Smart Polymer Surfaces

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14. ABSTRACT

In many materials applications it is highly desirable to design and control the properties and behavior of surfaces. The task of modifying surfaces to control properties is a daunting one because many surface characteristics are related to the nature of chemical and physical structure on a molecular level. The overall goal of this research is to develop new methods for the molecular design and fabrication of smart surfaces with properties that can be controlled by exposure to light of appropriate wavelength. The approach involves the synthesis of smart molecules

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Technical Accomplishments

I. Fabrication and Patterning of Block Copolymer Monolayers on Polymeric Substrates

We have successfully illustrated that monolayers of surface-active, smart block copolymers can be created on both hard and soft/polymeric substrates by a simple supercritical fluid (SCF) processing method. The coating is made by placing a small amount of block copolymer and the polymeric substrate in a pressure chamber. Once the pressure chamber is charged with supercritical CO_2, a monolayer spontaneously forms on the substrate. A patent has been applied for regarding this new process. To our knowledge, this is the first industrially feasible method by which monolayers of polymers may be deposited onto substrates in order to modify their surface characteristics. There are four unique and important advantages to the new method:

- since there are no capillary forces with supercritical fluids the process can be used to coat even the internal surfaces of nanopores, something that cannot be done with other coating methods
- the method works on substrates of arbitrary shape, not just on flat substrates
- if end-functional block copolymers are used, the number of functional groups at the surface can be quantitatively controlled
- if a photoactive block copolymer is employed, surface patterns of functional groups can be created.

Using this method we have been successful in quantitatively functionalizing the surfaces of flat substrates, microspheres and fabrics.

Dr. Dongman Cho in his PhD thesis first showed that this process could be used to coat poly(styrene-b-dimethylsiloxane) copolymers onto the surface of polystyrene substrates, and this work was published: “Deposition of Block Copolymer Thin Films onto Polymeric Substrates by Adsorption from Supercritical Carbon Dioxide”, D. Cho, J. T. Koberstein, Macromolecules, 38, 1829-1836, 2005.

Dr. Peng Wang then showed in his PhD thesis, that poly(styrene-b-*tert*-butylacrylate) block copolymers could also be coated onto polystyrene substrates using supercritical CO_2. A patent, “Methods of Modifying Surfaces”, which includes this invention, has been filed. A current PhD student, Mr Yong Chen, is following up on this work. He has shown that the solubility of the block copolymer can be increased by adding hexane to the solvent. The importance of this block copolymer system is that it provides a smart surface that is initially hydrophobic due to self-assembly of the copolymer into a bilayer at the surface that presents a poly(tert-butyl acrylate) (PtBA) surface layer. When the PtBA surface layer is exposed to UV radiation in the presence of a photoacid generator, the exposed regions are converted to polyacrylic acid (PAA), a functional hydrophilic substrate. When exposed through a mask, the surface chemistry can be patterned and subsequently used to template the spatial surface assembly of a variety of biological molecules of interest, as described in the publication: "Photochemical Modification and Patterning of Polymer Surfaces by Surface Adsorption of Photoactive Block Copolymers" F. Pan, P. Wang, K. Lee, A. Wu, N. J. Turro, J. T. Koberstein, Langmuir, 21, 3605-3612, 2005. The surface carboxylic acids serve as sites for covalent grafting of peptides. Mr. Chen is currently preparing peptide modified surfaces for cell interaction studies with fibroblasts (in collaboration with Prof. H. Lu at Columbia Biomedical Engineering Department).

Mr. Chen has also shown that the block copolymers can be coated onto polystyrene microspheres using the same technique. After coating, the PtBA surface is converted to PAA and then decorated with cell adhesion peptides to create a water dispersable cell growth media. The cell growth properties of these coated microspheres have been studied in collaboration with Prof. Susan Sharfstein from Rensselaer Polytechnic University.

Finally, Mr. Chen is currently collaborating with Dr. Lars Piehler, a chemist from the Multifunctional Materials Branch of the Materials Division of the US Army Research Laboratory on the development of antimicrobial surfaces. We are applying the SCF technique to coat fabrics used in soldier protection. The idea here is to use SCFs to deliver chemical agents to the clothing that would kill biological warfare agents as a deterrent to soldier infection. A postdoctoral associate, Dr. Christian Grigoras, has synthesized poly(dimethyl siloxane) polymers containing anitimicrobial end groups for this purpose. Our first forays into this field have been promising: uniforms coated by SCF with the first generation antimicrobials have achieved cell kill ratios greater than 50%. A new collaboration with Prof. Karthik Chandran from Columbia is developing to examine if these same coatings might be useful in preventing the formation of bacterial films. Dr. Grigoras has also developed the first method for covalent layer-by-layer assembly based upon the toolkit we have assembled for surface modification. The method uses 1,3 dipolar cycloaddition or click chemistry to covalently bond successive monolayers to surfaces.

II.Light-Activated Polymer Systems

A second aspect of our efforts to create smart surfaces involves collaboration with Prof. Nick Turro from the Columbia Chemistry Department to combine his expertise with photochemistry with Prof. Koberstein's expertise in polymer surface design and modification. The new surfaces we are developing are designed to respond in a prescribed fashion when exposed to light. The idea is to transform surface properties of materials using light as the only reagent. The initial work started with an illustration that chemical amplification photoresist methodologies could be used to perform surface modification. Self-assembled monolayers terminated with a tert-butyl ester were exposed to UV radiation to produce surface carboxylic acid groups. The surface acid groups were successfully micropatterned by exposure through a mask, and this work was published: "Photolithographic Technique for Direct Photochemical Modification and Chemical Micropatterning of Surfaces", K. Lee, F. Peng, G. T. Carroll, N. J. Turro and J. T. Koberstein, Langmuir, 20, 1812-1818, 2004. Similar work on photoactive block copolymers is described in the preceding section.

Mr. Greg Carroll, in his thesis completed in June of 2007, has now carried these studies further into two exciting new directions: the development of the first surface photochemistry that is capable of covalent immobilization of almost any carbohydrate ("Photochemical Micro-patterning of Carbohydrates on a Surface", G. T. Carroll, D. Wang, N. J. Turro and Jeffrey T. Koberstein, Langmuir, 22 (6): 2899-2905 (2006).), and the development of a photocrosslinking agent that can crosslink virtually any preexisting polymer film simply by exposure to light ("Photoactive additives for cross-linking polymer films: Inhibition of dewetting in thin polymer films", Carroll, Gregory T., Sojka, Melissa E., Lei, Xuegong, Turro, Nicholas J., Koberstein, Jeffrey T. *Langmuir, 22 (18)*, 7748-7754 (2006).). In both cases, the chemistry can be patterned by exposure through a mask. A number of invention disclosures have been filed and patents are being constructed on both inventions. (M03069- Method for modification of surfaces by coating photoactive block copolymers onto surfaces with supercritical carbon dioxide and other supercritical solvents. M03006-Block copolymers that can be used to create surface layers on solid substrates whose functional character may be altered by exposure to light. M07085-Method for covalent attachment of organic and functional layers on surfaces. M05091-Photochemical method for patterning cross-links in thin polymer films. M06046-Photo-generation of carbohydrate microarrays. M05092-Photochemical method for patterning the covalent immobilization of sugars to self assembled monolayers.)

In collaboration with Dr. Denong Wang from Stanford University, we have employed the photoimmobilzation method to create the world's first generation of covalently bound carbohydrate microarrays. Such microarrays have tremendous potential to revolutionize the field of glycomics since they can be applied to solve important problems such as rapid disease detection and identification. We already have illustrated ("Photo-generated glycan arrays identify immunogenic sugar moieties of Bacillus anthracis exosporium", Denong Wang, Gregory T. Carroll, Nicholas J. Turro, Jeffrey T. Koberstein, Pavol Ková, Rina Saksena, Roberto Adamo, Leonore A. Herzenberg, Leonard A. Herzenberg and Lawrence Steinman, Proteomics, 7, 180-184 (2007).) that our novel microarrays can be applied to determine the surface receptors on *bacillus anthracis*, and achievement that could lead to more rapid identification of anthrax threats or to methods for the destruction of anthrax spores.

The photocrosslinking method was developed during interactions with engineers at Sandia National Laboratories. For five out of the past six years, Prof. Koberstein has spent at least one month per summer at Sandia conducting collaborative research programs with Sandia personnel. One area of common interest has been the fabrication of polymer thin film sensors. The problem that was encountered at Sandia was that the polymer films, designed to have specific interactions with particular warfare agents, would dewet the surface of a surface acoustic wave based sensor, when exposed to a carrier vapor such as an alchohol. We were able to solve this problem by developing bis-difunctional additives that would crosslink the preexisting polymer film simply by exposure to UV radiation. We have since employed this method to also pattern crosslinking or dewetting. Patterned dewetting constitutes a completely new way of generating micro thin film structures that might be useful in microfluidics applications.

State of the Art Research

The research projects currently under investigation in the Koberstein group are at the forefront in several areas:

- First supercritical fluid based method for quantitative surface modification and functionalization
- First spin on coatings for creating surfaces with quantitative areal density of surface functional groups
- First covalently bound carbohydrate microarrays
- First methods for quantitative patterning of surface functional groups
- First method for covalent layer-by-layer-assembly

These fundamental achievements are being employed in a wide breadth of applications requiring quantitative surface modification ranging from microarray and sensor construction to the development of antimicrobial surfaces.

Technology Transfer

A large number of patent disclosures and patent applications have been filed as discussed in the preceding sections. There continue to be discussions with several companies regarding implementation of the new technologies.

Significant Awards

In 2006, Prof. Koberstein received the Stine Award from the American Institute of Chemical Engineers, recognizing his contributions to materials science. The national award, presented by the Division of Materials Engineering and Science Division, is the most prestigious award ptrdrnyrf by the Society in the field of materials.

In 2006, Prof. Koberstein was also elected as a fellow of the American Institute of Chemical Engineers, a distinction afforded to only a small fraction of the society membership. The Grade of Fellow is a special category of AIChE membership, reserved for those tenured Institute members who have displayed significant service to AIChE and the profession, and who have achieved significant accomplishments in Chemical Engineering.

Publications funded by ARO (last 5 years)

1. "Optimal Chain Architectures for Polymer Surface Properties", P. O'Rourke-Muisener, S. Kumar and J. T. Koberstein, Macromolecules, 36,771-781 (2003).
2. "Surface Segregation in Miscible Blends of Polystyrene and Poly(vinylmethylether): Comparison of Theory and Experiment", C. Forrey, J. J. Koberstein, David Pan, Interface Science, 11(2), 211-223, 2003.
3. "Measurement and Modeling of End Group Concentration Depth Profiles for ω-Fluorosilane-terminated Polystyrene and its Blends", P. O'Rourke-Muisener, C. A. Jalbert, C. Yuan, J. Baetzold, R. Mason, D. Wong, Y. J. Kim, J. T. Koberstein, Binnure Gunesin, Macromolecules, 36 (8), 2956-2966, 2003.

4. "Adhesion Hysteresis in Polydimethylsiloxane gels" R. Mason, J. Emerson and J. T. Koberstein, J. of Adhesion, 80, 119-143, 2004.
5. "Photolithographic Technique for Direct Photochemical Modification and Chemical Micropatterning of Surfaces", K. Lee, F. Peng, G. T. Carroll, N. J. Turro and J. T. Koberstein, Langmuir, 20, 1812-1818, 2004.
6. "Morphology of Immiscible Polymer Blend Thin Films Prepared by Spin-Coating, P. Wang, J. Koberstein, Macromolecules, 37, 5671-5681, 2004.
7. "Molecular Design of Functional Polymer Surfaces", J. T. Koberstein, Highlight Article, Journal of Polymer Science Polymer Physics Edition, 42, 2942-2956, 2004. (Invited Submission)
8. "Deposition of Block Copolymer Thin Films onto Polymeric Substrates by Adsorption from Supercritical Carbon Dioxide", D. Cho, J. T. Koberstein, Macromolecules, 38, 1829-1836, 2005.
9. "Adhesion of PDMS Elastomers to Functional Substrates", R. Mason, J. T. Koberstein, J. Adhesion, 81, 765-789, 2005.
10. "Photochemical Modification and Patterning of Polymer Surfaces by Surface Adsorption of Photoactive Block Copolymers" F. Pan, P. Wang, K. Lee, A. Wu, N. J. Turro, J. T. Koberstein, Langmuir, 21, 3605-3612, 2005.
11. "Adhesion Enhancement of Polymer Blend Interfaces by Reactive Block Copolymer Brushes", W. Hu, H. R. Brown, J. T. Koberstein, R. Bhatia, J. P. Lingelser, Y. Gallot, Compte Rendus Chimie Academie des Science (Invited Submission), 9, 45-59 (2006).
12. "Photochemical Micro-patterning of Carbohydrates on a Surface", G. T. Carroll, D. Wang, N. J. Turro and Jeffrey T. Koberstein, Langmuir, 22 (6): 2899-2905 (2006).
13. "Photoactive additives for cross-linking polymer films: Inhibition of dewetting in thin polymer films", Carroll, G. T; Sojka, M. E; Lei, X. G; Turro, N. J; Koberstein, J. T Langmuir (2006) 22 (18), 7748-7754.
14. "Synthesis and Surface Properties of End- and Center-Functional Poly (D,L-lactide)", Derek A. Wong, Patricia A.V. O'Rourke-Muisener and Jeffrey T. Koberstein, Macromolecules, (5), 1604-1614 (2007).
15. "Photoactive additives for cross-linking polymer films: Inhibition of dewetting in thin polymer films", Carroll, Gregory T., Sojka, Melissa E., Lei, Xuegong, Turro, Nicholas J., Koberstein, Jeffrey T. Langmuir, 22 (18), 7748-7754 (2006).
16. "Photo-generated glycan arrays identify immunogenic sugar moieties of Bacillus anthracis exosporium", Denong Wang, Gregory T. Carroll, Nicholas J. Turro, Jeffrey T. Koberstein, Pavol Ková, Rina Saksena, Roberto Adamo, Leonore A. Herzenberg, Leonard A. Herzenberg and Lawrence Steinman, Proteomics, 7, 180-184 (2007).
17. "Photogeneration of Carbohydrate Microarrays", G. Carroll, N. Turro, D. Wang, J. T. Koberstein, in A book in the series Modern Microanalytical Systems Title: Microarrays: New Development Towards Recognition of Bio-signals, Eds: Kilian Dill, Robin Liu and Piotr Grodzinski (Springer, New York, 2007, Chapter 13).

Other high visibility events

Because of the impact of the groups' recent research output, we have been invited to submit a number of prestigious highlight/review articles describing our work. One in the area of the carbohydrate microarrays have already been accepted ("Photogeneration of Carbohydrate Microarrays", G. Carrol, N. Turro, D. Wang, J. T. Koberstein, Invited book chapter, in press.). One highlighting our general work has been published ("Molecular Design of Functional Polymer Surfaces", J. T. Koberstein, Highlight Article, Journal of Polymer Science Polymer Physics Edition, 42, 2942-2956, 2004. (Invited Submission), and two are in preparation (Soft Materials and Polymer).