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Exploration of Layer by Layer Assembly of Flexible Phosphonium Polymers with Anionic Polythiophene

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I. Introduction

Ionic polymers that contain ammonium and phosphonium units have demonstrated outstanding ability to form supramolecularly organized films via facile layer-by-layer deposition as well as antibacterial properties. This Creative Inquiry project involved the synthesis of a series of phosphonium polyelectrolytes via polymerization of a variety of diphosphines with bis[bromomethyl]arene comonomers, leading to the cationic polyelectrolytes of interest. The spacer between charged units was varied to include flexible, rigid, and electroactive moieties. The influence of polymer structure on film formation, supramolecular assembly and antibacterial properties are discussed in this contribution.

II. Initial Synthesis and Characterization of Phosphonium Polymers

From the initial phosphonium polymers, it was determined that the more flexible the spacer is, the more linear the film grows. It was also found that film growth continues in a linear fashion indefinitely. Further exploration was conducted to determine the optimal flexible spacer length of five carbons. An additional polymer series was synthesized to determine whether hydrophobic side chains have an impact on film growth. The most prominent trend from these final two series of phosphonium polymers was the impact of odd versus even numbered methylene spacers. Odd spacers formed consistently smoother films than their even counterparts. Future exploration includes layer-by-layer with additional thiophene polymers as well as study of the antibacterial properties. Preliminary trials have been run with both E coli and S aureus.

III. LX and LO Synthesis and Analysis

The layer-by-layer absorbance of a) EtOHx with APPV, b) PhOHx with APPV and c) FcOHx with APT.

Figure 1: Synthesis scheme of EtOHx, PhOHx, and FcOHx.

Figure 2: The layer-by-layer absorbance of a) EtOHx with APPV, b) PhOHx with APPV and c) FcOHx with APT.

Figure 3: Synthesis scheme of LX and LO polymers

Figure 4: Absorbance and Linear Plot of Layer-by-Layer Analysis of LX5 with Unique Polystyrene.

Figure 5: RMS Roughness versus polymer spacer length a) LX polymers and b) LO polymers.

Figure 6: 1×1 µm AFM 2D-height (left column) and 3D (right column) images of layer by layer films of LO polymers with Pc12-100% made from AIST software: LO2 (A), LO3 (B), LO4 (C), LO5 (D), LO8 (E) and clean glass slide (F).

IV. Conclusions

From the initial phosphonium polymers, it was determined that the more flexible the spacer is, the more linear the film grows. It was also found that film growth continues in a linear fashion indefinitely. Further exploration was conducted to determine the optimal flexible spacer length of five carbons. An additional polymer series was synthesized to determine whether hydrophobic side chains have an impact on film growth. The most prominent trend from these final two series of phosphonium polymers was the impact of odd versus even numbered methylene spacers. Odd spacers formed consistently smoother films than their even counterparts. Future exploration includes layer-by-layer with additional thiophene polymers as well as study of the antibacterial properties. Preliminary trials have been run with both E coli and S aureus.

V. Acknowledgements and References

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Cheers!

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References