REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	25 June 1993	FINAL 12 Feb. 90 - 11 Feb. 93

4. TITLE AND SUBTITLE
Ultrastructure Processing of Macromolecular Materials

5. FUNDING NUMBERS
61102F
2303/CS

6. AUTHOR(S)
Professor Frank E. Karasz

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Dept. of Polymer Science and Engineering
University of Massachusetts
Amherst, MA 01003

8. PERFORMING ORGANIZATION REPORT NUMBER
AFOSR-TR- 93 0404

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NC
110 DUNCAN AVENUE SUITE B115
BOLLING AFB DC 20332-0001

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
F49620-90-C-0019

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The effects of microstructure on miscibility of **polymer blends** has been investigated in a number of model systems by thermal, mechanical and novel spectroscopic techniques. An understanding of the fundamental basis of the metastable miscibility found in large number of high temperature systems, i.e. these typically involving polyimides or related materials with high Tg's has also been gained. In a complementary investigation we have performed **computer simulation** studies of the equilibrium behavior of various blends, and under several types of constraint, to provide insights into behavior in binary systems at the segmental level. This study also investigated dynamic aspects, including phase separation. In another investigation, we have studied **electro-optically active conjugated polymers**, principally poly(*p*-phenylene vinylene) and its derivatives, modifications and blends. The emphasis has been on gaining a detailed understanding of the structural properties and concurrently exploiting the several electro-optical effects for which these polymer systems are noted. These include non-linear optical phenomena and electroluminescence. Certain **solution properties** of polymer systems have also been studied. We have continued to use quasi-elastic light-scattering measurements to investigate **translational diffusion of solvated polymers** in porous media and other properties of polar and non-polar macromolecules. A synthetic effort in **side-chain liquid crystal polymers** has led to the systematic study of the thermal, mechanical, and dielectric properties of several representative series and of their mixtures.

14. SUBJECT TERMS	15. NUMBER OF PAGES
polymer blends, computer simulation, electro-optically active conjugated polymers, translational diffusion of solvated polymers, side-chain liquid crystal polymers	22
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED

FINAL TECHNICAL REPORT

ULTRASTRUCTURE PROCESSING OF MACROMOLECULAR MATERIALS

MIRP GRANT AFOSR 90-C-0019

10 February 1990 - 11 February 1993

Frank E. Karasz
Department of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01003

FINAL TECHNICAL REPORT

ULTRASTRUCTURE PROCESSING OF MACROMOLECULAR MATERIALS

MIRP GRANT AFOSR 90-C-0019

10 February 1990 - 11 February 1993

Frank E. Karasz
Department of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01003

ACKNOWLEDGEMENT

The Principal Investigator would like to express his sincere thanks to Dr. Donald Ball, Director of Chemical Sciences, Air Force Office of Scientific Research, to the late Dr. Donald R. Ulrich, Senior Program Manager, Directorate of Chemical Sciences, to Dr. Charles Y-C Lee and to other members of the Directorate, for their unfailing cooperation, help and courtesy extended to him during the period of this grant.

CONTENTS

I. TITLE: Ultrastructure Processing of Macromolecular Materials

II. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz
Polymer Science & Engineering
University of Massachusetts
Amherst, Massachusetts 01003

III. GRANT NUMBER: AFOSR 90-C-0019
February 10, 1990 - February 11, 1993

IV. FACULTY ASSOCIATES: Professor W. J. MacKnight (PSE)
Professor Paul Lahti (Chemistry)
Professor K. H. Langley (Physics)

SENIOR RESEARCH PERSONNEL:

Dr. T. Bleha
Dr. W. Liang
Dr. S. O'Donohue
Dr. P. Musto
Dr. L. Wu
Dr. D. Rice
Dr. R. McCoy
Dr. Z. Chai
Dr. A. Waddon
Dr. I. Teraoka
Dr. R. Sun
Dr. J. Rutt
Dr. C. Imrie
Dr. V. Janarthanan
Dr. L. Litauszki
Dr. G. Ruggeri
Dr. M. Connolly
Dr. F. Kuchenmeister
Dr. I. Sokolik
Dr. Z. Yang
Dr. B. Hu
Dr. B. Jin

V. JUNIOR RESEARCH PERSONNEL:

R. Gregorious
S. Li
M. Masse
Y. Guo
F. Denton
J. Neill
J. Simpson
F. Papadimitrakopoulos
A. Sarker
B. Ma

VI. ABSTRACT

The report covers the operation of an AFOSR MIRP at the University of Massachusetts for the period 10 February 1990 to 11 February 1993.

The research has concurrently involved several areas of investigation in the physical chemistry of macromolecules. A major theme has been the study of the properties of **polymer blends**. Experimentally we have investigated the effects of microstructure on miscibility in a number of model systems by thermal, mechanical and varied novel spectroscopic techniques, and have also gained a wide understanding of the fundamental basis of the metastable miscibility found in an unexpectedly large number of high temperature systems, i.e. these typically involving polyimides or related materials with high Tg's. In complementary investigation we have performed **computer simulation** studies of the equilibrium behaviour of various blends and under several relevant constraints. Such calculations provide substantial insights into molecular behavior in binary systems at the segmental level. The work also investigated dynamic aspects, particularly phase separation at differing effective quench depths. Another line of investigation has concerned itself with **electro-optically active conjugated polymers**, principally poly(*p*-phenylene vinylene) and its derivatives, modifications and blends. Here the emphasis has been on gaining a detailed understanding of the structural properties and concurrently exploiting the several electro-optical effects for which these polymer systems are noted. These include non-linear optical phenomena and electroluminescence. Certain **solution**

properties of polymer systems have also been studied. In particular we have continued to use quasi-elastic light-scattering measurements to investigate **translational diffusion of solvated polymers** in porous media and other properties of polar and non-polar macromolecules. A synthetic effort in **side-chain liquid crystal polymers** has led to the systematic study of the thermal, mechanical, and dielectric properties of several representative series and, in some cases, of their mixtures. Other syntheses have aimed at providing **new polyimides**. A number of theoretical investigations related to the above projects have also been completed.

During the grant period some ninety-nine manuscripts were published or have been submitted as a result of AFOSR support, see Section VIII.

VII. DESCRIPTION OF RESEARCH UNDERTAKEN

The ninety-nine manuscripts published or submitted during the grant period and listed in Section VIII present full details of the research undertaken. Previous Annual Reports also describe results obtained. A further discussion of selected significant projects is presented below.

A. Miscibility in Model Copolymer Systems

Miscibility in blends of random copolymers of *o*-chlorostyrene and *p*-chlorostyrene [P(*o*ClSy-co-*p*ClS$_{1-y}$)] with eight atactic polystyrene (aPS) fractions has been studied at temperatures ranging from 150°C to 300°C. From these data, the temperature dependence of the three segmental interaction parameters required to describe this system were obtained using this technique for the first time.

In addition, the miscibility and phase behavior in 50/50 wt % blends of chlorinated poly(vinyl chloride) (CPVC) and poly(acrylonitrile-*co*-butadiene) (AN-BT) copolymer have been investigated. It was found that the extent of miscibility of the CPVC/(AN-BT) system becomes larger with increasing chlorine content of CPVC, compared to that of the PVC/(AN-BT) system. The maximum miscibility region was found around 63 wt % Cl in the CPVC blend system. By assuming a random copolymer structure for both components and applying first-order mean field theory to the experimental results, the respective segmental interaction parameters, χ_{ij}'s were determined. The theoretical phase boundary is consistent with

experimental data. By studying the temperature effect on the phase behavior of this blend, lower critical solution temperature behavior was identified as evidenced by the contraction of the miscibility region at 170 °C.

This work was extended theoretically and experimentally to study sequence distribution effects (microstructure) in copolymer miscibility. Such effects can dominate the phenomenon under certain conditions.

Solid state NMR techniques were employed in novel fashion to study the micro-morphology of miscible blends. It is tacitly assumed, without direct evidence, that fulfillment of the "single Tg" criterion of miscibility implies complete inter-segmental mixing. Advanced NMR methodologies provide more definitive information about segmental distribution in such systems and in the case of the model PPO/PS system indicate that homogeneity at the segmental level is probably absent even in systems characterized by a substantially negative χ_{ij}.

B. Computer Simulations of Miscibility in Binary Systems

Interactions play a decisive role in polymer-polymer miscibility. However, direct elucidation of interactions from thermodynamic mixing properties is experimentally cumbersome because of high viscosity and glass transition temperature effects in polymer systems, and because there are theoretical problems attributable to the mean-field approximation. Therefore we are interested in Monte Carlo (MC) simulations which overcome some of these restrictions and are an alternative to the

experimental and purely theoretical approaches. Results of such simulations are available for only a few model systems. MC simulation provides insight into these systems in two ways. First, simulation is an independent method that is free of mean-field approximations, so it enables us to account both for connectivity of monomers within the chains and for concentration fluctuations due to nonrandom mixing. Second, this method is a useful supplement to the standard copolymer theory because it enables us to investigate χ_{blend} over the complete polymer composition range. This flexibility allows us to see whether χ_{blend} behaves according to the quadratic mixing rule over the total composition range $0 < x < 1$. In other words, we can determine whether the segmental interaction parameters χ_{ij} obtained from miscibility boundaries at two copolymer compositions accurately represent χ_{ij} over this range. During the grant period we have studied a range of binary systems by the MC technique in two and (mostly) three dimensions. The results have enabled us to cover a wide range of interaction energies and to "observe" mixing-demixing transitions in binary homopolymer and copolymer situations. The effect of chain flexibility and relative component concentrations on solvent and solute conformations (as well as on miscibility) have also been studied. In the later portion of the grant period we have extended these concepts to variable density situations (technically, grand or semi-grand canonical ensembles *vis-á-vis* the canonical ensembles of the initial work) especially appropriate for

homopolymer or miscible blend surfaces or immiscible blend interfaces. The results obtained are somewhat "ahead of experiment" and we are currently attempting to verify certain predictions regarding the surface effects. Dynamic situations -- phase separations -- have also been explored. By changing the reduced segmental interaction energy from attractive to repulsive at time t = 0 we can simulate quenching experiments below the UCST -- and vary "quench depths" -- and thus observe the initial stages of phase decomposition. Good agreement with Cahn-Hilliard theory was obtained in regimes where direct experimental observation is difficult or impossible.

C. Polyarylene Vinylenes

Polyarylene vinylenes constitute the most chemically versatile π-conjugated macromolecule systems and have interest in their basic structure and properties as well as a wide variety of potential applications.

It has been known that doped (i.e. oxidized or reduced) members have high electrically conductivity, the exact nature of these complexes is one area of interest that has been investigated. The stage-1 phases of Cs-doped poly(*p*-phenylene vinylene) (PPV) have been investigated by *in situ* x-ray diffraction, using highly oriented vapor-doped samples. While the relative guest-host sizes are nearly equivalent, the resulting equatorial structures, as determined by structure-factor calculations, exhibit pronounced differences in the location and orientation of the polymer chains. PPV

samples are dominated by uniform chain-axis rotations within a base-centered orthorhombic lattice of the Cs^+ ions while polyacetylene undergoes displasive translations within a centered tetragonal lattice of the Rb^+ ions. Significant differences in the dopant-ion organization within the quasi-one-dimensional alkali-metal ion channels are also found. These temperature insensitive and polymer specific variations are indicative of local guest-host interactions which stabilize the respective structures. Further comparisons suggest that systematic intermediate-length-scale deviations from planarity by the polymer chains are probable. As a result, the electronic excitations may couple to polymeric torsional degrees of freedom.

In addition, solid-state ^2H quadrupole echo nuclear magnetic resonance (NMR) spectra and measurements of ^2H spin lattice relaxation times have been obtained (for example) for films of poly(*p*-phenylene vinylene) deuterated in the phenylene ring positions (PPV-d_4). NMR line shapes show that all the phenylene rings of PPV undergo 180° rotational jumps about the 1,4 ring axis ("ring flips") at 225°C. The temperature dependence of the ^2H line shapes show that the jump motion is thermally activated. The jump rate was also determined from the magnitude of the anisotropic T_2 relaxation associated with ^2H line shapes and from the curvature of inversion recovery intensity data. The experimental activation energy for jumps is comparable to the intramolecular potential barrier for rotation about phenylene vinylene bonds. ^2H NMR provides a method for

determining the phenylene vinylene rotational barrier in pristine PPV, and may potentially be used to study conjugation in conducting films.

Copolymers of various analogous structures incorporating hetero-atoms have been synthesized. Their characterization provided additional information regarding the effect of chemical and micro-structure on these π-conjugated systems.

D. Diffusion of Solvated Macromolecules in Constrained Media

The dynamics of a one-dimensional Brownian particle have been treated theoretically over a wide time scale in the presence of random reflecting barriers to complement our experimental studies. Green functions for particle motion with two kinds of barriers were formulated, one being diffusion with fixed random barriers and the other with stochastic random barriers. The stochastic barriers appear randomly on the time axis as well as with positional disorder and then, after a while, disappear. To treat these problems, we first developed a mean-field Green-function (MFG) theory. The effects of many barriers, regarded as a multiple perturbation to the free diffusion of the particle, were decomposed into many elements. Their average effects (the first cumulant of the random perturbation elements) were sequentially incorporated into the unperturbed Green function up to the number of the elements. The first-cumulant MFG was thus obtained and covers the whole range of the perturbation intensity of the mean element. Taking into account a higher-order correlation among

the perturbation elements yielded a higher-order cumulant MFG. By applying the first-cumulant and the second-cumulant MFG theories to the particle diffusion with fixed and with stochastic barriers, we calculated the mean-square displacement as a function of time. It was found that the first-cumulant MFG describes qualitatively the dynamic behavior of the particle on all the time scales, whereas the second-cumulant MFG gave a more accurate numerical coefficient in the estimation of the time-dependent mean-square displacement.

The complementary experimental program investigated the diffusion of macromolecules in a porous network of silica glass. The essential point is that a solvent iso-refractive with the silica (2-fluorotoluene) could be chosen which thus renders the motion of the solute (i.e. the polymer chains) visible. These measurements provided (often for the first time) data for comparison with theory and also revealed more subtle effects (e.g. with regard to concentration and bimodality) which have yet to be accounted for. We believe these measurements will have important applications in polymer separation science and technology.

E. Side-Chain Liquid Crystal Polymers

A series of side-chain liquid-crystalline copolymers, the poly[4-[1-(4-methoxy-4′-oxyazobenzene)-8-octyl]oxystyrene]-*co*-poly[4-[α-(4-methoxy-4′-oxyazobenzene)-ω-alkyl]oxystyrene]s, has been prepared in which the second spacer is varied in length from three methylene units up to twelve. The

properties of the copolymers are compared with those of the homopolymers, the poly[4-[α(4-methoxy-4′-oxyazobenzene)-ω-alkyl]oxystyrene]s. All the polymers exhibit smectic behavior with the exception of the propyl homopolymer, for which no mesophase is observed. The transition temperatures of the copolymers are similar to the mean values of the homopolymers. The largest deviations from this behavior were observed for copolymers containing either propyl or butyl spacers. In contrast the transitional entropies exhibited by the copolymers show significant negative deviations with the exception of dodecyl-octyl copolymer, for which a small positive deviation is observed. We interpret these differences in terms of steric factors. Electrically induced alignment of the LC polymer was also investigated.

F. Other Studies

The AFOSR grant provided opportunities for a considerable number of investigations in addition to the central themes outlined above (see Section VIII). Many of these concerned new materials (e.g. polyimides) or binary systems involving ultimately issues of heterogeneous non-polar or polar segment-segment interaction. Thus understanding the effect of microscopic interactions on macroscopic behavior may be considered the ultimate goal and achievement of the research.

VIII. PUBLICATIONS

1. Polymer 31, 1321-28 (1990) (with T. Bleha and P. Cifra) "The Effects of Concentration on Partitioning of Flexible Chains Into Pores".

2. Macromolecules 23, 3675-82 (1990) (with M.A. Masse, R.J.Composto, and R.A.L. Jones) "Dopant Concentration in Conducting Poly(*p*-phenylene vinylene) by Rutherford Backscattering Spectrometry".

3. Makromol. Chem., Rapid Commun. 11, 145-50 (1990) (with G. Attard) "Phase Studies of Blends of Polystyrene-Based Liquid Crystalline Side-Chain Polymers with Low Mass Mesogens".

4. MRS Proceedings, Volume 175, Material Research Society, Pittsburgh, 227-237 (1990) A. Buckley, G. Gallagher-Daggitt, F.E. Karasz, D.R. Ulrich, Eds., (with G. Williams and A. Nazemi) "Dielectric Relaxation Properties and Alignment Behaviour of Liquid Crystalline Side-Chain Polymers".

5. Multifunctional Materials, Ed. (with A. Buckley, G. Gallagher-Daggit and D.R. Ulrich), Materials Research Society, Pittsburgh, (1990).

6. J. Polym. Sci.: Part A: Polym. Chem., 28, 2867-2875 (1990) (with W.B. Liang, R.W. Lenz) "Poly(2-methoxyphenylene Vinylene): Synthesis, Electrical Conductivity, and Control of Electronic Properties".

7. J. Polym. Sci.: Part B: Polym. Phys., 28, 1859-1869 (1990) (with J.H. Simpson, N. Egger, M.A. Masse, D.M. Rice) "Solid-State ^{13}C NMR Characterization of Annealed Poly(*p*-phenylene vinylene) Films".

8. Makromol. Chem. 191, 1623-1631 (1990) (with J. Kressler, H. Kammer, and U. Morgenstern) "Miscibility in Blends of Random Copolymers of Styrene and Acrylonitrile With Block Copolymers of Styrene and Methyl Methacrylate".

9. Materials Science Progress 4, 357-363 (1990) (with X. Jin, Y. Luo and R. Huo) "Thermal Degradation of Poly(Aryl Ether Ether Ketone)".

10. J. Chem. Phys. 93, 3593-3603 (1990) (with H. Mattoussi and K.H. Langley) "Electrostatic & Screening Effects on the Dynamic Aspects of Polyelectrolyte Solutions".

11. Macromolecules 23, 4076-4082 (1990) (with T. Bleha and J. Gajdos) "Energetics of Strain-Induced Conformational Transitions in Polymethylene Chains".

12. Makromol. Chem. 191, 2111-2119 (1990) (with G. Guerra, P. Musto and W.J. MacKnight) "Fourier Transform Infrared Spectroscopy of the Polymorphic Forms of Syndiotactic Polystyrene".

13. Journal of Liquid Chroma. 13, 2581-2591 (1990) (with N. Segudovic and W.J. MacKnight) "Solvent Effect on the Separation Mechanism in HPGPC of Polyimide and Polyethersulfone".

14. New Polymeric Materials 2, 75-91 (1990) (with M. Masse, J. Hirsch and V. White) "A Multi-Technique Investigation of AsF_5-Doping Chemistry in Poly (*p*-phenylene vinylene).

15. J. Chem. Phys. 93, 7457-7462 (1990) (with Y. Guo and K. Langley) "Time Scale Dependence of Diffusion in Porous Material: Dynamic Light Scattering and Computer Simulation".

16. Science in China, Series B, No. 5, 460-470 (1990) (with X. Jin, Y. Luo and R. Huo) "Thermal Degradation of Sulfonated PEEK".

17. Contemporary Topics In Polymer Science, Vol. 6., Multiphase Macromolecular Systems (Bill M. Culbertson, Ed.), Plenum Press Publishers, New York, 493-504 (1989) (with S. Choe and W.J. MacKnight) "Phase Behavior in Miscible Polybenzimidazole/Polyetherimide Blends".

18. Proceedings of the Electrochemical Society, 88-6 747-753 (1988) (with J.B. Schlenoff and J. M. Machado) "Improved Mass Transport in Rechargeable Electrodes Employing Conducting Polymer Blends".

19. MRS Proceedings, Volume 171, Materials Research Society, Pittsburgh, 197-202 (1990) D.W. Schaefer, J.E. Mark, Eds., (with H. Yamaoka, N. Aubrey, W.J. MacKnight) "Miscibility in Blends of Polybenzimidazole and Fluorine Containing Polyimides".

20. Acta Polymerica Sinica No. 4, 426-433 (1990) (with R. Huo, Y. Luo, L. Liang and X. Jin) "Kinetic Studies on Thermal Degradation of Poly(Aryl Ether Ether Ketone) and Sulfonated Poly(Aryl Ether Ether Ketone) by TGA".

21. Liquid Crystals 9, 47-57 (1991) (with C.T. Imrie and G.S. Attard) "Side-Chain Liquid Crystalline Copolymers Containing Charge Transfer Groups".

22. Polymer 32, 3-11 (1991) (with P. Musto, L. Wu, and W.J. MacKnight) "Fourier Transform Infrared Spectroscopy Investigations of Polybenzimidazole/poly(bisphenol-A carbonate) Blends".

23. Polym. Comm, 32, 30-32 (1991) (with G. Guerra, C. De Rosa, V.M. Vitagliano, V. Petraccone and P. Corradini) "Blending Effects in the Polymorphism of Syndiotactic Polystyrene Crystallized from the Quenched Amorphous Phase".

24. Liquid Crystals, 9, 307-320, (1991) (with A. Nazemi, E.J.C. Kellar and G. Williams) "Electric Field Induced AC Alignment and Realignment: A Study of A Liquid-Crystalline Copolymer Having Longitudinally and Laterally Attached Mesogenic Groups as Side Chains Monitored Through Dielectric Spectroscopy and Optical Thermomicroscopy".

25. Progress in Pacific Polymer Science, B.C. Anderson, Y. Imanishi (Eds.), Springer-Verlag Berlin, 213-225 (1991) (with K. Liang, L. Wu, J. Grebowicz and W.J. MacKnight) "Miscibility Behavior in Polyethersulfone/Polyimide Blends with and without Solvents".

26. Polymer 32, 605-608 (1991) (with C.J. Wung, Y. Pang and P.N. Prasad) "Poly(*p*-phenylene vinylene)-Silica Composite: A Novel Sol-Gel Processed Non-Linear Optical Material for Optical Waveguides".

27. J. Polym. Sci.: Part B: Polymer Physics,29, 649-657 (1991) (with K. Liang, G. Banhegyi, and W.J. MacKnight) "Thermal, Dielectric, and Mechanical Relaxation in Poly(benzimidazole)/Poly(etherimide) Blends".

28. Polym. Commun. 32, 185-188 (1991) (with W. Salomons and G. ten Brinke) "Copolymer Blends of Styrene and *ortho*-fluorostyrene".

29. Mechanical Behavior of Materials - VI. Masahiro Jono and Tatsuo Inoue, Editors, Pergamon Press, Tokyo, (1991), 263-268 (with Z. Chai and R. Sun) "Aspects of Miscibility in Copolymer Blends".

30. J. Macromol. Sci.-Chem. A27 (13 & 14), 1693-1712 (1990) (with H. Ueda) "Critical Miscibility Phenomena in Blends of Chlorinated Polyethylenes".

31. Polym. Plast. Technol. Eng., 30 (2 & 3), 183-225 (1991) (with G. Banhegyi, P. Hedvig, Z. Petrovic) "Applied Dielectric Spectroscopy of Polymeric Composites".

32. Polymer 32, 2363-2366, (1991) (with W. Liang), "Molecular Orientation of Highly Drawn Poly(*p*-2-methoxyphenylene vinylene)"

33. Makromol. Chem. 192, 1495-1508 (1991) (with G. Attard, J. S. Dave, A. Wallington, C.T. Imrie), "Transitional Properties of Liquid-crystalline Side-chain Polymers Derived from Poly(*p*-hydroxystyrene)".

34. Synthetic Met. 41, 341 (1991) (with M. J. Winokur and D. Chen), "Structural Studies of Alkali-doped Poly(*p*-phenylene vinylene)".

35. Polym. Eng. and Sci. 31, 936-943 (1991) (with S. Havriliak and G. Banhegyi), "Determination of Unblended Chain Dynamic Parameters of a Polar Discontinuous Phase in an Immiscible Polymer Blend".

36. Polym. Eng. and Sci. 31, 981-987 (1991) (with J.H. Kim and M.F. Malone) "Effects of Phase Separation on the Mechanical Properties of Polystyrene/Poly(vinyl methyl ether) Blends".

37. Macromolecules, 24, 4762-4769 (1991) (with P. Musto and W.J. MacKnight), "Hydrogen Bonding in Polybenzimidazole/Poly(ether imide) Blends: A Spectroscopic Study".

38. Macromolecules, 24, 4820-4822 (1991) (with A. Bielecki, D.P. Burum, and D.M. Rice), "Solid-State Two-Dimensional ^{13}C-^{1}H Correlation (HETCOR) NMR Spectrum of Amorphous Poly(2,6-dimethyl-*p*-phenylene oxide)".

39. J. Polym. Sci.: Part B: Polym. Physics, 29 1389-1395 (1991) (with P. Cifra and W.J. MacKnight), "Short-Range Order in Miscible Polymer Blends: A *Monte Carlo* Study".

40. Macromolecules, 24, 5134-5140 (1991) (with G. Williams, A. Nazemi, J.S. Hill, D. Lacey and G.W. Gray), "Dielectric Relaxation Properties and Alignment Behavior of a Liquid-Crystalline Polymer Having Laterally Attached Mesogenic Groups".

41. Polymer, 32, 2340-2344 (1991) (with J. H. Simpson and D. M. Rice), "Investigation of H_2SO_4-doped, Ring-Deuterated Poly(*p*-phenylene vinylene) Using Solid State ^{2}H Quadrupole Echo NMR Spectroscopy".

42. Chemistry of Materials, 3, 941-947 (1991) (with R. K. McCoy, A. Sarker and P. M. Lahti) "Synthesis and Characterization of Ring-Halogenated Poly(1,4-phenylene vinylenes)".

43. Polymer Communications, 32, 430-432 (1991) (with G. Guerra, M. Iuliano, A. Grassi, D. M. Rice and W. J. MacKnight) "Solid-State High-Resolution ^{13}C Nuclear Magnetic Resonance Spectra of Syndiotactic Poly(*p*-methyl styrene)".

44. Phys. Review B, 44, 2507-2515 (1991) (with P. A. Heiney, J. E. Fischer, D. Djurado, J. Ma, D. Chen, M. J. Winokur, N. Coustel and P. Bernier) "Channel Structures in Alkali-Doped Conjugated Polymers: Broken-Symmetry 2-D Intercalation Superlattices".

45. MRS Proceedings Vol. 227, 335-340 (1991) (with J. L. Goldfarb, R. J. Farris, and Z. Chai) "A Calorimetric Evaluation of the Peel Adhesion Test".

46. J. Polym. Sci.: Part B: Polym. Physics, 30, 11-18 (1992) (with J. H. Simpson and D. M. Rice) "^{2}H NMR Characterization of Phenylene Ring Flip Motion in Poly(*p*-phenylene vinylene) Films".

47. J. Polym. Sci.: Part B: Polym. Physics, 30, 49-60, (1992) (with S. Cimmino and W. J. MacKnight) "Miscibility and Phase Behavior in Atactic Polystyrene and Poly (*o*-chlorostyrene-co-*p*-chlorostyrene) Blends: Effect of Polystyrene Molecular Weight and Copolymer Composition".

48. Polymer Bulletin, 27, 261-266 (1991) (with J.S. Rutt and Y. Takahashi) "Phase Behavior of Thermotropic Liquid Crystalline/Conducting Polymer Blends".

49. Macromolecules, 25, 192-194 (1992) (with P. Cifra and W. J. MacKnight) "Expansion of Polymer Coils in Miscible Polymer Blends of Asymmetric Composition".

50. Macromolecules, 25, 1057-1061 (1992) (with W. Huh) "Miscibility Behavior in Blends of Poly(acrylonitrile-*co*-butadiene) and Chlorinated Poly(vinyl chloride)".

51. Macromolecules, 25, 743-749 (1992) (with H. Mattoussi and S. O'Donohue) "Polyion Conformation and Second Virial Coefficient Dependencies on the Ionic Strength for Flexible Polyelectrolyte Solutions".

52. Macromolecules, 25, 1278-1283 (1992) (with C.T. Imrie and G.S. Attard) "Side-Chain Liquid-Crystalline Copolymers Containing Spacers of Differing Lengths".

53. Netsu Sokutei, 19 (1). 1-20 (1992) (with P. Cifra) "The Effect of Interactions in Polymer Blends Studied by Monte Carlo Simulations".

54. Phys. Rev. B., 45 (5). 2035-2045 (1992) (with D. Chen, M.J. Winokur, Y. Cao and A.J. Heeger) "Stage-1 Phases of Alkali Metal-Doped Conducting Polymers".

55. J. Polym. Sci.: Part B: Polymer Physics, 30, 465-476 (1992) (with K. Liang, J. Grebowicz, E. Valles, and W.J. MacKnight) "Thermal and Rheological Properties of Miscible Polyethersulfone/Polyimide Blends".

56. Integration of Fundamental Polymer Science and Technology-5, P.J. Lemstra and L.A. Kleintjens, Editors, Elsevier Pub. (1991) 3-11 (with W.J. MacKnight), "Phase-Behavior in Polymer Blends: The Effect of Microstructure".

57. Colloid & Polymer Science, 270. 113-127 (1992) (with B. Banhegyi, G. Marosi and G. Bertalan) "Studies of Thermally Stimulated Currents in Polypropylene/Calcium Carbonate/Surfactant Systems".

58. Frontiers of Polymer Research, (1991) 489-495 P.N. Prasad and J.K. Nigam, Eds., Plenum Press (with W.J. MacKnight and H.S. Kang) "Dynamic Mechanical and Dielectric Properties of Sulfonylated Poly(2,6-Dimethyl-1,4-Phenylene Oxide) Copolymers".

59. Macromolecules, 25. 2099-2106 (1992) (with J.H. Simpson and D.M. Rice) "Characterization of Chain Orientation in Drawn Poly(*p*-phenylene vinylene) by ^{2}H Quadrupole Echo NMR Spectroscopy".

60. Phys. Rev. A, 45, 5426-5446 (1992) (with I. Teraoka) "One-dimensional Diffusion with Stochastic Random Barriers".

61. Polymer Communications, 33, 1780-1782 (1992) (with W.B. Liang, D.M. Rice, F.R. Denton III and P.M. Lahti) "Preparation of Poly(*p*-phenylene vinylene) Deuterium Labelled in the Vinylene Positions".

62. J. Polym. Sci.: Part A: Polymer Chemistry, 30. 1227-1231 (1992) (with L. Litauszki, K. Grünberg, and W. Berger) "Thermal Behavior of Copolyimides Containing Bisbenzoylamine Groups".

63. Macromolecules, 25, 3068-3074 (1992) (with J.H. Simpson, W. Liang and D.M. Rice) "Solid-State ^{2}H Quadrupole Echo NMR Characterization of Vinylene-Deuterated Poly(*p*-phenylene vinylene) Films".

64. Chemical Processing of Advanced Materials, John Wiley & Sons, New York, 637-646 (1992) (with G.S. Attard and C.T. Imrie) "Multifunctional Polymers".

65. Chemical Processing of Advanced Materials, 647-662 (1992)John Wiley & Sons, New York, (with R.Ma.S. Gregorius) "Developments in the Synthesis of Polyarylene Vinylenes".

66. Macromolecules, 25, 4175-4181 (1992) (with Diane B. Scott, Alan J. Waddon, Je-Gang Lin and H. Henning Winter) "Shear-Induced Orientation Transitions in Triblock Copolymer of Styrene-Butadiene-Styrene with Cylindrical Domain Morphology"

67. Polym. Eng. and Sci., 32, 1047-1051 (1992) (with B. deJong, A.J. Waddon and W.J. MacKnight) "Blending of Poly(benzimidazole) (PBI) With a Low Molecular Weight Ether Imide Model Compound"

68. New Polymeric Materials, 3, 163-173 (1992) (with K. Jeremic and W.J. MacKnight) "Influence of Solvent and Temperature on the Phase Behavior of Polyarylsulfone/Polyimide Blends".

69. Polymer, 33, 3101-3107 (1992) (with W.B. Liang and M. A. Masse) "Highly Conductive Crystalline Poly(2-methoxy-*p*-phenylene vinylene)".

70. Polymer, 33, 3116-3122 (1992) (with D. Chen, M.J. Winokur and M.A. Masse) "A Structural Study of Poly(*p*-phenylene vinylene)".

71. J. Polym. Sci. A., Polym. Chem., 30, 2223-2231 (1992) (with F.R. Denton III and P.M. Lahti) "The Effect of Radical Trapping Reagents Upon Formation of Poly(α-Tetrahydrothiophenio *para*-xylylene) Polyelectrolytes by the Wessling Soluble Precursor Method".

72. J. Polym. Sci. A., Polym. Chem., 30, 2233-2240 (1992) (with F.R. Denton III, A. Sarker, P.M. Lahti and R.O. Garay) "*Para*-Xylylenes and Analogues by Base-Induced Elimination from 1,4-Bis-(Dialkylsulfoniomethyl)arene Salts in Poly(1,4-Arylene Vinylene) Synthesis by the Wessling Soluble Precursor Method".

73. Polymer, 33, 3388-3393 (1992) (with V. Janarthanan and W.J. MacKnight) "Miscibility in Polybenzimidazole/Polyimide Sulfone Blends: A Comparison of Blends Containing Fluorinated and Non-fluorinated Polyimide Sulphone".

74. Macromolecules, 25, 4716-4720 (1992) (with Z. Chai) "Miscibility in (A-B)/C-D) Copolymer Blends".

75. Polymer, 33, 3783-3789 (1992) (with A.J. Waddon) "Crystalline and Amorphous Morphologies of an Aromatic Polyimide Formed on Precipitation from Solution".

76. Phys. Rev. A, 46, 3335-3342 (1992) (with Y. Guo, S.J. O'Donohue, and K.H. Langley) "Polymer Diffusion in Porous Media of Fumed Silica Studied by Forced Rayleigh Scattering".

77. Macromolecules, 25, 4902-4904 (1992) (with Y. Guo and K.H. Langley) "Restricted Diffusion of Highly Dense Starburst-Dendritic Poly(amido amine) in Porous Glasses".

78. Macromolecules, 25, 4895-4901 (1992) (with P. Cifra and W.J. MacKnight) "Surface Segregation in Polymer Blends: A Monte Carlo Simulation".

79. MRS Proceedings Vol. 248, 477-482 (1992) (with H. Mattoussi and S. O'Donohue) "Static and Hydrodynamic Dimensions of Flexible Polyions in Solutions".

80. J. Serb. Chem. Soc. 57, 653-661 (1992) (with R. Stankovic and R.W. Lenz) "Electrical Conductivity of Doped Poly(Butadiene-co-2-vinyl Pyridine) Diblock Copolymers: Macrostructured Polymeric Semiconductors".

81. J. Polym. Sci. 30, 1401-1407 (1992) (with P. Cifra and W.J. MacKnight) "Polymer Miscibility in Capillaries".

82. Phys. Rev. B 46, 9320-9324 (1992) (with E.L. Frankevich, A.A. Lymarev, I. Sokolik, S. Blumstengel, R.H. Baughman and H. H. Hörhold) "Polaron-pair Generation in Poly(phenylene vinylenes)".

83. Polymers for Advanced Technologies, 3, 157-168 (1992) (with A. Nazemi, G. Williams and G.S. Attard) "The Alignment of LC Side-chain Polymers in Directing Electric Fields: Theory and Practice".

84. Macromolecules, 25, 6106-6112 (1992) (with I. Teraoka and K.H. Langley) "Reptation Dynamics of Semirigid Polymers in Porous Media".

85. Macromolecules, 25, 6113-6118 (1992) (with Z. Chai and R. Sun) "Miscibility in Blends of Copolymers: Sequence Distribution Effects".

86. Macromolecules, 25, 6664-6669 (1992) (with R. Gregorius and P.M. Lahti) "Preparation and Characterization of Poly(arylenevinylene) Copolymers and Their Blends".

87. Chemistry of Materials, 4. 1246-1253 (1992) (with G.S. Attard and C.T. Imrie) "Low Molar Mass Liquid-Crystalline Glasses: Preparation and Properties of the α-(4-Cyanobiphenyl-4′-oxy)-ω-(1-pyreniminebenzylidene-4′-oxy)alkanes".

88. Synthetic Metals, 53, 11-19 (1992) (with R. Gregorius) "Conduction in Poly(arylene vinylene) Copolymers and Blends".

89. Eur. Polym. J., 29, 159-162 (1993) (with R. Gregorius) "Orientation in Poly(Arylene Vinylene) Copolymers and Blends: An Infrared Dichroism Study".

90. Polymer Journal, 12, 1363-1369 (1992) (with Hiroyoshi Ueda) "Miscibility in Blends of Chlorinated Polyethylene and Chlorinated Poly(vinyl chloride)".

91. Polymer 34, 214-217 (1993) (with S. Cimmino, E.D. Pace, E. Martuscelli, C. Silvestre, D.M. Rice) "Miscibility of Syndiotactic Polystyrene/Poly(vinyl methyl ether) Blends".

92. Macromolecules, 26, 177-181 (1993) (with Antonin Sikora) "Solution-Phase Equilibria for Block Copolymers in Selective Solvents".

93. J. Chem. Phys. (with G. Mao, J.E. Fischer and M.J. Winokur) "Nonplanarity and Ring Torsion in Poly(*p*-phenylene vinylene): A Neutron-Diffraction Study" (in press).

94. J. Appl. Polym. Sci., (with S. Li) "Preparation and Characterization of Aromatic Polyimides and Related Copolymers"(in press).

95. Macromolecules, (with I. Teraoka and K.H. Langley) "Diffusion of Polystyrene in Controlled Pore Glasses: Transition from the Dilute to the Semidilute Regime" (in press).

96. J. Appl. Polym. Sci., (with N.S. Schneider and J.L. Illinger) "The Interaction of Water with Polyurethanes Containing Block Copolymer Soft Segments" (in press).

97. Macromolecules, (with C.T. Imrie, T. Schleeh and G.S. Attard) "Dependence of the Transitional Properties of Polystyrene-Based Side-Chain Liquid-Crystalline Polymers on the Chemical Nature of the Mesogenic Group" (in press).

98. Macromolecules, (with C.T. Imrie and G.S. Attard) "Comparison of the Mesogenic Properties of Monomeric, Dimeric, and Side-Chain Polymeric Liquid Crystals" (in press).

99. Polymer International, (with N. Segudovic, R. Vukovic, V. Kuresevic and W.J. MacKnight) "Solution Properties of Poly(fluorostyrene-*co*-chlorostyrene) Copolymers. I. Light Scattering, Differential Refractometry and Viscometry" (in press).