Title: Multi-Functional Pi-Conjugated Macromolecules Based on Poly(Phenylene Vinylene)

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Abstract:
This report, for the period 15 Mar 93 TO 14 Mar 94 and covers all AFOSR supported research under the P.I.'s direction. The principal thrusts of the research are in four relatively disparate areas related only by a polymeric theme: conjugated macromolecules; thermodynamics of inorganic-organic block copolymers; hyper-branched (dendritic) macromolecules; theoretical dielectric strength of polymers. However, because the present grant was the successor to a series of more widely focused AFOSR funding periods the opportunity was taken to complete numerous projects which originated earlier. As a result some forty-six AFOSR-supported manuscripts were published or were in press during the grant period. The focus of attention with respect to conjugated macromolecules was their electroluminescent (EL) properties. The fact that poly-p-phenylene vinylene (PPV) displayed EL has been known since 1992, and in the present work, based on many years of AFOSR-supported PPV research, derivatives of PPV were synthesized and characterized in terms of their electro-optical properties. In particular a series of conjugated-nonconjugated multi-block copolymers with extremely promising EL properties were studied and EL devices constructed. In these materials the "hard" blocks were short, monodisperse, phenylene vinylene...
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oligomers, or derivatives thereof, while the "soft" block were oligomethylene spacer units designed to impart solubility and film formation to the materials. By varying the nature of the "hard" block EL emission throughout the visible spectral range was achieved.
TECHNICAL REPORT

MULTI-FUNCTIONAL $\pi$-CONJUGATED MACROMOLECULES BASED ON POLY(PHENYLENE VINYLENE)

DIELECTRIC STRENGTHS/DENDRITIC POLYMERS

GRANT AFOSR F49620-93-1-0178

March 15, 1993 - March 14, 1994

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ACKNOWLEDGEMENT

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CONTENTS

I. TITLE
II. PRINCIPAL INVESTIGATOR
III. GRANT NUMBERS/DATES
IV. SENIOR RESEARCH PERSONNEL
V. JUNIOR RESEARCH PERSONNEL
VI. ABSTRACT OF ACCOMPLISHMENTS
VII. DESCRIPTION OF RESEARCH UNDERTAKEN
VIII. PUBLICATIONS
I. TITLE: (1) Multi-Functional π-Conjugated Macromolecules Based on Poly(Phenylene Vinylene) (2) Dielectric Strengths/Dendritic Polymers

II. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz
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March 15, 1993 - March 14, 1994

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VI. ABSTRACT OF ACCOMPLISHMENTS

This report is for the period 15 March 1993 - 14 March 1994 and covers all AFOSR supported research under the P.I.’s direction. The principal thrusts of the research are in four relatively disparate areas related only by a polymeric theme: \( \pi \)-conjugated macromolecules; thermodynamics of inorganic-organic block copolymers; hyper-branched (dendritic) macromolecules; theoretical dielectric strength of polymers. However, because the present grant was the successor to a series of more widely focused AFOSR funding periods the opportunity was taken to complete numerous projects which originated earlier. As a result some forty-six AFOSR-supported manuscripts were published or were in press during the grant period.

The focus of attention with respect to \( \pi \)-conjugated macromolecules was their electroluminescent (EL) properties. The fact that poly-\( p \)-phenylene vinylene (PPV) displayed EL has been known since 1992, and in the present work, based on many years of AFOSR-supported PPV research, derivatives of PPV were synthesized and characterized in terms of their electro-optical properties. In particular a series of conjugated-nonconjugated multi-block copolymers with extremely promising EL properties were studied and EL devices constructed. In these materials the "hard" blocks were short, monodisperse, phenylene vinylene oligomers, or derivatives thereof, while the "soft" block were oligomethylene spacer units designed to impart solubility and film formation to the materials. By varying the nature of the "hard" block EL emission throughout the visible spectral range was achieved.

Inorganic-organic di-block copolymers were designed in which the inorganic
elements were silicon based Si(OR)$_2$O units while the organic block consists of oligomeric -Si(CH$_3$)$_2$O-. The general theory for microphase separation of the diblock polymer with a second homopolymeric component of dimethyl siloxane, ie in an A-bl-B/B system has been treated by us and has become available to analyze this system with minor modification.

Substantial progress has been achieved in synthesizing hyperbranched (dendritic) polymers of high molecular weight. After some initial exploratory work the system finally chosen is a polyarylester made in gram quantity by a novel suspension polymerization route. These polymers have been converted by graft polymerization into a series of stable copolymer micelles with a wide range of properties.

Finally, in the fourth project, a theory of Zener tunneling has been applied to linear chain polymers to derive a new theory of intrinsic dielectric strength. In essence, a uniform and static electric field is applied in the direction of the chain extension. Thus the wavefunctions are deformed and a transition of the electrons in the valence bands to the conduction bands is seen. The transition takes place in the absence of charged impurities at absolute zero, and therefore such Zener tunneling is related directly to the inherent breakdown strength of materials of periodic structure. We have combined this Zener tunneling treatment with LCAO theory to derive the transition probabilities of polymers in fully extended conformations. Calculations have been performed for real systems such as polyethylene, polyvinylfluoride, polyvinylidenefluoride, and polytetrafluoroethylene.
In addition work has been completed in a variety of other AFOSR projects from previous grant periods as already stated. These include studies of a) polymer diffusion in confined geometries, b) halogenated polymer blends, c) side chain liquid crystalline polymers, d) novel polyimide systems, e) Monte Carlo simulations of polymer blends, f) solid state properties (other than electro-luminescent) of conjugated chain polymers, g) copolymer-copolymer miscibility and h) 2-D NMR studies of polymer blends. Further details can be obtained from the publications listed in Section VIII.
VII. DESCRIPTION OF RESEARCH UNDERTAKEN

A. \(\pi\)-Conjugated Macromolecules

A strong effort has been made in the area of electro-luminescent polymers. A number of polymer light-emitting diode (LED) devices have been constructed by us using a variety of conjugated polymers, using poly(\(p\)-phenylene vinylene) (PPV). LED devices have also been made using low molar mass molecules dispersed or dissolved in an inert polymeric matrix. We have reported on a series of conjugated-nonconjugated (CNCPs) containing multiple uniformly alternating conjugated rigid and nonconjugated flexible blocks which exhibit blue electroluminescence with a spectral maximum at 465 nm. and at longer wavelengths. It may be noted that CNCPs have unique advantages in that the conjugated rigid blocks may be of specified and uniform conjugation length, factors which are crucial for tailoring the electronic transition band gap which in turn determines the spectral properties of the light-emitting chromophore. The flexible blocks, on the other hand, contribute to the solubility and the film forming properties of the system. The advantage of the block copolymer structure over blends of small molecules in an inert polymeric matrix is that it is necessarily homogeneous (on a nanometer scale) and obviates the problem of recrystallization or elution of the small molecules in the matrix. We also predicted that a judicious modification of the molecular structure in the conjugated blocks of the copolymers provides convenient color tuning in the polymer LED without drastic change of the other properties. We
demonstrated for example that changing the aromatic ring structure in the conjugated blocks of a given CNCP causes band-gap shifts in which light emission changed from blue to yellow. We also showed that simply extending the conjugation length in the conjugated block of a previously described copolymer yields a copolymer with a red-shifted UV absorption, photoluminescent (PL) and electroluminescent spectra. Thus a new copolymer (with 3.5 PV units) emits green light with maximum intensity at 513 nm. It was synthesized using a Wittig reaction and characterized with elemental analysis, FTIR, NMR, GPC, UV, photoluminescent spectroscopy and DSC. The high solubility and excellent film forming properties of the copolymer enabled us to readily fabricate LED devices. The emission brightness of the resulting device permitted direct observation in a brightly lit room. Other systems, and blends with improved properties, have also been constructed and studied.

B. Thermodynamics of Inorganic-organic Block Copolymers

In this component of the overall project we have concentrated an synthesizing an inorganic-organic diblock copolymer based respectively on -[SiO(OR)₂]ₙ and [Si(CH₃)₂-O]ₙ blocks. This requires an anionic polymerization strategy and an optimization of reaction conditions to minimize hydrolysis of the Si-OR bond. This has proved difficult in practice and further studies to improve structural homogeneity are underway.

The theory applicable to this system has been completed. We have employed a model in which an homopolymer is allowed to interact with a block
copolymer, and with micelles of the block copolymer, and thereby profoundly affects the order-disorder transition of the latter. The phase complexities of this system (for example as in the well-studied styrene-bl-butadiene/polystyrene system) make this a rich source of morphological variants.

C. Hyperbranched (Dendritic) Polymers

In the initial proposal poly(amidoamine) dendrimers were selected as initial candidates for blend and other studies because of their availability and partial characterization. It was already recognized at an early stage that PAMAM polymer suffered from poor thermal and chemical stability which would make solid state studies difficult. In fact PAMAM polymers proved to be inaccessible in gram quantities and the focus of the project was change to a more robust chemical structure of polyaryl esters which could be made in relatively large quantity. A novel suspension polymerization of HO.Ø(COOH)$_2$ with (CH$_3$CO)$_2$O produced -AB$_2$- units which would further react to form multi-generation dendrimers in a "one-pot" reaction scheme. The resulting polyarylester can be regarded as a high density spherical structure with -COOH surface groups. These surface groups are susceptible to further reaction and can be capped or grafted with ester, ether, amine, linkages to produce a wide range of materials. We have shown that, for example, the Tg of the modified dendrimers can be varied from 150°C to -50°C by grafting. At the same time the miscibility of the systems can be varied over a wide range
of polarities. Work is under way to fractionate the polyarylesters for subsequent detailed characterization.

D. Intrinsic Dielectric Strength of Polymers

Electrical breakdown, its phenomenological aspects as well as mechanism, of insulators, has been studied for decades. Many of the studies have been performed for polymers, as they provide a breakdown strength far larger than other insulators such as gases, liquids, and ceramics. The mechanism have been classified into the following three categories: 1) electronic breakdown in which kinetic energy gained by a charged carrier between collisions against lattice exceeds the energy gained by a charged carrier between collisions with the lattice exceeds the energy lost by the collision, the energy equilibrium collapses, leading to catastrophic breakdown. 2) mechanical breakdown in which the electric force between two electrodes exceeds the mechanical force against compression, the insulator yields, and 3) thermal breakdown produced by dc conduction or by dielectric loss (in case of ac field) exceeds the loss of energy by thermal conduction and radiation.

The first mechanism assumes that there are charged carriers already present in the insulator. They are supplied by impurities in the system generated by thermal excitation or radiation. At absolute zero of temperature in the absence of radiation, there are no carriers in the insulator, if there are no impurities. The third mechanism does not contribute to the breakdown either when a dc field is applied to an insulator free of charged impurities. In
the absence of defects or stress concentration, the breakdown field by the second mechanism is given by \( E_M \approx 0.6 \sqrt{G_E/\varepsilon_0\varepsilon_r} \), where \( G_E \) is the elastic modulus, \( \varepsilon_0 \) is the vacuum permittivity, and \( \varepsilon_r \) is the dielectric constant of the polymer. A modest estimate for extended polyethylene gives \( E_M \approx 20 \) GV/m. This value is much larger than the breakdown field for the mechanism we consider in this research. Zener breakdown which takes place when an electron in the valence band is excited into the conduction band simply by an electric force acting on the electron. The tunneling by dc field excitation does not assume any inherent charged carriers in the conduction bands or in the midgap states. Zener breakdown is therefore regarded as the ultimate mechanism for electric breakdown in the absence of charged carriers or radiation. Once the electrons are excited through this mechanism, it may lead to breakdown through other mechanisms such as electronic breakdown. The formulation has been extended to include time-dependent but uniform electric field. In recent years, there has been controversy regarding the legitimacy of the formulations. Estimation of tunneling probabilities in real systems based on this formulation have not been verified partly because real insulators break down at lower fields (~ a few hundred MV/m, at best) through the mechanism mentioned earlier.

In the present work Zener tunneling probabilities in linear chain polymers, when a dc field is applied parallel to the chain backbone have been calculated. We study how the difference in the atomic sequence in the unit cell
of infinitely extended linear chain polymer (perfect lattice) affects the tunneling. Zener breakdown in the direction perpendicular to the backbone does not involve the lattice periodicity, and hence is equivalent to the breakdown of small molecules. We have summarized the formulation of the tunneling probabilities of electrons from the valence band to the conduction band and have applied the molecular orbital theory in linear combination of atomic orbitals (LCAO) formulation to the Zener tunneling of a linear chain polymer. Using this result, we can estimate the inter-band transition probabilities in polymer systems. We have made quantum mechanical calculations using MOPAC version 6.0, in its approximation, i.e. MNDO, modified to yield physical quantities necessary to calculate the transition probabilities. We apply the modified MOPAC to polyethylene, polyvinylfluoride, polyvinylidenefluoride, and polytetrafluoroethylene in all-trans configuration. Although MOPAC is not necessarily superior to other packages, availability of the source codes is the primary reason for its choice. Modified MOPAC can predict the relative magnitude of the transition probabilities for different polymer chains.
VIII. PUBLICATIONS IN PERIOD WITH AFOSR SUPPORT


36. ACS Symposium: Polymers of Biological and Biomedical Significance 102-115 (1993) (with N.S. Schneider and J.L. Illinger) "Interaction of Water with Polyurethanes Containing Hydrophilic Block Copolymer Soft Segments".


42. Macromol. Symp. (with Said Djadoun and F. Matref) "Miscibility of Poly(butyl methacrylate-co-methacrylic Acid) or Poly(styrene-co-4-vinylpyridine) or Poly(butyl methacrylate-co-4-vinylpyridine)" (in press).


44. Macromolecules, **27**, 2211-2218 (1994) (with S. Li and D.M. Rice) "Two-Dimensional NMR Characterization of Short-Range Order in a Miscible Blend of Polystyrene and Poly(2,6-dimethyl-p-phenylene oxide)" (in press).

46. Polymer, (with P.M. Lahti, A. Sarker, R.O. Garay and R.W. Lenz) "Polymerization of 1,4-bis(tetrahydrothiopheniomethyl)-2-cyano-5-methoxybenzene Dibromide: Synthesis of Electronically 'push-pull' Substituted Poly(p-phenylene vinylene)s" (in press).