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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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Online publication date: 30 November 2001

To cite this Article Kim, Myunghwan and Sandman, D. J.(2001) 'POLYICATION EFFECTS ON ELECTRONIC SPECTRA OF CONJUGATED POLYMERS IN PROGRAMMED ELECTROSTATIC ASSEMBLIES', Journal of Macromolecular Science, Part A, 38: 12, 1291 – 1304

To link to this Article: DOI: 10.1081/MA-100108384

URL: <http://dx.doi.org/10.1081/MA-100108384>

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POLYCATION EFFECTS ON ELECTRONIC SPECTRA OF CONJUGATED POLYMERS IN PROGRAMMED ELECTROSTATIC ASSEMBLIES

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

A polysaccharide, chitosan, has been used to study polycation effects on electronic spectra of conjugated polymers in programmed electrostatic assemblies. Conjugated polyelectrolytes, poly[2-(3-thienyl)-ethanolhydroxycarbonylmethylurethane] (HPURET) and polydiacetylene from 5,7-dodecadiyn-1,12-bis-(hydroxycarbonylmethylurethane) (HP4BCMU), were assembled from aqueous solution alternately with the polycation, poly (diallyldimethylammonium) chloride [PDADMAC], and with the polysaccharide cation, chitosan. Switching polycations did not significantly change the visible absorption spectra for HP4BCMU multilayers. The optical properties of the regiorandom polythiophene, HPURET, depend distinctly on the polycation and the pH of the solution, showing significant differences on visible absorption maxima of the assemblies ranging from 435 nm to 516 nm. After the assemblies were exposed to vapor of aqueous ammonia, they showed UV-vis maxima further red shifted and an enhanced emission intensity, compared to those of the original assemblies. A chitosan/HPURET complex was prepared as a precipitate from solution. Its visible absorption maximum is at 536 nm with a shoulder at 580 nm, reminiscent of regioregular poly(3-alkylthiophenes). This unusual

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sensitivity of conjugated polymers to polycations may have potential application in sensor devices.

Key Words: Programmed electrostatic assemblies; Conjugated polymers; Cation effects on electronic spectra; Chitosan

INTRODUCTION

The sequential adsorption of oppositely charged polyelectrolytes [1], an example of a programmed supramolecular assembly [2], has attracted considerable attention in recent years as a simple, well-defined, and potent nano-architectural strategy for various optical device applications [3], especially for the study of optical and electronic phenomena in conjugated materials [4, 5, 6, 7]. It is also noted for weak polyelectrolytes that not all of the repeating units need to have a 1:1 stoichiometry of anionic and cationic complex [8], and that the surface roughness of an assembly can be annealed to smaller values in post-assembly processing (or post-preparation treatment) [1]. Examples of such post-assembly processing reported include thermal treatments [9], photochemical polymerization [5], and chemical treatment [10]. Each electrostatic assembly of polyelectrolytes has its own programmed history of the deposition procedure. Therefore, post-assembly processes can change polymeric structures to a different morphology in order to adapt to their new environment [11]. A few studies of these post-assembly processes for desirable applications have been reported, such as, pH-switchable adsorption of nucleic acids to a surface [12] and a nylon-like film stable over a wide pH range through chemically induced amide formation [9].

Recently, it was suggested that fluorescence of pyrene could be used as a probe of the polarity of polyelectrolyte multi-layer films [13]. In a previous study [14], HPURET and HP4BCMU, were processed under the same assembly conditions to programmed electrostatic assemblies (PEA), respectively, with two different polycations that have significantly different refractive indices—one is PDADMAC, the other poly(4-vinyl pyridine) quaternized with dimethylsulfate (QPVP), in order to study the effects of the polarizability of polycations on the electronic spectra of conjugated polymer backbones. Even though the absorption maxima of polydiacetylene and polythiophene solutions are sensitive to the refractive indices of solvents [14, 15], the local refractive index of the different polycations does not significantly affect the maximum of the electronic absorption spectra of PEAs of HP4BCMU and of HPURET. Apparently, the conjugated polymer chromophores are not intimately involved with these polycations. Assemblies of HP4BCMU with PDADMAC, post assembly processed at pH 1 in aqueous solution, exhibit vibronic structure, comparable to the LB film of P4BCMU [16] and the PDA of Tieke's work [5]. The PEA of HPURET, followed by post-assembly processing with aqueous ammonia vapor, also leads to a significant red shift of the electronic spectrum, moving the absorption maximum from 440 nm to 496 nm. The addition

of polycations caused the red shifts of the electronic absorption spectra of HPURET in solution at pH 12 by polyelectrolyte complex formation between HPURET and polycations. The absorption maximum shift of the PEA by post-assembly processing was compared to that of the HPURET complex in solution.

On the basis of the above information, it is conceivable that the optical properties of conjugated polymers in PEAs can be manipulated by the introduction of different polyelectrolytes or by post-assembly processing, using various adaptations of conjugated polyelectrolytes with different polycations at certain pH. In this paper, chitosan was used for the study of polycation effects on electronic spectra of conjugated polymers in programmed electrostatic assemblies. It was possible to control the position of visible absorption maxima of chitosan/HPURET assemblies from 435 nm to 536 nm by changing assembly procedures and post-assembly-processing. These electronic spectra of HPURET were compared to that of a self-assembled chitosan/HPURET complex precipitated from solution. However, to our knowledge, there has been no systematic attempt to modify the optical properties of programmed assemblies of conjugated polymers by post-assembly-processing or by switching polymeric counterions.

Chitosan, the modified polysaccharide from naturally abundant chitin, has received much attention as a functional biopolymer in various areas, since it is readily soluble in acidic water, is biodegradable, and complexes with transition metals or with biomass. These chitosan complexes are accompanied by diverse molecular conformations of chitosan, including a reported helical conformation with acetic acid [17]. Due to those unique properties, chitosan has applications as a removal agent of toxic metals [18], artificial skin, surgical thread, drug delivery system, anti-cholesterol agent, encapsulating enzymes, gas masks, and contact lenses [19, 20, 21, 22, 23]. These functions of chitosan polyelectrolyte complexes come from the chemical structure, the supramolecular chain structure of chitosan, as well as its packing arrangement in the solid state.

EXPERIMENTAL

Chemicals and Electrostatic Assembly Procedures

HP4BCMU ($M_n = 7 \times 10^5$ g/mol) [24] and 60% HT-HPURET ($M_w = 3.2 \times 10^4$ g/mol) [25] were prepared according to the literature. PDADMAC ($M_n = 1.2 \times 10^5$ g/mol) and 75-85% deacetylated chitosan ($M_w = 1.9\text{-}3.1 \times 10^5$ g/mol) were purchased from Aldrich Chemical Company. The structures for these polymers are shown in Figure 1. Substrates (quartz or glass slides) are cleaned ultrasonically for 3 hours with 1% Chem-Solv[®], purchased from Aldrich Chemical Company, washed with distilled water and dried by nitrogen gas. HP4BCMU in 10^{-4} M aqueous solution at different pH values was deposited on glass slides up to an appropriate thickness with PDADMAC in 2×10^{-3} M aqueous solution or with chitosan in 0.1 wt% solution at pH4, with each alternating for 10 minutes dipping time.

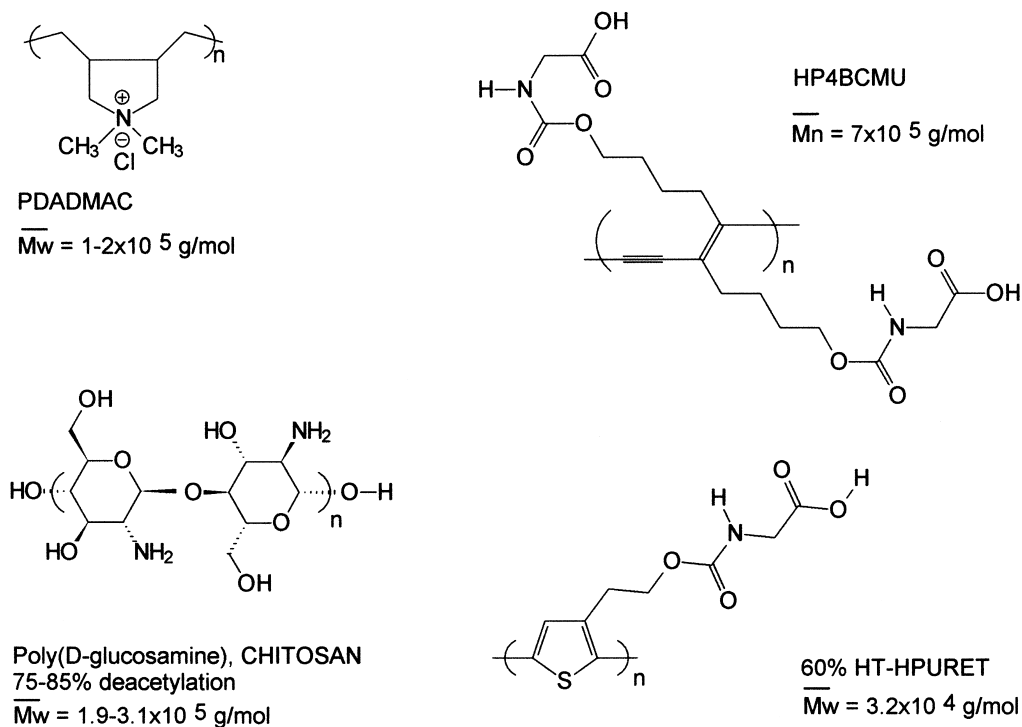


Figure 1. Chemical structures of polyelectrolytes.

HPURET in 10^{-3} M aqueous solution was deposited by the same procedure as HP4BCMU.

Preparation of Chitosan/HPURET Bulk Complex

A bulk Chitosan/HPURET complex was prepared as follows: first, 1 liter of 1% chitosan solution at pH 1 and 1 liter of 10^{-3} M HPURET solution in distilled water were prepared. Both solutions were mixed together and the pH was increased 12 by NaOH. After 24 hours, the precipitate was collected using a centrifuge and dried in a vacuum oven at room temperature for 8 hours. Elemental analysis showed the complex contained 1.74% sulfur (13.6 wt% of HPURET). X-ray powder patterns were recorded for the chitosan reprecipitated form at pH12, HPURET salt, and the complex. IR spectra of PDADMAC/HPURET 15 bilayers on the CaF_2 were recorded before and after base treatment of those assemblies. The thickness of the chitosan/HPURET assembly was measured using a DekTak profilometer.

RESULTS AND DISCUSSION

HP4BCMU in 10^{-4} M aqueous solution at pH 12 was processed by PEA on glass slides up to 10 bilayers with chitosan 0.1% aqueous solution at pH 4, with

each alternating 10 minutes dipping time. Figure 2 shows the linear increase of optical density as bilayers are built up from 7 to 10. The spectrum shifted slightly to longer wavelength as the bilayers were built up. This is possibly due to a reorganized structure. The overall spectra are quite similar to the HP4BCMU/PDAD-MAC assemblies reported previously [14]. Post-assembly processing was performed by soaking the 10 bilayer assembly in pH 1 solution for 12 hours. Vibronic structure developed which was similar to that found in the HP4BCMU/PDAD-MAC assemblies or HP4BCMU/Quaternized poly(4-vinylpyridine) assemblies in the previous study [14]. Unlike the previous study, soaking the assembly for 30 minutes was not enough time to accomplish the development of vibronic structure of the HP4BCMU in the assembly and there was no loss of absorbance intensity of the polydiacetylene chromophores even after 12 hours soaking in pH 1 solution. Apparently, the structural order of chitosan slows down acid diffusion at pH 1 compared to the polycations previously studied. The electronic structure of HP4BCMU is not affected by different polycations, such as, chitosan, PDAD-MAC, and quarternized poly (4-vinylpyridine), possibly due to its relatively rigid conjugated backbone.

The visible absorption maxima of HPURET were found at diverse positions, depending on assembly-processing conditions, such as pH of the solutions and polycations. When HPURET was assembled with chitosan each at pH 4 in Figure

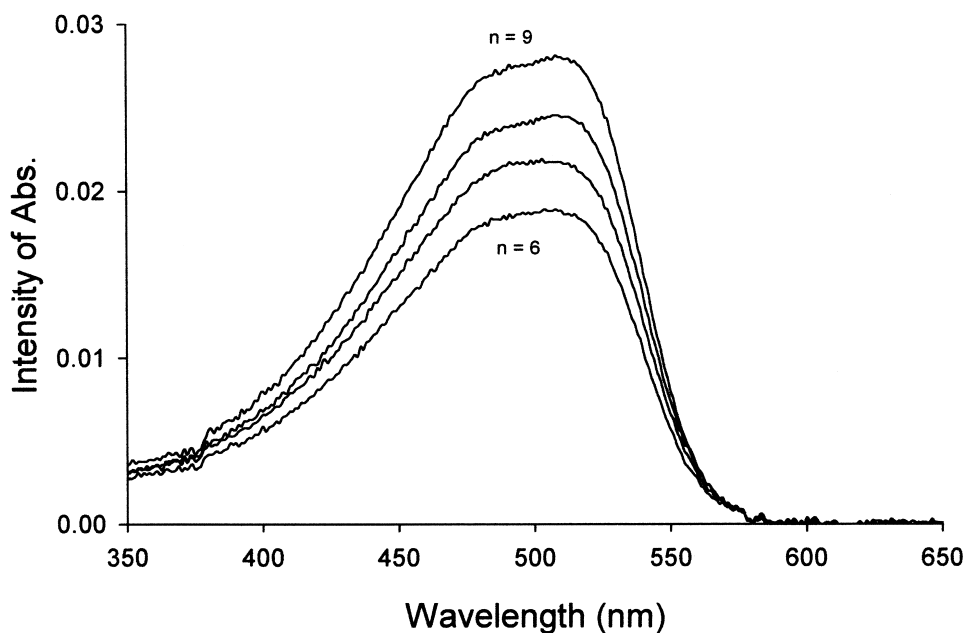


Figure 2. Visible absorption spectra of [chitosan/HP4BCMU]*n*/chitosan assemblies (*n* = 6, 7, 8, 9). The notation [chitosan/HP4BCMU]*n*/chitosan assemblies implies that the number of *n* bilayers are sequentially deposited and out most layer is chitosan. Chitosan and HP4BCMU were deposited, at pH 4 and pH 12, respectively, with 10 minutes dipping time.

3, the visible spectrum of the assembly was similar to those of HPURET assemblies with QPVP or with PDADMAC, showing an absorption maximum at 435 nm. The intensity of absorbance was 2.32 at 435 nm. The thickness of the 30 bilayer assembly was $2,650 \pm 150 \text{ \AA}$ ($88 \pm 5 \text{ \AA}$ per bilayer).

On the other hand, the featureless overall visible spectra of HPURET red shifted significantly, showing an absorption maximum at 516 nm, when pH12 HPURET solution was used for the assembly processes in Figure 4. The absorbance at 516 nm was 0.30. The thickness of the 30 bilayer assembly was $660 \pm 15 \text{ \AA}$ ($22 \pm 2 \text{ \AA}$ per bilayer). The change of absorption maxima of HPURET assemblies prepared from different procedures is shown in Figure 5, plotted as a function of the number of layers. There is a fluctuation in the position of the absorption maximum as the pH of solutions is switched from 4 to 12. Also, as depicted in the inset diagram in Figure 4, there is a systematic fluctuation of the intensity of absorption maxima. When the pH of each solution is kept at pH4, the position of absorption maximum and its absorbance increase are relatively constant as chitosan is deposited (Figure 5). However, the shift of absorption maximum (Figure 3 vs. Figure 4) does not seem to come only from pH effect, since HPURET does not show the same electronic absorption spectra when it was fabricated in assemblies with PDADMAC under the same conditions, even though there are red shifts of the absorption maximum to 455 nm (shown Figure 6), as layers are built up. However, when this HPURET/PDADMAC PEA is treated with ammonia vapor for 9 hours, the absorption maximum shifts to 490 nm.

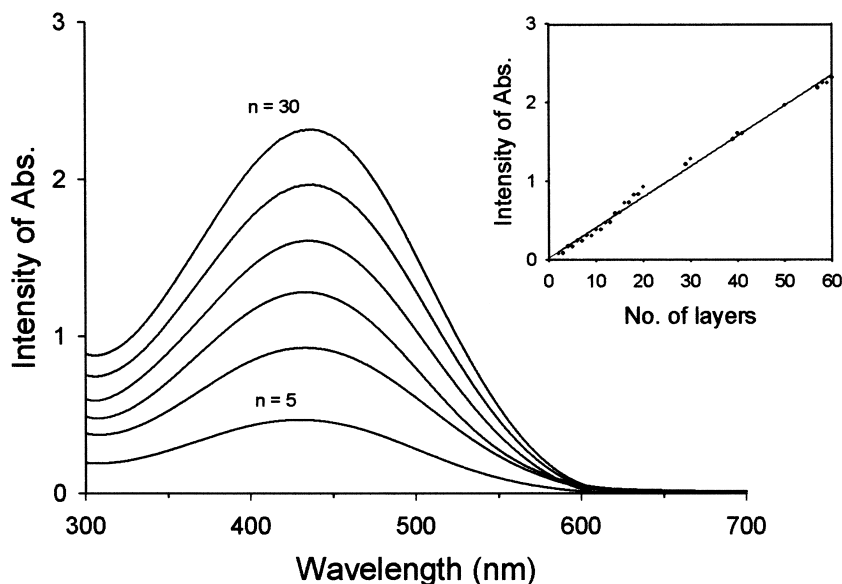


Figure 3. Electronic spectra of [chitosan/HPURET]_n assemblies ($n = 5, 10, 15, 20, 25, 30$). Chitosan and HPURET were deposited each at pH 4 with 10 minutes dipping time. Inset diagram shows the linear increase of absorption intensity of the assemblies at 435 nm, where odd number layers are chitosan and even numbers are HPURET.

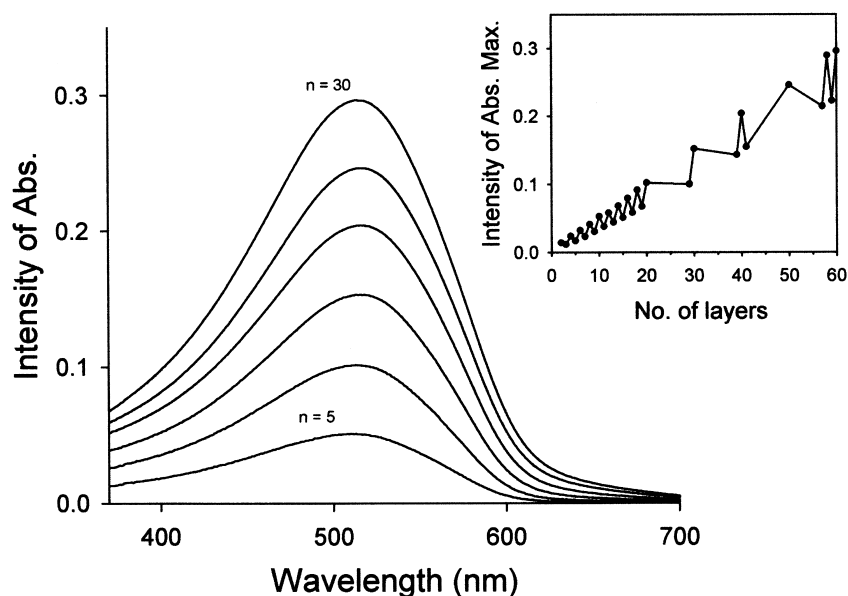


Figure 4. Electronic spectra of [chitosan/HPURET]_n assemblies (n = 5, 10, 15, 20, 25, 30). Chitosan and HPURET were deposited, at pH 4 and 12, respectively with 10 mins dipping time. Inset diagram shows the linear increase of absorption intensity of the assemblies at 516 nm (pH12, HPURET deposition) and at 486 nm (pH4, chitosan deposition) where odd numbered layers are chitosan and even numbered layers are HPURET.

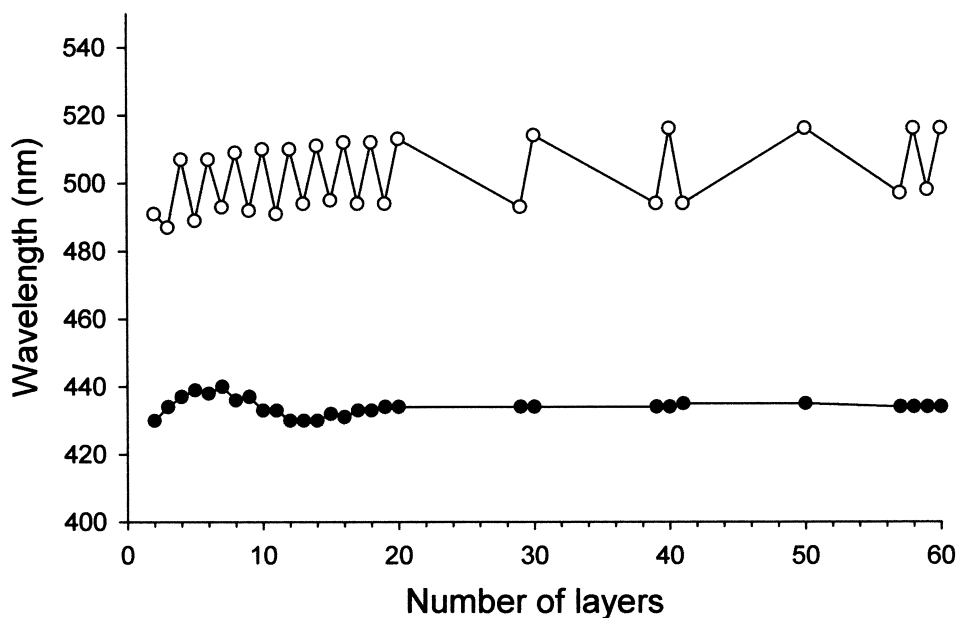


Figure 5. The shifts of visible absorption maxima of Chitosan/HPURET assemblies as a function of the number of layers. Open circle: chitosan and HPURET were deposited, respectively, at pH4 and pH12, fluctuating from 486 nm to 516 nm. Closed circle: chitosan and HPURET were deposited at pH4 each.

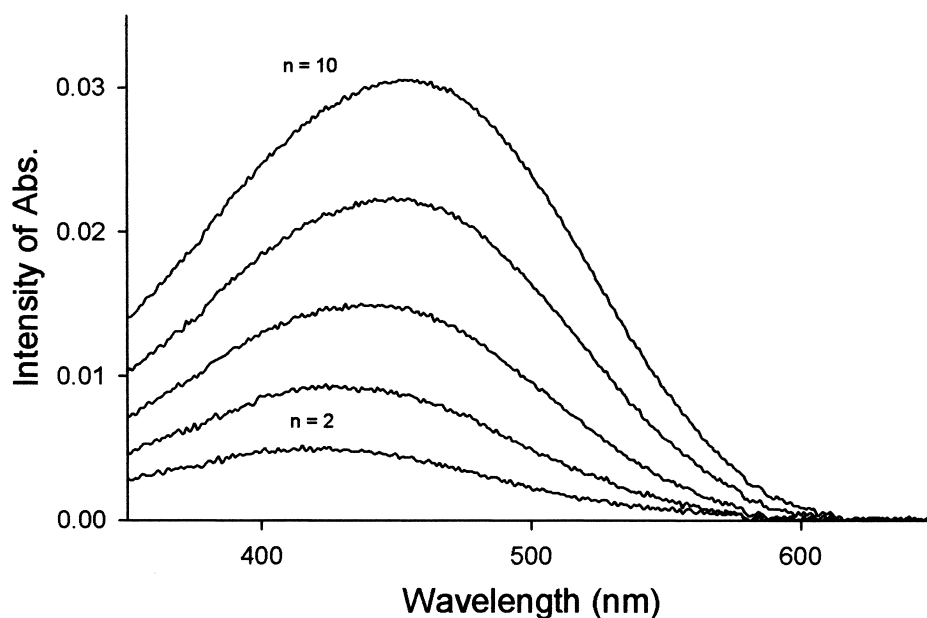


Figure 6. Visible absorption spectra of [PDADMAC/HPURET] $_n$ /PDADMAC assemblies ($n = 2, 4, 6, 8, 10$) showing shift of maximum. PDADMAC and HPURET were deposited, respectively at pH 4 and pH 12 with 10 minutes dipping time.

The IR spectra of the HPURET/PDADMAC PEA before and after ammonia treatment are shown in Figure 7. Clearly, the enhanced asymmetrical and symmetrical stretching bands of carboxylate ions appear after ammonia treatment, implying deprotonation of carboxyl.

We are interested in comparing the spectral and structural properties of a self-assembled complex of chitosan and HPURET precipitated from solution [26] with those found in PEA. 0.03% Chitosan and 0.3 mM HPURET solution were prepared each at pH 4.2 and combined together. The absorption maximum of the combined chitosan/HPURET solution was 422 nm. The pH of this solution was increased to 12 until precipitation occurred. The precipitate was redissolved by decreasing the pH of solution to 1. Finally, the pH of the solution was set to pH 4.2 again and the visible absorption spectra exhibited a maximum at 453 nm, as shown in Figure 8. The chitosan/HPURET complex was prepared as described in the experimental. This complex dispersed in nujol exhibits a visible absorption maximum at 542 nm with a shoulder at 588 nm (Figure 9, C). The frequency difference between the peak and shoulder is 1443 cm^{-1} , suggesting the involvement of an aromatic ring in the vibronic structure. The chitosan /HPURET complex in solution showed remarkably similar behavior to those of chitosan/HPURET assemblies with respect to electronic spectra. First, the absorption spectrum of the initially combined chitosan/HPURET solution exactly matches to that of HPURET aqueous solution at pH 4, which exhibits λ_{max} at 423 nm. Second, the

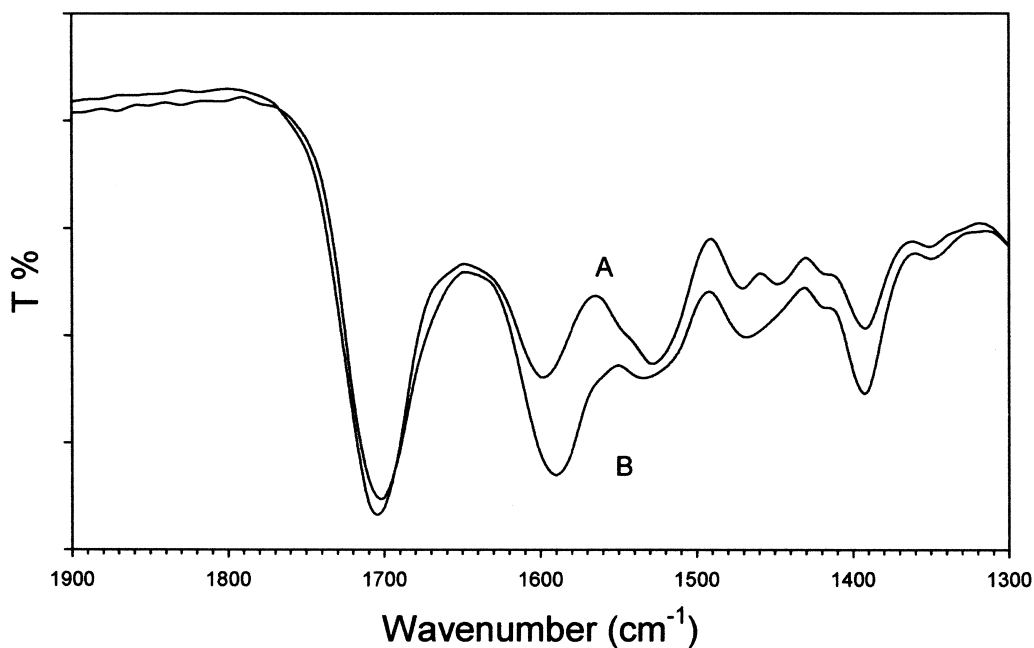


Figure 7. IR spectra of 15 bilayer HPURET/PDADMAC programmed electrostatic assembly on CaF2 (A) before and (B) after ammonia treatment.

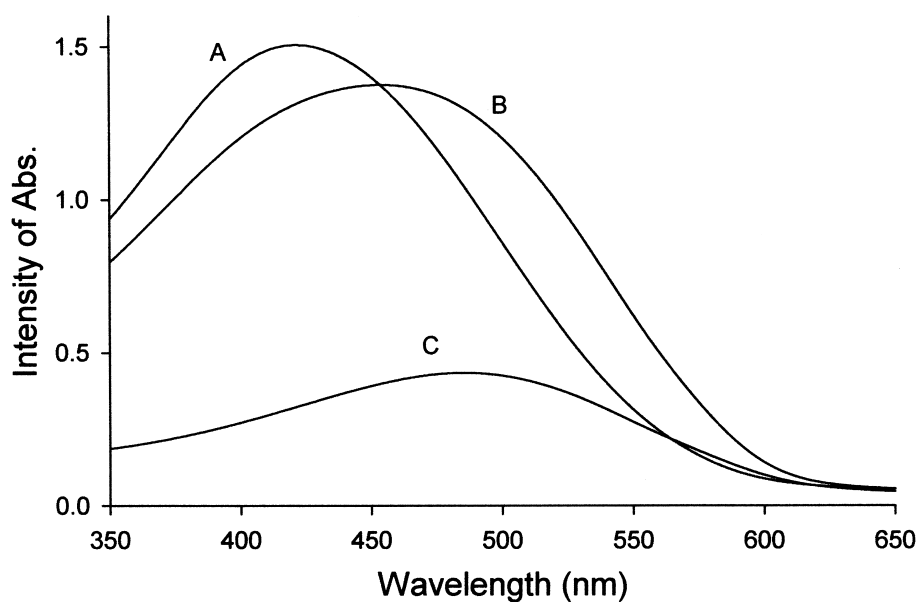


Figure 8. Electronic spectra of HPURET/Chitosan complexes in pH 4.2 solution. 0.03% chitosan and 0.3 mM HPURET solutions each at pH 4.2 were combined showing absorption maximum at 422 nm (A). The pH of this solution was increased to pH 12 and readjusted to pH 4.2 showing $\lambda_{\max} = 453$ nm (B). Chitosan/HPURET complex containing 13.6% HPURET was dissolved pH 4.2 (0.134 mg/ml) showing $\lambda_{\max} = 486$ nm (C).

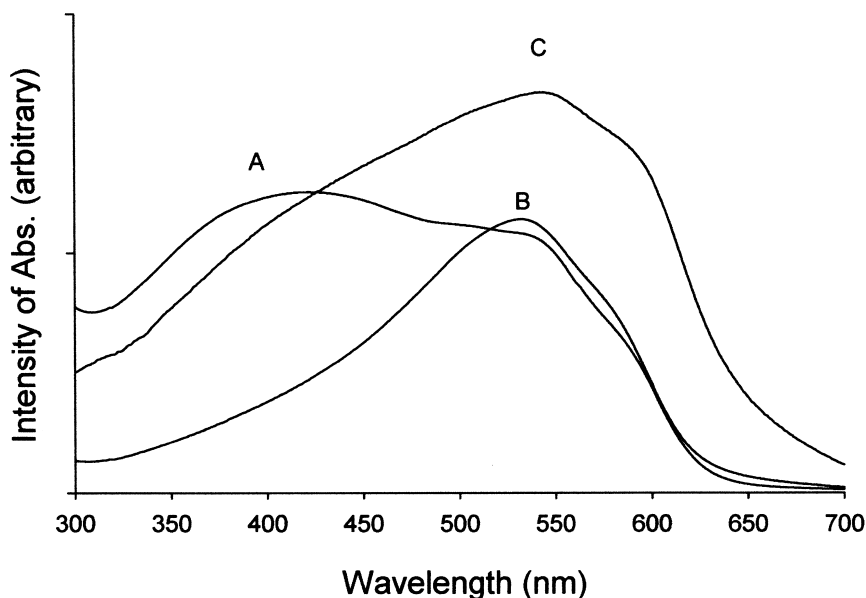


Figure 9. Electronic spectra of 30 bilayers Chitosan/HPURET assemblies after post-assembly-processing (A and B, see text) and of chitosan/HPURET complex dispersed in nujol (C).

redissolved chitosan/HPURET solution from pH12 to pH 4.2 shows similar electronic spectrum of the assembly which is analogous to chitosan/HPURET assembly, fabricated at same pH 4 with an absorption maximum at 435 nm (Figure 3). Finally, the powder of the chitosan/HPURET complex (13.6 wt% HPURET) was dissolved in pH 1 solution and pH was set to 4.2. This complex solution with maximum at 486 nm, matches the absorption spectrum of $[\text{chitosan/HPURET}]_{30}/\text{chitosan}$ whose outermost layer is chitosan, where, $[\text{chitosan/HPURET}]_{30}/\text{chitosan}$ is 30 bilayer assembly fabricated from pH4 chitosan solution and pH12 HPURET solution and the outermost layer is chitosan layer deposited at pH 4 (note the captions of Figure 5 and Figure 8, C).

Post assembly processing was performed for the two 30 bilayer assemblies using aqueous ammonia vapor in a desiccator. An assembly which was fabricated using pH4 chitosan solution and the same pH of HPURET solution, showed shoulders at 540 nm and 580 nm after 1 week of ammonia treatment (Figure 9, A), and the other assembly fabricated at pH 4 chitosan solution and pH 12 HPURET solution showed a red shift of the absorption maximum to 536 nm with a shoulder at 580 nm in Figure 9, B, after a 16 hour ammonia treatment. The frequency gap between the shoulder and the maximum is 1415 cm^{-1} . Both showed peaks or shoulders near the absorption maximum position of the complex dispersed in nujol in Figure 9, C.

Emission spectra are plotted in Figure 10 for 30 bilayer chitosan/HPURET assemblies, which are deposited using different conditions. When chitosan and HPURET are deposited respectively at pH 4 and 12, the intensity of the fluores-

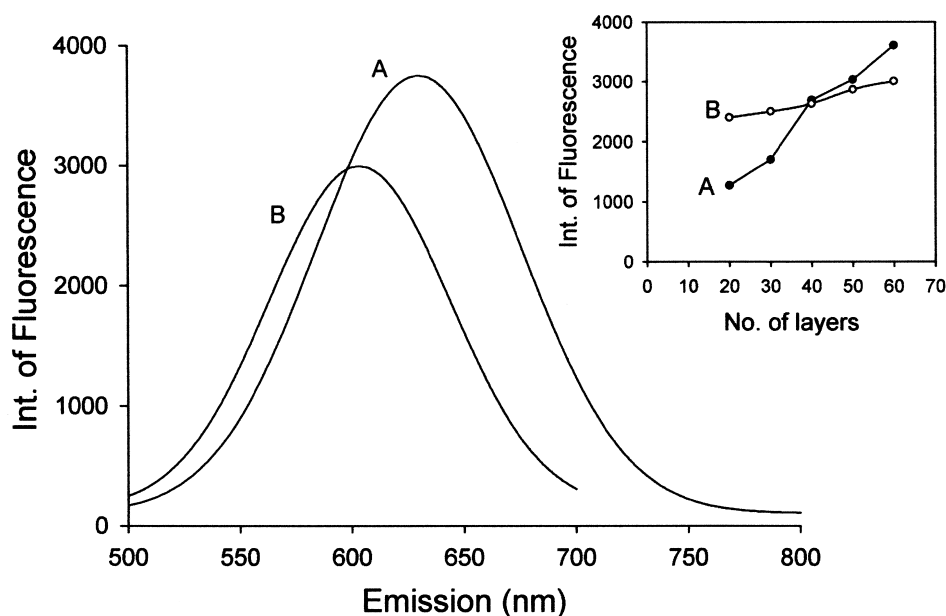


Figure 10. Emission spectra of 30 bilayer Chitosan/HPURET assemblies and inset diagram showing increase of the intensity of fluorescence of assemblies as built up, where the assembly A was deposited respectively at pH 4 (chitosan) and 12 (HPURET) (A, intensity of λ_{\max} 0.30 at 516 nm, and the assembly B both at each pH 4 (B, intensity of λ_{\max} 2.32 at 435 nm).

cence of the assembly shows 25% enhancement relative to that of the assembly deposited both at each pH4, even though the latter has about 8 times more absorbance. In addition, the assembly fabricated at pH 4 and pH 12 exhibits a linear increase of fluorescence intensity as the layers are built up and when the number of bilayers extrapolates to zero, the intercept of the fluorescence intensity is zero, indicating there is no saturation of fluorescence or quenching. Elemental analysis of chitosan/HPURET complex (1.74% sulfur, 13.6 wt% HPURET) shows that the ratio of chitosan to HPURET is 10 to 1 on the basis of repeating units of chitosan and of HPURET, where Mw of chitosan is 1.9-3.1 wt% 10^5 g/mol and that of HPURET is 3.2×10^4 g/mol. However, the ratio of the number of chitosan polymer molecules to that of HPURET polymer molecules is 0.75-1.2 to 1, suggesting an approximate 1:1 stoichiometry of anionic and cationic polymer molecule complex.

X-ray powder patterns were recorded for chitosan, HPURET and the chitosan/HPURET self-assembled complex. A chitosan powder sample was precipitated when the pH of the chitosan solution was increased from 1 to 12 using NaOH. The HPURET powder sample was the sodium salt form. Chitosan/HPURET complex isolation was accomplished at pH12 solution as described in the experimental. X-ray powder d-spacings (\AA) of chitosan ($2\theta = 10 - 50^\circ$) are 4.43 (S), 2.78(W), 2.37 (W), and 2.05(W), where S is strong intensity and W weak

intensity. The HPURET sodium salt sample shows an amorphous pattern. Powder X-ray d-spacing (\AA) of chitosan/HPURET ($2\theta = 10 - 50^\circ$) are 4.37 (S), 3.17 (W), 2.99 (W), 2.62 (W), 2.54 (W), and 2.36 (W). The observed reflections in the chitosan/HPURET complex correspond to those of well-oriented chitosan annealed by stretching [27]. In our X-ray powder data, the chitosan/HPURET complex shows broader diffraction near 4.40 \AA than our precipitated chitosan, implying less ordered structure for the complex. Nevertheless, the chitosan/HPURET complex exhibits more reflections than our precipitated chitosan.

CONCLUSION

The optical properties of the conjugated polyelectrolyte (regiorandom polythiophene, HPURET) in programmed electrostatic assemblies, depends distinctly on the polycation and the pH of the solution, showing significant differences in the visible absorption maxima of the assemblies. By switching polycations, by changing pH, or by post-assembly-processing, it is possible to tune the optical properties of HPURET assemblies from those of relatively disordered structures to a more-ordered structure reminiscent of those of regioregular poly(3-alkylthiophene) cast film [28]. In the present work, vibronic structure is observed in HPURET spectra only after post-assembly processing of PEA with ammonia vapor or in the self-assembled complex. However, HP4BCMU does not show significant change on the electronic spectra, possibly due to its relatively rigid conjugated backbone. We were initially motivated to study chitosan because of its chirality. Chitosan-induced-circular dichroism of achiral conjugated polymers is under investigation and will be separately reported [29].

ACKNOWLEDGMENTS

We thank the Office of Naval Research for partial support of this work through the Multidisciplinary University Research Initiative. We thank Mr. J. M. Downey for furnishing X-ray powder diffraction data.

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