

Synthesis and self-assembled multilayer film fabrication via layer-by-layer deposition of water-soluble aromatic polyimines

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SUMMARY :

A new series of water-soluble conjugated aromatic polyimines containing sulfonate groups have been synthesized via polycondensation reaction between diamines and dialdehydes at room temperature. Self-assembled multilayer films consisting each polyimine as a polyanion and poly(diallyldimethylammonium hydrochloride) as a polycation were fabricated successfully by alternate deposition in corresponding aqueous solutions.

Introduction

Currently the research interest in the synthesis and application of conjugated polymers with useful electronic, optoelectronic, and photonic properties has been increased during the last two decades.^{1,2} A lot of researches on the electronic, electrochemical, linear optical, or nonlinear optical properties of these materials such as polyacetylene, poly(*p*-phenylene) (PPP), and poly(*p*-phenylene vinylene) (PPV) have been reported so far.^{3,4} These properties may lead to various practical applications such as information storage and optical signal processing and materials for solar energy conversion. Besides the practical uses, electroluminescence (EL) from conjugated polymers is gaining a lot of interest. One of the π -conjugated polymers that is less studied with respect to electronic, optical, and nonlinear optical properties is the aromatic *polyimines* also known as *polyazomethines* or *poly(Schiff bases)*.⁵ However the infusibility and insolubility of conjugated aromatic polyimines in common organic solvents prevent their being processed. Some reports have been made to improve the poor processability of polyimines.^{6,7}

Ultrathin organic films are currently gaining widespread interest because of the potential applications in integrated optics, sensors, and friction reducing coatings. Recently new thin film fabrication technique based on the alternating adsorption of

molecular layer of oppositely charged polymers (anionic and cationic polyelectrolytes) can be successfully applied to manipulate a wide variety of electroactive materials including conjugated polymers.⁸

In this report we have synthesized new series of conjugated aromatic polyimines containing sulfonate groups. The preparation, characterization, and self-assembled multilayer fabrication of the newly synthesized polyimines are described in detail.

Experimental

Polymer synthesis The chemical structures of the polymers are shown in Scheme 1. Polyimines were prepared via low temperature interfacial polymerization under vigorous agitation.

Thin film fabrication through self-assembled layer-by-layer deposition The formation of self-assembled multilayers of polyimines were carried out by using a aqueous solution of each polyimine with a concentration of 3mM (Ultrapure Millipore water was used.). Multilayer formation was accomplished by using suitable polycation (poly(diallyldimethylammonium hydrochloride), PDH) since the sulfonate groups in the polyimine backbone were negatively charged in water. The final concentration of PDH solution was prepared at 3mM. A glass substrate with a negatively charged surface is immersed in the aqueous solution containing the cationic polyelectrolyte (PDH) and then a monolayer of the polycation is adsorbed onto the glass surface. After thorough rinsing in Millipore water the glass substrate is immersed in the solution containing the anionic polyelectrolyte (polyimine). Again a monolayer is adsorbed with polyanions, which is negatively charged. By repeating those steps in a cycle, alternating self-assembled multilayer of both polymers (PDH and each polyimine) was obtained (Fig.1.).

Results and Discussion

The solubility of diamine monomers (4,4'-diaminostilbene-2,2'-disulfonic acid and 2,5-diaminobenzenesulfonic acid) in organic solvents commonly used in solution polymerization reaction such as DMF and NMP is very low and they have limited solubility in water as well. We, therefore, conjectured the conversion of sulfonic acid groups in the diamine monomers into sodium sulfonate groups by using equimolar

amount of base. Finally the diamine monomers with sodium sulfonate groups were dissolved in water in the presence of a base (Sodium hydroxide was used in this experiment.) and reacted with a dialdehyde dissolved in chloroform to accomplish interfacial polycondensation reaction. Benzyltributylammonium chloride as a phase transfer catalyst (PTC) was used to increase the rate of polymerization. We found that four polyimines as synthesized were soluble in water, DMF, and DMAc. We convinced that the sulfonate groups played an important role in improving solubility in above solvents. Therefore the GPC measurement of each polymer was performed in DMF solution. The results were shown in Scheme 1. In **SIP** and **SIT**, the molecular weights are relatively high compared to those of **PIP** and **PIT**. FT-IR spectra of the polymers showed characteristic bands of the functional groups expected such as imine group (C=N) near at 1620cm^{-1} and sulfonic acid salt near at 1120cm^{-1} .

Table 1 shows the absorption and fluorescence maxima of the polymer solutions in water. We could obtain the emission maxima which were excited at their absorption maxima of the polymer solutions respectively. We, however, could not observe fluorescence from **SIP** and **SIT** solutions excited at each absorption maximum. But when excited at lower wavelength (lower than 350nm), high intensity of fluorescence was observed from the both solutions, which was thought that this fluorescence did not result from conjugated polymer backbone but from the low molecular weight fractions in the polymer.

We could fabricate alternating layers onto glass slide with four polyimines containing sulfonate groups as polyanions and PDH as a polycation, respectively. By UV-VIS spectroscopy, it is demonstrated that the consecutive adsorption of layers is stepwise as shown in Fig. 2 (for **SIP**). Linear relationship between the number of bilayers deposited and the absorbance of the multilayer film upto 5 bilayers. It was found that each bilayer makes an equal and reproducible contribution to the absorbance of the assembled multilayer films. This suggests that the sulfonate groups of polyimines were binded with cations in PDH resulted in the formation of self-assembled multilayer thin films.

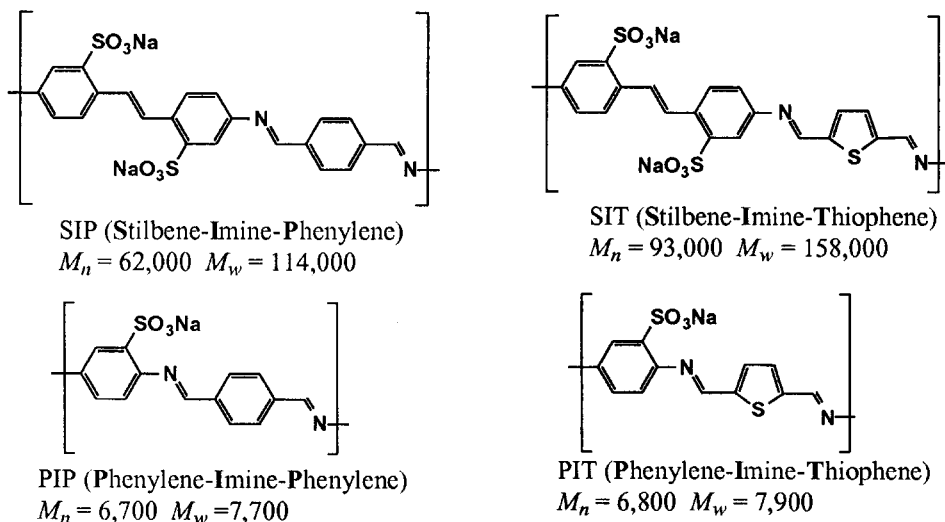
Conclusion

We are reporting the synthesis via interfacial polycondensation reaction and the characterization of specially designed series of conjugated aromatic polyimines

containing sulfonate groups in their backbones. Due to the presence of sulfonate groups in the polymer backbones, they showed much improved solubility in water and DMF. The polyimines showed different absorption maxima (400-480nm) in water according to the molecular backbone structures. We also demonstrated the fabrication of optical quality multilayer thin films of anionic (polyimine) and cationic (PDH) polyelectrolytes on glass slides. The self-assembled films are fabricated by adsorption from both polyelectrolyte aqueous solutions. Absorbances in UV spectra were increased linearly with the number of adsorption step, which implying that the spontaneous adsorptions of the polyimines containing sulfonate groups and cationic polyelectrolytes were performed by ionic interaction.

References

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Scheme 1. Chemical structures of the polyimines

Table 1. Absorption and fluorescence maxima of the polymers in water

	Absorption (nm)	Fluorescence (nm) ^{a)}
SIP	455	-
SIT	480	-
PIP	373	431
PIT	399	457

^{a)} excited at each absorption maximum

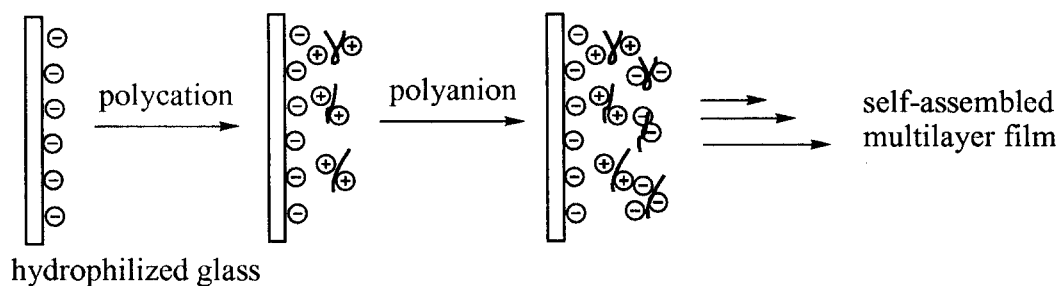


Fig.1. Schematic diagram for multilayer film formation process by layer-by layer deposition.

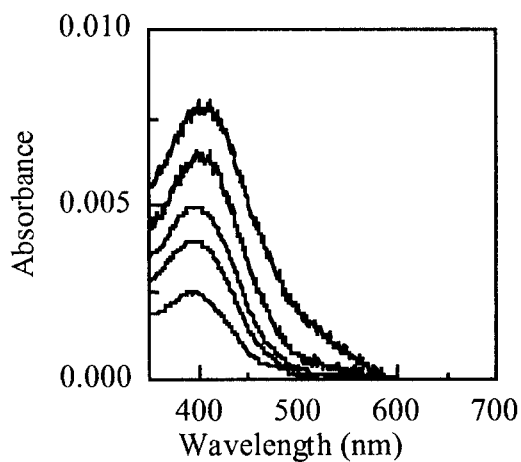


Fig. 2. Absorption spectra of SIP multilayer films with an increasing number of bilayers.