

High-Quality Conductive Polypyrrole Within a Secondary Crosslinked Interpenetrating Polymer Network

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ABSTRACT: A high-quality conductive polypyrrole was prepared within a secondary crosslinked interpenetrating polymer network by chemical oxidative polymerization, whose conductivity is high up to 0.25 S/cm only with 0.9% polypyrrole. The "microfiber" structure of polypyrrole was characterized by scanning electron microscopy, polarizing microscopy, and small angle X-ray diffraction. The formation of the microfiber was strongly dependent on the structure of the matrix. This might provide a new method for the preparation of conductive microfibers. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1–4, 1997

Key words: polypyrrole; secondary crosslinked interpenetrating polymer network

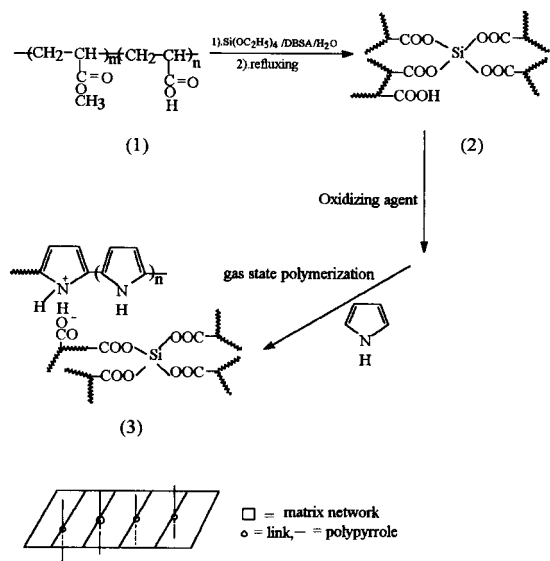
Conjugated polymers generally tend to be infusible and insoluble, so many researchers have concentrated on improvement in conducting material quality.^{1–4} Control over molecular architecture is a critical challenge in the design of new materials of sufficient quality.⁵ As a result of the intrachain π -bonding of the conjugated structure and the relatively strong interchain electron transfer interactions, the mechanical properties (Young's modulus and tensile strength) of conjugated polymers are potentially superior to those of saturated polymers, such as polyolefins. However, the electrical and mechanical properties are currently limited by defects and disorder, so improvement in material quality that enables the exploration of intrinsic properties has become an important goal of conducting polymer research.^{6–8} The key question is whether processing methods can be developed that will lead to chain-extended and chain-aligned materials of sufficient quality. Many highly ori-

ented conducting polymers with good conductivity and mechanical properties have been synthesized by the electrochemical oxidative polymerization method^{9,10} or by the drawing procedure.^{11,12}

On the other hand, conductive composites based on rigid conducting polymers and flexible matrices have drawn many scientists' attention to enhancing the processability and mechanical properties of the rigid conducting polymers.^{13,14} Many conductive composites with good processability and mechanical properties have been obtained successfully by electrochemical oxidative polymerization or by chemical oxidative polymerization.^{15,16} However, few chain-extended and chain-aligned conductive polymers of sufficient quality in the conductive composites have been obtained, especially by the chemical oxidative polymerization method. The previous paper¹⁷ reported on a new composite of conducting secondary crosslinked interpenetrating polymer network (IPN) which combined the properties of rigid conducting polymer and flexible matrix. Maeda and colleagues¹⁸ and Mehrotra and associ-

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Scheme 1 Formation of conducting secondary cross-linked IPN network.

ates¹⁹ have reported on conducting composites based on polypyrrole and sol-gel silica matrices which have specific applications, such as immunodiagnostic assays. We report here on a new kind of conducting “microfiber” polypyrrole within a poly(methyl acrylate-co-acrylic acid) (PMAA)/polypyrrole secondary crosslinked IPN system.

PMAA (1) was synthesized as described earlier.²⁰ PMAA (M_n 1×10^4 , group molar ratio $\text{COOCH}_3/\text{COOH}=6:1$) and tetraethyl orthosilicate (TEOS) were added to 10 g tetrahydrofuran (THF) in the weight ratios of 95 : 5 and 80 : 20, respectively, to prepare 9% PMAA + TEOS of THF solutions. With addition of 0.01 g dodecyl benzene sulfonic acid as catalyst and 0.01 g H_2O , the crosslink reaction of PMAA with TEOS was allowed to proceed for 1 h at the reflux. After the solution was refluxed and cooled, 2.2 g $\text{FeCl}_3/0.09$ g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (molar ratio, 3 : 0.1) was added to the 95 : 5 and 80 : 20 PMAA/TEOS solutions. For comparison with the above 95 : 5 PMAA/TEOS solution, 2.2 g $\text{FeCl}_3/0.9$ g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (molar ratio, 3 : 1) was added into another solution of 95 : 5 PMAA/TEOS. The solutions were then cast onto the film, placed in air for 24 h at room temperature, and cured in a bake oven at 80°C for 1 h under nitrogen. The preparation of freestanding conductive IPN films (3) was carried out at -8°C by exposing crosslinked PMAA films (2) containing $\text{FeCl}_3/\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ to pyrrole vapor for 24 h, washing the films several times with methanol until solvent remained colorless, and then press-

ing with glass plate and drying in vacuum for more than 12 h.

The conductive films of PMAA/TEOS in the ratios of 95 : 5 ($\text{FeCl}_3/\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; 3 : 0.1), 95 : 5 ($\text{FeCl}_3/\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; 3 : 1) and 80 : 20 ($\text{FeCl}_3/\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$; 3 : 0.1), correspondingly coded as $\text{P}_{2\text{H}}\text{-F}$, $\text{P}_{2\text{H}}\text{-F}_3$, and $\text{P}_{4\text{H}}\text{-F}$, exhibited conductivities of 0.13, 0.09, and 0.25 S/cm, respectively. Elemental analyses of $\text{P}_{2\text{H}}\text{-F}$, $\text{P}_{2\text{H}}\text{-F}_3$, and $\text{P}_{4\text{H}}\text{-F}$ indicated that these conductive IPN films (3) contained ca. 8%, 17% and 0.9% polypyrrole. These results show that the conductivity of IPN films (3) does not increase with increase in the content of polypyrrole but strongly depends on the structure of polypyrrole as in the other systems.²¹ Polypyrrole with low bulky density possesses poor conductivity, whereas with chain-extended and chain-aligned structure it exhibits good conductivity.²²

Scanning electron microscopy (SEM) micrographs for $\text{P}_{2\text{H}}\text{-F}$, $\text{P}_{2\text{H}}\text{-F}_3$, $\text{P}_{4\text{H}}\text{-F}$, and $\text{P}_{4\text{H}}$ ($\text{P}_{4\text{H}}\text{-F}$ without incorporating polypyrrole is called $\text{P}_{4\text{H}}$, i.e. crosslinked flexible network) are shown in Figure 1. Microfiber was observed in $\text{P}_{2\text{H}}\text{-F}$, $\text{P}_{2\text{H}}\text{-F}_3$, and $\text{P}_{4\text{H}}\text{-F}$, but not in $\text{P}_{4\text{H}}$, indicating that the chain-aligned polypyrrole with good structure regularity was generated in the IPN films, especially in $\text{P}_{4\text{H}}\text{-F}$, which resulted in good conductivity.²² Through comparison of $\text{P}_{2\text{H}}\text{-F}$ with $\text{P}_{2\text{H}}\text{-F}_3$, we also found that the increase of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ caused the loss in the structural regularity of polypyrrole; that is, the amount of microfibrils in $\text{P}_{2\text{H}}\text{-F}_3$ was less than that in $\text{P}_{2\text{H}}\text{-F}$. It has been reported that the regular structure of polypyrrole could be obtained by addition of FeCl_2 to decrease the oxidative potential of FeCl_3 .²³ Therefore, the loss in the structural regularity of polypyrrole was caused by the increase of H_2O content in the PMAA/TEOS system. When the H_2O content increases, TEOS can be hydrolyzed and condensed to form a high-density network and many Si-OH groups left in TEOS have good affinity with pyrrole; these groups limit the growth of the regular structure of polypyrrole. The hydrolysis and condensation reaction of TEOS is too limited at low H_2O contents, and many Si-OC₂H₅ groups with larger volume left in TEOS results in the formation of a “relaxed” crosslink network or small “cage” structure with same functions as microporous materials, in which polypyrrole with good structural regularity can be obtained.²² The content of the Si-OC₂H₅ group left in TEOS becomes larger at the higher amount of TEOS in $\text{P}_{4\text{H}}\text{-F}$ and the conductivity is high, up to 0.25 S/cm despite the polypyrrole content as low as 0.9%, indicating

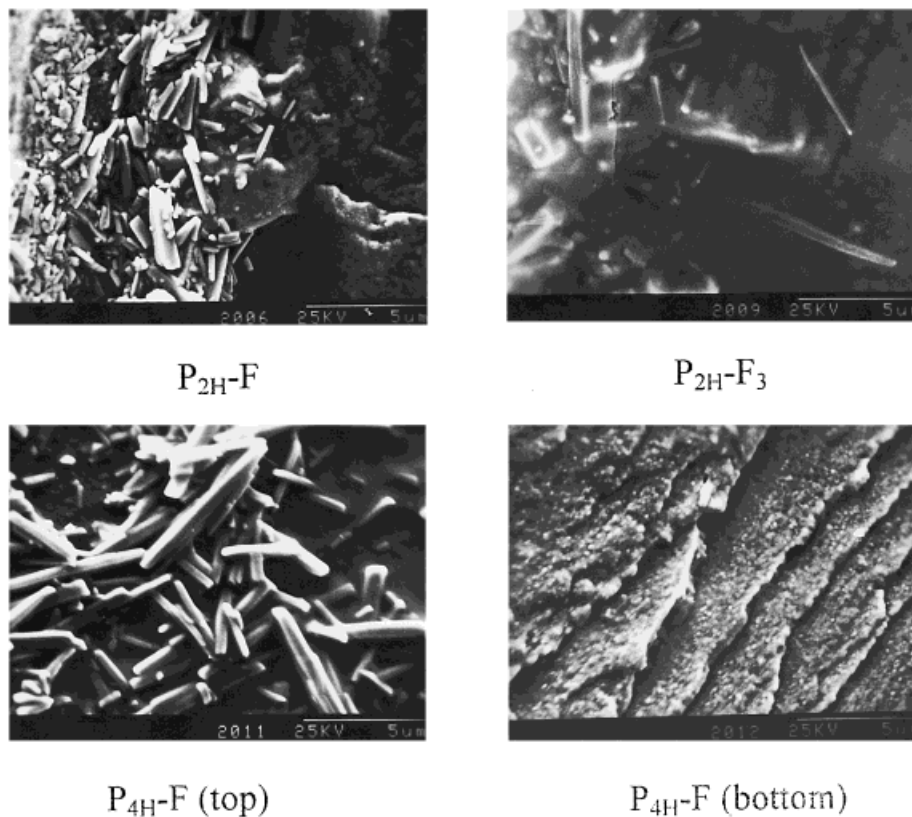


Figure 1 SEM of P_{2H-F} , P_{2H-F_3} , P_{4H-F} and P_{4H} .

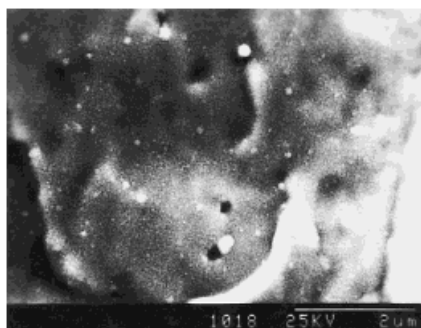
that microfiber can be easily formed in P_{4H-F} (see Fig. 2) and supporting the above results. The bright fiber/fragment in P_{4H-F} could be also observed under a polarizing microscope, suggesting that the microfibers phase in P_{4H-F} is further substantiated and may be composed of crystalline of polypyrrole.

Information on the microcrystalline in P_{4H-F}

was obtained by small-angle X-ray diffraction. Table I lists the observed reflections and the corresponding d -spacings. The d -spacings in P_{4H-F} are completely different from those in $FeCl_3$ or $FeCl_2$,²⁴ denying the possibility of the microcrystalline produced by $FeCl_3$ or $FeCl_2$ left, and supporting the above result that microcrystalline of polypyrrole existed in P_{4H-F} .

Table I Observed X-ray Reflections and Corresponding d -Spacing for P_{4H-F}

Code	Number	d -Spacing (nm)	Intensity
P_{4H-F}	1	3.01	strong
	2	2.26	middle
	3	2.08	middle
	4	1.91	middle
	5	1.59	weak
$FeCl_3$ ²⁴	1	2.68	strong
	2	2.08	weak
	3	5.9	weak
$FeCl_2$ ²⁴	1	2.54	strong
	2	5.9	weak
	3	1.8	weak



P_{4H}

Figure 2 SEM of P_{2H-F} , P_{2H-F_3} , P_{4H-F} and P_{4H} (cont'd).

There are great differences between the two surface morphologies for P_{4H}-F (Fig. 2), namely, the microfibril is not observed in the bottom, perhaps because the structure of the air surface is different from that of the bottom.²⁰ The ratio of N/C (0.06) in the surface measured by electron spectroscopy for chemical analysis was more than 3 times as large as that (0.018) in the bulk of P_{4H}-F measured by elemental analysis, suggesting that polypyrrole is mainly segregated in the two surfaces of P_{4H}-F and forms conductive layers, so that a film of "sandwich" structure has been generated, in agreement with the SEM results.

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