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Frank E. Karasz

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University of Massachusetts
Department of Polymer Science & Engineering
Amherst, MA 01003

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UNIVERSITY RESEARCH INITIATIVE

CENTER FOR ADVANCED ELECTRICAL AND STRUCTURAL POLYMERS

AFOSR/DARPA F49620-89-C-0027

1 November 1988 - 31 December 1989

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

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CONTENTS

I. TITLE

II. PRINCIPAL INVESTIGATOR

III. GRANT NUMBERS/DATES

IV. FACULTY ASSOCIATES AND SENIOR RESEARCH PERSONNEL - UMASS

V. JUNIOR RESEARCH PERSONNEL - UMASS

VI. EXTRA-MURAL SUBCONTRACTORS

VII. ABSTRACT OF ACCOMPLISHMENTS

VIII. DESCRIPTION OF RESEARCH UNDERTAKEN

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Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01003

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IV. FACULTY ASSOCIATES:
Professor K.H. Langley
Professor W.J. MacKnight
Professor E.L. Thomas (UMass/MIT)
Professor R.B. Hallock
Professor P. Lahti

SENIOR RESEARCH PERSONNEL:
Dr. Ray McCoy
Dr. Jeong Kim
Dr. Charles Dickinson
Dr. Wenbin Liang
Dr. Stephen O'Donohue
Dr. Pellegrino Musto
Dr. Phillipe Pradere (MIT)
Dr. Valerie Reid
Dr. Limeng Wu
Dr. Antonin Sikora
Dr. Gerard Smyth
Dr. Judit Simon
Dr. Hartmut Fischer
Dr. Robert Miller (WSU)
Dr. Jom Pin Chen (WSU)
Dr. Savithri Krishnamurthy (WSU)
Dr. David Rice

V. JUNIOR RESEARCH PERSONNEL:
J. Simpson
W. Nachlis
M. Lux
Y. Guo
R. Tomlinson (WSU)
J.D. Peak (WSU)
M. Carran (WSU)

Continued...

K. Paulvannan (WSU)
F. Denton
A. Sarker
S. Li
E. Douglas

VI. SUBCONTRACTORS:

Profs. J.J. Kane; W.A. Feld
Wright State University,
Dayton, Ohio (WSU)

Mr. R. Lusignea,
Foster-Miller, Inc.,
Waltham, MA

Prof. E.L. Thomas,
M. I. T.
Cambridge, MA

VII. ABSTRACT OF ACCOMPLISHMENTS

This report covers an additional thirteen months of research at the URI Center for Advanced Electrical and Structural Polymers at UMass. The research is organized into five main thrust areas and comprises collateral and coordinated investigators in three departments at UMass and at three sub-contractors. Electrical properties of polymeric materials are the focus of one thrust and continue to center on the prototypical conjugated system, poly-p-phenylene vinylene (PPV), and its analogs, derivatives, copolymers and blends. The electrical, structural, morphological, mechanical and processing properties of these materials have been investigated by advanced techniques including, for example, solid state NMR, specialized microscopies, X-ray diffraction, etc. Optical properties (which constitute a second URI thrust) of PPV and the related materials listed have focused on third order non-linear optical effects and on methodologies for increasing the desirable optical properties of these materials by processing and blending. New conjugated systems have been synthesized in systematic fashion to explore structive-property relationships, (WSU).

A central theme of the UMass URI has been the study of high temperature polymer blends and their ultrastructure. The systems studied have included polybenzmidazoles, polyimides, polysulphones and other high Tg or Tm macromolecules, in several combinations. The research has sought to understand on the one hand the basic principles of miscibility and structure-properties in these systems and on the other more application - processing protocols have been studied. Interaction with industrial researchers Celanese, GE, Lockheed has been an important component. Also included in the blend thrust are computer simulation calculations of multi-component systems, in which canonical Monte-Carlo simulation techniques have sought to calculate, without resort to mean field approximations, static and dynamic properties of representative systems. The fourth thrust has sought to elaborate on novel macromolecular architectures and characterization and includes, for example, studies of the block copolymer morphologies as a function of architectural parameters. New NMR techniques for studying interactions in blends have been developed as have new initiatives and analyses (Thomas, MIT). Forced Rayleigh light scattering techniques have been developed to study polymer diffusion in constrained media. The fifth thrust comprises new processing technologies and is largely centered on FMI investigations of PPV film processing optimization and on the difficult problem of larger scale processing of semi-intractable high temperature blends. [The AI vision/processing project, discussed in the previous report, has been deleted.]

As always, the five thrusts are dynamic and overlapping; some projects can be categorized by two or more thrust designations. During the year emphasis in several studies has invariably changed on the basis of results obtained to date and opportunities for productive new directions have been taken whenever appropriate. The URI program continues to play a major role in education and instrumentation at UMass and at the sub-contractual sites. At least thirty graduate students or post-doctoral fellows have received full or partial stipend support while a considerably greater number have had direct benefit by access to URI facilities and instrumentation.

VIII. DESCRIPTION OF RESEARCH UNDERTAKEN

1. INTRODUCTION

This report covers a thirteen month continuation URI program organized as The Center for Advanced Electrical and Structural Polymers at the University of Massachusetts and sub-contractual sites. At the end of the present reporting period this Center had been in operation for 36 months.

The organization of the URI is based on five research thrusts:

1. Electrical and Magnetic Properties of Polymers
2. Non-Linear Optical Properties of Polymers
3. Advanced Ultrastructural Polymers
4. Novel Macromolecular Architecture and Characterization

   and

5. New Processing Technology

It involves the interaction of the PI and Faculty Associates from several academic departments at UMass and from three extra-mural subcontractors.

In addition the Center has maintained a close interaction with numerous outside industrial/academic/government research sites. Those directly involved include Hoechst-Celanese, Lockheed, G.E., Wright-Patterson Materials Laboratory, and NASA Langley.

The educational object has been emphasized through the support of graduate students and post-doctoral fellows.

Instrument acquisition was largely completed during the first two years of the Center but some additional major facilities were acquired or constructed during the present reporting period. A forced Rayleigh light scattering facility may be mentioned in this context. Major cost sharing from the respective institutions has continued to raise the productivity of the Center.

Additional details of these features have been provided in earlier reports.

Productivity in terms of scientific manuscripts also continues to be high. Some <u>seventy-six</u> publications and one patent application have appeared or are in press as a result of complete or partial URI support during the reporting period.

2. ELECTRICAL AND MAGNETIC PROPERTIES OF POLYMERS

Numerous studies (see Publications) of PPV and related polymers have been carried out. An example is in processing which has been used to produce oriented films of poly(phenylene vinylene) by simultaneous thermal elimination and uniaxial stretching of the poly(sulfonium salt) precursor polymer. The method provides precise control over drawing conditions (temperature, draw ratio, etc.) allowing the preparation of high quality film with draw ratios up to twelve. The evolution of molecular orientation with increasing draw ratio has been examined using infrared dichroism and the results compared to theoretical predictions. The high efficiency of orientation allows the preparation of film processing nearly perfect uniaxial molecular orientation (orientation function ≥ 0.95). Chemical doping studies have been performed relating the electrical conductivity in both the machine and transverse directions to the draw ratio and degree of orientation. Conductivities, measured in the machine direction, up to 10^4 S/cm and electrical anisotropies up to 80 have been obtained.

The mechanical properties of uniaxially oriented poly(p-phenylene vinylene) film prepared by simultaneous thermal elimination and uniaxial extension of the poly(sulphonium salt) precursor have been measured both in the machine and transverse directions. The mechanical properties are anisotropic and dependent upon the degree of molecular orientation. Young's modulus varies between 2.3 and 37GPa as a function of draw ratio in the machine direction and between 2.3 and 0.5 GPa in the transverse direction. The effect of chemical doping on mechanical properties has also been determined. A comparison between mechanical and electrical anisotropy in oriented samples has been made.

Some studies of other conducting systems have also been made. Thus defined AB poly(butadiene-co_2-vinyl pyridine) block copolymers with different compositions were prepared by anionic polymerization reactions. The morphologies of solution cast films of these diblock copolymers were investigated with electron microscopy. Semiconducting materials with conductivities as high as 10^{-3} Scm^{-1} were obtained upon exposure of films of these block copolymers to iodine vapor. A specimen with lamellar morphology was subjected to solid state coextrusion at 150°C, and good orientation of lamellae was achieved, but this sample, upon exposure to iodine vapor, did not show electrical anisotropy.

3. NON LINEAR OPTICAL POLYMERS

Several studies of PPV and PPV analogs have shown the intensity non-linear optical behavior of these materials (with P. Prasad, SUNY Buffalo). Thus large linear refractive index birefringence, strong dichroic behavior, and highly anisotropic $\chi^{(3)}$ have been observed for a uniaxially oriented poly (2,5-dimethoxy paraphenylene vinylene) film. A subpicosecond time-resolved degenerate four-wave mixing study reveals an unusual behavior. Along the draw direction $\chi^{(3)}$ is complex with a negative real part and has a response time that is longer than the optical pulse resolution. In contrast, $\chi^{(3)}$ along the transverse direction is largely real and positive. Its response time is much faster, and is limited by the laser pulse width of ~400 fs.

Other optical properties are also of interest. We have reported the observation of a large birefringence in an as-cast unoriented film of poly-p-phenylene vinylene, a material which has a large third-order nonlinear optical susceptibility. A wave guide technique in TE and TM polarization are used to obtain in-plane and out-of-plane refractive indices at several wavelengths. At 633 nm the measured refractive index values are $n_{TE} = 2.085$, $n_{TM} = 1.612$. No dependence of the in-plane refractive index on the direction of film spreading is found indicating an in-plane isotropic behavior. No anomalous dispersion of refractive index is found in the wavelength range 633 nm to 1064 nm.

All these measurements are in the framework of a total approach by several techniques. For example coordinated study on electrochemical, magnetic, optical, and transport properties of poly(1,4-dimethoxy phenylene vinylene) (PDMPV) using *in situ* electrochemical doping techniques is presented. Properties are correlated through a common axis of applied voltage. Electrochemical doping shows ≈ 100% Coulombic efficiency up to an applied potential of 3.8 V versus lithium in propylene carbonate electrolyte. Conductivity increases in a reversible manner to a maximum of 250 Ω^{-1} cm $^{-1}$ and an applied potential of 3.9 V. Potentials in excess of 3.9 V cause an irreversible decrease in conductivity. Spin and charge show a 1:1 relation only to very low doping levels. Two paramagnetic species are produced on doping. A maximum spin concentration is observed at ≈ 3.7 V. The ultraviolet-visible-near-infrared spectra of doped PDMPV show at least five absorption bands, at 4.8, 3.7, 2.5, 1.7, and 0.6 eV. The first three bands decrease with doping and the latter two increase. When analyzed by the polaron or bipolaron model, the optical data imply significant symmetry breaking. Contributions to the optical activity from polarons and bipolarons are determined from the EPR results and are found to be different for both peaks, implying greater symmetry-breaking effects for polarons. An electrochemical analysis of EPR results suggests that polaron interaction energies are ≈0.45 eV greater than those for bipolarons.

4. ADVANCED ULTRASTRUCTURE POLYMERS

Blends (Karasz, MacKnight)

To elucidate the nature of the specific interactions occurring in polybenzimidazole (PBI)/polyimide (PI) miscible blends, an FTIR investigation on these polymers in the presence of low molecular weight monofunctional compounds was undertaken. In the case of PBI the probe compounds were proton accepting molecules (aliphatic ketones) able to form hydrogen bonding interactions with the polymeric substrate. In the case of the two investigated polyimides, poly[(2,2′-bis(3,4-dicarboxyphenoxy)phenyl propane)-2-phenylene bisimide] (Ultem 1000) and the condensation product of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BIDA) and 5(6)-amino-1-(4′-aminophenyl)-2,3,3′-trimethylindane (XU218), the carbonyl functional group in the probes was replaced by a hydroxyl group. This approach allowed us to conclude that in PBI/PI blend systems a hydrogen bonding interaction occurs between the polymeric components.

In addition, we have investigated related systems by high resolution NMR. Thus miscible blends of polybenzimidazole with an aromatic polyimide and a polyetherimide have been studied by high-resolution ^{13}C CPMAS NMR in the solid state. the observed resonance signals in the spectra of individual components of the blends have been assigned, and these assignments have been supported by interrupted decoupling experiments. The blending of PBI with polyimide induces a broadening and a downfield shift of the aromatic polyimide phthalimide carbonyl resonance with respect to that of the pure material. The difference between the spectra of the blends and those of the respective mechanical mixtures has been interpreted to be the result of the formation of specific hydrogen bonds between the PBI imidazole amine function and the polyimide phthalimide carbonyl function. Miscibility in the blend of PBI with the aromatic polyimide has also been confirmed by a study of the proton rotating frame spin-lattice relaxation behavior.

Similarly, NMR evidence has been obtained for miscibility on a molecular scale in blends of the poly(ether sulphone) (PES) and the polyimide (PI) XU 218 (the condensation product of 3,3′-4,4′-benzophenonetetracarboxylic dianhydride and 5(6)-amino-1-(4′aminophenyl)-1,3,3′-trimethylindan). Changes in the imide carbonyl line of the ^{13}C CP/MAS spectrum of XU 218 indicate an increase in polarity of the environment of this carbonyl which is the result of solvation of polyimide by the PES chain. The presence of XU 218 in a blend with PES results in a decrease in the value of $T^{H}_{1\rho}$ for the polyimide from 14.3 ms for the pure component to 7.1 ms for a 25/75wt% PES/PI blend. The $T^{H}_{1\rho}$ of pure PES is 4.5 ms. Log plots of the decay in the ^{13}C CP/MAS resonance intensity with contact time are linear. This relaxation behavior is consistent with miscibility in these blends with a domain size less than 20 Å.

Model systems have also been investigated. Thus phase behavior in blends of random copolymers of styrene and acrylonitrile with block copolymers of styrene and methyl methacrylate was studied by light scattering, light microscopy and glass transition temperature measurements. The results are compared with those of respective blends containing random copolymers of styrene and methyl methacrylate. In terms of macro-phase separation, the block copolymers display a more extended miscibility domain with styrene/acrylonitrile copolymers than the random copolymers. However, the extent of the miscibility domain varies as a function of temperature. Unlike the random copolymer blends, all blends containing block copolymers exhibit lower critical solution temperature behavior. Finally, it is established that the systems studied here undergo spinodal decomposition leading to macro-phase separation.

Computer simulation studies of multi-component systems have increased in this reporting period. For example, interactions in copolymer-homopolymer (A_xB_{1-x}/B) and copolymer-copolymer (A_xB_{1-x}/A_yB_{1-y}) mixtures containing equal amounts of the two respective components were studied as a function of the copolymer compositions x and $|x-y|$ respectively, and of segmental interaction energies using computer simulations of chains on a planar square lattice. The effective interaction parameter χ_{blend} for regimes corresponding to miscibility was less strongly dependent on x (or $|x-y|$) than predicted by the mean-field square power rule, and the number of heterocontacts varied widely from that calculated by random mixing. In the immiscibility regime the effective χ_{blend} becomes asymptotic as a result of phase separation.

Dynamic studies have also yielded information. Thus, isothermal demixing after an instantaneous quench to below the spinodal of a binary polymer mixture was studied using computer simulation methods. Short range fluctuations, corresponding to a large wavenumber ν, were followed during the demixing. The results obtained provide a useful supplement to those based on a linearized version of Cahn's theory of spinodal decomposition (SD). The latter theory applies to small ν regimes and to scattering experiments which cover a range of fluctuation wavelengths typically larger than the size of the polymer coils. However, fluctuations in wavelength on the order of the interaction range, i.e. the nearest neighbor distance in the mixture, are not adequately described by the linearized theory; deviations are observed at very early stages of phase decomposition. In this regime thermodynamic, rather than diffusional, factors are paramount. In the present study spinodal decomposition for mixtures on a three dimensional cubic lattice were simulated, and the corresponding kinetics were evaluated for a range of quench depths.

Another example is the study of equilibrium partitioning between bulk solution and pores by computer experiment using the Monte Carlo technique. In a multichain athermal system, self-avoiding walks of up to 60 steps were generated on a simple cubic lattice with variable pore size and chain concentration. The results demonstrate that the constraints imposed by the pores and/or neighboring chains reduce the chain entropy. The entropy related parameter, the partition coefficient K (the equilibrium pore-to-bulk concentration ratio) increases linearly with bulk concentration ϕ. A maximum concentration dependence of K was found for large pores characterized by a coil-to-pore dimension ratio λ of about 0.1-0.3. In this range the increase in bulk concentration brings about a dramatic enhancement of partitioning into pores. The results of computer experiments are compared with predictions of hard-sphere solutes theory and with static and gel-chromatographic measurements of the partitioning equilibrium. The implications of the concentration-dependent coefficient K for hindered transport of flexible polymers inside pores are briefly discussed.

5. NOVEL MACROMOLECULAR ARCHITECTURE AND CHARACTERIZATION

a. Diffusion (Karasz, Langley)

We continue to use novel instrumentation to study macromolecular dynamics. Thus, the diffusion of a flexible polymer (polystyrene) in fluid-filled pores of silica controlled pore glasses has been studied by using dynamic light scattering. Each measurement was carried out inside a single porous glass fragment that was immersed in a solution of polymer in a good solvent (2-fluorotoluene). Fickian diffusion was observed up to confinements as high as $\lambda_H=R_H/R_P = 1.4$, where R_H and R_P are the polymer and pore radius, respectively. The macroscopic diffusion coefficient D in the porous medium (measured on length scales compared to R_P) is found to decrease monotonically with increasing molecular weight and λ_H. At $\lambda_H < 0.3$, the diffusion coefficients are in good agreement with those predicted by the hydrodynamic theory for the hindered diffusion of a flexible macromolecule in cylindrical pores. At $0.2 < \lambda_H < 0.5$, D decreases approximately as M^{-1}, a result which is attributed to the hydrodynamic screening effect of the pore walls. At $\lambda_H > 0.6$, a stronger molecular weight dependence emerges, which is inconsistent with the "elongated cigar" model. At large values of λ_H, irregularities in local pore size lead to alterations in polymer conformation and hence changes in entropy as the chain moves. The experimental data agree qualitatively with predictions of the recent entropy barrier theory which is a scaling analysis of the diffusion hindrance based on entropy changes.

The same technique has been used for polymers of more complex architecture; the study of the macroscopic diffusion coefficient D_∞ (at low q) of linear, 4-arm star and 8-arm star polyisoprene in silica controlled pore glass, for values of the confinement parameter $\lambda_H = R_H/R_P < 0.1$, where R_H is the hydrodynamic radius of the polymer and R_P is the radius of the pores in the glass has been completed. The reduced diffusion in the pores is found to depend on the molecular architecture of the polymer. For a given λ_H. the branched polymers diffuse slower than the linear polymer; it is also found that 8-arm stars diffuse more slowly than 4-arm stars of the hydrodynamic radius. The results are compared to hydrodynamic theories for hard spheres in isolated cylindrical pores. Our results indicate that the hydrodynamic radius of a polymer derived from its diffusion coefficient in dilute unbounded solution does not uniquely describe the hydrodynamic effects of a constraining wall on its diffusion behavior. We also report measurements of the macroscopic diffusion D_∞ of strongly confined linear polystyrene chains with λ_H varies up to 0.74. Over the range of confinement investigated, an asymptotic region described by a power law relationship between D_∞ and molecular weight is not observed. Our data suggest that the presence of two length scales in the porous material could play an important role in the diffusion of strongly confined chains, in accordance with the theoretical model of Muthukumar and Baumgartner.

b. Structural Studies (Thomas, MIT)

Studies on the packing and organization of macromolecules at the molecular and supramolecular levels utilizing high resolution electron microscopy (HREM) and conventional TEM and small angle x-ray scattering techniques have provided considerable new information during the last year. Work has concentrated on kink band formation in rigid rod fibers poly(para phenylene benzobisthiazole) PBZT, and poly (para phenylene benzobisoxazole) PBZO as well as the appearance of the ordered bicontinuous double diamond structure in binary blends of diblock copolymers and homopolymer.

Structure-Property Relationships of Rigid Rod Fibers

The tensile strengths of fibers of the rigid-rod polymers poly(paraphenylene benzobisthiazole) (PBZT) and poly(paraphenylene benzobisoxazole) (PBZO) are excellent, and therefore make these materials of particular interest for high performance structural applications. However, the fibers are a factor of ten weaker in compression, with failure occurring by strain localization in well defined kink bands. We have studied the morphology of PBZT and PBZO kink bands in detail in order to help elucidate the molecular mechanisms involved in this deformation process. We find that the typical dimension of a kink in the direction of the fiber axis (~30nm) is smaller than the length of an average PBZT or PBZO molecule (100nm). Also, the boundary between the kink and unkinked regions is well-defined. Low dose, high resolution electron microscopy (HREM) of the kink interior reveals local, high angle changes in the chain orientation, indicative of covalent bond bending or breaking. A model for kink nucleation and propagation in terms of edge dislocations was developed. A stress analysis using this model suggests that kinks tend to propagate toward regions of higher compressive stress. This observation is interpreted in terms of dislocation pinning (in areas of hydrostatic tension) and the nucleation of dislocation pairs (in areas of hydrostatic compression) due to the asymmetric nature of the intermolecular energy potential.

The ultrastructure of PBZO fibers was studied as a function of processing condition by Wide Angle X-ray Scattering (WAXS), Selected Area Electron Diffraction (SAED), Dark Field Transmission Electron Microscopy (DF), and High Resolution Electron Microscopy (HREM). The development of single crystal texturing in thin films made it possible to index the PBZO scattering patterns to a non-primitive (N=2) monoclinic space group Pc (No. 7). The new unit cell parameters are a=1.120 nm, b=0.354 nm, c=1.205 nm, γ=101.3 degrees, with a crystal density of 1.66 gms/cm^3. Neighboring chains are placed at relative axial translations of +/- 1/4 c in the a-direction. HREM images of the 0.55 nm (200) and 0.35 nm (010) lateral spacings between PBZO molecules enabled the crystallite size, shape, and relative orientations to be directly determined. Defects within and between PBZO crystallites were observed, and molecular models presented which are consistent with these observations.

Structural Investigations of Block Copolymers and Block Copolymer/Homopolymer Blends

The goal this past year in this area was to establish if the ordered bicontinuous double diamond (OBDD) morphology occurred in binary blends of diblock copolymer and homopolymer. Our previous work showed the OBDD morphology occurred for composition windows of 28-33% and 62-66 volume % polystyrene (PS) in linear polystyrene/polyisoprene (PS/PI) diblock copolymers.

A systematic study of over 120 different blend compositions has indeed revealed that the OBDD morphology is present at approximately the same overall volume fractions (total polystyrene content in the blend) as occurs in the pure diblock materials. Moreover, the work showed for the first time how one can tailor the microdomain structure by blending in substantial amounts of low molecular weight homopolymer so as to alter the PS/PI interface curvature. We found that if the molecular weight of the homopolymer were less than or equal to that of the corresponding block of the diblock, the system had a large solubility of the homopolymer in the respective block microdomain and that the addition of the homopolymer could alter the interface area per junction which in turn caused changes in the length scale of the domains and interface curvature.

c. New Polymer Synthesis (Feld, Kane, WSU)

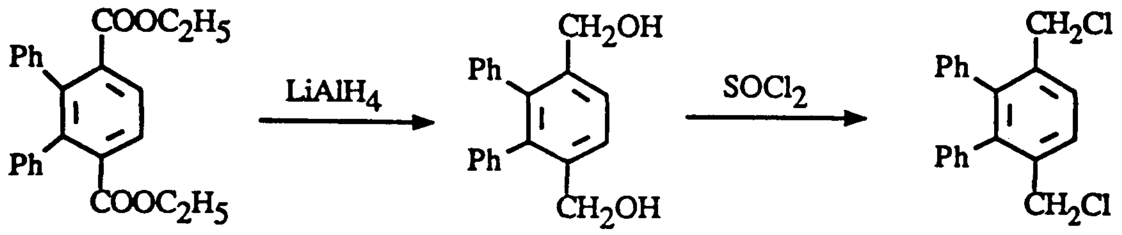
Phenylated Poly(Phenylene Vinylene)s

Highly conjugated polymeric systems represent important challenges to both synthetic and theoretical chemists because of the current interest in conductive polymers. Applications include semiconductors and photosensitive systems. The conjugated poly(xylylidenes) also known as the poly(phenylene vinylene)s (PPV)s (1), are highly fluorescent and have conductive potential. However, due to the limited solubility and molecular weight, most of these polymers are neither melt nor solution processible, an important consideration for the majority of potential commercial applications. In general, unmodified polymers of conjugated hydrocarbons are insulators or, at best, semiconductors, but they can be rendered electrically conductive by doping with suitable electron acceptors or donors, i.e., with oxidizing or reducing agents. PPV has been shown to display metal like conductivities after reaction with AsF_5.

The difficulty in attaining high molecular weights is common to all polymerization reactions which form conjugated polymers because of the potential premature precipitation of an insoluble, unsaturated, oligometic chain. This problem can be overcome by the synthesis of a soluble, polymeric precursor which can be cast into a film and subsequently converted by thermal or chemical means to the conjugated polymer.

Accordingly, the objectives of the poly(p-phenylene vinylene) research were to: (1) modify poly(p-phenylene vinylene) by adding pendent phenyl groups to increase organic solubility (see compound 2), (2) to synthesize the phenylated poly(p-phenylene vinylene) from soluble precursor film by the sulfonium salt method, (3) to study the effect of different counter ions in the polymerization, and (4) to study the effect of monomer/reagent concentrations on the course of the polymerization.

The synthesis of a phenylated phenylene vinylene monomer involved several steps. First, diethyl 2,3-diphenyl-1,4-benzenedicarboxylate (3) was reduced to the diol 3,6-bis(hydroxymethyl)-1,2-diphenylbenzene (4). Second, the diol 4 was converted to the dihalide 3,6-bis(chloromethyl)-1,2-diphenylbenzene (5). Third, the dihalide 5 was reacted with dimethyl sulfide to produce 2,3-diphenyl-p-xylenebis(dimethylsulfonium chloride) (6). All of the previously mentioned compounds were completely characterized and identified. Polymerization of 6 was carried out under a variety of conditions and resulted in the reproducible preparation of a tough, stable polyelectrolyte film (7). The conversion of the



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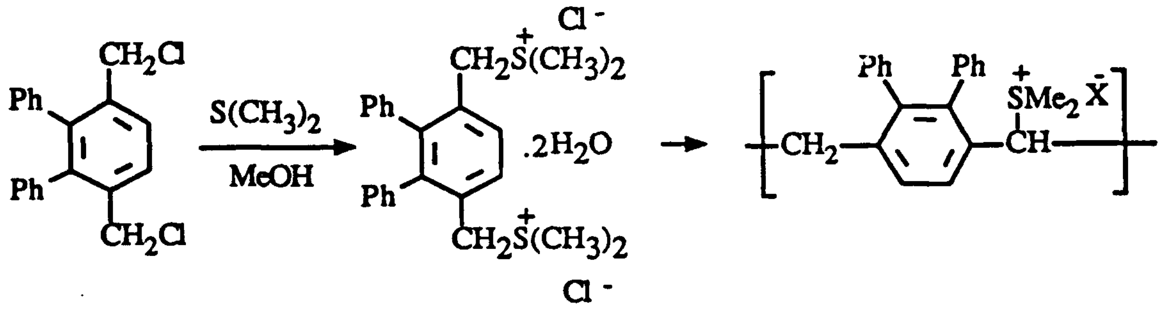

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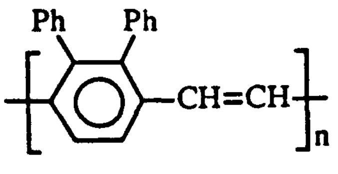

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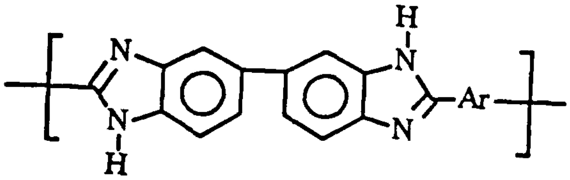
polyelectrolyte film to phenylated poly(phenylene vinylene)(PPPV) (2) was carried out with sodium hydroxide as the base. The PPPV is currently being characterized and the synthesis is being scaled up to provide additional material for NLO and electrical conductivity measurements.

Poly(benzimidazole) Synthesis (Kane)

Polybenzimidazole (8) (PBI) is a general name for polymers that contain the benzimidazole ring system in their backbone. This ring system gives rise to the polymer's retention of oxidative stability a temperatures up to 200°C beyond that of most common polymers. They also have the excellent resistance to hydrolytic attack in an acidic or basic environment. Adhesives and laminating resins based on polybenzimidazoles have high strength at elevated temperatures without the need for crosslinking. The absence of crosslinking contributes to the resistance to brittle failures by crack propagation. Since these polymers have glass transition temperatures greater than 400°C, only their thermal and oxidative stabilities permit reaching temperatures at which their thermoplastic behavior can be observed. These properties make polybenzimidazoles especially suitable for



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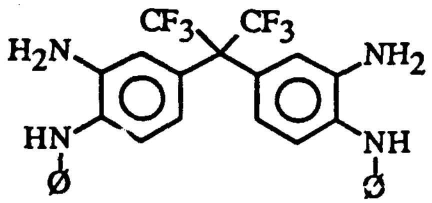
application in the aerospace field.

The goal of the present study was to assess the utility of PPSE (polyphosphoric acid trimethylsilyl ester) in the synthesis of N-phenyl polybenzimidazoles and to compare the yields and properties of these PBIs to those of the same polymers prepared by modification of a known two-step process. The tetraamine chosen for study was 2,2-bis(3-amino-4-anilinophenyl)-1,1,1,3,3,3-hexafluoropropane (9) which would not produce a rigid-rod system but would allow the determination of optimum polycondensation conditions.

The synthesis of the t-boc protected tetraamine 2,2 bis(3-t-butoxycarbonylamino-4-anilinophenyl)-1,1,13,3,3-hexafluropropane (10) was carried out in order to stabilize the amino groups of the parent compound 9. The utility of the t-boc group is that it can be quantitatively cleaved either thermally or with acid catalysis to yield the free amine. the by-products, gaseous butene and carbon dioxide are essentially unreactive. An efficient cleavage of the t-boc protecting group was developed to prevent any intramolecular reactions between the protected amino group and the anilino group. The model compound 2,2-bis(1,2-diphenylbenzimidazole-5yl)-1,1,1,3,3,3-hexafluoropropane (11) was prepared by the reaction of 10 with benzoic acid or by a two-step procedure that included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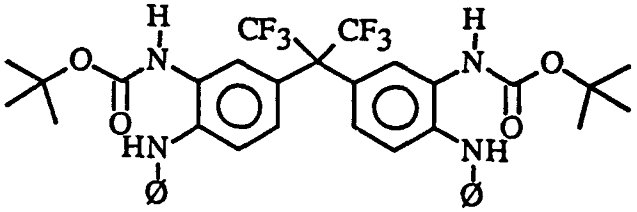
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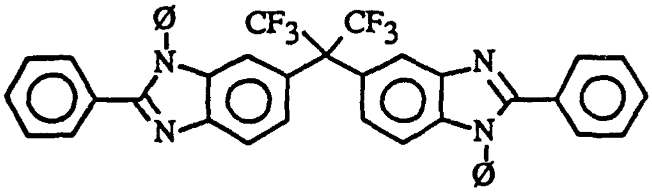
the reaction of freshly deprotected diamine 9 and benzoyl chloride followed by cyclization of the amide 11 in PPA.



11

Several factors may affect the one-step polymerization reaction, one of which is the decomposition of the tetraamine monomer by the acid formed from the hydrolysis of PPSE.

The two-step polybenzimidazole polycondensation procedure was improved by low temperature polyamide formation using lithium hydride to neutralize the hydrogen chloride by-product. Benzimidazole ring closure by dehydration in PPA gave the final product.

2. NEW PROCESSING TECHNOLOGY

Nonlinear Optical Polymers: Synthesis, Processing, and Characterization (FMI)

Certain conjugated rigid rod polymers possess interesting nonlinear optical properties. To date there exist several of these polymers. At Foster-Miller, in collaboration with the University of Massachusetts - Amherst and the State University of New York - Buffalo, we have investigated poly (p-phenylenebenzobisoxazole [PBO]), poly (p-phenylene vinylene[PPV]) and poly (dimethoxy-p-phenylene vinylene [DMPPV]), and a new class of NLO active polyimides. The overall goal of our efforts is to develop the requisite processing techniques to produce polymer films with high $\chi^{(3)}$ and low absorptive losses. The target value for many nonlinear optical applications is $\chi^{(3)}/\alpha = 10^{-7}$ esu-cm. The techniques employed at Foster-Miller, Inc. include derivatization of main chain polymers with NLO pendant groups, modification of NLO active mainchain polymers with electron releasing groups, and the synthesis of NLO active kinked semi-conjugated polymers.

Our research has established that modification of the polymer backbone in PPV with an electron donating group (such as methoxy) increases the π electron density along the polymer backbond. Upon orientation the value of $\chi^{(3)}$ parallel to the orientation direction is 2.4×10^{9} esu. This is six times greater than the value in highly oriented PPV. Additional research has resulted in the synthesis of new NLO active polyimides having values of $\chi^{(3)}$ exceeding 10^{-11} esu and low optical losses. These tailored NLO active polyimides represent a tenfold increase in NLO activity over LARC-TPI, a polyimide of moderate NLO activity. The detailed characterization of the linear optical properties of these new materials is in progress, as well as efforts to further enhance the NLO activity. Finally we have synthesized an NLO active vinyl substituted thiophene benzobisthiazole compound and work is in progress on its copolymerization with styrene monomer. The resulting mainchain polymer with NLO active pendants will be characterized for its NLO and linear optical properties.

Processing and Orientation of Plasticized Polyaniline Films

The mechanical and electrical properties of polyaniline films are strongly dependent on factors such as molecular weight and orientation of the material. In a collaborative effort with the University of Pennsylvania and The Ohio State University (ONR/DARPA URI), films of the emeraldine base form containing ~15% (wt.) of NMP plasticizer can be uniaxially drawn (4:1) and also biaxially (2:1) in orthogonal directions at 140°C. The tensile strength of the uniaxially drawn film was 145 MPa, the biaxially drawn film was 130 MPa, while that of the undrawn film was 60 MPa. Upon doping the 4:1 drawn film with 1M HCl the DC electrical conductivity was 50 S/cm and and the anisotropy in the conductivity was 10. X-ray diffraction of the 4:1 drawn films indicated a substantial increase in the molecular order of the polymer.

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Publications 48-76 are with the P.I. as author or co-author.

PATENTS: Applications, U.S. and Foreign

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