DOE-DE-FG05-91ER45374

INVESTIGATIONS OF THE EFFECTS OF ISOTOPIC SUBSTITUTION AND PRESSURE
ON MISCIBILITY IN POLYMER-POLYMER AND POLYMER-SOLVENT SYSTEMS.

Technical Progress Report for March 1991 to March 1992.
Description of Grantee's Plans for Year II of the Award, and
Request for Year II Continuing Support.

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for

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INTRODUCTION

DOE-DE-FG05-91ER45374 was awarded effective September 1, 1991 for a 38 month period. It continues as the renewal of an earlier DOE project, DOE-DE-FG05-91ER45374 which lasted from 9/1/88 to 8/31/91. The report which follows covers the period March 1991 through March 1992.

PERSONNEL

The following personnel were occupied or will be occupied with the research described below.

- (1) Professor Alexander Van Hook, Principal Investigator.
- (2) Dr. Luis Paulo Rebelo, Postdoctoral Associate, 9/1/90 through 2/1/92.
- (3) Dr. Marek Luszczyk, Postdoctoral Associate, 1/15/92 to 1/15/93 or beyond. (Replaces Rebelo).
- (4) Dr. Andrzej Zywockinski, Postdoctoral Associate, 11/1/90 to 1/1/93.
- (5) Dr. K. Rambabu, Postdoctoral Associate will join 6/1/92 and overlap with Dr. Zywockinski who leaves later in the year.
- (6) Mr. Ye Yijun, 1/4 time predoctoral candidate 9/1/88 to 12/31/91.

TECHNICAL PROGRESS

Significant progress has been made in several areas.

- (1) The design, construction and calibration of the polymer-solvent light scattering apparatus is complete. The basic design and technique (ref. 1, publications list), and improvements thereto (ref. 2), have been reported.
- (2) Preliminary results for the polystyrene-acetone system have been reported (ref. 3). In that same paper the theory necessary to rationalize the isotope effects was developed.
- (3) Detailed high precision measurements on the polystyrene-acetone and polystyrene-methyl cyclopentane systems have been completed. That work is nicely described in the abstract of

a paper ready to be submitted by us to Macromolecules, Spring 1992. (ref. 4).

ISOTOPE AND PRESSURE DEPENDENCE OF LIQUID-LIQUID EQUILIBRIA IN POLYMER SOLUTIONS. SOLUTE AND SOLVENT ISOTOPE EFFECTS IN THE POLYSTYRENE-ACETONE AND POLYSTYRENE-METHYLCYCLOPENTANE SYSTEMS. Cloud point and spinodal loci have been obtained as functions of pressure (P), temperature (T), molecular weight (MW) and molecular weight distribution (ρ_{mw}), weight (W_{ps}) or volume (φ_{ps}) fraction of the polymer, and H/D substitution on either solute (z_D) or solvent (y_D), for acetone-polystyrene and methylcyclopentane-polystyrene solutions. A light scattering technique was employed. The isotope effects and their pressure dependences are large. 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 molecular weight increases the region of miscibility. The solutions show both upper and lower branches, which, for acetone, join at an hypercritical point. The binodal diagrams are highly distorted in the hypercritical region but smooth as one moves away by appropriately varying pressure, H/D ratio, or solute molecular weight.

The curves describing the falloff from hypercritical conditions along the UCS and LCS loci, that falloff induced by varying pressure, reciprocal molecular weight, or H/D solvent ratio can be described within experimental error using scaling relations of the form $T^* = |1 - T_c/T_{hop}| = A(1/MW^*)^B + B(1/MW^*)^{0.5+B}$ with $B \approx 1/3$ and $1/MW^*$ the reduced reciprocal molecular weight. In the immediate vicinity of the multiple critical point, hypercritical distortion for polystyrene/ $(CH_3)_2CO$ solutions causes an highly unusual homogeneous one phase "hole" in the T, W_{ps} diagram. The "extra" one phase region appears close to the hypercritical point, and just inside the two phase region found immediately after the system collapses into its "hour-glass" configuration. The effect is not seen in $(CD_3)_2CO$ or mixed solvent solutions, but such solutions also show marked distortion in the T, W_{ps} plane. H/D substitutions (on either polymer or solvent) cause large effects, especially in the vicinity of the hypercritical point where isotope shifts as large as 40 K have been observed for the cloud points of the polystyrene/acetone system. The present results are discussed in the context of current theories of polymer solutions as modified by the theory of isotope effects in condensed phases.

(4) We have reported the occurrence of an unusual phase diagram in the acetone(h)-polystyrene(h) system in the vicinity of the hypercritical point. Near tri-critical behavior is exhibited in an highly unusual manner (ref. 5).

(5) Extensive data on phase separation in polymer-polymer solutions by light scattering using spinodal quench techniques have been obtained. Our instrument, built here in the Chemistry Department, is of a new design and allows the effect of pressure on the phase separation to be investigated. We are currently analyzing results for H/D and pressure dependences of the phase diagrams, as well as the precipitation kinetics in polyvinylmethylether/polystyrene and polystyrene/poly- α -chlorostyrene solutions. The results will be submitted for publication in the near future.

(6) Studies in polymer-solvent systems continue. Preliminary results have been obtained for polystyrene/propionitrile solutions.

(7) We have worked out methods to synthesize useful quantities of perdeutero-methylcyclopentane and 1,1 dideutero-propionitrile at affordable cost. About 80 grams of the first compound (catalog price $\approx$ \$300/gram) have been prepared for a cost of less than \$500 (not including graduate student time). Results from studies using this solvent have been discussed above. We are presently engaged in the synthesis of deuterio-propionitrile.

(8) In collaboration with G. Jancso, Rebelo and Van Hook have completed a review article summarizing the field of isotopomer solution thermodynamics, including results for H/D effects in polymer/polymer and polymer/solvent systems. The preparation of this review article afforded us the opportunity to clarify many points regarding the theory of isotope mixtures and the interpretation of results in isotopomer solutions. (Reference 6)

RESEARCH PLANS FOR YEAR II. 11/1/92 TO 10/31/93.

During the second year of this grant we will continue on the schedule described in the proposal for 1991-94 support.

(1). Measurements on demixing in polymer-solvent systems will continue. Measurements on acetone and methyl-cyclopentane are now complete. Propionitrile/polystyrene systems will be investigated, especially near the hypercritical point. Preliminary studies on mixed solvent systems are planned. The effects of varying MW distribution, heretofore pretty much ignored, will be studied.

(2). Polymer-polymer investigations will continue. The development of our new light scattering cell which will permit the introduction of tension as a new variable will continue.

(3). Theoretical efforts will continue. Development of mean-field interpretations of the phase diagrams using modern approaches to polymer solution theory and equally modern ideas concerning condensed phase isotope effects is our the priority.

PERSONNEL EXPECTED FOR YEAR II OF THIS GRANT.

Dr. Luszczyk will continue in this laboratory until June 1993 and Dr. Zywockinski until January 1993. Dr Rambabu will be here from June 1992 to May 1993. Dr Szydlowski who collaborated with us on the earlier grant will return for the final year and one-half of the present grant starting June 1993. It is not yet clear who, if anyone, will replace Zywockinski and Rambabu. We are currently looking for one or more graduate students to work on this project, thus replacing Mr. Ye Yijun who was forced to resign for personal reasons at the beginning of January 1992. It is clear from the brief description above that this grant will continue to be manned by experienced and skilled workers, and for that reason good progress is to be expected.

FINAL REMARKS.

The technical report detailed above demonstrates good progress on the research program described in the original and renewal proposals. Plans for the next year given above are entirely consistent with the ideas developed in those proposals. The progress we have described leads to the reasonable expectation that interesting and useful results will continue to be obtained from this project. I therefore respectfully request continued funding for DOE-DE-FG05-91ER45374 according to the proposed budget which is attached.

Alexander Van Hook
Principal Investigator
Professor of Chemistry
University of Tennessee

PUBLICATION AND PRESENTATIONS CONCERNING DOE SUPPORTED WORK.

I. PUBLICATIONS. (1991-1992).

1. Szydłowski, J.; Rebelo, L.; Van Hook, W. A.: "A new apparatus for the detection of phase equilibria in polymer solvent systems by light scattering." Rev. Sci. Ins. 1992, 63, 1717-1725.
2. Szydłowski, J.: Van Hook, W. A. "Glass capillary optical cell to determine the pressure dependence of polymer-solvent phase transitions at near critical conditions by light scattering." J. Polymer Sci., Polymer Phys. Ed. 1991, 29, 1437-1439.
3. Szydłowski, J.: Van Hook, W. A. "Isotope and pressure effects on liquid-liquid equilibria in polymer solutions. H/D solvent isotope effects in acetone-polystyrene solutions." Macromolecules 1991, 24, 4883-4891.
4. Rebelo, L.; Van Hook, W. A.: "Isotope and pressure effects on liquid-liquid equilibria in polymer solutions. Hypercritical phenomena in acetone-polystyrene and methylcyclopentane-polystyrene solutions." Macromolecules 1992. (For submission).
5. Rebelo, L. P.; Van Hook, W. A. "An unusual phase diagram: The polystyrene/acetone system in its hypercritical region; Near tricritical behavior in a pseudo-binary solution." J. Polymer Sci., Polymer Phys. Ed. 1992 (Submitted)
6. Jancso, G.; Rebelo, L.; Van Hook, W. A.: "Isotope effects in solution thermodynamics: Excess properties in solutions of isotopomers." Chemical Society Reviews 1992 (Submitted).

II. PRESENTATIONS (1991-1992).

"Isotope and pressure effects on critical demixing in some polystyrene solutions." 46th Annual Calorimetry Conference: DeKalb, Il. July 28-August 1, 1991. (with Rebelo, L; Szydłowski, J.).

"Influence of isotope substitution on mutual solubility of liquids. Study of α and β picoline in D₂O." National meeting, Polish Chemical Society. October, 1991. (with Jelinska-Kazimierczuk, M.; Szydłowski, J.)

Seminar. "Isotope and pressure effects on demixing in polymer-solvent systems. Experiment and theory." Florida Institute of Technology, February 6, 1992.

"Isotope and pressure dependences of demixing in polymer-solvent and polymer-polymer solutions." Gordon Conference on Chemistry and Physics of Isotope Effects. Ventura, CA, March 1992.

(Scheduled) "H/D isotope and pressure dependences of liquid-liquid equilibria in some polymer-polymer solutions. Kinetics of the spinodal decomposition." IUPAC Conference on Chemical Thermodynamics, Snowbird, Utah, August 1992. (with A. Zywockinski)

(Scheduled) "Isotope and pressure dependence of liquid-liquid equilibria in polymer solutions. Solute and solvent isotope effects in the polystyrene-acetone and polystyrene-methylcyclopentane systems. 1. Experimental measurements. 2. Results." IUPAC Conference on Chemical Thermodynamics, Snowbird, Utah, August 1992. (with L. Rebelo*).

(Scheduled) "Isotope and pressure dependence of liquid-liquid equilibria in polymer solutions. Solute and solvent isotope effects in the polystyrene-acetone and polystyrene-methylcyclopentane systems. 3. Interpretation; Theoretical correlation." IUPAC Conference on Chemical Thermodynamics, Snowbird, Utah, August 1992. (with L. Rebelo).

(Scheduled) Seminar. "Isotope and pressure effects on demixing in polymer-solvent systems. Experiment and theory." The Lubrizol Co., Cleveland OH, April 30, 1992.

(Scheduled) Seminar. "Isotope and pressure effects on demixing in polymer-solvent systems. Experiment and theory." Lycoming College, Westport, PA, Nov. 6, 1992.

END

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