Effect of a Surface Active Pyrrole on the Conductivity of Polypyrrole Composites

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SYNOPSIS

A surface active pyrrole, which has a long hydrophobic chain attached to the 3 position of the pyrrole ring, is used to modify the surface properties of the pores of a porous, crosslinked polystyrene. The latter is prepared starting from a concentrated emulsion (an emulsion with a large volume fraction of the dispersed phase, here 0.81) of water dispersed in a continuous medium composed of styrene, divinyl benzene, a suitable surfactant, an initiator, and the surface active pyrrole. This modified crosslinked porous medium is employed as the host for a polypyrrole composite that is prepared first by imbibing the host with a solution of pyrrole and subsequently with an oxidant solution. The latter plays the role of catalyst for polymerization as well as the role of dopant. The presence of the head groups of 3-alkyl pyrrole molecules on the surface of the pores of the host polymer increases the affinity of the surface for pyrrole. The improved wetting thus achieved for the pyrrole solution ensures a higher connectivity among the pyrrole films present on the internal surface of the host polymer and increases the conductivity of the polypyrrole composites by a factor of 2 to 14, depending upon the solvents employed for pyrrole and oxidant.

INTRODUCTION

Since Shirakawa et al.[1] demonstrated that polyacetylene can have semiconductor or metallic properties, many conjugated double bond polymers have been identified, which can be made conductive by adding oxidizing or reducing agents, such as iodine, bromine, $FeCl_3$, etc. Polymer-based conducting materials have received attention because they can substitute for conductors or semiconductors in a wide variety of electrical and electronic devices. Potential advantages of conductive or semiconductive polymers lie in their light weight and in the versatility with which their synthesis and manufacturing can be accomplished. Among these doping-induced conductive polymers, polypyrrole was extensively studied because of its higher chemical and thermal stabilities as compared with those of polyacetylene. It was also studied because of its reasonably high conductivities (> 100 S/cm).

Polypyrrole can be prepared electrochemically[2,3] as well as chemically.[4-6] The physical appearance and conductivity of polypyrrole strongly depend upon the preparation route employed. The chemical oxidation route leads to polypyrrole powder, while the electrochemical route provides free-standing polypyrrole films. The electrochemically prepared polypyrrole films generally possess higher conductivities and mechanical strengths than those prepared via the chemical oxidation method. The use of the electrochemical synthesis is, however, limited by the size, shape, and nature of the electrode involved, as well as the difficulty in preparing thick films. Methods, therefore, have been proposed to prepare composites that possess sufficiently high conductivities, good mechanical strength, and allow easy processibility (i.e., are readily able to be shaped or molded). Conducting polypyrrole composites have been prepared by polymerizing polypyrrole in a thin polymer matrix,[7,8] on polymer surfaces,[9] in porous thin filter papers,[10] and in thick porous media.[11]

Ruckenstein and Park[11] proposed a method for the preparation of thick conducting polymer com-

posites. In their method, a porous medium of cross-linked polystyrene was first obtained by the concentrated emulsion polymerization method (as described later in the article), and further employed as host for the conducting polypyrrole composites. The incorporation of polypyrrole was performed by: (1) imbibing the host polymer with a pyrrole solution, (2) partially drying the imbibed host polymer, and (3) imbibing again with an oxidant solution for polymerization to take place.

The conductivity of the composite can be ascribed to the network of polypyrrole formed inside the porous host polymer.[11] One possibility to achieve a higher conductivity is to improve the imbibing efficiency of the host polymer with the pyrrole solution. In this article, a way to improve the imbibing efficiency by modifying the internal surface properties of the host polymer is suggested. A surface active pyrrole, namely the 3-hexadecyl pyrrole, is used to modify the surface properties of the pores; this is expected to improve the spreading of the pyrrole solution over the surface of the pores. The experimental results show that the conductivities of the surface active pyrrole containing composites are 2 to 14 times higher than those free of the surface active pyrrole, depending upon the solvents employed for pyrrole and oxidant.

EXPERIMENTAL

Chemicals and Equipment

Pyrrole and styrene (Aldrich) were used as received. Ferric chloride ($FeCl_3$, anhydrous), chloroform, benzene, and ethyl ether were also products of Aldrich. Divinyl benzene (Polysciences) was distilled before use. Azobisisobutyronitrile (AIBN, Alfa) was purified by recrystallization in methanol. Sorbitane monooleate (Span 80) was purchased from Fluka.

The chemicals needed for synthesizing 3-alkyl pyrrole: pyrrole, potassium, tetrahydrofuran (anhydrous), benzene sulfonyl chloride, palmitoyl chloride, aluminum chloride, dichloromethane (anhydrous), ethyl acetate, propanol, and sodium borohydride (Aldrich) were used as received.

Nuclear Magnetic Resonance

The 3-alkyl pyrrole was characterized by proton NMR using a Varian VXR-400S NMR Spectrometer, operating at 400 MHz and at 18°C.

Scanning Electron Microscopy

The morphologies of the porous host polymers and conducting composites were examined by scanning electron microscopy (SEM, Hitachi S450). The samples of conductive composites were examined directly, while those of the nonconductive porous host polymers were coated with a thin layer of gold prior to observation.

Conductivity Measurement

For measuring the conductivity of polypyrrole, the powder was first pressed into a disc of about 0.25 cm thickness at an applied pressure of about 24 M Pa. The standard four-probe method was employed to measure the conductivity of polypyrrole and its composites at room temperature.

Synthesis of 3-Hexadecyl Pyrrole

Some pyrrole derivatives become surface-active when a long hydrophobic chain is attached to this heterocyclic, five ring structure. The pyrrole ring of the pyrrole derivatives is sufficiently hydrophilic, due to the presence of the N—H bond. The ring acts, therefore, like a hydrophilic head group of a surface active molecule. The surface-active pyrrole monomer used in this article, 3-hexadecyl pyrrole, has a long hydrophobic alkyl chain attached to the 3 position of the pyrrole ring. It is essential for the alkyl chain to be located at the 3 position of the pyrrole ring since the polymerization of pyrrole takes place at the 2,5 positions of the ring[12] and they must remain free in order to react. The surface-active pyrroles have been used to synthesize electrically conductive monolayer to multilayer films by employing the Langmuir–Blodgett technique. The chemical oxidation[13–15] or the electrochemical method[16] were used for polymerization.

The synthesis of 3-hexadecyl pyrrole is presented schematically in Figure 1. In this reaction, 1-(phenyl sulfonyl) pyrrole, denoted (b), is first prepared as suggested by Papadopoulos and Haidar.[17] Subsequently, the hydrophobic group (palmitoyl chloride, $CH_3 (CH_2)_{14} COCl$) is attached to the 3 position of the 1-(phenyl sulfonyl) pyrrole ring by the $AlCl_3$-catalyzed acylation reaction.[18] The final product was characterized by proton NMR.

Preparation of the Porous Medium (Porous Crosslinked Polystyrene)

The porous medium was prepared by the concentrated emulsion method.[19] In a concentrated emulsion, the volume fraction of the dispersed phase is very large, larger than 0.74 (which represents the volume fraction of the most compact arrangement of spheres of equal radius) and as large as 0.99. The
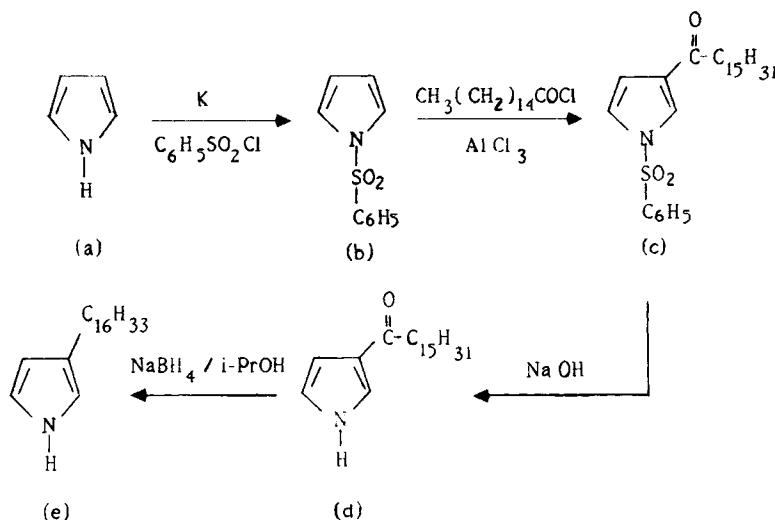
Figure 1   The synthesis of 3-alkyl pyrrole.

continuous phase has a low volume fraction and is in the form of a network of thin liquid films that separate polyhedral droplets of the dispersed phase. The concentrated emulsion is a kind of liquid–liquid foam and has the appearance of a gel. The concentrated emulsion was prepared as follows: A small amount of the continuous phase containing the appropriate initiator and a suitable surfactant was placed in a flask equipped with a mechanical stirrer and an addition funnel. The dispersed phase was placed in the funnel and added dropwise at room temperature into the stirred flask. In this study, water was the dispersed phase, while a mixture of styrene and divinyl benzene containing azobisisobutyronitrile (AIBN) as initiator, sorbitane monooleate (Span 80) as surfactant, and 3-hexadecyl pyrrole constituted the continuous phase. The gel thus obtained can be molded in any desired shape. Here it was molded as a pancake. Polymerization of the pancake was carried out at 55°C for 24 h. Subsequently, the water of the dispersed phase was evaporated by keeping the polymer at 100°C for 3 days.

Preparation of the Conducting Polymer Composite

The dried porous host polymer was imbibed with a pyrrole/organic solvent solution (0.4 g pyrrole/1 mL solvent) for 15 min. After partial drying in air for 80 min at room temperature, the host polymer was contacted with an excess amount of oxidant solution (FeCl$_3$/water or FeCl$_3$/methanol, 0.4 g FeCl$_3$/ 1 mL solvent) for 2 h. (The partial drying is employed in order to help the penetration of the oxidant solution into the host polymer.) Subsequently, the

composites were vacuum-dried for one day prior to the conductivity measurements.

Modification of the Surface of the Pores of the Host Polymer

The scope of this study is to modify the surface properties of the pores of the host polymer in order to achieve its better wetting by the pyrrole solution. A surface active pyrrole was chosen for this purpose. An effective way to incorporate the 3-alkyl pyrrole monomers into the surface of the pores with the pyrrole ring exposed to the void space is to use the surface active pyrrole as emulsifier when preparing the host porous polymer. Unfortunately, experiment showed that although the 3-alkyl pyrrole is surface active and able to form a stable monolayer at the air–water interface,[13] it is not powerful enough as an emulsifier to generate a concentrated emulsion. Therefore, another oil soluble surfactant must be mixed with the 3-alkyl pyrrole in order to prepare the concentrated emulsion. Table I lists the compositions of the porous media prepared in this study. The volume fraction of the dispersed phase was 0.81 in all these media. It is important to note that (1) the mechanical strength of these porous polymers decreases as the amount of 3-alkyl pyrrole increases, and (2) the porosity of all the specimens is almost the same (this was verified by their immersion in various liquids (Table II)).

RESULTS AND DISCUSSION

The conductivity of polypyrrole composites is expected to be strongly dependent on the following

Table I   The Compositions of the Host Polymers Employed

Polymer	Continuous Phase	Dispersed Phase
#1	0.1 g AIBN + 5 g sytrene + 1 g divinyl benzene + 1 mL Span 80	30 mL water
#2	0.1 g AIBN + 5 g styrene + 1 g divinyl benzene + 1 mL Span 80 + 0.05 g 3-alkyl pyrrole	30 mL water
#3	0.1 g AIBN + 5 g styrene + 1 g divinyl benzene + 1 mL Span 80 + 0.2 g 3-alkyl pyrrole	30 mL water
#4	0.1 g AIBN + 5 g styrene + 1 g divinyl benzene + 1 mL Span 80 + 0.4 g 3-alkyl pyrrole	30 mL water

two factors: (1) the penetration of the pyrrole solution into the pores to generate a pyrrole network, and (2) the contact between the oxidant solution and the pyrrole network, which leads to a polypyrrole network. The conductivity of the composite polypyrrole can be ascribed to the degree of connectivity of the polypyrrole network in the porous medium. Hence, it is important to ensure that the pyrrole solution can penetrate the entire pore space of the host polymer.

The Effect of Surface Active Pyrrole on Conductivity

The effect of the amount of surface active pyrrole on conductivity is presented in Figures 2–4. All these figures have a common trend, namely the conductivity of polypyrrole composites passes through a maximum when plotted against the concentration of 3-alkyl pyrrole. The optimum composition has a value of about 0.04 g 3-alkyl pyrrole/g styrene. The increase in conductivity, compared to that in the absence of 3-alkyl pyrrole, is by a factor of 2 to 14, depending upon the solvents employed for pyrrol and oxidant.

Because the 3-alkyl pyrrole is surface active, some of its molecules will be located on the internal interface of the concentrated emulsion with the hydrophilic head groups exposed to water and the hydrophobic tails extended in styrene. The exposure

of 3-alkyl pyrrole head groups to water alters the surface properties of the pores. Due to the presence of pyrrole head groups, the modified surface of the host polymer becomes more compatible with the pyrrole solution. Figure 5 shows that indeed the amount of pyrrole present in the porous host polymer increases with increasing content of surface-active pyrrole. This implies that 3-alkyl pyrrole-modified pores can absorb, spread, and retain pyrrole more efficiently, thus leading to a higher connectivity in the polypyrrole network.

The decrease in the conductivity of the composite polymer for greater amounts of surface-active pyrrole may be due to the loose structure, which is induced by the incorporation of large amounts of 3-alkyl pyrrole. Perhaps the presence of the less powerful surface active agent, 3-alkyl pyrrole, causes a partial collapse of the thin films of the continuous phase during polymerization, thus generating some cavities. As a result, the pyrrole solution is distributed less uniformly in the porous medium. The loose structure of the final composite that was observed may be due to these cavities. Another possibility is that, at high concentrations, a part of the surface active pyrrole dissolves into the pyrrole solution and interferes with the polymerization process.

Scanning electron microscopy experiments have been performed to examine the morphology of the host polymers and composites. Figure 6 presents the morphologies of the host porous polymers as a function of the amount of surface active pyrrole. The morphologies reveal a decrease in pore size in the presence of the 3-alkyl pyrrole, even though, as noted previously, the overall porosity is almost the same. The decrease in pore size might contribute to the increase in conductivity because the higher "capillary rise" and larger surface area of the porous medium can lead to a better distribution of the pyrrole and hence to a higher connectivity in the polypyrrole network. Of course, as soon as some pores collapse, generating cavities, the distribution of the liquid in

Table II   The Porosity of the Porous Media[a] (g Liquid/g Host Polymer)

Polymer	Water	Chloroform
#1	4.29	13.08
#2	4.39	12.73
#3	4.13	11.52
#4	4.27	13.79

[a] Note that, as expected, there is no swelling in water, but there is swelling in chloroform.
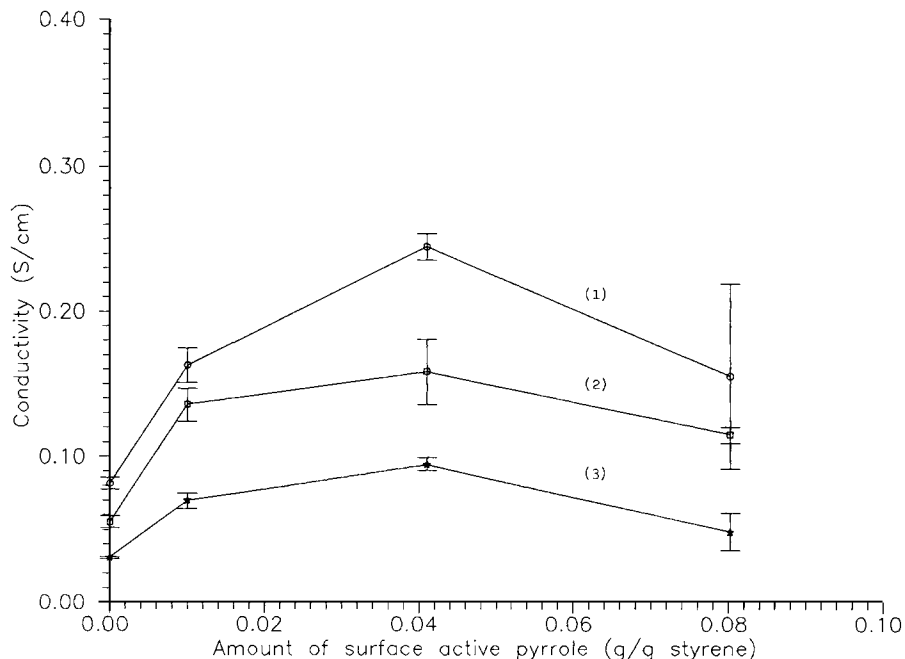
Figure 2   The effect of 3-alkyl pyrrole on the conductivity of polypyrrole composites. Methanol is the solvent used for the oxidant (0.4 g ferric chloride (anhydrous)/1 mL methanol). (1) Chloroform is the organic solvent used for pyrrole (0.4 g pyrrole/1 mL chloroform). (2) Benzene is the organic solvent used for pyrrole (0.4 g pyrrole/1 mL benzene). (3) Ethyl ether is the organic solvent used for pyrrole (0.4 g pyrrole/1 mL ethyl ether).
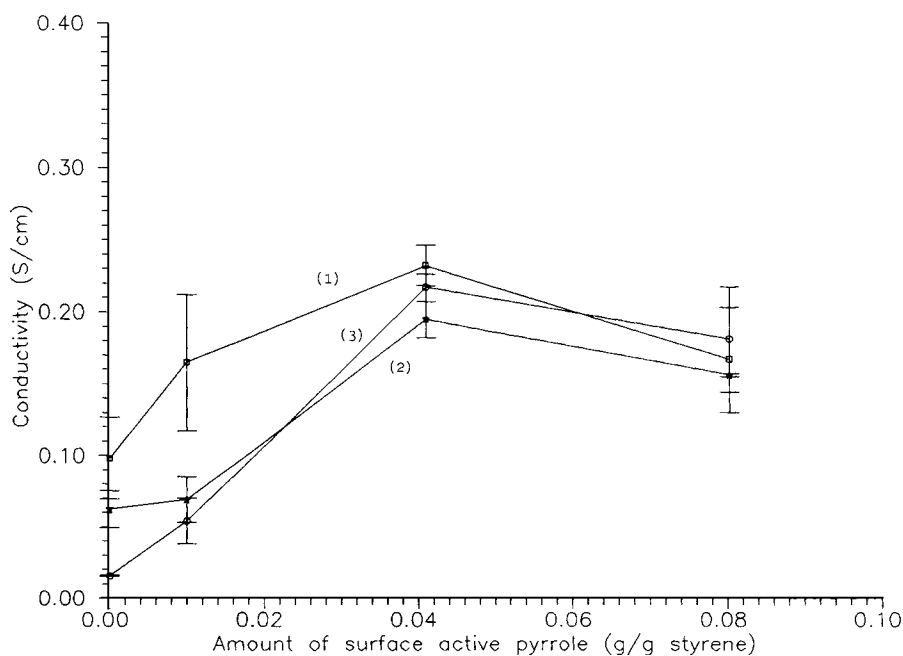

Figure 3   The effect of 3-alkyl pyrrole on the conductivity of polypyrrole composites. Water is the solvent used for the oxidant (0.4 g ferric chloride (anhydrous)/1 mL water). (1) Benzene is the organic solvent used for pyrrole (0.4 g pyrrole/1 mL benzene). (2) Ethyl ether is the organic solvent used for pyrrole (0.4 g pyrrole/1 mL ethyl ether). (3) Chloroform is the organic solvent used for pyrrole (0.4 g pyrrole/1 mL chloroform).
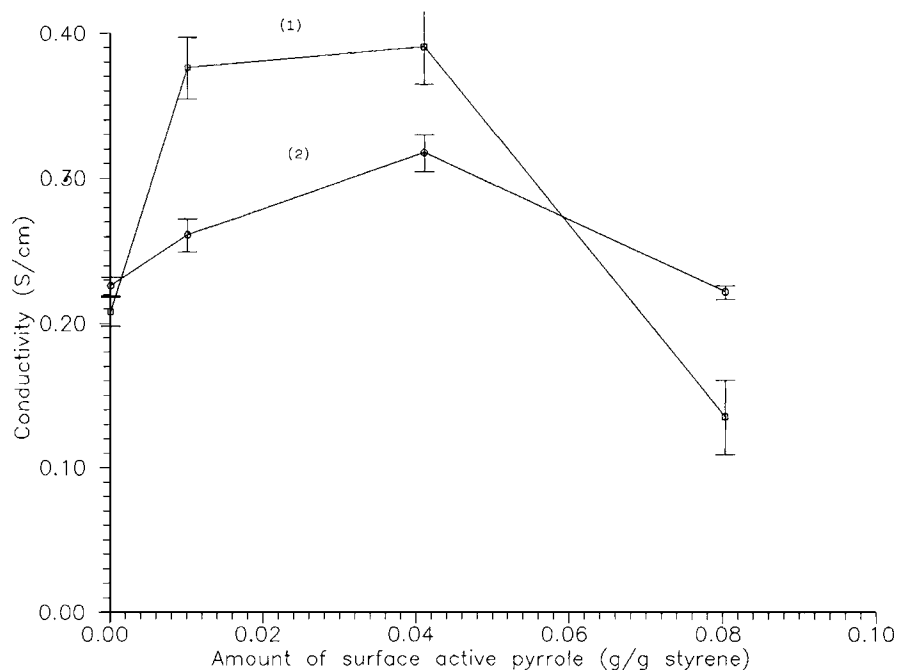
Figure 4 The effect of 3-alkyl pyrrole on the conductivity of polypyrrole composites. Pyrrole is used without a solvent. (1) Methanol is the solvent used for the oxidant (0.4 g ferric chloride (anhydrous)/1 mL methanol). (2) Water is the solvent used for the oxidant (0.4 g ferric chloride (anhydrous)/1 mL water).
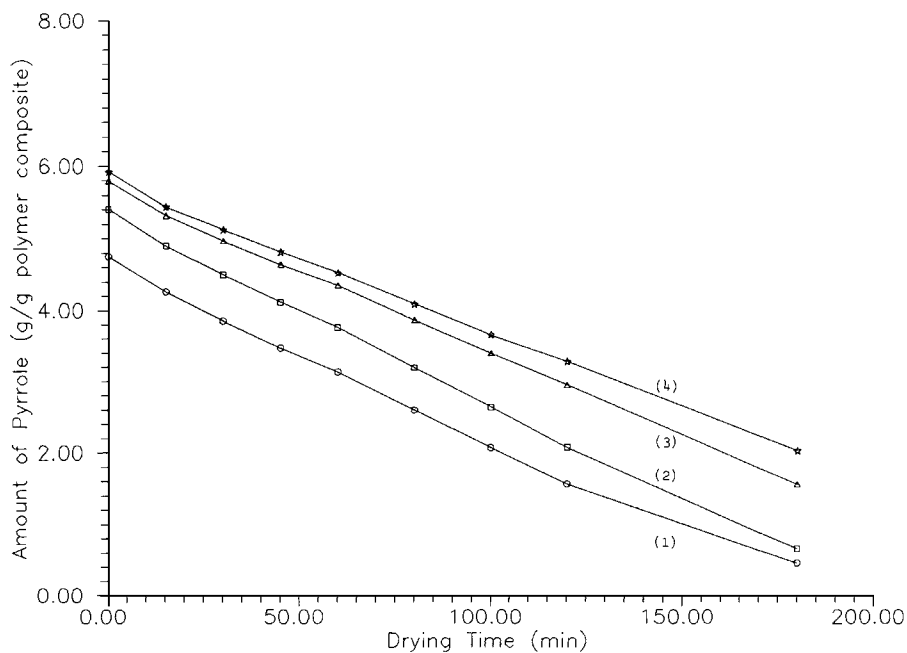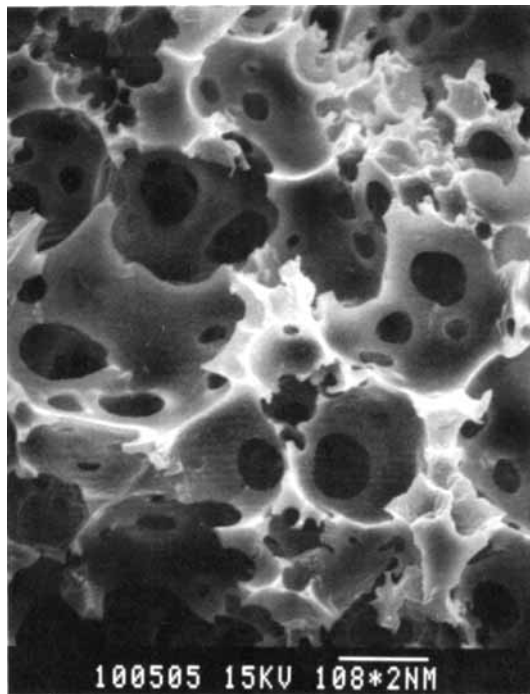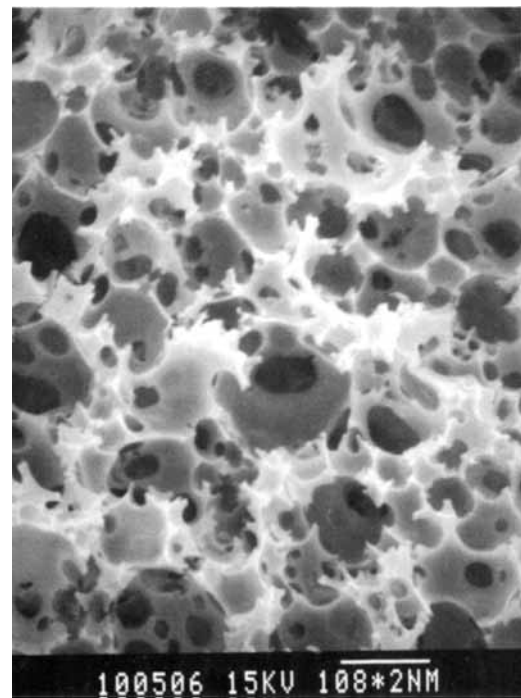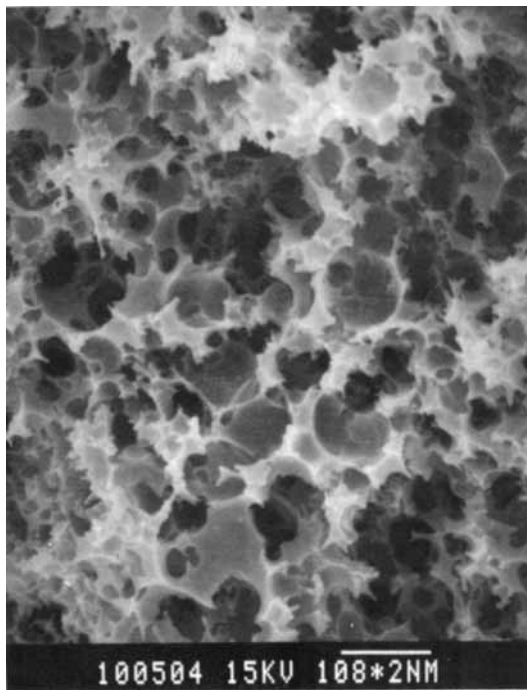

Figure 5 The effect of 3-alkyl pyrrole modified host on the absorption of pyrrole in the porous medium followed by desorption during drying at room temperature. Amount of pyrrole retained in the porous medium vs. drying time. (1) free of 3-alkyl pyrrole. (2) 0.01 g 3-alkyl pyrrole/g styrene. (3) 0.04 g 3-alkyl pyrrole/g styrene. (4) 0.08 g 3-alkyl pyrrole/ g styrene.
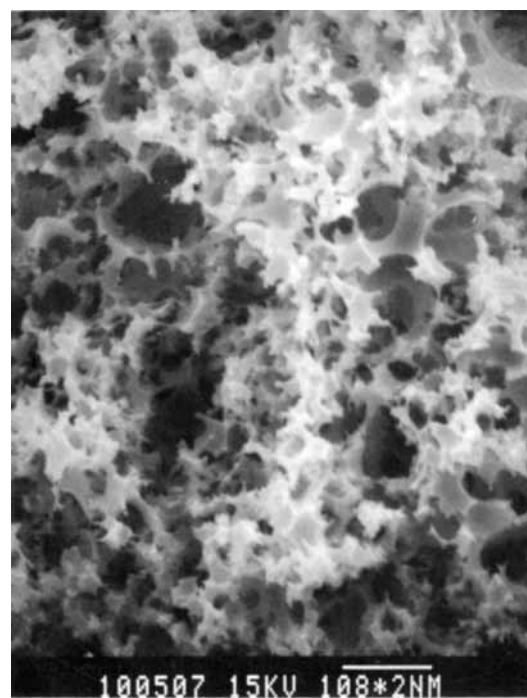
(a)

(b)

(c)

(d)

Figure 6 Scanning electron microscopy of porous crosslinked polystyrene. (a) free of 3-alkyl pyrrole. (b) 0.01 g 3-alkyl pyrrole/g styrene. (c) 0.04 g 3-alkyl pyrrole/g styrene. (d) 0.08 g 3-alkyl pyrrole/g styrene.

Table III The Effect of the Amount of Polypyrrole Incorporated in the Host Polymer on the Conductivity of Polypyrrole Composites[a]

Polymer[b]	Pyrrole Solution[c]	Oxidant Solution[d]	Conductivity (S/cm)	Polypyrrole (g polypyrrole/ g host polymer)
#1	Pyrrole/CHCl$_3$	FeCl$_3$/MeOH	0.08	3.06
#2	Pyrrole/CHCl$_3$	FeCl$_3$/MeOH	0.16	3.30
#3	Pyrrole/CHCl$_3$	FeCl$_3$/MeOH	0.25	2.48
#4	Pyrrole/CHCl$_3$	FeCl$_3$/MeOH	0.16	1.42
#1	Pyrrole/CHCl$_3$	FeCl$_3$/water	0.02	3.61
#2	Pyrrole/CHCl$_3$	FeCl$_3$/water	0.05	3.62
#3	Pyrrole/CHCl$_3$	FeCl$_3$/water	0.22	3.27
#4	Pyrrole/CHCl$_3$	FeCl$_3$/water	0.18	2.97
#1	Pyrrole	FeCl$_3$/MeOH	0.21	5.16
#2	Pyrrole	FeCl$_3$/MeOH	0.38	4.50
#3	Pyrrole	FeCl$_3$/MeOH	0.39	5.82
#4	Pyrrole	FeCl$_3$/MeOH	0.14	5.41

[a] Only selected data are listed.
[b] As in Table I.
[c] 4 g pyrrole/10 mL solvent.
[d] 4 g FeCl$_3$/10 mL solvent.

the host polymer is no longer as uniform and the degree of connectivity in the polypyrrole network is expected to decrease because a part of the liquid accumulates in the cavities. The connectivity among the polypyrrole films located upon the surface of interconnected pores, rather than the polypyrrole powder accumulated in the voids, contributes to conductivity. The fact that there is no direct relation between the amount of polypyrrole in the host polymer and conductivity (Table III) indicates that indeed the connectivity in the polypyrrole network, rather than the accessible porosity of the host, is responsible for conductivity. Figure 7 reveals a higher connectivity in the polypyrrole network (the brighter regions) when the surface active pyrrole is present. Figure 7(c) corresponds to the optimum composition and appears to have indeed the highest connectivity.

In summary, one can emphasize that the improved wetting induced by the alkyl-pyrrole has a positive effect on conductivity. However, the pore structure is also affected. While the overall porosity is almost the same, the average pore size changes, becoming smaller as the concentration of the surface active pyrrole increases. As noted previously, this may increase the extent of connectivity for low concentrations of the latter compound. At high concentrations, some pores collapse, thus generating cavities. This decreases the uniformity in liquid distribution and, hence, the connectivity of the polypyrrole network. These opposing effects may explain the occurrence of a maximum in conductivity.

The Effect of Reaction Medium on Conductivity

Two solvents have been used for the oxidant, namely water and methanol. Methanol is miscible with pyrrole, while water and pyrrole are almost immiscible (6 wt % pyrrole in water[20]). Three organic solvents (chloroform, benzene, and ethyl ether), which are miscible with methanol but immiscible with water, have been employed for pyrrole. Figure 2 indicates that when methanol is the solvent for the oxidant, the conductivity of the composite polymer changes with the solvent employed for pyrrole in the sequence chloroform > benzene > ethyl ether. Table IV lists the solubility parameters of the solvents used in this article. The sequence of conductivities coincides with that of the solubility parameters chloroform > benzene > ethyl ether, perhaps because the pyrrole solution becomes increasingly compatible with the surface active pyrrole modified pore surface as the solubility parameter increases. For pyrrole in any of the three solvents (insoluble in water) and oxidant in water, the sequence cannot be related to the solubility parameter (Fig. 3). The nature of the solvent employed for the oxidant also affects the conductivity.
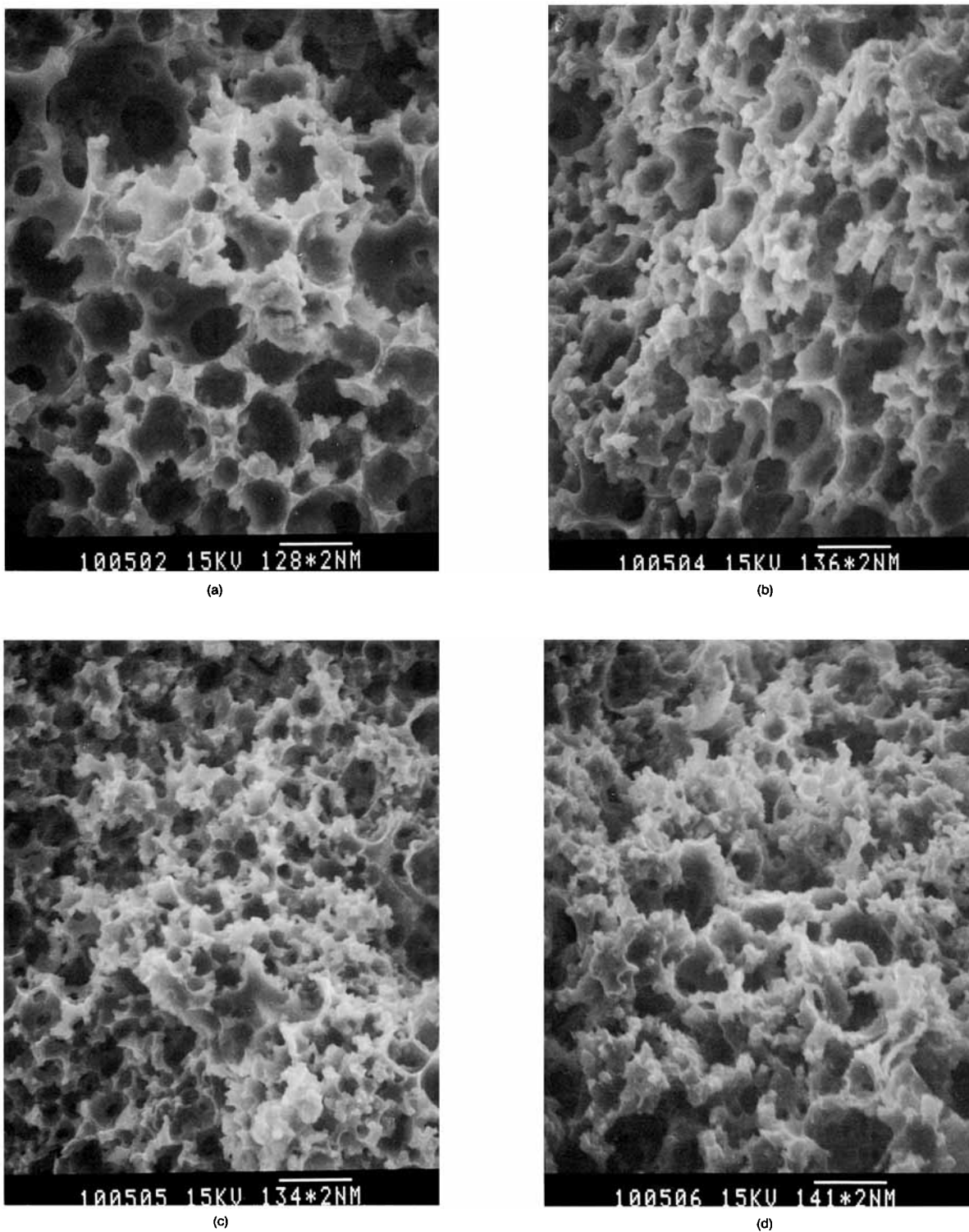
Figure 7 Scanning electron microscopy of polypyrrole composites. (a) free of 3-alkyl pyrrole. (b) 0.01 g 3-alkyl pyrrole/g styrene. (c) 0.04 g 3-alkyl pyrrole/g styrene. (d) 0.08 g 3-alkyl pyrrole/g styrene. The bright cloud-like network is polypyrrole. A higher connectivity in the polypyrrole network is observed when the surface active pyrrole is present.

Table IV   The Solubility Parameters at 25°C

Liquid	Solubility Parameter δ $(cal/cm^3)^{1/2}$	Reference
Chloroform	9.3	21
Benzene	9.15	21
Ethyl Ether	7.4	21
Methanol	14.5	21
Water	23.2	21
Pyrrole	12.16	a

a The solubility parameter is calculated using the following equation:

$$\delta = (d(\Delta H_v - RT)/M)^{1/2}$$

where δ, Solubility Parameter; d, Density of liquid; ΔH_v, Heat of vaporization (45.34 KJ/mol at 25°C[22]); R, Gas constant; M, Molecular weight; T, Temperature in °K.

CONCLUSIONS

The presence of 3-alkyl pyrrole molecules on the surface of the pores of the host polymer increases the affinity of the surface for pyrrole. This ensures a higher connectivity among the pyrrole films and increases the conductivity of polypyrrole composite from 2 to 14 times, depending upon the solvents employed for pyrrole and oxidant.

REFERENCES

1. H. Shirakawa, E. T. Louis, A. G. MacDirmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc. Chem. Commun.*, 578 (1977).
2. A. Dall'Olio, Y. Dascola, V. Varacco, and V. Bocchi, *C. R. Acad. Ser. C*, **267**, 433 (1968).
3. K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, *J. Chem. Soc. Chem. Commun.*, 854 (1979).
4. G. B. Street, T. C. Clarke, M. Krounbi, K. K. Kana-zawa, V. Lee, P. Pfluger, J. C. Scott, and G. Weiser, *Mol. Cryst. Liq. Cryst.*, **83**, 253 (1982).
5. F. Hautiere-Cristofini, D. Kuffer, and L. T. Yu, *C.R. Acad. Sci. Ser. C*, **277**, 1323 (1973).
6. R. E. Myers, *J. Electron Mater.*, **2**, 61 (1986).
7. M.-A. Paoli, R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 1687 (1985).
8. E. Ruckenstein and J. H. Chen, *Polym.*, **32**, 1230 (1991).
9. A. Pron, W. Fabianowski, C. Budrowski, J. B. Raynor, Z. Kucharski, J. Suwalski, S. Lefrant, and G. Fatseas, *Synth. Metals*, **18**, 49 (1987).
10. V. Bocchi, G. P. Gardini, and S. Rapi, *J. Mater. Sci. Lett.*, **6**, 1283 (1987).
11. E. Ruckenstein and J. S. Park, *J. Appl. Polym. Sci.*, **42**, 925 (1991).
12. G. P. Gardini, *Adv. Heterocyclic Chem.*, **15**, 67 (1973).
13. K. Hong and M. F. Rubner, *Thin Solid Films*, **160**, 187 (1988).
14. A. K. M. Rahman, L. Samuelson, D. Minehan, S. Clough, S. Tripathy, T. Inagaki, X. Q. Yang, T. A. Skotheim, and Y. Okamoto, *Synt. Metals*, **28**, C 237 (1989).
15. K. Hong, R. B. Rosner, and M. F. Rubner, *Chem. Mater.*, **2**, 82 (1990).
16. T. Shimidzu, T. Iyoda, M. Ando, A. Ohtani, T. Kaneko, and K. Honda, *Thin Solid Films*, **160**, 67 (1988).
17. E. P. Papadopoulos and N. F. Haidar, *Tetrahedron Lett.*, **14**, 1721 (1968).
18. R. Greenhouse and C. Ramirez, *J. Org. Chem.*, **50**, 2961 (1985).
19. E. Ruckenstein and J. S. Park, *J. Polym. Sci. Polym. Lett. Ed.*, **26**, 529 (1988).
20. A. R. Katritzky, *Handbook of Heterocyclic Chemistry*, Pergamon, New York, 1985.
21. R. C. Weast, Ed., *Handbook of Chemistry and Physics*, 68th Edition, CRC Press, Boca Raton, Florida, 1987.
22. D. R. Lide, Ed., *Handbook of Chemistry and Physics*, 71st Edition, CRC Press, Boca Raton, Florida, 1990.