Patterning of Conductive Polyaniline Films from a Polymerization-Induced Self-Assembled Gel

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Introduction. Conductive polyaniline (PAn) gels have been considered a novel class of plastic materials due to their well-known mechanical flexibility, which is useful for processing.[1−4] Most of these gels have usually been prepared by mixing the polyemeraldine base and suitable surfactant dopant such as camphorsulfonic acid (CSA), dinonylnaphthalenedisulfonic acid (DNNDSA), and dodecylbenzenesulfonic acid (DBSA) in a dry or wet condition.[5,6] Effective doping of the polyemeraldine base form of PAn to a conductive form, polyemeraldine salt, is very important. Recent studies reported that a decrease in conductivity occurs during heat treatment and annealing of PAn gels due to the degradation and segregation of dopants from the polymer.[7] In applications such as optoelectronics and microelectronics, it is essential to have uniformly deposited high-quality films, a requirement that is particularly problematic for conjugated polymers such as PAn where the rigid backbone is inherently difficult to process. Further advancement in gelation techniques is desired to achieve high-quality, processable gels. An attractive route, yet to be investigated, to obtain conductive PAn gels is to perform polymerization in the presence of surfactant acids. Despite the fact that a number of sulfonic acid-based polymerization protocols to form PAn in the form of nanostructures[8,9] and dispersions[10,11] have been reported, no synthetic efforts have been made to develop an in situ PAn gel.

In this study, we report an interesting phenomenon of gelation in an aqueous aniline−DBSA polymerizing system that allows the processing of high-quality conductive PAn films prior to gelation. The process can be described as a polymerization induced micellar interconnection that eventually transforms the solution to a solid gel.

Experimental Section. Polymerization-induced gel formation was observed only over a specific concentration range of DBSA−aniline complex (0.01−0.1 mol/L). Deviation from this concentration range resulted in either the solubilization or precipitation of PAn. In a typical synthesis, sodium salt of DBSA (100 mL, 0.025 M) was converted to the acid form, DBSA, by the addition of hydrochloric acid (3.3 mL, 1 M). To this 0.09 mL of aniline was added drop by drop and thoroughly mixed to form an aniline−DBSA complex (Figure 2). To the above turbid solution 0.62 g of ammonium persulfate was added as a polymerizing agent, and the reaction was conducted at 23 °C. After 15−25 min the solution turned light green. At this stage the solution was stirred for 30 s. The solution exhibited a gradual increase in the viscosity. Gelation was observed within 20 min in the final stage of the polymerization and resulted in a solid green gel which is a conductive form of PAn called polyemeraldine salt. The viscous solution phase observed prior to gelation can be utilized to dip-coat good quality films (Figure 1). After the completion of gelation, the gel gradually shrinks by expelling the trapped water. Scanning electron micrographs (SEM) of the films and gels were performed to analyze the morphology. Conductivities of the PAn films were measured using a four-point probe method at ambient temperature.

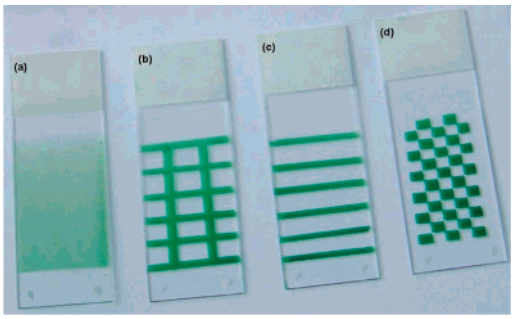

Figure 1. Thin films of polyemeraldine salt dip coated on (a) a glass slide and (b−d) dip coated on patterned glass slides, and later the patterns were removed.

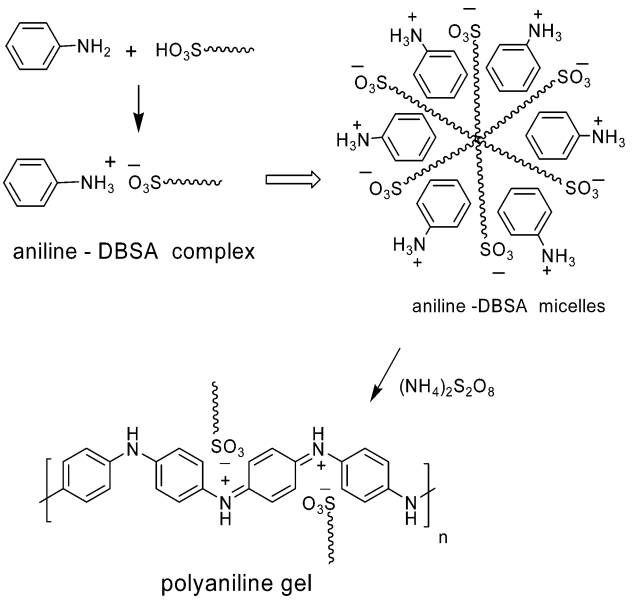

Figure 2. Illustration of polymerization of aniline−DBSA micelles to a conductive PAn gel.

Results and Discussion. Surfactants are capable of forming well-defined micellar structures in a solution. The characteristics of the micelles are dependent on the type of solvent, concentration of the surfactant, and the counterion. In an aqueous solution of DBSA−aniline complex, anilinium ions sit in the micellar interface with

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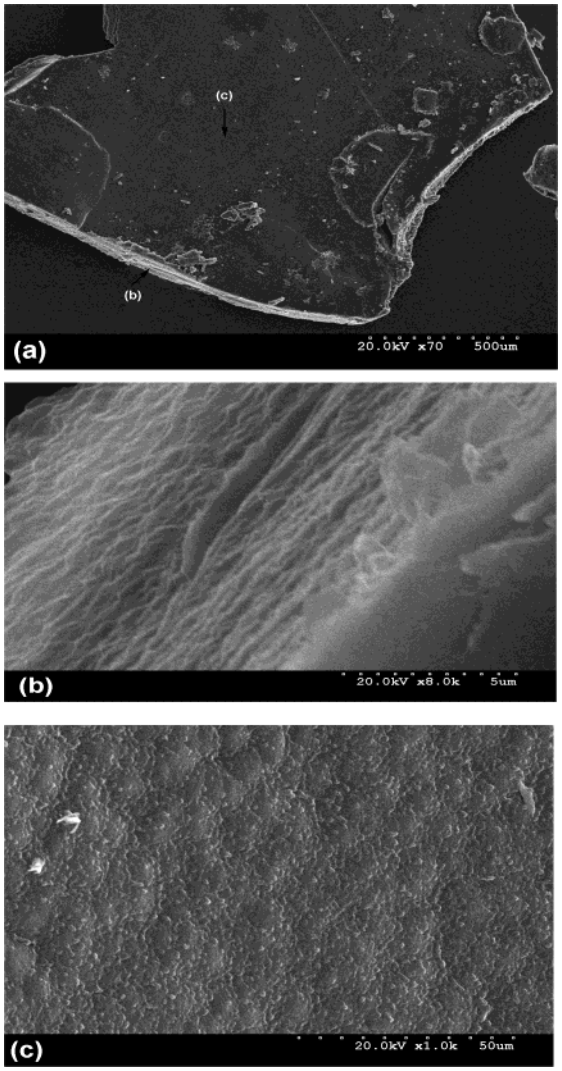

Figure 3. Scanning electron micrographs of (a) dried PAn gel, (b) illustrates a stacked-layer structure with each layer thickness ~100 nm along the edge, and (c) shows fibrillar morphology of the gel surface.

benzene parts penetrating into the hydrophobic core of the DBSA micelle as illustrated in Figure 2.

Aniline−DBSA complex at low concentrations (<0.01 mol/L) forms a clear solution in water with no noticeable change in the viscosity.[12] Polymerization of these systems resulted in the formation of PAn solutions. At these low concentrations, micelles are apart from each other, and as a result there is negligible chance to form a highly networked PAn structure. At concentration range 0.01−0.1 mol/L, a slight turbidity was observed in the solution, indicating micellar aggregation. Furthermore, a small increase in the viscosity was observed for aniline−DBSA complex compared to DBSA solutions of the same concentration. This implies that at this specific concentration range micelles are close enough to interact with each other, indicating intermicellar interaction. Anilinium ions in one micelle interact with DBSA anions in the neighboring micelles, establishing a weakly networked structure.[12] Polymerization performed in these systems induces the union of anilinium ions in the neighboring micelles to form PAn chains in an organized fashion that eventually leads to a stable, well-defined PAn gel structure. The measured conductivities for thin films processed from the gel (thickness 50−500 nm) were 1 S cm^{-1}.

SEMs of the dried gel showed an interesting morphology as shown in Figure 3. As illustrated in Figure 3b, along the edge of the gel, a stacked layer by layer morphology was observed with an approximate individual layer thickness of 100 nm. This observation indicates the transformation to a layered structure in the gel. The gel surface showed a fibrillar morphology as shown in Figure 3c. The formation of PAn precipitates above 0.1 mol/L implies that the micellar characteristics change with increasing concentration of aniline−DBSA complex in water.

Conclusion. A novel conductive PAn gel doped with DBSA is developed for the first time from an aqueous solution of aniline−DBSA complex using a polymerization-induced micellar self-assembly. The high quality of PAn patterns dip-coated prior to gelation demonstrates that in situ polymerization induced gelation is a simple and effective way to achieve a homogeneous system for easy processing. The thin films showed comparatively good conductivity (1 S cm^{-1}). This paper contributes to the current focus on patterning in conductive polymers for potential use in optoelectronic devices. The properties and structural characteristics of PAn gel films are currently under investigation.

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Supporting Information Available: Pictorial illustration of gelation, schematic illustration of intermicellar interactions, schematic of deprotonation of polyemeraldine salt film, UV−vis spectra of PAn, conductivity data, and SEMs of dried gel and films. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) See Supporting Information for pictorial representation of intermicellar interaction and viscosity studies.

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