# Pyrrole–Styrene Graft Copolymers

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The first graft copolymer of polypyrrole has been synthesized by electrochemically polymerizing pyrrole in the presence of pyrrole derivatized polystyrene; the copolymer produced exhibited an electrical conductivity comparable to that of polypyrrole.

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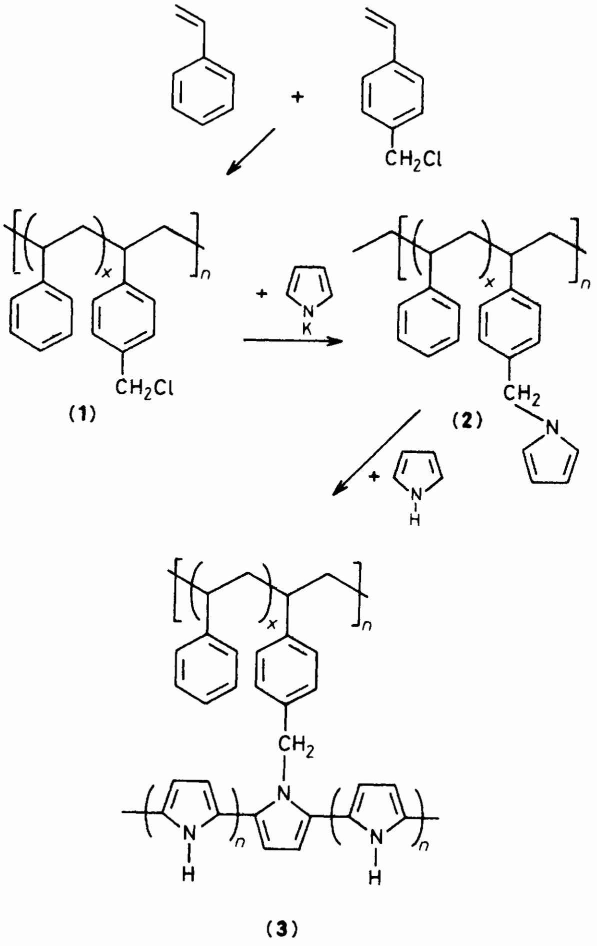
Electrochemically prepared polypyrrole films show good electrical conductivity, *ca.* 100 S/cm,[1] and they are relatively stable over long periods of time under ambient conditions[2] *e.g.* their conductivity decreases by an order of magnitude in a year. Their mechanical properties are enhanced by incorporating toluene-4-sulphonate as the counter ion[3] or by forming composite polymers by electrochemically incorporating polypyrrole within the matrix of a polymer whose mechanical properties are superior to polypyrrole,[4–6] *e.g.* poly(vinyl alcohol) or poly(vinyl chloride). Also copolymers of pyrrole with *N*-methylpyrrole have been used to modify the conductivity of polypyrrole.[1] We report here on copolymers with pyrrole where one of the components is not a pyrrole derivative and was chosen to provide versatility for systematic modification of physical properties.

Copolymers in general exhibit physical and mechanical properties far different from those of homopolymers, and different from those of blends of the same individual homopolymers. For example the butadiene–styrene copolymer in a 3 : 1 ratio (synthetic rubber) has desirable properties which cannot be achieved with either of the homopolymers or any of their blends. The properties of copolymers can also be modified by varing either the ratios of the various constituents or the manner by which they are chemically attached. A large variety of copolymers should thus be obtainable by varying the nature, number, and ratios of the polymers copolymerized with polypyrrole. We report here on the pyrrole–styrene copolymer system.

Styrene was copolymerized with 4-chloromethylstyrene[7] in a 9 : 1 ratio (neat) using 2,2′-azobis(2-methylpropionitrile) as a radical initiator (1%). The polymerization was allowed to proceed for 3 days at 80 °C and the copolymer was then purified by repeated precipitation from a dichloromethane solution by adding to hexane. No attempt was made to determine the molecular weight or molecular weight distribution of the polymer, but elemental analyses indicated that the copolymer (**1**) contained *ca.* 12% chloromethyl groups. The copolymer was dissolved in tetrahydrofuran (THF) and added to a THF solution of potassium pyrrole at reflux and allowed to react overnight. The new copolymer (**2**) was purified in a similar manner to (**1**). Elemental analysis of (**2**) indicated that about half of the chloromethyl groups had reacted with the potassium salt.

This copolymer (**2**) was then used to grow the graft copolymer (**3**) by electro-oxidation in a one compartment electrochemical cell with two platinum electrodes. The electrolyte solution consisted of 0.1 M tetrabutylammonium tetrafluoroborate, 0.1 M pyrrole, and a varying amount of (**2**) in dichloromethane. The films were grown at a constant current density of *ca.* 0.1 mA/$cm^2$. The films produced vary in their properties depending on the intial ratio of (**2**) to pyrrole. Films grown from a solution containing (**2**) and pyrrole in the ratio of 1 : 20 by weight were pyrrole-like in character with a conductivity of *ca.* 50 S/cm. Films grown from a solution containing a 1 : 1 mixture of (**2**) and pyrrole were very brittle and exhibited poor conductivity of *ca.* $5 \times 10^{-2}$ S/cm. Films with intermediate composition had properties in between, *e.g.* 1 : 6 ratio of (**2**) to pyrrole had a conductivity of 0.4 S/cm. Films grown from identical solutions but at different rates of growth produced films of similar properties indicating that (**2**) is incorporated chemically in the copolymer and not just physically dispersed in the polypyrrole matrix. Soaking the copolymer in a good solvent for (**2**) such as dichloromethane failed to extract any of the polymer, again indicating that it is chemically incorporated in the copolymer. Further, scanning electron microscopy indicated the films to be homogeneous in structure to a resolution better than 0.1 micron.



This polymer system is only one of several that can be synthesized in a similar manner. For example the chloromethylstyrene can be copolymerised with many commercially available vinyl-type monomers and combinations of these monomers. The chloromethyl group will still be available both before and after polymerization to be derivatized with pyrrole and then used in the manner described above to give a large variety of pyrrole copolymers.

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