

Polymerization of Pyrrole and Processing of the Resulting Polypyrrole as Blends with Plasticised PVC

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ABSTRACT: Polypyrrole was synthesized by chemical oxidation of pyrrole in water containing various sulphonic acids like toluene sulphonic acid (TSA), sulphosalicylic acid (SSA), and camphor sulphonic acid (CSA), as well as a combination of each sulphonic acid with sodium dodecyl benzene sulphonate (NaDBS) to investigate the effect of doping on conductivity, yield, and processability of the conducting polymer. Free-standing blend films of polypyrrole and plasticized polyvinyl chloride (PVC) were obtained by casting an homogeneous suspension of the two polymers in tetrahydrofuran. The maximum conductivity of the blend film is ~ 0.3 S/cm, corresponding to a weight fraction of 0.16 w/w polypyrrole. The blend film is semiconducting in the range 300–10 K. A TG-DTA scan indicates the blend film to be amorphous with a stepwise decomposition process similar to pristine PVC. The choice of a dual dopant system during synthesis and the plasticised polymer during subsequent processing were keys to obtaining homogeneous high-quality films. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1544–1548, 2001

Key words: polymerization; polypyrrole; processing

INTRODUCTION

Polypyrrole is a heterocyclic polymer which has received a great deal of attention for the following reasons: (1) oxidative polymerization of pyrrole by chemical means is easy; (2) it can be performed by a number of oxidizing agents¹; (3) the process yields a stable conducting polymer^{2,3} with good percentage of recovery; and (4) the solvent used for synthesis is water, which is very practical when considering bulk production of the polymer.


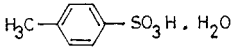
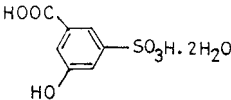
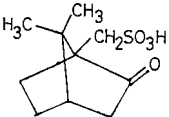
Although such properties suggest many practical applications of these materials, polypyrrole is obtained as an intractable powder and extremely difficult to process. This is attributed to the ex-

tensive conjugation in the main chain structure of the polymer, which gives rise to increased chain stiffness and chain interactions. We, therefore, reasoned that to synthesize polypyrrole and render it processable it would be necessary to reduce the intra- and intermolecular interactions between the polymer chains and enhance the interaction between the chains and the solvent. Crucial to this strategy was the choice of dopants used in the synthesis of the conducting polymer and the plasticized polymer used during subsequent processing. Results of this research targeted towards enhancing the processability of polypyrrole blends is presented in this article. The use of two dopants to improve thermal stability and enhance compatibility of the conducting polymer complex has been reported^{4,5} previously for polyaniline. Other methods employed in processing conductive blends like blending,⁶ swelling,⁷ and diffusion⁸ have their inherent drawbacks such as

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Table I Structure and Code of Chemicals

Chemical Structure	Formula Weight	Code
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	228.2	APS
	67.09	Py
	190.2	TSA
	254.2	SSA
	232.3	CSA
$\text{CH}_3-(\text{CH}_2)_{11}-\text{C}_6\text{H}_4-\text{SO}_3\text{Na}$	348.98	NaDBS

inhomogeneous mixing, high polymer loadings, or use methods not amenable to large-scale production.

EXPERIMENTAL

Pyrrrole was distilled and stored in a dessicator. The sulfonic acids were commercially available. Ammonium persulphate of reagent grade was used as received. Formula weight of the ingredients is given in Table I. Recipe for synthesis with weights of ingredients is given in Table II.

Synthesis

Aqueous solution of the oxidant (APS: 0.26 mol) was added instantly to a vigorously stirred solution of pyrrole (0.96 mol) containing 0.05 g of the appropriate sulphonic acid maintained at 5°C. The reaction mixture rapidly darkened and produced a fine dispersion of black particles. After the given reaction time, the precipitated polypyr-

role was isolated by filtration and rinsed successively with water, methanol, and acetone. The washed powders were finally dried in a vacuum dessicator at room temperature. The procedure was repeated to prepare polypyrrole powders using a mixture of each sulphonic acid with NaDBS.

Characterization

Polypyrrole powder samples were compressed into discs, typically 1 mm thick, using a 6-mm die at 100 psi, to ensure uniform packing density. DC conductivity measurements were performed using the "four-probe" technique. (ASTM D 991-89). Samples were coated with colloidal silver for electrical contacts. A programmable current source (Keithley 220) and a Keithley 1954 DMM was used for the four-probe measurements. Conductivities below room temperature were measured for one representative blend film by attaching the film to a four-probe dipstick cryostat that was evacuated to 0.05 Torr and then filled with helium exchange gas. Lakeshore 330 auto-tuning temperature controller was used to monitor the temperature. Thermal behaviour of the blend film was analyzed using a simultaneous TG-DTA thermal analyzer (Shimadzu-DT 40) at a heating rate of 10°C/min in an atmosphere of nitrogen.

RESULTS AND DISCUSSION

Polypyrrole is synthesized using ammonium persulphate in acidic aqueous media containing the appropriate sulphonic acid. In each case the conducting polymer is obtained as an insoluble bulk powder. The compressed bulk conductivity is shown in Table III. The values are comparable to these reported recently for chemically synthesised polypyrrole.^{9,10}

Table II Recipe for Synthesis

Ingredients	Weight (g)
APS : Py	0.15 : 0.5
TSA	0.05
TSA : NaDBS	0.045 : 0.005
SSA	0.05
SSA : NaDBS	0.045 : 0.005
CSA	0.05
CSA : NaDBS	0.045 : 0.005

Table III Effect of Dopants on Yield and Conductivity of Polypyrrole

Dopant	Dopant/Py (mol/L)	Reaction Time (min)	Yield (%)	Conductivity (S/cm)	
				Pellet	Blend Film ^a
TSA	1.27	5	45	0.66	0.14
TSA : NaDBS	1.19/0.12	30	75	0.6	0.04
SSA	1.69	5	45	0.59	0.12
SSA : NaDBS	1.58/0.15	30	80	0.52	0.03
CSA	1.55	5	45	0.87	0.17
CSA : NaDBS	1.55/0.14	30	80	0.7	0.3

^a Films cast from a homogeneous suspension of the synthesized powders with 20% PVC in THF. Polymerization temperature: 5°C.
 APS: 0.26 mol/L.
 Py: 0.96 mol/L.
 APS/Py: 0.26 mol/L.

Initially, the monomer and oxidant is dissolved in a homogeneous solution. Ammonium persulphate is chosen as the oxidant owing to its good solubility in water. As polymerization proceeds the system becomes heterogeneous owing to the precipitation of insoluble microscopic particles in the aqueous phase. In the absence of NaDBS, precipitation of polypyrrole was almost instantaneous. When NaDBS was added to the reaction mixture, a white flocculate was formed first and eventually turned to black. The effect of the type of dopant and the surfactant NaDBS on yield, conductivity, and processability of the resulting powders is shown in Table III. The main points that emerge from Table III are the following.

First of all, the values of conductivity and yield of the polymer obtained does not vary with the type of dopant used for polymerization. Secondly, the addition of a small amount of NaDBS to the reaction mixture has a profound effect in enhancing the yield as well as the processability of the resulting powders.

The reason for the increase in yield of polypyrrole in reaction mixtures containing NaDBS is explained in terms of interaction between the bulky anion and the conducting polymer particle. Briefly stated, the insoluble microscopic particles are stabilized by the bulky anion as it adsorbs onto the primary particles as a thick layer,¹² providing a barrier to particle aggregation. The enhanced processability is also attributed to the role of the bulky anion in locating itself between the primary particles, reducing both intra as well as intermolecular interactions^{11,13} between the chains.

Electrically conducting polymer blend films were prepared by mixing in a pestle and mortar

the powder particles in a tetrahydrofuran solution of plasticised PVC, and subsequently evaporating the solvent. Films cast from PPy prepared from reaction mixtures containing CSA as the doping species and NaDBS as the processing aid resulted in high-quality free-standing films. The blend film exhibited a maximum conductivity of 0.3 S/cm corresponding to a weight ratio of 0.16 w/w PPy.

A plot of conductivity vs. PPy content of the cast blend films is shown in Figure 1. The figure exhibits features characteristic of percolating systems with an onset of conductivity at 0.08 w/w of polypyrrole.

Temperature dependence of resistance was measured in the range 300–10 K for one representative blend film showing the highest conductivity. The data is shown in Figure 2. To interpret this R vs. T plot, the data is analyzed in terms of the hopping mechanisms obeying the relation

$$\rho \propto \exp(T_0/T)^{1/n}$$

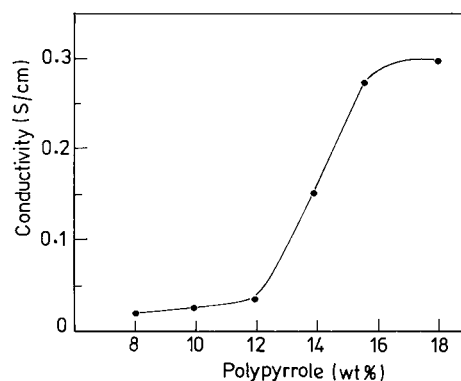


Figure 1 Electrical conductivity vs. polypyrrole content in PPy/PVC blend films.

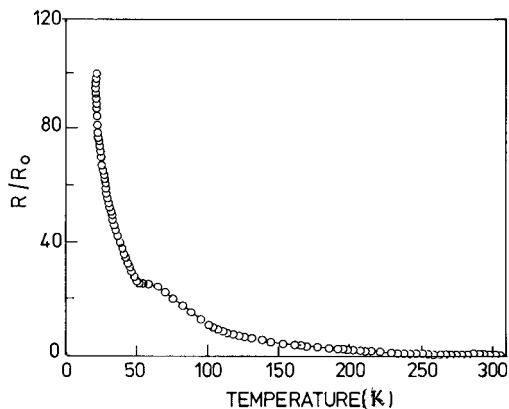


Figure 2 R/R_0 vs. temperature plot of PPy/PVC blend film (PPy 0.16 w/w).

where the power coefficient may be between 1 and 4. The analysis indicates that for the PPy/PVC blend film with PPy content 0.16 w/w, the data fits well with $n = 4$, i.e., the $T^{-1/4}$ dependence in the range 300–160 K, as shown in Figure 3. PPY generally exhibits structural disorder due to polymerization defects.¹⁴ Consequently, the charge carriers do not move as in a crystalline lattice. Thus, the dominant transport mechanism in PPY is hopping between the localized states. In the case of the blend films, an additional disorder results from distribution of conducting PPY domains within the polymer matrix. Conductivity is limited mainly by macroscopic hopping between the conducting domains.

Pressure dependence of resistance of the blend film (PPy : 0.16 w/w) is shown in Figure 4. This is the expected pressure dependence with the initial decrease in resistance and saturation at higher pressures. In polymeric materials the

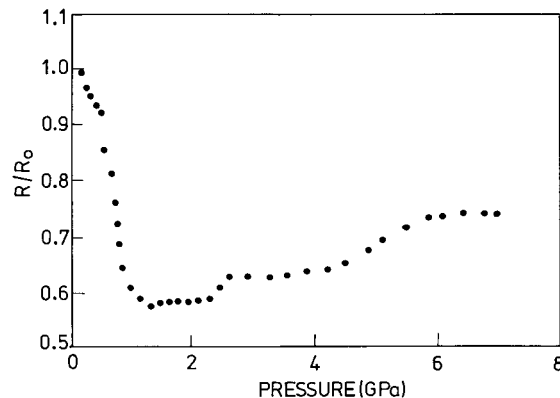


Figure 4 R/R_0 vs. pressure plot of PPy/PVC blend film (PPy 0.16 w/w).

free volume between chains could be reduced by pressure. If the mechanism of conduction is by hopping, then the temperature dependence should change with pressure, as seen in Figure 4, because the density of states at the Fermi level changes with applied pressure.¹⁵ Temperature dependence of resistance at 3 GPa shows a decrease in resistance in the range 300–50 K, as shown in Figure 5.

Finally, the thermal behavior of the blend film (PPy : 0.16 w/w) is shown in Figure 6. TG-DTA scan of pristine PVC is also shown for comparison. A TGA scan of the blend film reveals a stepwise decomposition process similar to pristine PVC. The initial weight loss of 10% observed upon heating the blend film is presumed to be due to loss of water. A TG thermogram of blend film shows a weight loss onset at 200°C due to polymer decomposition.

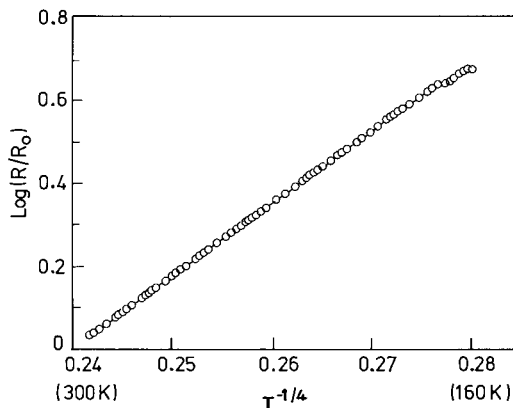


Figure 3 $\log R/R_0$ vs. $T^{-1/4}$ plot of PPy/PVC blend film (PPy 0.16 w/w).

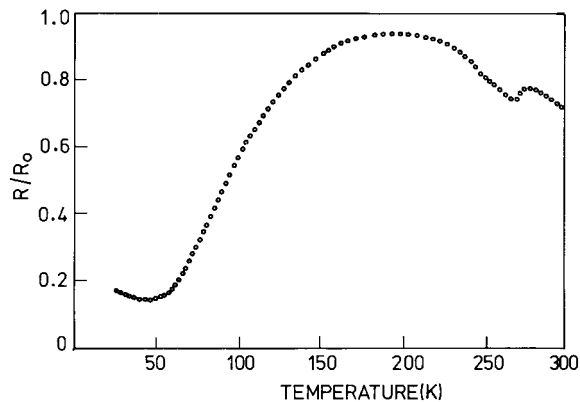


Figure 5 R/R_0 vs. temperature plot at 3 GPa of PPy/PVC blend film (PPy 0.16 w/w).

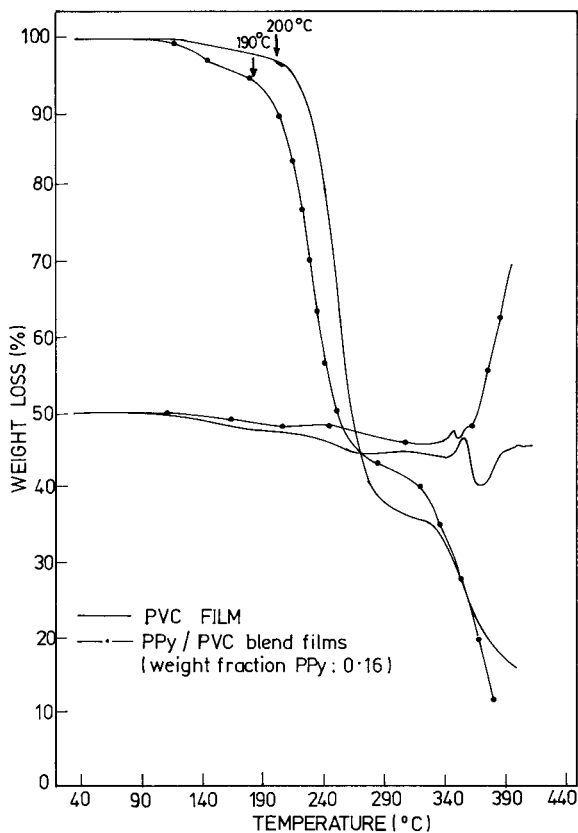


Figure 6 Simulation T.G-D.T.A curves of pristine PVC and PPY/PVC blend film (PPy 0.16 w/w).

CONCLUSIONS

By using a combination of dopants during synthesis we have been successful in enhancing the processability of polypyrroles.

Free-standing and flexible-blend films were obtained by casting a homogeneous suspension of the synthesized powders with plasticised PVC in tetrahydrofuran.

The maximum conductivity of the blend film is ~ 0.3 S/cm, corresponding to a weight fraction of 0.16 w/w polypyrrole and semiconducting in nature.

TG-DTA scan indicates the blend film to be amorphous with a decomposition pattern similar to pristine PVC.

As the blend films are stable and retain the mechanical characteristics of the plasticised polymer, it can be used as semiconducting tapes for cable claddings, shielding, and antistatic applications.

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