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13. ABSTRACT (Maximum 200 words)  We have extended in several ways the lattice cluster theory for the statistical thermodynamics of polymer systems. In addition to the previous treatments of the influence of monomer molecular structures, pressure, and non-random mixing, the new extensions consider the phase diagrams, the structural properties evidenced by small angle neutron scattering, the behavior of block copolymer systems, the stabilization of binary polymer blends by diblock copolymers, and the range of validity for mean field theories of polymer blends. Besides enabling the explanation of detailed, previously perplexing experimental data, the theory has been used to provide predictions, subsequently verified, concerning the pressure dependence of polymer properties and the possibility for ordering in block copolymers upon heating.				
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## FINAL REPORT

GRANT #: N00014-91-J-1442

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INSTITUTION: The University of Chicago

GRANT TITLE: Towards the Molecular Design of Composite Materials

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OBJECTIVE: To develop a theory of the statistical thermodynamics of polymer blends and block copolymer systems in which the theory relates microscopic and macroscopic properties and thereby assists in the molecular design of composite materials with desired macroscopic properties.

APPROACH: The lattice cluster theory for the statistical thermodynamics of polymer systems properly describes the influence of monomer molecular structure, pressure, and local non-random mixing upon the macroscopic thermodynamic properties. The theory has been applied to study the sensitivity of various blend properties, such as the effective Flory interaction parameters, excess thermodynamic properties, phase diagrams, correlation lengths, and effective chain sizes, to monomer molecular structure and thermodynamic state. Tests of the theory are made by comparison with experimental data for selected systems and by predicting novel general trends and specific behaviors.

ACCOMPLISHMENTS: The lattice cluster theory of corrections to Flory-Huggins theory has been applied to determine general dependence of the effective interaction parameter for high molecular weight binary compressible blends (at a pressure of one atmosphere) on composition, monomer molecular structure, microscopic interaction energies, and temperature. The theory has been extended to compute spinodals, and we demonstrate that a binary blend may, in principle, exhibit phase diagrams with either lower or upper critical solution temperatures or with a closed loop phase. Computed spinodals for PS/PVME blends (using no new adjustable parameters) agree well with experiment. The theory has been combined with our compressible random phase approximation to describe small angle coherent scattering from polymer blends and therefore the influence of monomer molecular structure, local correlations, and thermodynamic state upon correlation lengths and apparent radii of gyration of polymers in binary blends. In addition to elucidating general trends and deficiencies in the prior incompressible theory, our computations provide the first systematic understanding of the counterintuitive small values for the observed correlation lengths and their strong composition dependence in PS/PVME blends. The theory also demonstrates the alteration of chain dimensions in binary blends and thereby provides guidance into further developing microscopically predictive theories of condensed polymer materials. Including the generally observed composition dependence of the Flory interaction parameter, we predict the possibility for new types of phase behavior in which two pairs of coexisting phases may be present in the two-phase region.

The lattice cluster theory of corrections to Flory-Huggins theory has also been extended to describe the variation of the effective interaction parameter for diblock copolymers on composition, monomer molecular structure, microscopic interaction energies, and temperature. The theory demonstrates the existence of a large  $1/N$  contribution, where  $N$  is the polymerization index, to the diblock copolymer effective interaction parameter. This  $1/N$  contribution arises from the junction in the block copolymer and generally contributes a positive increment to the effective interaction parameter, thereby explaining the origin of the huge entropic contribution observed for the polystyrene-b-poly(methyl methacrylate) diblock copolymer system. The theory provides the first prediction for the general pressure dependence of microphase separation in block copolymers, a dependence that had not been measured previously but that may influence the behavior of block copolymers under typical polymer processing conditions. Subsequent experiments verify our general predictions concerning the pressure dependence of block copolymer phase diagrams. The polystyrene-b-poly(vinyl methyl ether) system is predicted to have a novel re-entrant phase diagram for microphase separation. Subsequently, Russell of IBM has confirmed our predictions with his observation of a diblock copolymer system with ordered phases occurring as the temperature is increased.

While the previous theoretical extensions have been applied to diblock copolymer melts, further lattice cluster theory computations have completed the task of computing the free energy for a ternary compressible system of diblock copolymers with their respective homopolymers. The theory has been used to study the stabilization of blends by block copolymers. Detailed computations for ternary systems with polystyrene-b-poly(methyl methacrylate), polystyrene-b-poly(vinyl methyl ether), and polystyrene(H)-b-polystyrene(D) diblock copolymers along with their respective homopolymers consider the limits of stability for the homogeneous phase as a function of the composition and molecular weights of the ternary system, demonstrating conditions under which the blend may be either stabilized or destabilized and exhibiting substantial differences from small molecule behavior for the influence of dilution on critical properties of binary mixtures. Substantially different behaviors are predicted for blends which display lower versus upper critical solution temperatures. The lattice cluster theory has also been used to study the molecular characteristics governing the domain in which mean field theories are not valid. Monomer molecular structure, equation of state effects, and local correlations are shown to exert a strong influence on the size of the non-classical region, and large departures are evidenced from the classic incompressible Flory-Huggins theory.

CONCLUSIONS: The lattice cluster theory is the first to establish the strong dependence of several thermodynamic properties of polymer blends on monomer molecular structure. The need for including compressibility is likewise strikingly demonstrated; otherwise, the phase behavior of PS/PVME blends could not be explained. The combination of monomer molecular structure, compressibility, and non-random mixing in the theory is shown to yield a much richer dependence of polymer properties on thermodynamic state, thereby providing more possibilities for using this richness to design novel materials with desired properties. It is particularly gratifying to see that the fitted interaction energies for PS/PVME blends are consistent with changes in chain dimensions - the first established theoretical connection between thermodynamic state

and molecular conformations in polymer blends.

The extension of the lattice cluster theory to diblock copolymers predicts and explains the existence of a substantial difference between the effective interaction parameter for blends and the corresponding block copolymers, in sharp contrast with the general assumption that the interaction parameter is identical for these two systems. Our predicted pressure dependence and re-entrant phase diagrams for microphase separation in diblock copolymers can have important implications in the design of new composite materials by control of pressure and temperature and by choice of monomer structures.

The stabilization of blends by block copolymers is an important phenomenon in controlling the properties and morphology of polyolefins which are of importance as structural materials, such as high impact polystyrene which is a two-phase blend of polystyrene and polybutadiene, as well as block copolymers of these species. Our computations demonstrate that a much richer variation of the phase behavior (and hence of the physical properties) is predicted to arise from the combined influences of local correlations, monomer molecular structure, and equation of state effects. Such rich variation provides more opportunities for the design and control of new structural materials with improved adhesive characteristics. A theory for the size of the non-classical region in binary polymer blends is essential in interpreting experiments on the dynamics of phase separations in these systems. Very different theories apply in the classical, non-classical, and crossover domains. Our theory exhibits gross departures from the predictions of the classic, but over simplistic Flory-Huggins theory, and we explain the origins for the observed lack of universality of the previously derived expressions for the size of the non-classical domain.

SIGNIFICANCE: Our theory describes how monomer molecular structure may be used as a tool for designing and controlling the physical properties of complex polymer materials. This will impact on the development of new materials and will eventually be translated into biological applications as have previous significant conceptual advances in polymer science.

PATENT INFORMATION: None

AWARD INFORMATION: None

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