

Synthesis of Polymers with Electro-optical Properties

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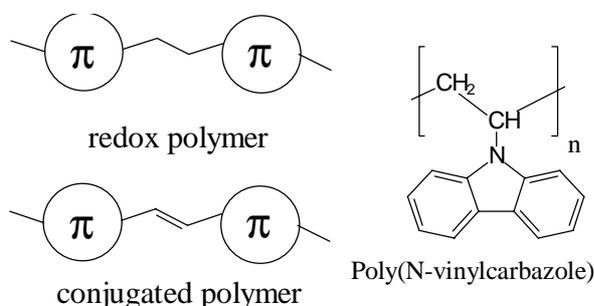
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The electro-optical properties of organic and polymeric materials are regarded as holding potential for developments in charge storage, analytical sensors, electroluminescent devices, optical data processing and integrated optics. For example, nowadays it is clear that sensor sensitivities and specificity can be increased by using redox polymers [1] or that the parameters characterizing the relative strength of nonlinear optical, NLO, effects are typically 50 or 100 times greater in organic molecular systems than in inorganic dielectric insulators and semiconductors [2].

In addition, because of the availability of a enormous variety of organic molecules and of liquid crystalline oriented films or other ordered environments, the properties of polymeric materials may be tailored to optimize other parameters such as anisotropy, mechanical strength, processability, thermal stability, laser damage threshold, etc., while preserving intact the electronic structure responsible for the electro-optical effects. While the potential for applications is great indeed, the development of appropriate electro-optical polymeric materials is a combination of interdisciplinary tasks: (1) synthesis of macromolecules with π -electron systems, (2) control of the molecular morphology and the detailed nature of the electronic environment of the medium, and (3) characterization of the polymer material properties.

Electro-optical Polymers

The key structural feature of almost all the electro-optically active polymers is that they have π -electron systems as building blocks imbedded in its structure. These unsaturated systems can be considered either as chromophores or as electrophores depending on the kind of particles, light or electrons, they interact with. While charge uptake can lead to electric conductivity, charge storage or electro

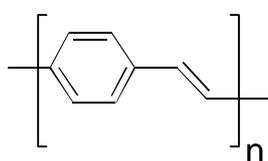


luminescence (after ion recombination) [3]; the interaction with electromagnetic waves gives origin to photoconductivity, photovoltaic effects, em shielding, NLO effects and so on.

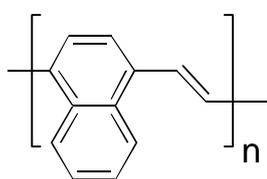
Another fundamental structural feature which defines the polymer electro-optical properties is the type of unit linking the π -electron systems [4]. In **redox polymers**, the active units are

linked by saturated spacers that isolate the π -electrons. Therefore, the polymer electro-optical properties [oxidation potentials, fluorescence, band gaps, etc.] are rather similar to their low molecular building blocks whereas the polymeric state is of importance by its contribution to the mechanical properties of the material. Poly(vinylcarbazole) that has been used as the photoconducting layer in photocopiers is an early example of this type of polymers. On the other hand, **conjugated polymers** have unsaturated linking units. As a result, the π -conjugation is extended over long segments of the polymer main chain until a defect, i.e. a saturated unit, interrupts the electron delocalization. The conjugated polymer electro-optical properties are intrinsic and they often differ substantially from the redox polymers[5]. Conjugated polymers have also received the name of conducting polymers which focuses on its ability to transport electrical charges upon oxidation or reduction, i.e. “doping”.

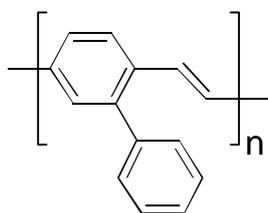
The Precursor Route to Poly(Arylene Vinylene)s



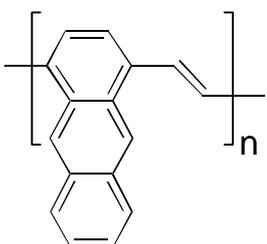
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In this report the focus will be placed on the synthesis of poly(arylenevinylene)s, PAV's, of general formula $[-Ar-CH=CH-]_n$. Some of the conjugated polymers such as polyaniline or polypyrrol are electrosynthesized on an electrode surface from which a film can be peeled off. This procedure permits to circumvent the biggest problem in the conjugated polymers synthesis, that is, its lack of processability. Due to the rigid main chain structure all this polymers are insoluble in all kind of solvents and decompose before melting. However, for some conjugated polymers, including the PAVs [6], an alternative synthetic route has been designed. The common feature of these procedures is that a processable precursor polymer is first obtained and later converted into the conjugated polymer. A great

variety of PAVs as well as its copolymers have been obtained using this synthetic route, some of the homopolymers are listed in the scheme.

References and Notes

1. Ivaska, A. *Electroanalysis* **1991**, 3, 247.
2. Nalwa, H. S. In: *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S. and Miyata, S., Eds.; CRC Press Inc., 1997; p 611.
3. Kraft, A. C.; Grimsdale, A.; Holmes, B. *Angew. Chem. Int. Ed.* **1998**, 37, 402.
4. Bohnen, A.; Rader, H.J.; Mullen, K. *Synth. Met.* **1992**, 47, 37.

5. Mathy, A.; Ueberhofen, K.; Gregorius, H.; Garay, R. O.; Müllen., K.; Bubeck, C. *Phys. Rev. B* **1996**, *53*, 4367.
6. Garay, R.O.; Lenz, R.W. *Makromol. Chem., Suppl.* **1989**, *15*, 1.
7. Garay, R.O.; Karasz, F.E.; Lenz, R. W. *J. Macromol. Sci.* **1995**, *A32*, 905.
8. Stenger-Smith, J.D.; Lenz, R.W.; Wegner, G. *Polymer* **1989**, *30*, 1048.
9. Garay, R.O.; Naarmann, H.; Müllen, K. *Macromolecules* **1994**, *27*, 1972.