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13. ABSTRACT *(Maximum 200 words)*

We have greatly extended and applied our theory to describe the thermodynamic properties of mixtures of polymers (polymer blends), with applications to explaining experimental data that cannot be explained by any other theories. The extensions involve elucidating general trends in the pressure dependence of polymer phase diagrams, the development of a new theory for random copolymer systems with explicit evaluation of the entropic contributions to the effective interaction parameter, a description of the synergistic roles of asymmetries in interactions, chain stiffness, and monomer structures, and the development of a simplified version of the theory that contains many essential features in a form readily usable by experimentalists. Applications have included the explanation of puzzling data for binary polyolefin blends, for blends of random copolymers containing cyclo-olefins, and for the remarkable variation of the phase behavior (upper vs. lower order-disorder transition temperature) in poly(n alkyl methacrylates) as a function of the alkyl chain length n.

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1. Description of research project:

The research is designed to develop and elaborate theories for molecular modeling the phase behavior and thermodynamic properties of multicomponent polymer systems which are useful to the Army as potential candidates for materials applied as protective coatings, poison protection suits, and novel sensors. Based on interactions with researchers at ARL and others supported by Dr. Kiserow's research program, we are developing plans for extending our research to study 1) the long standing question of the miscibility of linear and branched polymers, such as polyethylene, which is of interest to the Army, and 2) the sorption of gases by polymers, which is of relevance to the fabrication of improved flexible barriers.

2. Description of scientific progress and accomplishments:

Paper 1 (see list in section 4 below) provides a key to understanding general trends in the pressure dependence of polymer blend miscibilities. Our findings of a predominant increase of polymer-polymer heterocontacts with increasing pressure explain the general trends that systems, which are described within our theory using positive exchange energies, i.e., with an upper critical solution temperature (UCST), generally are destabilized by increasing pressure. In contrast, blends described with negative exchange energies, i.e., with a lower critical solution temperature (LCST), generally become more compatible with elevated pressure. Exceptions to this trend have been anticipated for UCST blends composed of components with very disparate self-interaction energies, and this prediction has recently been verified experimentally for blends of poly(alkyl siloxanes). This work provides a means for rapidly estimating the pressure dependence of blend miscibilities from rather limited data for the blend components, a feature of use to experimentalists and designers of polymeric materials with specific pressure sensitivities.

Paper 2 discusses the possibility for substantial deviations from available theories for the phase behavior of random copolymer systems, systems quite prevalent in industrial polymers and in many (current and future) crucial polymer systems for the Army. The paper also describes our initial attempt towards devising a group additive model for interaction energies to treat homologous systems with minimal experimental inputs. The theory demonstrates the possibility for dramatically controlling the phase behavior of random copolymer blends by introducing small changes in the copolymer compositions. Other papers below represent a continuation of the study of random copolymer systems, with applications to explain particular puzzling experimental data.

Paper 3 demonstrates unequivocally that the phase behavior of polymer blends is governed by a synergistic combination of three types of asymmetries between the blend components: asymmetries in interaction energies, in monomer structures, and in degree of chain stiffness. While one of these asymmetries may dominate over the others, in general, all these factors should be considered simultaneously in modeling the phase behavior. The fact that our theory provides the means for assessing these individual molecular factors makes the theory a useful tool for modeling the thermodynamic properties of polymer systems.

Papers 4 and 5 represent a major advancement in developing a readily assessable molecular theory for modeling the influence of monomer molecular structure and interactions upon the phase behavior of polymer systems. The simple theory readily explains the disparate miscibilities of head-to-head and head-to-tail poly(propylene) with other polyolefins, the prevalence of LCST phase diagrams for blends of poly(isobutylene) - the primary component in poison protection suits, - with other polyolefins, and more. This simplified theory is readily usable by experimentalists and modelers and has numerous applications. Both its simplicity and utility are evidenced by the recent inclusion of the simplified theory in a general service graduate course in polymer physics at U. Mass, Amherst.

Papers 6-9 present some overviews of the above works, along with several additional illustrations of the molecular modeling capabilities of our theory. They have been published in conjunction with invited talks given by Dudowicz and Freed in two separate ACS symposia, one with an industrial orientation and the other directed towards academic researchers.

Paper 10 is a joint effort with the experimental group of MacKnight, U. Mass., Amherst, to explain their data for binary blends of ethylene-co-norbornene random copolymers. These cycloolefin systems are of particular interest because they have higher glass transition temperatures and better thermal stability than polyethylene while still retaining excellent optical clarity. MacKnight sought our assistance because his data conflict strongly with the existent theories (which he had developed!) for the miscibility of random copolymers. We provide a major extension of random copolymer theory in a form that is readily usable by experimental groups. The theory is based on the more realistic united atom models for the monomer molecular structures. The entropic portion of the Flory χ parameter is computed with no adjustable parameters, while the interaction portion of χ is determined using an extension of Flory type counting to the united atom models. The theory explains the experimental data reasonably well and shows that the observed miscibilities in these systems are dominated by the entropic part of χ, a quantity whose explicit computation (without adjustable parameters) is totally inaccessible to earlier theories.

Paper 11 provides a detailed description of the theory used in papers 10 and 12, along with new applications to binary mixtures of saturated poly(butadienes) with differing microstructures (described more extensively in paper 12). The saturated poly(butadienes) are random copolymers by virtue of varying degrees of 1,2 and 1,4 additions during the polymerization. Prior attempts at describing the extensive small angle neutron scattering data of Graessley, Lhose, and coworkers use simple solubility parameter theory, which reduces a set of n^2 temperature (and, in general, composition) dependent binary interaction parameters to a set of n temperature (and, in general, composition) dependent single component solubility parameters (where n is the number of samples with different microstructures.) While the solubility parameter approach produces a large reduction in the data set, it offers no molecular understanding that may be transferred to other systems. In addition, the manner in which solubility parameter theory is applied is thermodynamically inconsistent when the χ parameter has a significant entropic component. Our theory, on the other hand, describes *all* these systems with only *two* adjustable parameters, the 1,2 and 1,4 unit interaction energies,

and this success provides encouragement towards developing a more comprehensive theory that can treat homologous systems. The theory has also been applied to data for the identical systems as studied by Klein and coworkers whose a nuclear reaction analysis. The agreement with experiment is even better and improves significantly with the use of an extra adjustable parameter (describing a very small deviation of the heterocontact interaction energy from the geometric mean.) The information gained from the study of these systems ties in well with our proposed project to understand the miscibility of blends of linear and branched polymers.

Our earlier prediction (1990) that diblock copolymers could undergo an order-disorder transition upon *heating* has subsequently been verified experimentally for poly(styrene)-b-poly(butyl methacrylate) diblock copolymers. The experiments also confirm our predictions of a strong pressure sensitivity of the ordering transition, a pressure sensitivity that may be useful to the Army in devising a new class of sensors. Further experiments also reveal a remarkable dependence of the phase behavior of poly(styrene)-b-poly(n-alkyl methacrylate) diblock copolymers on the length n of the alkyl chain, a dependence that is explained in paper 13. More specifically, experiments by Russell (U. Mass., Amherst) and Mayes (MIT) show that the diblock polymers undergo a traditional order-disorder transition upon cooling for n =1 (as is well known), but the transition occurs on *heating* for n = 2, 3, and 4, before shifting to a transition on *cooling* for n = 6, 8, and 12. A 50-50 (by weight) random copolymer made from n = 1 and n = 12, each of which yield diblocks with PS that order on *cooling*, produces a diblock that orders on *heating*. Our explanation for the striking variation of phase behavior with alkyl chain length n (which defies explanation by all previous theories) further illustrates the ability of our theory in molecular modeling polymer materials of interest to the Army.

3. Technology transfer:

All reports and publications are sent to
Dr. Nora Beck-Tan
U. S. Army Research Laboratory
Materials Directorate-Delaware Site
ATTN: AMSRL-MA-H
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Dr. Donald Rivin
Natick Research, Development and Engineering Center
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Kansas Street
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U. S. Army Research
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P. O. Box 12211
Research Triangle Park, NC 27709-2211

In addition, all publications are sent to
Drs. Charles Han and Jack Douglas, Polymers Division, NIST, Gaithersburg, MD

Some publications have been sent to Dr. David Lhose, Exxon research, Annandale, NJ with whom we have had some discussions concerning the analysis of his experimental data for polyolefin blends. Exxon has a strong research program in polyolefins because the new metallocene catalysts now enable unprecedented control of the chemical structure of the polyolefins, thereby focusing attention on understanding the relation between molecular structure and performance of high commodity polyolefins in order to improve existing products and to develop new ones. Our improvements in the theory of random copolymer systems should be of more widespread industrial interest since many commodity and specialty polymers are random copolymers.

For a theoretician "technology transfer" is a process of transferring theoretical advancements to experimentalists for further implementation and development of new technologies. The 1998 summer workshop "Polymer Theory vs. Polymer Experiment", co-organized by K. F. Freed, was designed to promote this type of "technology transfer" on a wider scale. Anna Balazs (also funded by ARO through Kiserow) was an invited speaker as was Jacek Dudowicz. On a more direct level, we have been in contact with Bill MacKnight (U Mass), Tom Russell (U. Mass), David Lhose (Exxon), Dietmar Schwahn (Julich), and Kalman Migler (NIST) concerning our interest in analyzing their experimental data and in using our theory to design new experiments as an aid towards developing novel materials. The work of the latter three experimentalists concerns the pressure dependence of polymer blends, which is of particular interest to the Army and has been the subject of study by us as described above. The incorporation of our simplified theory, mentioned above, in a general polymer physics graduate course will serve technology transfer as the students take up positions in industry and research laboratories.

Freed has made two visits to ARL and has had several e-mail contacts with Dr. Nora Beck Tan there. Freed's visit this autumn has been delayed due to family illness. Dudowicz has made one visit to ARL.

Dr. Tan has suggested that our theory might be helpful to indicate potential substitutes for the polyisobutylene in butyl rubber, which is used as the material to protect soldiers against poison warfare. The present butyl rubber suits are found to be very uncomfortable to wear, and their impermeability to water and heat makes them dangerous to wear for extended periods in ultra hot dessert environments. Perhaps, blending polyisobutylene with another polyolefin will improve the wearability of the suits constructed from a polyisobutylene blend without degrading the low permeability to poisons. I have suggested that one of the factors contributing to the impermeability of polyisobutylene is its higher density compared to other polyolefins. The ability of polyisobutylene to form very miscible blends (negative χ parameter) with several other polyolefins probably arises on a molecular scale from a preponderance of "surface" methyl groups, which have stronger attractive interactions than other CH_n groups, n = 0, 1, or 2. A negative χ generally implies a negative volume change on mixing and higher densities, so some of these blends should be candidates for replacing simple butyl rubber. I also expect that the solubility of polar organic substances (most poisons) will be less if the polyolefin blended with polyisobutylene also has a small or vanishing dipole moment for each monomer unit.

The ability of our theory to predict the variations of critical temperatures with pressure may have important ramifications for Army applications. Upon an increase in pressure, many blends are anticipated to change from one phase systems to two phase blends, and Dr. Tan suggested that this phenomenon might be used as a means for absorbing energy and thereby for protecting against ballistics. The polymer phase separation would be too slow for this application, but a system-containing polymer, perhaps in gel form, and entrapped small molecules might be more promising. When Dr. Tan elaborates this idea further, she will contact us for further theoretical input.

Discussions with Dr. Kestutis Chesonis at ARL also alerted us to another important problem that we plan to address in the future. Many coatings are formed from multicomponent polymer solutions, such as a miscible ternary system of two polymers in solution. When the solvent is removed, the resultant binary polymer blend may or may not be phase separated. Only a one-phase blend can provide useful transparent coatings, and systems are tested on a costly purely trial and error basis. Our theory could be applied to the bulk phase diagrams for both the ternary and binary systems in order to eliminate many systems (and ranges of concentrations) without performing expensive experimental tests. A longer-range interest would involve devising a theory for the phase behavior in thin films. In the interim, we were able to provide a preprint on experimental methods for stabilizing thin polymer films that would otherwise phase separate when solvent evaporates.

We met Steve Bunte and Cary Chabalowski from the ARO modeling group and discussed common interests in electronic structure theory. Cary asked for advice on the modeling of polymers containing high-energy propellants. We made some suggestions on how to adopt the potential functions that they are developing into the generalized Rouse description that we have formulated.

Freed attended the first Army workshop focusing on flexible barrier materials for the soldier system, held April 14-15, 1999, at the Natick Research, Development, and Engineering Center. At this meeting Freed and Mays (Alabama) developed plans to combine Mays' ARO supported work to synthesize carefully branched polyolefins and finally resolve important questions concerning the miscibility of linear and branched polymers. Dr. Charles Han, NIST will perform the small angle neutron scattering experiments on Mays samples, while Freed and Dudowicz will apply (extending if necessary) their theory to the SANS data. Freed also discussed with Barbari (Johns Hopkins) the application of our theory to his data on gas sorption by polymer blends. While these preliminary discussions have not progressed further, Freed and Dudowicz plan to study the general questions related to the alteration of blend phase diagrams by small molecules. Gas sorption is one application, and the influence of supercritical CO_2 is one specific system of interest for sorption studies as well as for the general solvent problems raised by Dr. Chesnonis at ARL.

As described in the year one technical report, our research for the first year was heavily leveraged; thereby contributing strongly to the large publication output the first and second years. The research in years two and three has not been leveraged.

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4. Papers published:

1. Nonrandom mixing in polymer blends: Implications for phase behavior. K. W. Foreman, K. F. Freed and I. M. Ngola. J. Chem. Phys. 107, 4688 (1997).

2. Energetically driven asymmetries in random copolymer miscibilities and the pressure dependence. J. Dudowicz and K. F. Freed, Macromolecules 30, 5506 (1997).

3. Influence of stiffness, monomer structure, and energetic asymmetries on polymer blend miscibilities: Applications to polyolefins. K. W. Foreman and K. F. Freed, Macromolecules 30, 7279 (1997).

4. Molecular mechanisms for disparate miscibilities of poly(propylene) and head-to-head poly (propylene) with other polyolefins. K. F. Freed, J. Dudowicz, and K. W. Foreman, J. Chem. Phys. 108, 7881 (1998).

5. Lattice cluster theory for pedestrians: The incompressible limit and the miscibility of polyolefin blends. K. F. Freed and J. Dudowicz, Macromolecules 31, 6681-6690 (1998).

6. Modeling the Phase Behavior of Random Copolymer/homopolymer Polyolefin Blends. J. Dudowicz and K. F. Freed, Polym. Mat. Sci. Eng. 79, 240 (1998).

7. Miscibility Patterns in Random Copolymer/homopolymer Mixtures. J. Dudowicz and K. F. Freed, Polym. Mat. Sci. Eng. 79, 118 (1998).

8. Molecular Factors Governing Miscibility of Polymer Blends. K. F. Freed, J. Dudowicz, and K. W. Foreman, Polym. Mat. Sci. Eng. 79, 68 (1998).

9. Molecular Modeling as an Aid to Controlling the Miscibility of Polymer Blends. K. F. Freed, J. Dudowicz, and K. W. Foreman, Polym. Mat. Sci. Eng. 79, 238 (1998).

10. Molecular Factors Affecting the Miscibility Behavior of Cycloolefin Copolymers. C. Delfolie, L. C. Dickinson, K. F. Freed, J. Dudowicz, and W. J. MacKnight, Macromolecules **32**, 7781 (1999).

11. Lattice Cluster Theory for Pedestrians: Models for Random Copolymer Blends. K. F. Freed and J. Dudowicz, Macromol. Symp. (in press).

12. Lattice Cluster Theory for Pedestrians: II. Random Copolymer Systems. J. Dudowicz and K. F. Freed, Macromolecules (in press).

13. Explanation for the Unusual Phase Behavior of Polystyrene-b-Poly(n-alkyl methacrylate) Diblock Copolymers: Specific Interactions. J. Dudowicz and K. F. Freed, Macromolecules (in press).

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5.Scientific personnel and honors:

K. F. Freed, PI
J. Dudowicz, coPI
K. W. Foreman, graduate student

Dudowicz was promoted to Senior Research Associate, our highest research level position, in recognition of his outstanding research accomplishments.

Dr. Foreman received a prestigious Sloan Foundation/DOE postdoctoral fellowship to enter the field of computational biophysical chemistry.

Freed was chairman of the 1996 Gordon Research Conference of Polymer Physics and co-chairman of a new conference on "Polymers: Theory versus Experiments." He will also co-organize a polymers conference at Argonne National Laboratory, June 19-23, 2000 which is designed by the Argonne co-organizers to interest DOE in increased funding for polymer research at Argonne. Freed was also an invited speaker (for the third successive time) at the European Symposium on Polymer Blends, Mainz, Germany, the primary international conference on polymer blends.