Articles

Solid-State Polymerization of Pyrrole within a Langmuir–Blodgett Film of Ferric Stearate

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Ultrathin, highly conductive films have been formed by inducing the polymerization of pyrrole within the structure of a Langmuir–Blodgett film. The synthesis proceeded through the sequential exposure of a ferric stearate multilayer to hydrogen chloride gas and pyrrole vapor. Both steps resulted in significant chemical and structural changes. The first reaction converted the multilayer to stearic acid and hydrated ferric chloride and resulted in the partial disordering of the LB organization. In the second step, the oxidizing ferric chloride polymerized the pyrrole monomer and doped the resultant polypyrrole polymer. The film thickness doubled, and conductivities as high as 10 S/cm were attained after polymer aggregates were created in the multilayer. Infrared and ultraviolet–visible spectra indicated that the newly formed polymer chains showed little or no preferential orientation within the LB matrix. Electrical measurements confirmed that the polypyrrole phase separates into microdomains.

Introduction

Since their discovery, electrically conducting polymers have attracted a considerable amount of attention as possible alternatives for metals and semiconductors. Potential applications for these new polymers range from power distribution equipment[1] to electrical devices.[2] Increasingly, efforts have focused on incorporating these novel materials into highly organized, well-defined structures with the ultimate goal of fabricating nanoscale[3] and even molecular-scale electronic devices.[4] Progress toward this end, however, has been limited by their relatively poor stability and processability. Once rendered conductive by exposure to an oxidizing or reducing agent, these polymers become insoluble and nearly impossible to manipulate. A great deal of effort, therefore, has been directed toward improving these characteristics by means of new processing methods. Ideally, the process should not only improve the physical properties of the conductor but also provide a means of controlling the structure and morphology of the resulting product. One method of achieving these goals is by mixing the conducting polymer with a second, inert material to form a conductive composite. In this way, the matrix material not only strengthens the composite and provides a structural framework, it also serves to protect the polymer from ambient moisture and air.

This approach has been particularly successful with polypyrrole. Pyrrole is readily polymerized and doped by a variety of oxidizing agents including ferric chloride ($FeCl_3$).[5] The chemistry is straightforward and involves first impregnating a matrix material with the oxidizing salt and then exposing it to pyrrole vapor to induce the solid-state polymerization reaction. The technique has shown great versatility with a host of materials being used as templates for polypyrrole synthesis including glasses,[6] ceramics,[3] and polymers.[7–11]

This process also provides a rare opportunity to control the morphology and structure of the composites. During the polymerization reaction, the conductive chains will only form in regions rich in oxidizer. By controlling the location and concentration of the oxidizing agent within the matrix, one can dictate where the polymerization will take place and thereby control which regions of the composite become conducting and which remain insulating. While many matrix materials are amorphous and therefore incapable of generating composites with sophisticated structures, new substrates and techniques have been developed which are capable of producing complex architectures with novel electrical properties.[3] Among these new methods, the Langmuir–Blodgett (LB) technique, which represents one of the few ways of fabricating organic films of controlled thickness and structure, shows great promise.[12,13]

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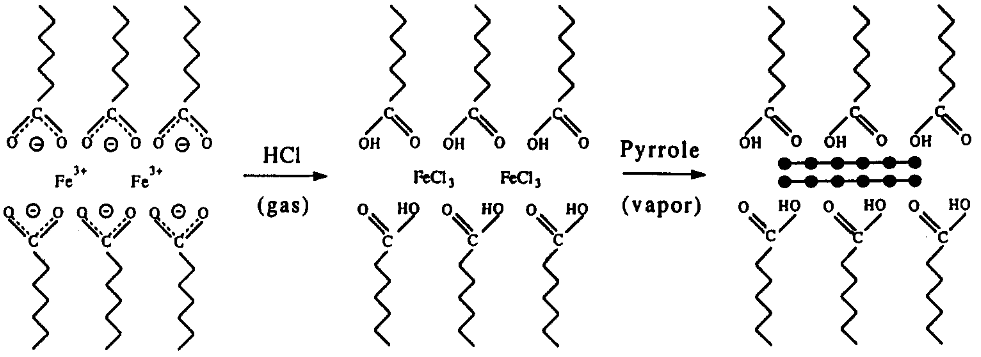

Figure 1. Idealized scheme showing the solid-state reactions of ferric stearate multilayers with hydrogen chloride gas and pyrrole vapor to form conductive polypyrrole. Connected black dots symbolize polypyrrole.

In this paper we present a novel method of incorporating conductive polypyrrole into a Langmuir–Blodgett multilayer through a series of solid-state reactions. Here, an LB film of ferric stearate acts as the template or matrix for the polymerization reaction. The polymerization occurs by the sequential exposure of the multilayer film to hydrogen chloride gas and pyrrole vapor. An idealized schematic of this reaction is shown in Figure 1. The first step results in the conversion of the ferric salt to stearic acid and hydrated ferric chloride. In the second step, conductive polypyrrole is formed after the acid-treated film is exposed to the monomer vapor. While other methods have been developed to manipulate conductive polypyrrole on an LB trough,[14,15] this is the first to take advantage of this facile chemistry. The structural and chemical changes that accompany each step of the reaction have been investigated, and the structure and morphology of the resulting films are discussed.

Experimental Section

Fabrication of Ferric Stearate Multilayers. A monolayer of ferric stearate was formed by first spreading a solution of stearic acid in chloroform (1 mg/mL) onto a Langmuir–Blodgett trough containing a dilute ferric chloride solution (1.5 mg/L).[16a] The surface layer was then compressed to a pressure of 32 mN/m. Films were deposited on a variety of substrates by the standard vertical dipping technique. Slower than normal dipping rates (5–10 mm/min) and longer drying times between dips (1 h) were used to accommodate these stiffer films and to ensure that the dipping ratio remained at unity. For additional information on the LB manipulation of ferric stearate, see also ref 16b.

Solid-State Polymerization of Pyrrole. After drying for several days, the completed films were ready to undergo the two-step conversion process. The first step, acidification of the stearate salt, was performed by suspending the clear, slightly yellow films in a desiccator charged with hydrochloric acid solution (5 mL, 37%). After brief exposure to the HCl gas evolving from the solution (2–4 min), the films became somewhat foggy and attained a slightly grainy texture though their yellow color persisted. The films were then removed to a second desiccator charged with pyrrole (5 mL). This system was sealed and partially evacuated (0.5–2 Torr) to allow the monomer vapor to saturate the chamber atmosphere. After standing under these conditions for 17 h, the samples attained a light gray color and displayed conductivities in the range 1–10 S/cm; far higher than similar LB films of conducting materials. To verify that conductive polypyrrole is formed only through this process and not by the HCl treatment alone, we subjected LB films of ferric stearate and cadmium stearate to the acid and pyrrole treatments outlined above. Under identical experimental conditions the ferric stearate multilayers produced conductive films while the cadmium stearate films exhibited no conductivity. This experiment demonstrates that HCl exposure alone could not have resulted in the formation of electrically conductive polypyrrole, i.e., iron(III) is necessary for the reaction to occur.

Spectroscopic Analysis. The electrical and optical properties and X-ray diffraction patterns and thickness were recorded at each stage of the reaction process in order to ascertain how the structure and chemistry of the films were affected by the solid-state reactions. Transmission/reflection FTIR and visible spectra were used to determine the organization of the amphiphilic molecules and polymer chains within the multilayer. Both methods provide important structural information by probing the sample in different orientations with respect to the plane of the film and substrate. In the case of FTIR, transmission experiments were performed with films deposited on infrared transparent (zinc selenide) plates in order to probe the dipole moments oriented parallel to the plane of the substrate. Films deposited on platinum-coated glass were used for reflection experiments. In this configuration, the beam struck at an angle of 78° from the surface normal and selectively coupled with dipoles oriented perpendicular to the substrate. A comparison of the relative intensities of absorption peaks seen in both experiments revealed how these vibrations, and therefore the corresponding molecular moieties, were oriented relative to the plane of the substrate. For example, an absorption strong in transmission but weak in reflection suggests a preferred orientation that is parallel to the planar surface, whereas equal peak intensities would indicate that the dipoles are either randomly oriented or situated at a 45° angle.[17,19] Similarly with the UV–visible spectra, two different polarizations of the beam were used to examine the orientation of the polypyrrole chains. With the sample held at 45° from the beam, S-polarization produces an electric field that is parallel to the substrate while P-polarized light contains an element that is perpendicular to the plane. Again, comparison of peak intensities in each mode yielded information about the orientation of the polymer chains with respect to the plane of the surface.

Structural information on a larger scale was attained with small-angle X-ray and profilometric thickness measurements. The X-ray diffraction patterns were recorded from 1.2 to 6° and from 3 to 16°. The locations of the Bragg diffraction peaks were used to calculate the stacking distance between monolayers. A Sloan Dektak profilometer was used to measure the overall thickness of the multilayers.

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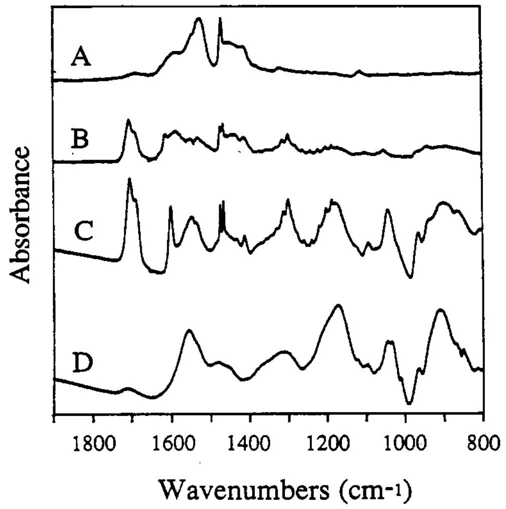

Figure 2. FTIR spectra of multilayers at each stage of the reaction process starting with pristine ferric stearate (A), after exposure to hydrogen chloride gas (B), after reaction with pyrrole vapor (C), and polypyrrole prepared in bulk (D).

In-plane dc conductivity was measured by a variation of the four-point probe method known as the Van der Pauw technique.[20] The temperature dependence of the conductivity was determined by measuring the resistance of a sample while it was in a cryostatic chamber. The low-temperature electric field behavior was investigated using films deposited on a special substrate containing electrodes spaced 5 μm apart. The electric field was calculated from the voltage buildup between the electrodes and the conductivity determined from the resulting current. Details concerning these various measurements can be found in previous papers.[4]

Results and Discussion

The polymerization of pyrrole within a multilayer could manifest itself as any one of several different morphologies. The possibilities range from the laminate structure implied by Figure 1 in which layers of polymer are alternately stacked with those of the fatty acid, to one in which the polymer forms randomly dispersed aggregates in the aliphatic matrix. A thorough investigation of the chemistry and molecular orientation of the samples at each step was made in order to confidently assign a structure and explain the electrical behavior of these novel composites.

FTIR Results. The chemical changes that take place during the solid state reactions were confirmed with conventional FTIR experiments. Figure 2 shows the infrared spectrum of a multilayer in its three forms: pristine ferric stearate (A), the multilayer after acid treatment (B), and the polypyrrole charged sample (C). Comparison of the first two spectra (Figure 2A,B) provides strong evidence that the ferric stearate salt has been converted to stearic acid by exposure to HCl. The presence of absorption bands at 1540 and 1580 cm^{-1} (Figure 2A) due to the carboxylate ions and the absence of the corresponding acid peak at 1700 cm^{-1} suggests that the original LB film was composed mostly of ferric stearate. The spectrum of the acid-treated film, however, shows an increased absorption at 1700 cm^{-1} due to the formation of carboxylic acid groups accompanied by a diminution of the salt peaks indicating that exposure of the films to the acid fumes was effective in converting most of the salt to the acid. The additional development of a shoulder peak at 1600 cm^{-1} as well as a broader absorption at 3500 cm^{-1} (not shown) due to the formation of hydrated ferric chloride ($FeCl_3 \cdot xH_2O$) adds further proof of this conversion.

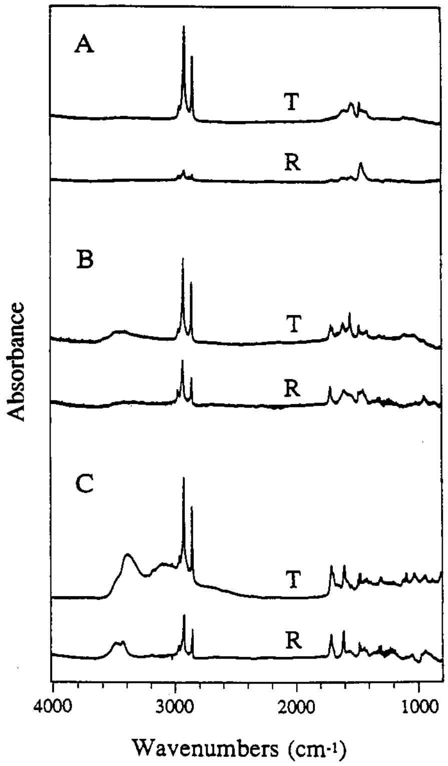

Figure 3. Transmission (T) and reflection (R) FTIR spectra of the pristine ferric stearate (A), after exposure to hydrogen chloride gas (B), and after reaction with pyrrole vapor (C).

Exposure of the acid-treated films to pyrrole vapor produced further significant changes in the infrared spectrum (Figure 2C) which were attributed to the presence of polypyrrole. A new set of peaks, seen at 890, 1040, 1186, and 1300 cm^{-1}, closely match the ring vibrations observed in polypyrrole films. These similarities are easily recognized by comparing the IR spectrum of the fully treated LB film (Figure 2C) with that of pure polypyrrole made by oxidation with ferric chloride (Figure 2D). These four FTIR spectra prove that the chemistry shown in Figure 1 is correct, but further evidence is needed before structures can be assigned.

One of the most powerful tools for determining molecular orientation is transmission/reflection FTIR spectroscopy. Three sets of such spectra, each representing a stage in the reaction process, is displayed in Figure 3. The first two sets indicate a high degree of order in the pristine ferric stearate multilayers that is significantly modified after exposure to the acid fumes. The intensities of the asymmetric and symmetric CH_2 stretching vibrations of the unexposed films (Figure 3A) at 2917 and 2851 cm^{-1} are significantly greater in transmission than reflection. This type of polarization dependence is characteristic of a structure in which the hydrocarbon tails of the amphiphiles are rigidly aligned normal to the substrate surface; an arrangement commonly found in LB films of stearate salts.[18] The spectrum of the acid-treated films, now consisting of stearic acid and hydrated ferric chloride (Figure 3B), shows greatly enhanced methylene absorptions in the reflection mode revealing that the hydrocarbon tail groups have now tilted away from the normal of the

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substrate. This conclusion is in agreement with prior studies of stearic acid LB films which have found that the hydrocarbon tails of a stearic acid multilayer tilt by as much as 58° from the normal.[21] The ratio of the methylene absorptions did not change in the third set of spectra (3C). This suggests that no further changes in the orientation of the fatty acid molecules occurred during the final step in the process despite the addition of the polymer chains.

The fact that intensities of the vibrational bands associated with the newly formed polypyrrole chains (found in the 800–1300-cm^{-1} range of Figure 3C) are not significantly different in reflection and transmission indicates that the polypyrrole chains are randomly oriented within the LB film. This is in contrast to prior methods of synthesizing the conductive polymer directly on an LB trough and subsequently fabricating multilayers.[14b] Polypyrrole-loaded multilayers made by such techniques show significantly stronger absorption bands in the transmission mode evincing a preferred orientation of the chains within the plane of the surface.

UV–Visible Spectroscopy. Radiation within the ultraviolet and visible region is of high enough energy to excite the charge-carrying bipolarons of a doped conductive polymer. As such, it is particularly well suited to studying of the orientation of the polypyrrole chains independent of the matrix. This was done on the fully reacted films, after the polymerization treatment was complete. Separate experiments were devised in order to probe the chain orientation along the length of the substrate and normal to it. The first experiment showed that the absorption of polarized light by polypyrrole was the same in all directions parallel to the substrate. This indicates that the polymer chains radiate outward equally in all directions within the plane of the substrate. The second set of experiments, using S- and P-type polarization, also failed to discern any difference in the absorption of the polymer parallel and perpendicular to the substrate. Taken together, these results suggest that the polymer chains reside within the fatty acid matrix with little or no preferred orientation.

X-ray Diffraction Studies. The structural evolution seen in the spectroscopic results was corroborated by the X-ray diffraction patterns of these films. The diffraction patterns also reflect the disruption of the initial Langmuir–Blodgett structure by the acid treatment and provide further evidence of the conversion to the less ordered stearic acid system. Figure 4 gives the small-angle X-ray diffraction patterns recorded from 1.2 to 16° at each stage of the reaction. The pristine ferric stearate (Figure 4A) exhibits a highly pronounced, well-defined pattern. The peaks located at 1.60, 3.16, 4.74, and 6.36° correspond to the first four reflections of the Bragg diffraction and yield a bilayer repeat distance of 54 Å. This value, exactly twice the length of a stearate molecule, confirms the rigid head-to-head configuration expected in a well-ordered Langmuir–Blodgett film of ferric stearate. The second set of X-ray patterns, generated by the acid-treated films, dramatically illustrate the changes brought about by the HCl fumes. The original pattern of the stearate salt is completely wiped out and replaced by a new series of far weaker peaks. As predicted by the spectroscopic results, the new pattern closely resembles that of stearic acid. In fact, a closer inspection reveals that there are actually two separate patterns here; one with peaks at 3.95 and 5.82°, giving a repeat distance of 45 Å, and the second, more intense pattern at 2.16, 4.33, and 6.52° yielding a bilayer spacing of 40.5 Å. This type of diffraction pattern is often seen with stearic acid which is known to organize into two distinct molecular organizations with different tilt angles and thereby generate a mixed morphology.[21] The weakness of the patterns suggests an overall loss of order and further that the actual thickness of the films are not necessarily reflected in the new bilayer spacing values.

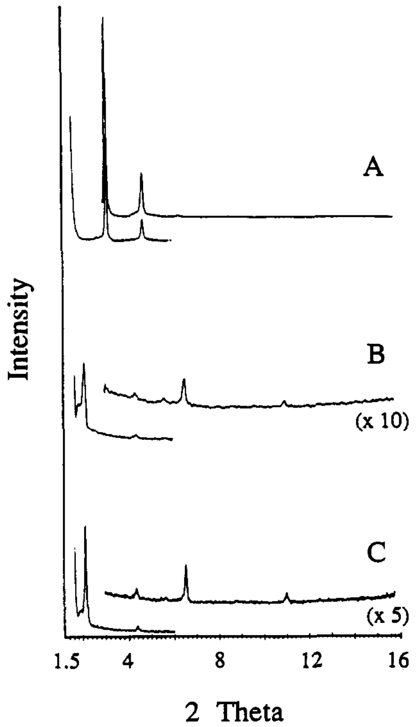

Figure 4. Small-angle X-ray scattering curves recorded from 1.2° to 6° and from 3° to 16° for a ferric stearate multilayer in pristine form (A), after treatment with HCl gas (B), and after reaction with pyrrole vapor (C). Multiplication factors below each curve indicate intensity scale relative to curve (A).

The X-ray diffraction patterns of the polypyrrole-loaded films (Figure 4C) are nearly identical to those generated from their acid-treated precursors. Thus, according to the X-ray diffraction results, no further structural changes occur as a result of the formation of the polymer. This seemingly conflicting result can be explained by recognizing that the newly incorporated polymer chains are randomly oriented and phase separated within the LB matrix and, as such, are incapable of greatly influencing the Bragg reflection of the stearic acid matrix. Had the polypyrrole formed in an ordered fashion, say as thin layers between the fatty acid matrix, the diffraction patterns would have changed to reflect this new organization. However, because the polymer acts as a random and unordered element (as already evinced by the UV–visible spectra) its influence on the X-ray pattern is minimal. This is not to say that a change in structure has not occurred but rather that the introduction of the polymer has not altered the basic structure of the stearic acid domains nor their X-ray diffraction pattern. In fact, the addition of the polymer may be evident from the profilometric thickness measurements.

The profilometer simply measures the overall thickness without regard to the film's underlying structure. According to these tests, the final thickness of the fully reacted multilayers ranged between 108 and 132 Å/layer, nearly

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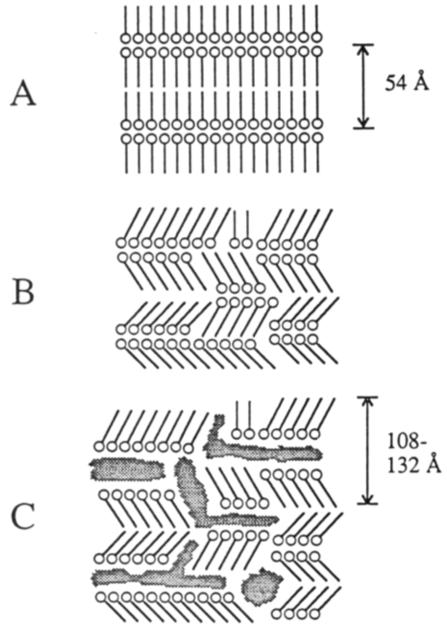

Figure 5. Schematic of the structural changes undergone by the ferric stearate multilayer starting with the original Langmuir–Blodgett construction (A), and conversion to stearic acid by treatment with HCl (B), and the final structure containing conductive polypyrrole aggregates (C).

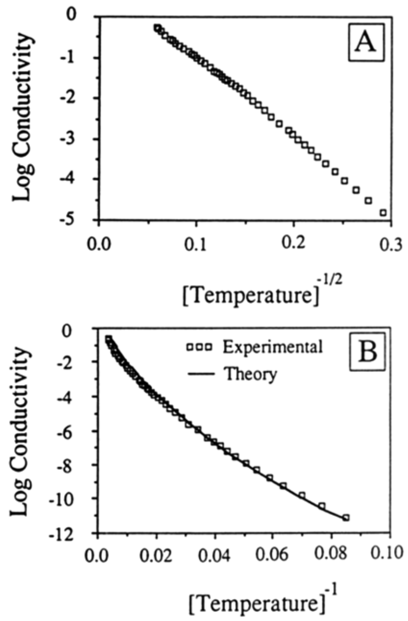

Figure 6. Comparison of the temperature dependence of the conductivity with two models; the charging energy limited tunneling model which proposes a $T^{-1/2}$ dependence (A) and the best fit by the thermally induced voltage fluctuation model (eq 1) where T_0 is set at 8.6 K and T_1 at 225 K (B).

twice their initial bilayer spacing of 54 Å. This increase in thickness is probably due to a combination of factors including the disordering of the film upon acid treatment and later by the addition of polypyrrole.

When all the structural data are taken into account, a general picture of the evolution of these unusual films may be presented. A schematic of the structural changes is shown in Figure 5. Initially, the ferric stearate molecules were formed into a rigid head-to-head structure by the action of the Langmuir–Blodgett trough. This structure, however, was drastically changed after exposure to hydrochloric acid fumes (Figure 5B). The stearic acid chains became tilted and formed into two less ordered morphologies. This treatment and the polymerization which took place after exposure to pyrrole (Figure 5C) resulted in a swelling of the film to nearly twice the original thickness. The polymerization occurred without significant change in the order of the fatty acid structure.

It appears that the polymer chains are randomly configured but the spectroscopic data fail to contribute anything more to the understanding of this important element. The polypyrrole could form aggregates (as illustrted by Figure 5), two-dimensional plates or even thread through the multilayer as individual chains. Arguments based on minimizing the surface energy of the precipitate would suggest a spherical shape for the polymer aggregates.[22,23] One way of discerning between these various possibilities is through a study of the electrical properties.

Electrical Properties. Differences in the chemistry and structure of conductive organic systems are often revealed in the electrical properties.[24] The present example of conductive polypyrrole aggregates within an insulating matrix were modeled after similarly structured composites of carbon black in PVC. In the original application of this theory the carbon particles act as the conductive element while in the present case it is the polymer aggregates which are responsible for carrying a charge. Nonetheless, the two models developed for this system represent reasonable approximations to the stearic acid/polypyrrole system at hand.

The first theory, called charging energy limited tunneling, best describes systems in which the conductor forms small aggregates (less than 200 Å in diameter) in close proximity to each other. Conduction of electricity occurs after an electron hops or tunnels from one aggregate to the next and in so doing, produces a charged aggregate pair. The creation of such a pair, like the charging of a capacitor, requires energy. In a system consisting of small particles, the energy requirement is significant and becomes the rate limiting step in conducting a charge. Such a system shows a $T^{-1/2}$ temperature dependence. From this, and a study of the electric field behavior, one can determine a value for the sum of s and d ($s + d$) where s is the average interparticle distance and d is the average particle diameter.[25-27] While the temperature dependance of the experimental data closely followed theory (Figure 6A), calculations based on the electric field dependence produced disappointing results. The application of this model yielded a sum value ($s + d$) of 3.4 Å, a nearly impossible number.

The second theory, known as fluctuation-induced tunneling conductivity, produced better results. This theory best predicts the behavior of composite systems made up of larger particles ($d > 200$ Å). As the size of the conductive particles increase, the charging energy becomes negligible and the rate at which an electron hops from neighbor to

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neighbor becomes a function of the energy barrier for the jump. Materials that follow this behavior exhibit a temperature dependence that is defined by the equation

$$1/\sigma = 1/\sigma_0 \exp[T_1/(T + T_0)] \qquad (1)$$

where σ represents conductivity, T is temperature, and σ_0, T_0, and T_1 are constants. Evaluation of this temperature dependence in conjunction with the electric field behavior yields individual values for s and d, the critical dimensions of the composite.[28-30]

As shown in Figure 6B, the theoretical curve that best fits the experimental data gave T_1 and T_0 values of 225 and 8.3 K respectively. This information was enough to determine the interparticle distance s through the relationship[28]

$$s\pi/\delta = 2(T_1/T_0) \qquad (2)$$

where δ is the electron penetration depth.[31] This parameter was assigned a value of 4.35 Å and is based on the same potential energy barrier height (V_0) of 200 meV used in the PVC/carbon black system.[28] When this value was put back into eq 2 the interparticle distance was found to be 75 Å.

The diameter of the particles was estimated from the electric field behavior of the conductive LB films. This behavior exhibits both a temperature and electric field dependence[28] and is given by the equation

$$j = j_0 \exp\{-a(T)[(\epsilon/\epsilon_0) - 1]^2\} \qquad (3)$$

where

$$a(T) = T_1/(T_0 + T)$$

In these equations, ϵ and j represent the electric field and current at temperature T, j_0 is a constant, and ϵ_0 is the fitting parameter necessary for the determination of the particle size d. The best fit to the experimental curves at 10 and 30 K occur when ϵ_0 is assigned a value of 1800 V/cm.

While this value of ϵ_0 can be interpreted as the average field strength across the sample, the actual field encountered by the electrons is greater. This is because the electric field cannot exist within the conductive regions such as carbon black particles or, in the case of the present study, polypyrrole aggregates and must be dissipated in the insulating regions between aggregates. The true potential drop seen by an electron is estimated by dividing the barrier height V_0 by the interparticle distance s[29] according to the equation

$$\epsilon_B = 4V_0/es \qquad (4)$$

Putting in the values for V_0 and s results in an interparticle field strength of 1.1 MV/cm. Thus we attain two values of the field strength; one reflecting the average value over the entire sample ϵ_0, the second giving the actual or resulting electric field that develops between the conductive particles ϵ_B. A relationship exists between the ratio of the electric field values and the ratio of particle size to nearest neighbor distance. This takes the form[27]

$$\epsilon_B/\epsilon_0 = d/s \qquad (5)$$

The experimental results indicate that the ratio of ϵ_B to ϵ_0 is 590. This value must also represent the difference between the nearest neighbor distance (75 Å) and the particle diameter. When eq 5 is applied to these results, the particle diameter is found to be about 4.4 μm, a much more reasonable number than that provided by the charging energy theory.

In summary, application of the tunneling mechanism yields a value of 3.4 Å for $(s + d)$. This result seems dubious considering it represents a combination of the particle diameter and interparticle distance. The thermally induced voltage fluctuation model gave better results. The interparticle distance was calculated to be 75 Å, while the particle diameters were on the order of 4 μm. The better fit provided by this model suggests that the actual morphology of the film is one dominated by larger polypyrrole aggregates and separated by distances on the order of 100 Å. One must be very cautious, however, in interpreting these results as they frequently give size estimates that are not very close to actual values (due to the various assumptions that are made). The electrical measurements are therefore presented primarily to show that the polypyrrole has aggregated into separate domains and that this type of phase-separated molecular organization strongly influences charge transport. Perhaps the best conclusion that can be drawn from these results is that the morphology of the conductive multilayers is more complicated than the structures suggested by either theory.

Conclusions

A new method has been developed by which ultrathin, highly organized films of conductive polypyrrole can be synthesized within the structure of a Langmuir–Blodgett multilayer. The polymerization occurs through a series of facile solid-state reactions with the LB film acting as a template. In the first of two reactions, the ferric stearate film is converted to stearic acid and ferric chloride by exposure to hydrogen chloride gas. The reaction also results in a significant change in the structure of the films; the amphiphilic chains become tilted away from the normal of the film and the multilayer construction loses much of its initial order. In the second and final reaction, pyrrole vapor reacts with the iron chloride in the matrix to form conductive polypyrrole. This causes further changes in the structure of the film and contributes to a near doubling in thickness. The presence of the polymer also manifests itself in the electrical properties of the films with conductivities as high as 10 S/cm being recorded. A combination of spectroscopic evidence and modeling of the electrical properties point to a final structure in which the polypyrrole resides as aggregates up to a micron in diameter within the partially ordered stearic acid matrix.

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