW/MCE
239000	387	482	<1.1	v	84COW/MCE
860000	402	466	<1.1	v	84COW/MCE
2000000	417	452	<1.1	v	84COW/MCE

TABLE 27. PS in ethylcyclohexane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
43600 [b]	320 x		?	? (0.1)	51FOX/FLO
92000 [b]	326 x		?	? (0.1)	51FOX/FLO
123900	325.8		1.05	?	63DEB/WOE
152880	327.7		1.04	?	63DEB/WOE
238680	330.4		1.08	?	63DEB/WOE
360000 [b]	336 x		?	? (0.1)	51FOX/FLO
568980	335.1		1.09	?	63DEB/WOE
1270000 [b]	339 x		?	? (0.1)	51FOX/FLO
infinite*	343			?	89ELI

TABLE 28. PS in *trans*-decalin.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000	274.5		1.06	v	76NAK/HIG
90000	281.5		1.04	0.1	95PFO/HIN
97000	281.8		1.06	v	76NAK/HIG
100000	282		?	?	85KRÄ/WOL
110000	283		1.06	0.1	77WOL/JEN,77WOL/SEZ
164000	288		1.1	?	93ARN/BER
200000	285.0		1.06	v	76NAK/HIG
233000	287.1		1.06	0.1	95PFO/HIN
305000	288		3.9	?	87ARN/BER,93ARN/BER
390000	289		1.1	0.1	77WOL/JEN
400000	287.9		1.06	v	76NAK/HIG
670000	289.0		1.1	v	76NAK/HIG
1700000	290.4		?	?	85KRÄ/WOL
1971000	291.5		1.26	0	95IMR/VAN2
2000000	291		1.3	0.1	77WOL/JEN
2050000	289		?	?	74VER/PHI
2700000	291.3		1.1	v	76NAK/HIG
infinite*		1584		?	76NAK/HIG
infinite*	294	>633		v	75KON/SAE
infinite*	293			?	72LEC/SCH
infinite*	293			?	77WOL/JEN

TABLE 29. PS in benzene.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000		538.7	<1.06	v	73SAE/KUW2
97200		532.5	<1.06	v	73SAE/KUW2
200000		530.5	<1.06	v	73SAE/KUW2
400000		528.3	<1.06	v	73SAE/KUW2
670000		527.0	<1.1	v	73SAE/KUW2
2700000		525.0	<1.1	v	73SAE/KUW2
infinite*	100			?	51FOX/FLO, 90BAR
infinite*		523		v	73SAE/KUW2

TABLE 30. PS in toluene.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000		567.2	<1.06	v	73SAE/KUW
97200		559.9	<1.06	v	73SAE/KUW
200000		557.2	<1.06	v	73SAE/KUW
400000		554.9	<1.06	v	73SAE/KUW
670000		553.1	<1.1	v	73SAE/KUW
2700000		552.0	<1.1	v	73SAE/KUW
infinite*		550		v	73SAE/KUW
infinite*	160			?	51FOX/FLO, 90BAR

TABLE 31. PS in diethyl malonate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000	262.7		1.06	v	75KON/SAE
62600	291 x		?	?	50JEN/KEL
97200	278.3		1.06	v	75KON/SAE
102000	277.1		1.02	?	90STA/PLO
102000	276.3		1.02	?	88TVE/GRE
102000	275.2		1.02	?	90GRU/HAB
107000	280.1		1.02	?	87GRU/GRE
200000	283.9		1.02	?	77HAM/KUW, 80HAM/KUW 79HAM/KUW
200000	285.8	589.6	1.06	v	75KON/SAE
400000	293.3	586.2	1.06	v	75KON/SAE
600000	294		1.1	0.1	81WOL/GEE
670000	296.3	584.1	1.15	v	75KON/SAE
2700000	301.8	580.9	1.1	v	75KON/SAE
infinite*	309	578	?	?	75KON/SAE
infinite*	304–309		?	?	89ELI

TABLE 32. PS in diethyl oxalate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
16700	261.9		1.06	0.1	86SAE/KUW
50000	280.0		1.06	0.1	86SAE/KUW
62600	259 x		?	?	50JEN/KEL
110000	292.5		1.1	0.1	86SAE/KUW
300000[xx]	318/308 [a]		1.06	0.1	95HAA/TOR
600000	309.9		1.1	0.1	86SAE/KUW
600000[xx]	312.8[x]		1.1	?	94SATKUW
2000000[xx]	334/322[a]		1.3	0.1	95HAA/TOR
infinite*	324.5–332.5			?	89ELI

[a]Two dimensional measurement of film between glass cover slip comparing wet (first entry) and dry solvents (second entry), (i.e., water contaminated vs water free).

TABLE 33. PS in ethyl-n-butyrate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000		514.9 x	1.06	v	75KON/SAE
110000		490.8	1.06	v	75KON/SAE
200000		486.5	1.06	v	75KON/SAE
670000		479.9	1.06	v	75KON/SAE
2700000	180.3	···	1.1	v	75KON/SAE
3450000	180.6	474.8	?	v	75KON/SAE
infinite*		471		v	75KON/SAE

TABLE 34. PS in diethyl ether.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
4800		407.3	<1.06	v	72SIO/DEL
10000		353.0	<1.06	v	72SIO/DEL
19800	235.6	314.5	<1.06	v	72SIO/DEL
20400	230 x	316 x	<1.06	v	74COW/MCE, 74COW/MCE2
20400	228.4 x	314.5 x	<1.06	0	76SAE/KUW

TABLE 35. PS in dioctyl phthalate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
280000	281		3	?	74VER/PHI
280000	281		3	?	84RAN/MET
900000	283.6		?	?	84RAN/MET
1800000	285		1.3	?	84RAN/MET
1800000	286		?	?	74VER/PHI
1850000	284		1.06	?	94WIR
1971000 [a]	281 x		1.26	0	95IMR/VAN2
2050000	285		?	?	74VER/PHI
infinite*	295			?	94WIR
infinite*	295			?	67BER

TABLE 36. PS in ethyl formate.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
2200	230		<1.1	v	75KON/SAE
4000	244	480	<1.1	v	75KON/SAE
10000	272	451	<1.06	v	75KON/SAE
20400	294	428	<1.06	v	75KON/SAE
37000	316	410	<1.06	v	75KON/SAE

TABLE 37. PS in acetone.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
2510	232 [d]	480	<1.1	v	91SZY/VAN
4800	222 x	465 x	<1.06	v	72SIO/DEL
5110	263 [d]	448	<1.07	v	91SZY/VAN
5770 [a]	251	452	<1.05	v	91SZY/VAN
7500	253.3 x	442 x	~1.05	0.5	95LUS/VAN
7820	271 [d]	438	1.19	v	91SZY/VAN
7820	254		1.19	0 ?	92SZY/REB
8000	260 x	437 x	1.09	0.5	95LUS/VAN
10300	271	414	<1.06	v	72SIO/DEL
11500	273 [d]	419	1.07	v	91SZY/VAN
11500	286		1.07	0 ?	92SZY/REB
11687	274.8 x	421 x	1.03	0.5	95LUS/VAN
13502	289 [d]	396	1.06	v	91SZY/VAN
13502	285.3 x	400 x	<1.06	0.5	95LUS/VAN
19800	no T_c at $p=v$		<1.06		72SIO/DEL
20000	338		1.03	0	94CAS/RUB
20400	no T_c at 0 MPa		<1.2		72ZEM/PAT, 74COW/MCE
22000	no T_c at 0 MPa		1.03		93REB/VAN
22901	341.2 x	351.7 x	1.03	0.5	95LUS/VAN

TABLE 38. PS in deutero-acetone.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
5110 [a]	259	444	<1.07	v	91SZY/VAN
5770 [a]	270	436	<1.05	v	91SZY/VAN
7800 [a]	286.1	428	1.19	v	91SZY/VAN
7820	286		1.19	0 ?	92SZY/REB
8000 [a]	282	420	<1.09	v	91SZY/VAN
11500	284		1.07	0 ?	92SZY/REB
11500	290	408	1.07	v	91SZY/VAN
13502	350.3	367.3	<1.06	v	95LUS/REB

TABLE 39. PS in methyl ethyl ketone.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
37000		463.2	<1.06	v	73SAE/KUW2
97000		445.8	?	?	73BAB/FUJ
97200		448.8	<1.06	v	73SAE/KUW2
110000		447	?	?	74NAK/HAM
200000		441.1	<1.06	v	73SAE/KUW2
200000		439.2	?	?	73BAB/FUJ
212000		440	?	?	74NAK/HAM
342000		436	?	?	74NAK/HAM
400000		434.5	<1.06	v	73SAE/KUW2
533000		432	?	?	74NAK/HAM
670000		431.8	<1.1	v	73SAE/KUW2
860000		428.0	?	?	73BAB/FUJ
2000000		426	<1.3	?	74NAK/HAM
2000000		422.9	?	?	73BAB/FUJ
2700000		425.7	<1.1	v	73SAE/KUW2
11000000		422	?	?	74NAK/HAM
infinite*		422		v	73SAE/KUW2
infinite*		418.8		?	74NAK/HAM
infinite*		418		?	73BAB/FUJ
infinite*	0			?	51FOX/FLO

TABLE 40. PS in dimethoxymethane.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
51000		413.7	<1.06	v	72SIO/DEL
97200		406.1	<1.06	v	72SIO/DEL
160000		401.2	<1.06	v	72SIO/DEL
411000		395.0	<1.06	v	72SIO/DEL
860000		391.6	<1.06	v	72SIO/DEL

TABLE 41. PS in propionitrile.

M_w	UCST(K)	LCST(K)	M_w/M_n	p (MPa)	Ref.
8000	273		~1.05	0	95LUS/VAN
13500	312		1.06	0	95LUS/VAN
22000	359 x	401 x	1.03	0	94IMR/VAN
22091	364	400	1.03	0	95LUS/VAN
25000	no T_c at $p=0$		?	0	95LUS/VAN

TABLE 42. Other PS/solvent systems.

Solvent	M_w	UCST(K)	LCST(K)	Ref.
bromobenzene	infinite*	115		90BAR
n-butanol**	62600	(454)?	(454)?	50JEN/KEL
i-butyl acetate	infinite*	227		89ELI
sec-butyl acetate	infinite*	210	442	75KON/SAE
n-butyl formate	infinite*	264		89ELI
butyl stearate**	62600	(387)?	(387)?	50JEN/KEL
capronic acid**	62600	(448.1)?	(448.1)?	50JEN/KEL
1-chloro-*n*-decane	infinite*	279.7		89ELI
1-chloro-*n*-dodecane	infinite*	331.7		89ELI
1-chloro-*n*-undecane	infinite*	305.9		89ELI
cyclohexanone	infinite*	170		90BAR
o-dichloro benzene	infinite*	220		90BAR
dichloro ethane	infinite*	190		51FOX/FLO, 90BAR
2.5-dimethyl furan	infinite*	145		90BAR
dimethyl malonate**	62600	(409)?	(409)?	50JEN/KEL
dimethyl oxalate**	62600	(453)?	(453)?	50JEN/KEL
dimethyl succinate**	62600	(335)?	(335)?	50JEN/KEL
1,4-dioxane	infinite*	198		90BAR
ethyl acetoacetate	infinite*	381.6		89ELI
ethyl benzene	infinite*	156		90BAR
ethyl chloroacetate	infinite*	255		90BAR
n-hexanol**	62600	(425)?	(425)?	50JEN/KEL
hexanol-3**	62600	(396.5)?	(396.5)?	50JEN/KEL
hexyl-*m*-xylene	infinite*	285.6		89ELI
isoamyl alcohol**	62600	(444)?	(444)?	50JEN/KEL
dl-menthol	infinite*	388.1		89ELI
methyl *n*-amyl ketone	infinite*	210		90BAR
3-methyl cyclohexanol	infinite*	371.1		89ELI
nitroethane	48000	303		91KAW/IMA
1-nitropropane	infinite*	272		90BAR
octadecane	4000	403		74KON/KLE
octadecyl alcohol**	62600	(448.6)?	(448.6)?	50JEN/KEL
octene**	62600	(355)?	(355)?	50JEN/KEL
n-pentane	1100	292		88KIE/BOR, 88KIE/BOR2
	1000	332 **	405 **	72HOR
1-phenyldecane	infinite*	301.1–303.7		89ELI
	600000	295.5		81WOL/GEE
pyridine	infinite*	161		90BAR
dl-terpineol	infinite*	351.6		89ELI
vinyl acetate**	62600	(284)?	(284)?	50JEN/KEL

*Obtained from fit of CP data to Eq. (1) or extrapolation of 2nd virial coefficient data.

**Results reported in these references (50JEN/KEL, 72HOR) are strange. It is not clear whether the mol.weight is reported as M_v or M_w. The T_c's are quite different from the trends reported by other workers, and it is sometimes not clear whether the reported T_c refers to UCS or LCS. Perhaps the sample was partly cross-linked or the solvents dirty?

infinite* Obtained from fit of CP data to Eq. (1) or extrapolation of 2nd virial coefficient data. PS/acetone phase diagram in the vicinity of the hypercritical point has been carefully studied. In this region T_c/concentration diagrams are highly distorted (95LUS/REB, 93REB/VAN) and it is possible that actual critical temperatures differ from temperature maxima in T/concentration diagrams by as much as several degrees. (See Tables 37–39, and 42; Fig. 12.)

4.11. Terpenes

Solubility data have been reported for two terpenes (dl-

TABLE 43. Least squares parameters of fit to Eq. (2). $X = M_w^{-1/2} = AT^4 + BT^3 + CT^2 + DT + E$. The pressure is held at the solution vapor pressure except for the marked cases where $p=0$. M_w has units of amu and T is in K. The solutions are at the critical concentration so $T=T_c$.

Solvents	10^{11} A	10^8 B	10^5 C	10^4 D	E	M_w range	Temp. range
acetone$^{p=0}$	3.6524	−5.30626	2.91007	−71.2001	0.661744	2510–20000	232–480
acetone$^{p=0}$ (deuterated)	4.71845	−6.63738	3.52871	−84.0202	0.76422	5110–13502	259–444
benzene^{L}				3.4021	−0.178082	37000–2700000	525–538.7
n-butyl acetates^{L}				1.56122	−0.07505266	233000–600000	489–494
tert-butyl acetate	−0.21902	0.23518	−0.03394	−2.30745	0.05832	37000–3450000	253.6–422
cyclodecane^{U}				−4.0639	0.117394	153000–10000000	282.5–287.8
cycloheptane^{U}				−3.24293	0.0940258	51000–10000000	278.9–287.8
cyclohexane	−1.0822	1.63851	−0.795433	12.8409	−0.022394	20400–3500000	279.6–510.9
cyclohexane (deuterated)^{U}			−0.1020116	4.123266	−0.02961988	131000–625000	297.5–304.8
cyclohexanol^{Ud}				−4.21263	0.15093	84000–5500000	350–357
cyclooctane^{U}				−3.79986	0.1089	51000–10000000	275.2–285.5
cyclopentane	1.23548	−6.17153	3.12989	−85.889	0.813273	37000–2700000	267–455
trans-decalin^{U}				−2.80691	0.0823462	37000–2700000	274.5–291.5
diethyl ether		−0.332029	0.363871	−12.4293	0.141387	4800–19800	235.6–407.3
diethyl malonate	0.78138	−1.25729	0.76891	−21.51096	0.23028	37000–2700000	262.7–589.5
diethyl oxalate^{U}			0.135233	−9.06514	0.152371	16700–600000	261.9–309.9
1,4 dimethyl cyclohexane	2.56717	−4.44156	2.94302	−88.4247	1.01481	110000–2000000	374–494
dimethoxy methane^{L}				1.51305	−0.0581971	51000–860000	391.6–413.7
dioctyl phtalate^{U}			5.69692	−325.354	4.646	280000–2050000	281–285
ethyl acetate	1.14767	−1.65899	0.938139	−23.9563	0.224465	37000–2700000	204.1–451
ethyl-*n*-butyrate	−1.63419	2.137603	−0.91964	14.41844	−0.068427	37000–2700000	180–491
ethyl cyclohexane^{U}				−1.6462	0.0564762	123900–568980	325.8–335.1
ethyl formate	2.451272	−3.583992	2.017385	−51.64271	0.5090744	2200–37000	230–480
n-heptane		0.164309	−0.0910598	−1.05719	0.0937232	2030–4800	311–515
n-hexane		0.169164	0.107588	−16.4537	0.382228	900–2030	296–490
n-hexyl acetate^{L}				1.951525	−0.1037011	233000–600000	532–542
isoamyl acetate	−1.78401	2.50692	−1.17729	20.7302	−0.110658	37000–2700000	199.4–526.2
isobutyl acetate	−0.397448	0.451411	−0.113655	−1.51999	0.0509085	37000–2700000	197.9–487.4
isopropyl acetate	0.808317	−1.14824	0.650321	−16.8097	0.161456	10000–2700000	206–6–468.5
methyl acetate	2.1153	−3.06061	1.71909	−44.063	0.4308795	37000–2700000	266.6–434
methyl cyclohexane$^{p=0}$	0.136884	−0.08142638	0.07168329	−5.518922	0.1189158	761–20000000	189–497
methyl cyclopentane	0.383305	−0.611338	0.468517	−17.6164	0.247594	2510–2000000	255–500
methyl cyclopentane (deuterated)^{U}				8.55935	0.268374	25000–106280	310.0–339.4
methyl ethyl ketone^{L}				1.14313	−0.0479875	37000–11000000	425.7–463.2
n-octane			0.0809112	−7.12018	0.164954	2030–4800	309–527
n-pentyl acetate^{L}				1.131629	−0.05665654	233000–1971000	507–519
propionitrile$^{p=0}$			0.0415382	−3.17393	0.0672377	7500–22000	273–400
n-propyl acetate	−0.402924	0.32354	0.0404934	−6.9662	0.101776	37000–2700000	183.7–481.4
toluene^{L}				2.96112	−0.162705	37000–2700000	552–567.2

L = LCS branch only. U = UCS branch only. We used 4th-degree polynomial, when we had UCS *AND* LCS data, and linear fitting, when we had only UCS *OR* LCS data. Sometimes the number of points was not enough for a 4th-degree fitting, then we used 3rd- or 2nd-degree expressions, and sometimes the linear fitting was not good enough to describe the data for a single branch, in which case we used 2nd-degree fitting.
d=Reported molecular weight is $M_n = M_{viscosity}$.

menthol and dl-terpineol). Both are theta solvents with rather high values for Θ_{UCS} but without reported Θ^{lcs}'s. (See Table 42.)

4.12. Other Compounds

Dimethoxymethane is a theta solvent with a rather low Θ^{lcs} and no reported Θ^{ucs}. A single point is available for capronic acid. Propionitrile is a poor but thoroughly studied solvent. The pressure, molecular weight, and isotope dependencies of the UCS and LCS solubilities are all available. (See Tables 40–42; Fig. 13.)

5. Solubility and Solvent Quality

5.1. Correlations

Traditionally correlations of polymer solubility with solvent properties have been based on the ideas of Hildebrand (50HIL/SCO) or their elaborations (67VAN/HOF, 89GRU). An excellent review of the present status of the "solubility parameter" approach has been given by Barton (90BAR, 91BAR). He discusses many of the one, two, three, and four parameter representations suggested over the past half cen-

TABLE 44. Scaling coefficients (T^*, X^*, and A) for demixing of PS/solvent mixtures at solution vapor pressure for solvent systems with both UCS and LCS branches (in order of increasing T^*). Hypercritical molecular weights derived from X^*. These least squares parameters refer to Eq. (3).

Solvent	T^*	X^*	M_w^*	A	Remarks
diethyl ether#	275	0.006416	24300	0.416995	
benzene#	311.5	−0.034743	not real	0.680081	
isopropyl acetate	318	−0.0022966	not real	0.202275	
ethyl acetate	324	−0.00567	not real	0.276047	
n-propyl acetate	324	−0.009487	not real	0.389742	
ethyl-*n*-butyrate	327	−0.007455	not real	0.433163	
tertbutyl acetate	332.5	−0.000766	not real	0.115016	$p=0$
isobutyl acetate	337.5	−0.00692	not real	0.320163	
acetone	346	0.005008	40000	0.209425	
methyl acetate	351/346	−0.001195/ −0.0010434	not real	0.098788/ 0.099362	$p_{vap}/p=0$
d-acetone	353	0.008271	14600	0.32285	
toluene#	355	−0.027495	not real	0.547436	
isoamyl acetate	360	−0.01068	not real	0.370552	
cyclo-pentane	360	−0.00487	not real	0.182699	
ethyl formate	362	0.00275	130000	0.146864	
propionitrile	382	0.006606	23000	0.330838	$p=0$
methyl-cyclopentane	385	−0.00115	not real	0.083214	
n-hexane#	393.5	0.00445	50000	0.096895	
cyclohexane	398	−0.00978	not real	0.22804	
methyl cyclohexane	413/405	−0.0038/ −0.003053	not real	0.163591/ 0.144462	$p_{vap}/p=0$
n-heptane#	416	0.01053	9000	0.232997	
1,4-dimethyl-cyclohexane	434	0.000454	4800000	0.058592	
n-octane#	440	0.00831	14500	0.230319	
diethyl malonate	440	−0.006368	not real	0.300939	

#Relatively few data points; parameters uncertain.

tury. The parameters usually derive from empirical correlations of properties like refractive index, dipole moment, cohesive energy, spectroscopically derived hydrogen bond strengths, etc., with solubility or other thermodynamic properties of solution. Barton presents extensive numerical tables for the various schemes which he discusses. The original Hildebrand development introduced a parameter, δ, which scales as the square root of the cohesive energy density, $\Delta E_{vap}/V_{liq}$. Solubility correlates with δ in the sense that it becomes more likely as the difference $(\delta_{solvent}-\delta_{solute})$ becomes small, but this oversimplified approach does not work well enough to be consistently useful for predictions of solubilities in polymer/solvent systems. In fact, the Hildebrand one parameter approach is often not able to predict whether the polymer (PS) and solvent are even compatible, let alone to make an estimate of the molecular weight dependence of the solubility. This accounts for the elaboration into two, three, and more parameter representations. It appears the most successful, or at least the most commonly used, of the multiparameter representations is the one due to Hansen (89GRU, 90BAR, 91BAR). Hansen suggested that dividing the solubility parameter into dispersive (δ_d), dipole-dipole (δ_p), and hydrogen bonding (δ_h) contributions greatly improves correlation. The parameters δ_d, δ_p, and δ_h are obtained from a variety of empirical, semiempirical, or theoretical correlations of solubility and/or other thermodynamic properties of solution with the electrical and/or other physical properties of the component molecules. A commonly used variant of the Hansen approach introduces a "cohesive radius parameter," R_{12}, as a square root of the linear combination of squared differences (89GRU, 90BAR, 91BAR),

$$R_{12}=[a(\delta_{d1}-\delta_{d2})^2+b(\delta_{p1}-\delta_{p2})^2+c(\delta_{h1}-\delta_{h2})^2]^{1/2}. \quad (4)$$

As before, the idea is that if R_{12} is small the polymer and solvent are compatible. Subscripts 1 and 2 refer to polymer and solvent respectively. A common choice (89GRU, 90BAR, 91BAR, 94UZO/ODO) is $a=4$ and $b=c=1$. It is useful to discuss solubility in terms of the "volume-of-solubility" carved out in $(\delta_d;\delta_p;\delta_h)$ space (91BAR), and the factor, $a=4$, was introduced in an effort to make this volume approximately spherical.

We desired a function, empirical if necessary, to quantitatively correlate solubility with solvent quality. In addition we wanted to employ already tabulated solubility parameters when possible, both to minimize labor in arriving at correlations, and to avoid the arbitrary choice of parameter which would be implied in any new table of δ values. To begin we made trial plots of X^* or T^* obtained from the present scaling fits (Table 44) against the Hildebrand parameter, the Hansen parameters, and the cohesive radius R_{12} (first setting $a=4$ and $b=c=1$, later using $a=b=c=1$), but without useful result. We used the scaling fits because those representa-

TABLE 45. Solubility parameters [$MPa^{1/2}$] (at room temperature, from 89GRU), cohesion radii [$MPa^{1/2}$], solvent quality integral I and $X_{300} = M_w^{-1/2}$ [$amu^{-1/2}$], at the solution vapor pressure and 300 K.

Solvent name	$\delta_{Hildebrand}$	δ_d	δ_p	δ_h	R_{12}	R_{12}^S	I	X_{300}
n-pentane	14.5	14.5	0	0	9.4	8.4	···	positive
n-hexane	14.9	14.9	0	0	8.9	7.8	15.5	0.03121
diethyl ether	15.8	14.5	2.9	5.1	6.9	6.8	37.0	0.00672
n-heptane	15.3	15.3	0	0	8.3	7.2	22.4	0.02561
n-octane	15.6	15.6	0	0	8.0	6.8	27.6	0.02417
methyl cyclohexane	16	16	0	1	6.9	5.5	34.6	0.006821
isoamyl acetate	17.2	15.3	3.1	7	5.7	5.6	45.9	−0.00852
dioctyl phtalate	18.2	16.6	7	3.1	4.3	3.2	···	negative
cyclohexane	16.8	16.8	0	0.2	6.7	5.3	32.1	0.001622
sec-butyl acetate	16.8	···	···	···	···	···	···	negative
isobutyl acetate	16.8	15.1	3.7	6.3	5.8	5.7	43.3	−0.00608
isopropyl acetate	17.2	···	···	···	···	···	41.2	−0.00212
methyl *n*-amyl ketone	17.4	···	···	···	···	···	···	negative
ethyl *n*-butyrate	17.4	···	···	···	···	···	55.2	−0.00718
n-butyl acetate	17.4	15.8	3.7	6.3	4.4	4.4	···	negative
diethyl oxalate	17.6	···	···	···	···	···	···	around 0.002
cyclopentane	17.8	···	···	···	···	···	30.3	−0.00082
n-propyl acetate	18	···	···	···	···	···	45.2	−0.00914
ethyl benzene	17.8	17.8	0.6	1.4	5.1	3.6	···	negative
trans decalin	18	0	0	0	6.5	5.0	···	negative
n-butyl formate	18.2	···	···	···	···	···	···	negative
toluene	18.2	18	1.4	2	4.1	3.0	54.0	−0.02529
ethyl acetate	18.2	15.8	5.3	7.2	4.9	4.7	38.7	−0.00526
benzene	18.8	18.4	0	2	5.3	3.2	57.8	−0.03464
methyl ethyl ketone	19	16	9	5.1	6.1	3.8	···	negative
ethyl formate	19.6	15.5	8.4	8.4	7.2	5.9	28.2	0.00649
methyl acetate	18.8	15.5	7.2	7.6	6.2	5.5	30.1	0.00139
bromobenzene	21.7	20.5	5.5	4.1	5.4	5.3	···	negative
acetone	20.1	15.5	10.4	7	8.1	5.2	27.2	0.00794
cyclohexanone	19.6	17.8	6.3	5.1	2.1	0.2	···	negative
o-dichloro benzene	20.5	19.2	6.3	3.3	3.7	3.1	···	negative
1,4-dioxane	20.5	19	1.8	7.4	4.0	3.3	···	negative
1-nitropropane	21.1	···	···	···	···	···	···	negative
pyridine	21.7	19	8.8	5.9	5.2	2.4	···	negative
propionitrile	22.7	15.3	14.3	5.5	11.4	5.2	40.0	0.009387
nitroethane	22.7	16	15.5	4.5	11.9	3.8	···	positive
n-butanol	23.3	···	···	···	···	···	···	unknown
dimethyl oxalate	22.5	···	···	···	···	···	···	unknown
tertbutyl acetate	···	···	···	···	···	···	41.2	−0.00021
diethyl malonate	···	···	···	···	···	···	54.8	0.000751
cyclohexanol	22.5	17.4	4.1	13.5	8.6	8.6	···	positive
polystyrene	19.0	17.9	4.2	5.0	···	···	···	———

tions have the fewest number of least squares parameters and therefore the smallest correlation error.

A better empirical measure of the extent of solution, and thus of the quality of the solvent, is given by the area enclosed by the scaling function. By integrating Eq. (3) from $X_{monomer}$ to X^* we empirically define a "solvent quality integral," I, in the (X,T_c) plane, where I is the area enclosed by the scaling function, Eq. (3), corresponding to the one phase part of the diagram (see the shaded areas in Fig. 2). Obviously the larger I, the greater the homogeneous region of solubility,

$$\left[I = \frac{4}{3} \frac{T^* A}{\sqrt{|X^*|}} \left(\frac{1}{162} - X^* \right)^{3/2} \right]. \tag{5}$$

In Eq. (5) 162 is the sum of the molecular weights of a PS monomer unit plus butyl and H terminating groups. The least squares parameters required to numerically evaluate Eq. (5) are found in Table 44. We have found that the solvent quality integral, I, correlates reasonably well with cohesive radius R_{12} ($a=4$, $b=c=1$). That plot is shown in Fig. 14. To determine R_{12} values we used the Hansen coefficients recom-

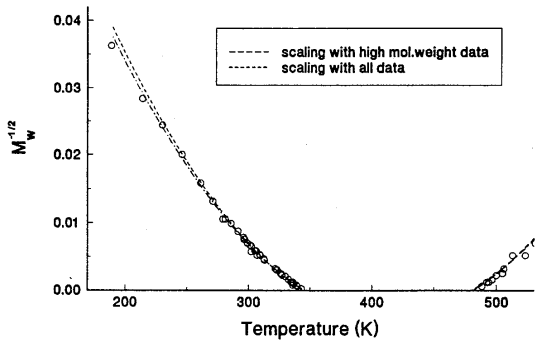


FIG. 3. A comparison of scaling fits [see Eq. (3)] for demixing of PS/methylcyclohexane for different ranges of polymer molecular weight. Dashed line = fits to Eq. (3) where data is limited to $M_w > 10^4$. Dot-dash line = fits to Eq. (3) for M_w in the range $2\times10^7 > M_w > 7\times10^2$. The comparison demonstrates the one term formalism is adequate for our purposes.

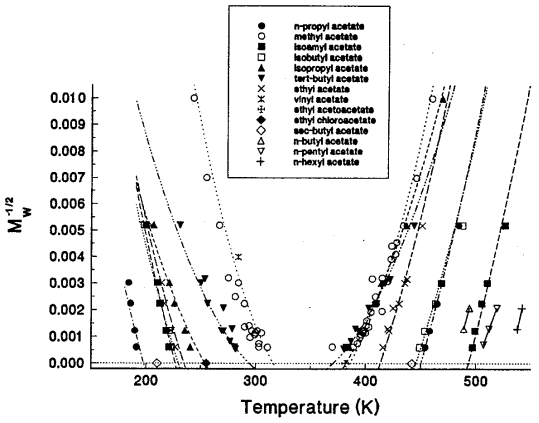


FIG. 5. Demixing data in PS/organic acetate solutions. See Tables 3–12 and 42.

mended by Grulke for the solvents (89GRU). Literature values of R_{12} for polystyrene are scattered, and we elected to consider δ_d, δ_p, and δ_h for PS as adjustable parameters to arrive at the best possible correlation. In this way we find $\delta_d = 17.9$, $\delta_p = 4.2$ and $\delta_h = 5.0$, and $\delta = 19.0$ MPa$^{1/2}$. These values are in good agreement with the Hansen parameters for polystyrene recently suggested by Mieczkowski (88MIE). The resulting R_{12} parameters calculated for some solutions are very sensitive to the δ parameters selected for PS. The error bars in Fig. 14 correspond to a 3% uncertainty in (δ_d, δ_p, and δ_h)$_{solvent}$ parameters, which is typical of the variation from author to author, and between different editions of the tables. Although for the δ parameters the errors are symmetric, the algebraic combination of δ's sometimes causes asymmetric errors in R_{12} and $R_{12}^{\$}$ (see next paragraph) as is evident in Figs. 14–16, see especially the error bars for benzene and toluene which are markedly larger to one side. From Fig. 14 one deduces $R_{12}^{*} = 6.9$ MPa$^{1/2}$ which almost perfectly divides the solubility plane according to a "poor solvent"/"good solvent" dichotomy (there is but one exception, cyclohexanol, not plotted in Fig. 14 because LCS data are not available, and therefore the solvent quality integral cannot be calculated). For $R_{12} > R_{12}^{*}$ one is in the "poor solvent" region, the solutions show hypercritical demixing and no Θ points are observed, but for $R_{12} < R_{12}^{*}$ every solvent is a Θ solvent. The separation $\Delta\Theta = (\Theta^{lcs} - \Theta^{ucs})$ increases as R_{12} falls toward zero.

A closer examination of Fig. 14 reveals that the outliers are solvents with high dipole moments, (propionitrile—marked as PPN in Figs. 14 and 15—is the most extreme example). It seems that it is the contribution of the term involving δ_p which is the most uncertain. We therefore elected to correlate I with R_{12} ($a=4$, $b=0$, $c=1$) $= R_{12}^{\$}$ and found the $(I, R_{12}^{\$})$ correlation markedly better than the (I, R_{12}) one. Figure 15 is a plot of the $(I, R_{12}^{\$})$ correlation, once again using 3% error bars. The equation which expresses this correlation, $I = (75.8 \pm 7.6) - (7.2 \pm 1.3)\ R_{12}^{\$}$ using δ_d (PS) = 17.9 and δ_h (PS) = 5.0, is the best description of the dependence of PS solubility on solubility parameters now available. It demonstrates that a two dimensional set of solubility parameters is adequate for the approximate description of demixing in

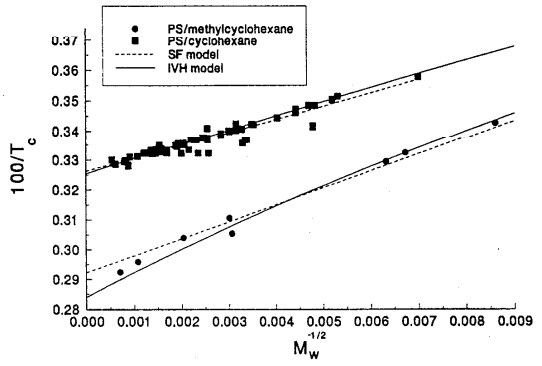


FIG. 4. A comparison of Eqs. (1) and (3) for the fitting of UCS data for the PS/methylcyclopentane and PS/cyclohexane systems. _____Eq. (3) (Imre–Van Hook model);---Eq. (1) (Schultz–Flory model).

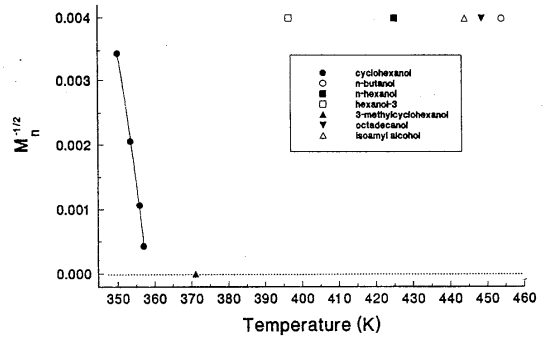
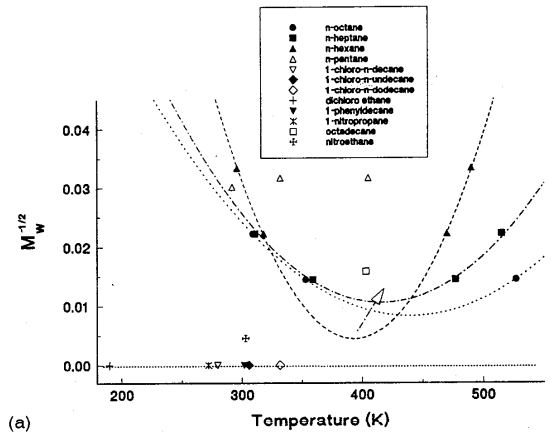
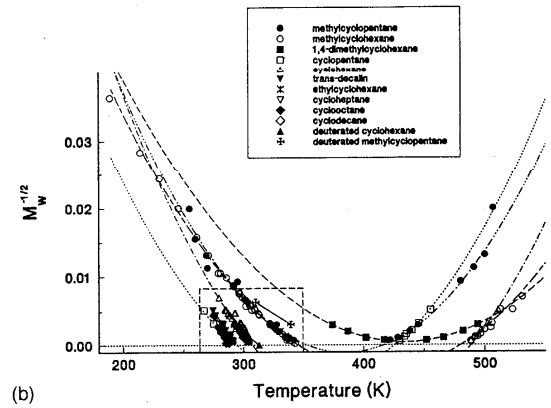


FIG. 6. Demixing data in PS/alcohol solutions. See Tables 13 and 42.





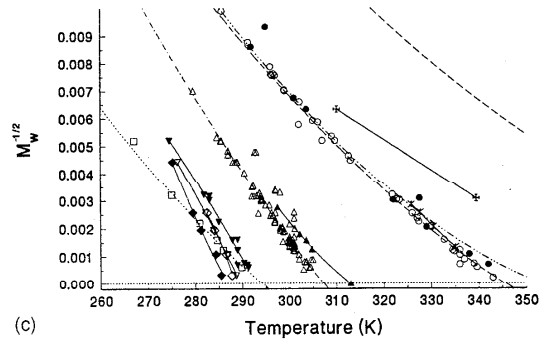


FIG. 7. Demixing data in PS/alkane solutions. See Tables 14–28 and 42. (a) Normal alkanes and derivatives. (b) Cyclic alkanes and derivatives. (c) A portion of the data from b at higher magnification. The arrow in a represents the solubility limit predicted by Cowie (83COW/MCE).

PS solutions. In our opinion the selection of Hansen's δ_d and δ_h for the correlating parameters is reasonable and well documented. We much prefer to use these well established and long tabulated values over a new reparametrization with its attendant uncertainties.

In the new correlation, I vs $R_{12}^{\$}$ (Fig. 15), there is no

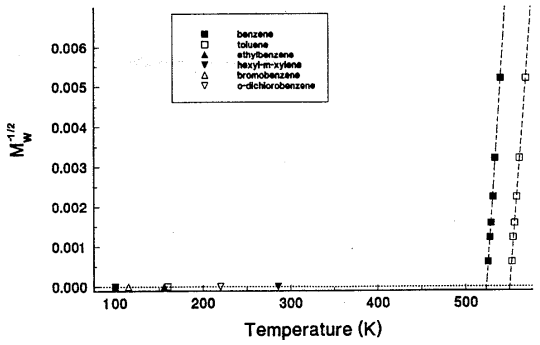


FIG. 8. Demixing data in PS/aromatic hydrocarbon solutions. See Tables 29, 30, and 42.

longer a clear dichotomy between "good solvent" and "poor solvent" regions, as there was in the I vs R_{12} correlation (we refer here to the dotted line in Fig. 14). Rather, in the I vs $R_{12}^{\$}$ correlation (Fig. 15) the "good solvent"/"poor solvent" boundary is found to be rotated and imperfect. The "good solvent"/"poor solvent" distinction is no longer defined by a unique value of the cohesive radius. We do not find this to be a significant concern. The strength of the present approach is that it describes solvent quality in terms of a continuum, and from that point of view any arbitrary dichotomy is necessarily inaccurate. The "good solvent"/"poor solvent" boundary in these diagrams, which diagrams correlate experimental data from widely disparate sources, is also smeared by uncertainties introduced by corrections for the effects of pressure, *MW* dispersion, etc., Van Hook and co-workers (91SZY/VAN, 94IMR/VAN, 95IMR/VAN, 95LUS/REB, 95LUS/VAN) have shown the demixing diagrams to be sensitive to such variables in the region of change from "good" to "poor" solvent character.

In Fig. 16 we show a second interesting correlation function, one which establishes an approximate linear relationship between R_{12} and X_{300} $[X_{300} = (M_w^{-1/2})_{300}]$. Here

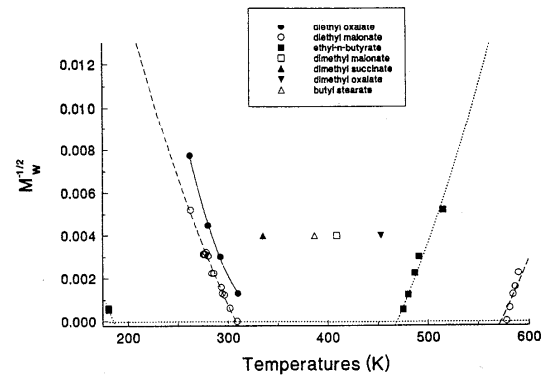


FIG. 9. Demixing data in PS/organic ester (other than formates and acetates) solutions. See Tables 31–33 and 42.

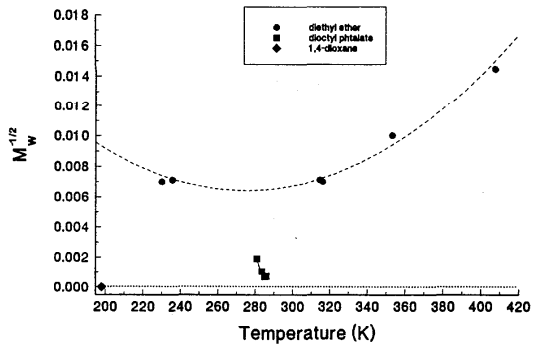


FIG. 10. Demixing data in PS/ether solutions. See Tables 34, 35, and 42.

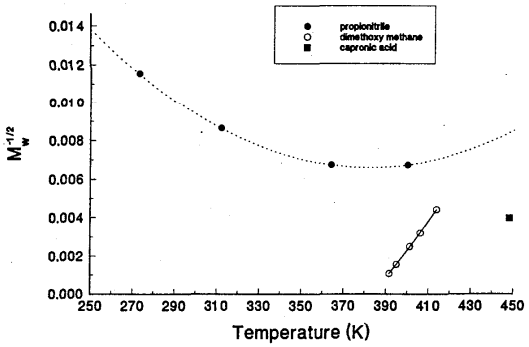


FIG. 13. Demixing data in some other PS solutions. See Tables 40–42.

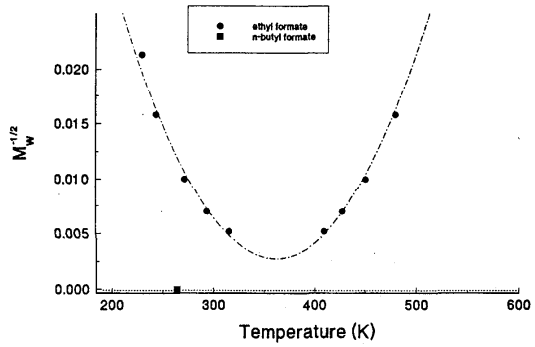


FIG. 11. Demixing data in PS/formate solutions. See Tables 36 and 42.

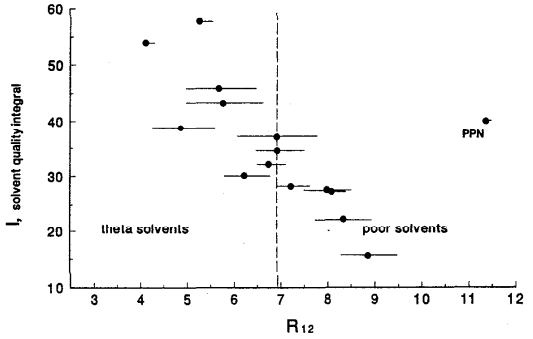


FIG. 14. Correlation of the solvent quality integral, I, (see text) with R_{12} as defined in Eq. (4) with $a=4$, $b = c = 1$ and using Hansen parameters quoted by Grulke (89GRU). I has units of K amu$^{-1/2}$, and R_{12} units of M Pa$^{1/2}$.

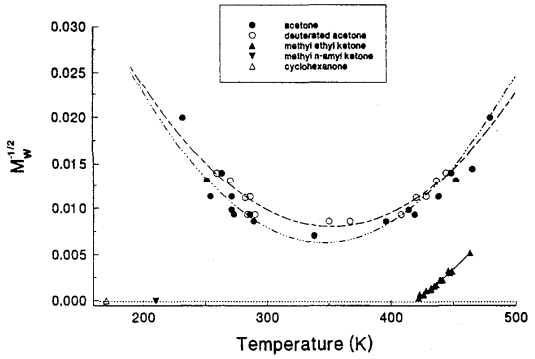


FIG. 12. Demixing data in PS/ketone solutions. See Tables 37–39 and 42.

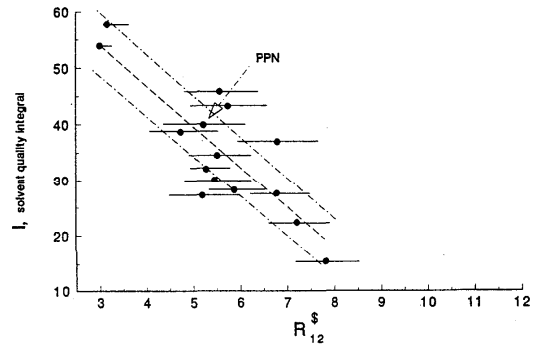


FIG. 15. Correlation of the solvent quality integral, I, (see text) with $R^{\$}_{12}$ as defined in Eq. (4) with $a=4$, $b=0$, and $c=1$ and using Hansen parameters quoted by Grulke (89GRU). I has units of K amu$^{-1/2}$, and $R^{\$}_{12}$ units of M Pa$^{1/2}$. Note the improved fit with fewer parameters as compared to Fig. 14. The lightly dashed lines lie above and below the best-fit line by one standard deviation.

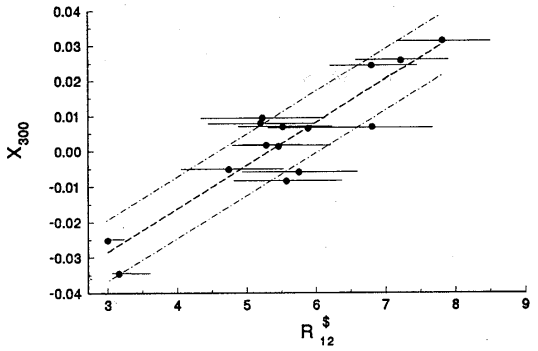


FIG. 16. Correlation of 300 K solubilities along the UCS branch, X_{300}, (see text) with $R^{\$}_{12}$ as defined in Eq. (4) with $a=4$, $b=0$, and $c=1$ and using Hansen parameters quoted by Grulke (89GRU). X_{300} has units of amu$^{-1/2}$, and $R^{\$}_{12}$ units of M Pa$^{1/2}$. The lightly dashed lines lie above and below the best-fit line by one standard deviation.

$(M_w)_{300}$ is the maximum weight average molecular weight PS which will dissolve at 300 K along the UCS branch. The correlation at 300 K is appropriate because the tabulated Hansen parameters refer to that temperature (room temperature), and also because it is particularly convenient for experimental observation. Once again the error bars represent a 3% uncertainty in the parameters used to calculate $R^{\$}_{12}$. The quality of the $(X_{300},R^{\$}_{12})$ correlation, $X_{300} = (-6.5\pm0.9)\times10^{-2} + (1.22\pm0.2)\times10^{-2}\ R^{\$}_{12}$ with (as before) δ_d (PS) = 17.9 MPa$^{1/2}$ and δ_h(PS) = 5.0 MPa$^{1/2}$, is commensurate with that of the earlier (I,R_{12}) correlation. It is unfortunate that we have been unable to develop a third independent correlation between solvent solubility parameters and some other attribute of the phase diagram. The scaling description, Eq. (3), uses three parameters, so a total of three correlations are required to permit the calculation of approximate phase diagrams purely from the table of parameters. However, for any particular solution of interest, given one piece of experimental information concerning the (T_c,X) demixing surface, that piece of information comfortably removed from 300 K along the UCS branch (and preferably on the LCS branch), the correlations we have presented permit an estimation of PS/solvent phase diagram over a wide range of M_w and temperature.

5.2. Demixing from Two Component Solvents

Although this review has been limited to demixing from two component PS/solvent mixtures, a few comments on precipitation from mixed solvent systems are worthwhile. The topic is of considerable practical interest, not the least because one well established method of molecular weight fractionation is by selective precipitation (to prepare polymer samples of increasingly narrow *MW* distribution) and involves the addition of a properly selected cosolvent. For example Kamide (90KAM) in his review shows purification of PS by a number of different PS/cosolvent systems, including for example solution in methylethylketone followed by partial precipitation with methanol. Bohassian and Delmas (92BOH/DEL) have developed a technique to determine *MW* distributions via measurements of partial solubilities in mixed solvents. According to the development in the last section we expect both the solvent quality integral, I, and the X_{300} UCS solubility to scale linearly with $R^{\$}_{12}$ at a useful level of approximation. However $R^{\$}$ itself is not a linear function of the solubility parameters δ_d and δ_h [see Eq. (4) remembering $a=4$, $b=0$, and $c=1$]. For mixed solvents it seems reasonable in first approximation to assume linear combining for the δ parameters, i.e., $\langle\delta_{i,23}\rangle = \Psi_2/(\Psi_2+\Psi_3)\,\delta_{i,2} + \Psi_3/(\Psi_2+\Psi_3)\,\delta_{i,3}$ where the subscripts "2" and "3" refer to the cosolvents, and the Ψ's are concentrations. However, even if the δ solubility parameters should scale linearly, the dependence on solvent properties via R_{12} or $R^{\$}_{12}$ is not at all linear as Eq. (4) shows. Large departures are to be expected depending on the specific values of the dispersive and hydrogen bonding δ parameters, and such predictions seem to be in at least qualitative agreement with experiment. Cowie and co-workers (72COW/MCC, 74COW/MCE, 74COW/MCE2, 83COW/MCE) have studied cosolvent systems (acetone/alkanes, acetone/cyclohexanol, and methylcyclohexane/diethyl ether) finding in each case the cosolvent mixture to be superior than simple linear combining, and in most of these cases superior to either solvent by itself. That observation is in agreement with the predictions of Eq. (4) following the formulation above. Perhaps one could find cosolvent systems where the opposite holds true (i.e., where solubility is much poorer than linear combining suggests), but very few investigators have joined in the search for extra-poor solvents; we cannot support this conjecture with literature citations. While on this topic it is worth pointing out that the hypersensitivity of polymer solubility to water impurity can be rationalized in terms of the above approach, most simply because δ_h for water is unusually large, and since it enters as the square in the expression for $R^{\$}_{123}$, precipitation is induced at unusually low concentrations. We suggest that more detailed experimental studies of precipitation from ternary polymer/cosolvent systems and/or reevaluation of extant data in the light of the Hansen parameters for the cosolvents and the combining rules suggested above might be of considerable practical interest.

6. Summary and Conclusions

The demixing of polystyrene/solvent mixtures has been discussed. The solutions show pressure dependent upper and lower branches which, for poor enough solvents, join at a hypercritical point. After discussing the nature of the diagrams, reviewing literature data for seventy-six different solvent systems, and presenting least squares parameters for scaling descriptions, we succeeded in developing a correlation between the Hansen solubility parameters, δ_d and δ_h, and the extent of the region of homogeneous solution in the (T_c,X) plane. It is to be emphasized that this new approach will permit the estimation of the phase diagram from the Hansen parameters over a broad temperature range, and over

the complete range of M_w's, given one experimental point, preferably on the LCS branch. It is a useful extension of present day methods of predicting polymer solubilities.

7. Acknowledgments

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