

Research News

Highly Conjugated Ionic Polyacetylenes: Thin-Film Processing and Potential Applications**

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1. Introduction

Polyacetylene (PA), structurally the simplest conjugated polymer, is endowed with one of the highest known delocalized π -electron densities. As a result of its unique backbone structure, very high values of third-order non-linear polarization susceptibility and conductivity (up to 10^3 S/cm) have been reported.^[1] Unfortunately, applications of this promising material have remained limited because the polymer is insoluble, infusible, and electrically unstable. The electrical instability is dramatic in that conductivity of p-doped PAs can fall several orders of magnitude within a few days, while the n-doped PA can revert to insulating levels within minutes upon exposure to air. This instability is due to easy access of chemical agents such as oxygen to reactive sites along the highly conjugated unsubstituted backbone. Attempts to overcome these limitations for eventual device fabrication have included the synthesis of blends of PA that exhibit elastic or plastic properties,^[2,3] and optimization of the thin-film morphology.^[4] Although mechanical properties of PAs could indeed be improved with these techniques, little progress was made towards improving the electrical stability.

Research then turned more towards modification of the actual chemical structure of PA through alkyl or phenyl substitution. Such substitution considerably enhances both the stability and processability of the PA films, but at the same time facilitates the formation of conformers in which

the double bonds are forced out of their planar trans arrangement because of steric repulsive effects between substituents. Thus the π -electron orbital overlap is decreased with concomitant reduction in optical nonlinearity and electrical conductivity.^[5] The overall extent of conjugation in such PAs is small, with a conjugation length rarely exceeding three monomer units.^[5] The values of conductivity obtained rank below those expected of polymeric conductors and semiconductors.

We have recently reported the synthesis and properties of a new family of mono- and di-substituted polyacetylenes that retain extensive conjugation.^[6-11] This conjugation is achieved by introducing one or two ionic charges into each repeat unit, thus endowing such PA polymers with one of the highest charge densities known. The electrostatic repulsion between segments favors backbones with extended conformations and hence conjugation lengths (often in excess of 10) are substantially higher than those of non-charged substituted PAs. In addition, this family of PAs offers unsurpassed tunability by simply changing the chemistry of the monomer, the nature of the quaternizing agent, and the type of the counterion used.^[6] An example based on the 2-pyridinium substituent is given in Figure 1. A wide spectrum of solubilities is possible, ranging from water to non-polar solvents. Amphiphilic systems are obtained when R is a long alkyl chain or with block copolymers incorporating an ionic PA and a hydrophobic block.

Mesogenic moieties can also be incorporated into the structure to bolster the liquid-crystalline and film-forming

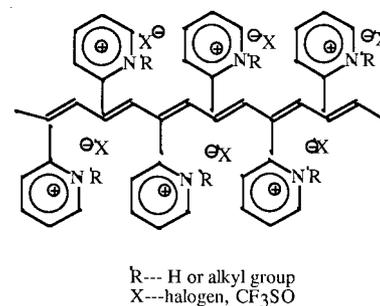


Fig. 1. Molecular structure of ionic polyacetylenes (IPAs) based on 2-ethylpyridinium substituents.

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properties of various ionic polyacetylenes (IPAs). Such an approach was attempted and led to films with a smectic organization.^[12]

2. Amphiphilic Systems

2.1. Long-Chain Derivatives

Polymer thin film architectures that combine extended molecular conjugation and two-dimensionality on a nanoscale are desirable for many optical and electronic applications.

Molecular films of conjugated IPAs can be obtained easily by using either amphiphilic acetylenic monomers polymerized in situ within the monolayer or amphiphilic polyacetylenes. The literature lacks examples of such monomeric films polymerized in situ, but examples of films of poly(*N*-octadecyl-2-ethynylpyridinium) salts have recently been studied in our laboratory.^[9,13] In the case of poly(*N*-octadecyl-2-ethynylpyridiniumyl bromide) (P2EPY/ODBr), very stable Langmuir monolayers were obtained at the air/water interface.^[9,13] The surface pressure–molecular area isotherms of these monolayers indicated that the long alkyl chains are oriented perpendicularly to the interface, while the rigid, conjugated polymer backbone is contained within the planar layer of the interface. Facile, Y-type multilayer Langmuir–Blodgett (LB) deposition was carried out on quartz substrates. Stable films containing $n = 60$ interdigitated double layers were transferred without significant deviations in the spectral absorption from linearity. In addition, the UV-vis spectra of LB multilayers displayed an absorption trailing out to 800 nm, which is indicative of increased conjugation induced by enhanced order in the LB film.^[9,13] We used Fourier transform infrared spectroscopy (FTIR), attenuated total reflection (ATR), grazing angle reflection (GAR), and ellipsometry measurements to characterize the molecular organization of these multilayer assemblies. It was determined that the polymer chains are oriented parallel to the substrate and are sandwiched between layers of interdigitated octadecyl groups.^[13] This is shown in Figure 2.

Layer-by-layer electrostatic treatment, involving alternate deposition of polycations and polyanions onto charged

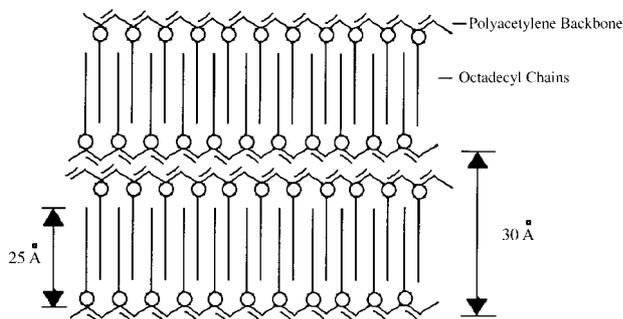


Fig. 2. Schematic representation of the interdigitated molecular structure of poly(*N*-octadecyl-2-ethynylpyridiniumyl bromide)

surfaces, is shown schematically in Figure 3. It was first reported by Decher et al.^[14] This technique, owing to its simplicity, has recently been expanded to a large number of polyelectrolytes with interesting opto-electronic properties for application in thin-film devices such as light-emitting devices and memory elements.^[15]

Given the ionic nature of these new polyacetylenic materials, it seemed reasonable to attempt to extend this simple

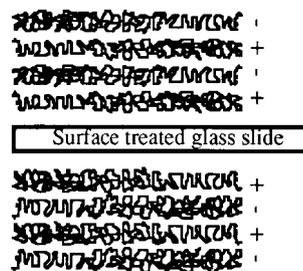


Fig. 3. Schematic layer-by-layer electrostatic deposition of polyelectrolytes.

processing technique to these systems. It was determined that the layer-by-layer self-assembly technique using poly(styrene sulfonate) as the polyanion led initially to similarly structured multilayers to those observed using the LB technique. But, in contrast to the uniformity of the LB multilayers, as observed spectroscopically, deterioration begins to occur after only $n = 10$ – 12 layers.

The conductivity of IPA films was found to increase substantially upon doping with iodine and the films exhibited good gas permeability and permselectivity to oxygen when deposited on Nafion membranes.^[13] However, despite these promising properties, both the LB and layer-by-layer films were found to be somewhat brittle, thus complicating the study of their mechanical properties and limiting their potential applications. This difficulty was addressed by improving their mechanical integrity through the formation of block copolymers, composites, and blends.

2.2. Block Copolymers

Block copolymers of ionic polyacetylenes with styrene (PS) and butadiene (PB) were synthesized in our laboratory by anionic initiation.^[16,17] These contained short sequences of four to eight acetylenic units attached to longer PS and PB blocks. Stable monolayers of these amphiphilic block copolymers were easily formed at the air–water interface. The pressure–area isotherms were characterized by steep slopes and high collapse pressures (50 mN/m). The isotherms and effects of pH and temperature change on the monolayer indicated that a layer of rigid, charged, and slightly disordered IPA sequences are submerged in the water subphase, while chains of the more hydrophobic PS or PB sequences are condensed and forced out of the water upon compression. LB deposition was carried out again and much more flexible multilayers were transferred onto various substrates for characterization. The molecular organization of the LB films reflects the organization of the

monolayers observed at the air–water interface: a double layer of disordered, ionic PA, followed by a layer of intermingled PS or PB chains. It was found that stable films of PS-PA copolymers with controlled thickness could be easily self-assembled onto various substrates using either the LB or layer-by-layer method. Interestingly, the presence of a counter polyanion layer was not necessary, as the amphiphilic nature of the bisequential copolymer provided the necessary cohesion between the layers and layer-by-layer assembly could be achieved simply by multiple dipping into the same solution of the block copolymers. Copolymers with a large sequence length mismatch, for example, IPA8/PS57, gave less uniform films than those with a better match, for example, IPA8/PS12.^[16,17]

3. Composites and Blends

3.1. Composites

Stable films of composites and blends of IPAs displayed improved mechanical properties, even with a very high (over 90 wt.-%) IPA component. Thus, stable films of interpenetrating networks of crosslinked poly(*N*-butyl-2-ethynylpyridiniumyl bromide) (PB2EPB) and poly(carbonate urethane) (PCU) were easily obtained^[18].

These films, while retaining a high degree of conjugation, displayed improved mechanical properties, solvent resistance, and thermal stability over the corresponding pure IPA. Electrical conductivities in the semiconducting range of the order of 10^{-4} S/cm were recorded after iodine doping.^[18]

Films of composites of the monomer 2EPY polymerized within a Nafion matrix displayed an increase in permselectivity with respect to oxygen and an excellent temporal stability of the permeation coefficients.^[19] LB films of amphiphilic IPA deposited on Nafion significantly enhanced both the permeability and permselectivity towards oxygen of the substrate itself, while maintaining a high degree of stability.^[13]

3.2. Blends

Films of blends of various IPAs and poly(vinylpyrrolidone) (PVP) displayed improved mechanical properties even at very small PVP content, at which concentration the conductive properties of doped IPA were not significantly altered. The mechanism of conduction in IPA is complex, with a strong component of ionic conductivity. Values between 10^{-2} and 10^{-3} S/cm were reached for films of poly(*N*-methyl-4-ethynylpyridiniumyl iodide) and disubstituted poly(1,2-bis(*N*-methyl-4-ethynylpyridiniumyl iodide)) with various dopants.^[20,21]

4. Conclusion

We have briefly described some of the features of films obtained from ionic polyacetylenes. By building the type of amphiphilic structures described, techniques such as LB or electrostatic layer-by-layer deposition may now be used for the processing of polyacetylenes into thin-film architectures for device fabrication.

The presence of a substituted but conjugated backbone combined with the proximity of charges gives such structures practical potential. The stability of the electric response, owing to strong dopant binding, is a feature especially useful in energy storage devices. Likewise the enhanced chemical and thermal stability, owing to the rigidity of the conjugated backbone, makes these compounds particularly valuable in technologies in which stability of response and processability are of importance, for example, in electron beam resists (the substitution provides for backbone stability and film processability, while the conjugation opposes charge build-up).

The conjugation, rigidity, and amorphous nature of these PAs and their affinity for oxygen combine to make such polymers good candidates for permselective membranes. The shift from the *cis* to *trans* conformation in IPAs favors a substantial increase in the nonlinear optical (NLO) response of such films. Values for third-harmonic generation (THG), $\chi^{(3)}$, in films of poly(2-ethynylpyridine) were increased upon quaternization from 1.5×10^{-13} esu to 5.7×10^{-7} esu.^[22]

The film-forming potential of these semiconducting, soluble, and stable polymers in their amphiphilic state is very high, making them excellent candidates for various surface modifications. The structural and electronic properties of these new materials are promising, but have yet to be extensively investigated.

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