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**THE EFFECT OF PRESSURE, ISOTOPIC (H/D)
SUBSTITUTION, AND OTHER VARIABLES ON
MISCIBILITY IN POLYMER-SOLVENT SYSTEMS.
THE NATURE OF THE DEMIXING PROCESS;
DYNAMIC LIGHT SCATTERING AND SMALL
ANGLE NEUTRON SCATTERING STUDIES.**

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**THE EFFECT OF PRESSURE, ISOTOPIC (H/D)
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INTRODUCTION

This proposal was awarded to study various aspects of liquid-liquid transitions in polymer-solvent and polymer-polymer solutions at the University of Tennessee, Chemistry Department. Polymer miscibility is an important research topic because the physical properties of polymer blends and solutions depend not only on the molecular parameters of each component, but also (and sometimes sensitively) on phase equilibria in the mixture. Polymer miscibility may determine the physical nature of block and graft copolymers, interpenetrating networks, and thermosetting networks. A thorough understanding of the physical properties of polymer mixtures would include detailed understanding of the conditions for phase separation, and that understanding should be at the molecular level. Only then can one proceed from the atomic and molecular properties of the base repeating unit, through bulk properties of individual components, to the details of the physical properties of the solution, mixture, or composite. Theoretically based design of mixtures and composites of desired characteristics becomes practical.

The Tennessee program was designed to contribute to this important area in several ways.

(1) Through studies on the effects of solvent quality, temperature, concentration, pressure, chain length, polydispersity, and isotope substitution on the demixing process, especially on the loci of the coexistence, cloud, and spinodal curves. It is a laborious but still straightforward modeling process to express demixing loci using an appropriate mean-field equation of state (EOS). This explains why phase transition data are used to probe excess free energies and related properties of solution. Once EOS is established the prediction of a plethora of interesting and important properties becomes possible.

(2) By employing scattering measurements to examine the tendency toward clustering as the demixing locus is approached from the one phase region. Interesting logarithmic divergences

in correlation lengths, scattering intensity, and other functions related to polymer-polymer interaction are observed, especially for solutions at or near critical concentration. Such studies are of broad general interest.

(3) Throughout the program we were especially interested in solvent and solute isotope effects on demixing loci and other properties of polymer solutions. This because H/D substitution is commonly used to tune the response (i.e. "set the contrast") in small angle neutron (SANS) investigations of polymer solutions. A thorough knowledge of the effect of isotope label on thermodynamic properties of the solutions is therefore critically important for proper interpretation of SANS data. We note that SANS is widely employed in studies of structure and properties of polymer solutions.

REVIEW

This grant began on 9/1/88 and ended 10/31/99 (including no-cost extension 11/1/98-10/31/99). This report documents significant progress in all areas for which funds were requested. That progress has been reported in 36 scientific papers in the technical literature (31 in print, 2 in press, 2 submitted for publication, 1 in preparation). Those papers are listed in the bibliography and reproduced in the Appendix of this report. The report itself is divided into several sections.

A. Development of equipment including pressure cells for scattering measurements (dynamic and static light scattering and neutron scattering), including studies of pressure induced precipitation.

B. Determination of pressure, solvent and solute isotope, and segment number dependences of cloud, coexistence, and spinodal loci for polystyrene demixing from a series of solvents (acetone, methylcyclopentane, propionitrile, methylcyclohexane, cyclohexane and others).

C. Mean-field analysis; scaling analysis: A practical computer program for theoretical rationalization of concentration, pressure, temperature, isotope, segment, and segment distribution dependences of polymer demixing data. Correlations with scaling expressions.

D. Mechanisms of liquid-liquid precipitation from PS/solvent solutions using DLS and SANS. Determination of size distributions, correlation lengths, and scattering intensities; ratios of DLS and SANS correlation lengths.

E. Other efforts: (1) Segment distribution effects, especially broadened and bimodal distributions. (2) Solutions under tension, negative pressure. (3) Solvent quality effects. (4) Demixing from polymer-polymer blends. (5) Osmotic pressure at elevated pressure.

F. Conclusions.

A. Instrumentation. DLS and SANS of polymer-solvent mixtures over wide ranges of P and T. Pressure induced demixing.

i. **First generation equipment:** We began with the design, construction and use of instrumentation to locate phase transitions. We employed a static light scattering (SLS) technique with fiber optic technology and restricted attention to relatively crude measurements of scattering intensity at low angle.^{1-3,10,13} In the beginning using glass capillary cells we determined cloud and spinodal loci for polymer demixing ($253 < T/K < 550$) and ($0.1 < P/\text{MPa} < 10$). More recently the pressure range has been extended by more than an order of magnitude, ($0.1 < P/\text{MPa} < 200$).²⁷⁻³⁰ Then or now, however, the SLS sensitivity is too crude to permit accurate experimental measurements of trends in SLS correlation lengths, virial coefficients, *etc.* as demixing is approached. Still, this first generation equipment has been (is being) employed to gather much of the thermodynamic demixing data summarized in this and earlier reports. That work includes measurements of the ψ , T , P , S_{O_2} , y_D , z_D , $\langle r \rangle$, and $W(r)$ dependences of CP and SD/P demixing surfaces for polystyrene in acetone,^{2,4,9} methylcyclopentane,⁹ propionitrile,^{8,13} methylcyclohexane^{11,20,21,22} and other solvents.^{14,18,19,27,29,30} Efficient software routines for temperature and pressure control, for automated data collection, and for numerical analysis of raw data, were developed as integral parts of the program, as were routines for thermodynamic interpretation of the corrected data using mean field analysis.^{1,9,13} The instrument continues in service depending on the availability of manpower.

ii. **New light scattering equipment:** With UTK/DOE support we purchased a Brookhaven Instruments Co. BI200SM light scattering system in 1995. This equipment permits accurate and precise studies of the details of particle size distribution, growth kinetics, correlation lengths, scattering intensities and related physical changes during temperature- or pressure-quench induced phase transitions using static (SLS) or dynamic light scattering (DLS). Like system-I, above, it can be used in simple fashion to locate CP and SD/P surfaces, but in addition, and more importantly, we are now able to examine the nature of demixing transitions by measuring DLS or SLS correlation lengths, scattering intensities, *etc.* as the transition is approached. Although location of CP and SD/P surfaces provides important thermodynamic information, we can now supplement that information with studies on the nature, mechanism, and (sometimes) the kinetics of phase transitions. An important part of the upgrade was the improvement in software used to analyze the scattering data, as well as to control the goniometer and other equipment. The commercial package did not include provide for measurements at other than 0.1 Mpa, or at extra-ordinary temperatures, and as part of the instrumental improvement we have built these capabilities in-house.

iii. **Pressure generating equipment:** The computer controllable pressure generator subsystem ($0 < P/\text{MPa} < 200$) is similar to one previously described by us,¹⁻³ but modified to operate to higher pressure. It employs mostly commercially available components, together with in-house constructed pressure cells of several designs.

iv. **Pressure cells for DLS measurements:** Scattering cells for high pressure LS measurements were a major problem. Thus, an important part of the upgrade was in-house development of DLS high pressure cells. A report on the design is published.^{29,30}

v. **High pressure SANS cell and sample handling:** In collaboration with ORNL researchers we have determined SANS intensities and correlation lengths for polymer/solvent mixtures in the vicinity of pressure induced liquid-liquid phase transitions. These experiments were carried out for the identical pressure/temperature data sets earlier investigated by DLS. The ORNL quartz-windowed SANS high pressure cell was used after fitting with modified pressure generating and bellows-type hydraulic-fluid-to-sample isolation units designed and constructed in Knoxville. The improvements enabled us to improve the efficiency of SANS data collection by about a factor of eight compared to preliminary runs.^{20,21,25}

B. Pressure, solvent and solute isotope, and segment number dependences for liquid-liquid demixing of polystyrene solutions.

Experimental results obtained in this program for liquid-liquid demixing of polystyrene from several different solvents have been reviewed.^{5-7,12,17,23,25,26,32,33} Usually the solutions show upper and lower demixing branches which join at hypercritical points. The analysis of the phase diagram yields a set of free energy parameters and their pressure, isotope, *etc.* coefficients. Given a sufficiently detailed mean-field model these, in turn, can be interpreted in molecular terms. The decision to focus attention on the complete phase diagram (*i.e.* upper and lower branches, hypercritical points, *etc.*) over broad ranges of all variables limits the number of possible model interpretations, and for any given model severely constrains the range of possible parameters. Isotope effect studies are of considerable help here since it is well established that isotopomers share a common potential energy surface. The decision to restrict attention mostly to PS as representing the general class of USC/LCS polymer solutions permitted the purchase of useful amounts of high purity well characterized polymer at reasonable prices.

i. **Propionitrile:** We have completed a thorough study of demixing from PS/propionitrile solutions^{8,13,36} including measurements of ψ , T , P , y_D , z_D , ρ_m , $\langle r \rangle$, and $W(r)$ dependences, sometimes extending to studies of solutions under tension (*i.e.* at negative pressure).^{6,8,15} An increase in pressure, an increase in H/D ratio in the solvent (or decrease in the polymer H/D ratio), or a decrease in polymer segment number increases the region of miscibility. The solutions show both upper and lower branches, which for $\text{CH}_3\text{CH}_2\text{CN}$ join at a hypercritical point found at negative pressure. In $\text{CH}_3\text{CD}_2\text{CN}$ the hypercritical point is at positive pressure (deuteration decreases solvent quality and moves the locus of critical demixing toward lower molecular weight). The results have been discussed in the context of current theories of polymer solution as modified by the theory of isotope effects in condensed phases (see below).¹³ An extensive data set exploring segment distribution ($W(r)$) effects for propionitrile solutions has been obtained and will be submitted for publication soon.³⁶

ii. **Acetone, methycyclopentane:** Studies on the ψ , T , P , y_D , z_D , ρ_m , and $\langle r \rangle$ dependences for demixing from PS/acetone and PS/methylcyclopentane solutions have been completed.^{2,4,9,30} In 1997 we carried out DLS and SANS measurements on PS/acetone solutions in the hypercritical region.^{20,21,30}

iii. **Cyclohexane, methylcyclohexane:** DLS and SANS measurements of CP and SD/P loci in these solvents have been reported.^{11,20,21,22}

iv. Methylacetate, ethylformate: As a part of the program examining the use of scaling equations to describe continuity of state as a function of P (including $P < 0$), $\langle r \rangle$, and S_Q (solvent quality), Imre and Van Hook^{12,15} reported demixing data for the PS/MA and PS/EF systems confirming that solvent quality is a sensitive function of pressure. The authors demonstrated solvent continuity between the heretofore arbitrary divisions "poor", "theta", and "good".

v. Acetaldehyde: Rebelo, de Sousa and Van Hook¹⁴ reported measurements on the phase diagram for PS/ acetaldehyde in $(P, T, \psi, \langle r \rangle)$ space. The experiments were carried out in Lisbon using techniques and equipment developed in Knoxville. We showed new evidence for double critical points and a window of miscibility, thereby confirming the earlier observation seen in PS/acetone-h/d phase diagrams.⁴ Successful modeling of the effects was achieved using temperature and concentration dependent interaction parameters.

C. A practical program for modeling the ψ , P , T , y_D , z_D , $\langle r \rangle$, ρ_m , and $W(r)$ dependences of polymer. Scaling analysis.

We developed computer programs^{9,13,14} to calculate phase equilibria as a function of the listed variables. The package includes a least squares routine to refine mean-field parameters using phase equilibrium data. This is important. It makes the present experimental information much more useful. The algorithm employs a modified Flory-Huggins model married to a Ratsch-Kehlen continuous thermodynamic formalism and uses the Bigeleisen-Wolfsberg-Van Hook description of condensed phase isotope effects. Cloud, shadow, and spinodal loci are obtained. The calculations are tedious, mostly because the free energy surface is flat near the phase change (particularly near the hypercritical point). The scaling analysis^{9,12} is described in a later section.

D. Studies of LL precipitation using DLS and SANS. Size distributions, correlation lengths, and scattering intensities.

i: Initial results at ambient pressure. Temperature quenches.

Using the newer instrumentation we made careful SLS and DLS measurements (mostly DLS) close to the LL transition at 0.1Mpa.^{18,19} We compared DLS correlation lengths, ξ_{DLS} , and intensities, I_{DLS} , near to and far from LL, making measurements in two concentration regimes, (i) at low concentration where precipitation is *via* nucleation/growth (NG) (and the 1-phase metastable region between CX and CP can be studied), and (ii) at higher concentrations where the phase transition occurs *via* a spinodal decomposition/percolation (SD/P) process. The shape of the DLS correlation diagram varies significantly in the different regions. Brown and Nicolai (among others) have commented on the scanty amount of DLS (and SLS) data available for polymers dissolved in poor solvents or in θ -solvents at temperatures between θ_L or θ_U and the coexistence surface (*i.e.* for solutions near or very near demixing).

ii: DLS and SANS studies of pressure induced transitions.

(a). DLS Studies. We recently completed DLS measurements of demixing in PS/cyclohexane, PS/methylcyclohexane, and PS/acetone solutions, ($0.1 < P/\text{MPa} < 200$) and ($283 < T/\text{K} < 383$),

supplementing that work with SANS measurements on some of the solutions, ($0.1 < P/\text{MPa} < 50$) and ($280 < T/\text{K} < 353$).^{29,30}

(b). SANS studies. Demixing in the $(T, P)_c$ plane: In collaboration with workers at ORNL we made SANS investigations of P and T induced demixing from PS/acetone, PS/cyclohexane, and PS/methylcyclohexane comparing SANS and DLS intensities and correlation lengths measured for identical conditions. The techniques sample widely different wave lengths, and thus examine different correlation lengths and/or particle sizes. The SANS experiments employed the ORNL quartz window high pressure cell coupled with UTK pressure generating and gaging equipment ($1 < P/\text{MPa} < 50$) and sample handling techniques. The data has been analysed in detail and published.^{20-22,25,26,29-33}

E. Other Efforts.

i. Segment distribution effects, especially broadened and bimodal distributions.

Mahlotra, Wilczura, and Van Hook³⁶ completed measurements on ρ_m and $W(r)$ dependences of PS/propionitrile demixing. Samples were constructed (1) to mimic broadened Schultz-Flory distributions, or (2) as examples of binodal MW distributions, in both cases with very different M_w and M_n . CP, shadow, and SP loci are sensitive to $W(r)$ and such data nicely test the mean-field model of solution properties. The experimental part of the effort is complete and a report is in preparation.³⁶

ii. Solutions under tension, negative pressure. Polymer liquids are commonly processed by methods involving extrusion, high speed flow, or other techniques which place the fluids in strain. There exists a considerable literature (not reviewed here) on the properties of liquids under tension. It was of interest to determine if (P, T) demixing loci carry over smoothly in the transition from pressurized fluids to fluids under tension. Imre and Van Hook have reported on demixing measurements in solutions under tension using a quasi-static method using of Bertholot tubes. The work has been reported.^{6,8,15,17} The experimental isopleths join smoothly with those at $P > 0$. This effort has been useful in the development of generalized scaling equations to describe LL demixing in multivariable format.¹²

iii. Correlation of LL demixing with solvent quality: Imre and Van Hook¹² reviewed low pressure demixing data in 76 solvent systems and developed scaling relations which correlate solubility in the $(T_c, \langle r \rangle^{-1/2})$ plane with S_Q , using Hansen parameters. The approach appears to be the best now available. In related experimental work the authors considered continuity of S_Q in polymer/solvent systems. They examined θ -to-poor transitions at negative pressure and poor-to- θ transitions at positive pressure demonstrating of continuity of state over extended regions of P , S_Q , etc. The approach exemplifies one practical applications of this DOE supported program. It permits convenient design of improved P and S_Q based fractionation schemes.

iv. Demixing from blends. Early on we reported on SLS studies of demixing of polymer/polymer solutions.¹⁰ In spite of initial success in determining P , T , and y_D or z_D dependences of blend demixing we lowered the priority for this work. We found LL transitions in films to be slow and difficult to reproduce. The samples are tedious to prepare and characterize, and the rate of data production is unacceptably low compared to studies in polymer solvent mixtures. The observation

is not meant to denigrate the practical importance, and the theoretical and industrial interest in polymer/polymer blend demixing, but simply rationalizes the decision to focus on studies of equal interest and equal import involving more efficient use of experimental time and facilities.

E. Conclusions.

The work described above and in the papers reproduced in the appendix clearly supports the claim that solid progress has been made and reported for this DOE supported effort.

(i) DLS and SLS instrumentation to measure demixing loci from polymer/solvent systems over wide ranges of T , P , and other variables has been developed and is in use.

(ii). Extensive data on phase equilibria for PS dissolved in a wide range of solvents have been obtained. The dependence of CP and SD/P on ψ , T , P , y_D , z_D , $\langle r \rangle$, S_Q , ρ_m , and $W(r)$ has been explored, and in considerable detail. DLS and SANS measurements have been compared in several solvents. DLS measurements have been extended into the metastable region and precipitation mechanisms in the NG and SD/P regions compared.

(iii). Both mean-field and scaling methods have been developed to describe the results. The data have been compared with other studies *via* a detailed and critical review of the extant literature. In that review extended scaling relations correlate the phase diagrams with S_Q , P , T , $\langle r \rangle$, $W(r)$, y_D , z_D , *etc.* In the alternate mean-field formalism we combined Bigeleisen-VanHook-Wolfsberg condensed phase isotope effect theory with a Ratsch-Kehlen continuous thermodynamic Flory-Huggins theory to express the location and shape of the phase diagrams in terms of a convenient set of excess free energy parameters. This is a useful and concise way to report, catalog, and order the data.

(iv). Neutron scattering measurements were made. A series of DLS and SANS runs comparing pressure induced precipitation in PS/solvent mixtures has been completed. The results should contribute to the understanding of exactly how these two techniques complement each other.

(v). We have described measurements of segment distribution effects, demixing at negative pressure, and demixing from polymer-polymer blends, and have critically reviewed and correlated literature data on PS/solvent demixing.

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