Parylene Polymers for Nanotechnology Applications

Rakesh Kumar* and Andreas Greiner**

*Specialty Coating Systems, 7645 Woodland Drive,
Indianapolis, IN 46278, USA, rkumar@scscoatings.com
**Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Str.,
D-35032 Marburg, Germany, greiner@staff.uni-marburg.de

ABSTRACT

This paper describes the use of Parylene polymers for nanotechnology applications, particularly as structured materials for hollow nano & mesospheres and nanotubes, and as protective coatings for nanostructured substrates, nanodevices, and nanoelectronics for functionality and reliability enhancement. Several attributes of the Parylene polymers are discussed in connection with nanotechnology applications. In addition, it briefly describes a model for manufacturing Parylene hollow fibers, and hollow nano and meso scale spheres having inner diameters from 50 nm to 20 microns. The unique coating process of Parylene and its properties can be exploited to protect nanodevices, nanofluidics, nanowire nanosensors, nanoelectronics and other nanostructured materials from various deteriorating agents.

Keywords*: Parylene, Nanodevices, Nanoelectronics, Nanocoating, Nanotubes*

1 INTRODUCTION

The role of vapor phase polymers is becoming more attractive in the nanotechnology area, particularly if any polymer can be formed or deposited at molecular level with desired physical and chemical properties. The number of nanoelectronic devices and materials are continuously growing, and in many areas commercial products are slowly becoming available. In the electronics area, nanoparticles have been used in a number of products to enhance mechanical, thermal or electrical performance. Although cabon nanotubes received increased interest for industrial applications initially, polymer and polymer composites are now getting more attention due to their excellent mechanical and thermal properties. As the growth of nanoelectronics and other devices are increasing, the challenges of making them safe and effective are also increasing.

In medical area, most nanodevices incorporate nanoelectronic components that might be placed inside the body to either sense or facilitate a physiological response. Several nanoelectronic devices may be used for diagnoses or analyses also come in contact with the human body. It is, therefore, not only very important that these nanoelectronics materials do not create any adverse effects upon contact with human body, but it is also essential that they have long-term resistance to corrosive body fluids, electrolytes, proteins, enzymes and lipids. Implantable nano surfaces generally require a protective coating to provide physical isolation from moisture, chemicals and other substances and to immobilize microscopic particles. They may also need passivation, electrical insulation and coating to reduce friction.

Advancements in materials technology have led to the development of several materials that are inherently stable but tend to degrade when subjected to harsh environments. Many potential nano devices including implantable and non-implantable have to be biostable in order to prevent their degradation and reduction in medical efficacy.

As size of components and parts are reducing in electronics, the required performance of these electronic devices in many different type of environments, both within and outside of the human body, has led many researchers and companies to the world of advanced nanomaterials and suitable protective polymeric coatings that can be applied at molecular level for long-term effectiveness.

Among the available polymers for nanotechnology applications, Parylenes (vapor phase deposited organic coatings) [1] offer a significant role in packaging and protection of nanoelectronic devices for safety and enhancing the overall electronics reliability within body tissues and fluids. Parylenes have also been very effective on non-implantable medical electronic devices by providing protection from adverse environmental effects. Although not exactly in the nano area, examples of Parylenes in medical electronic devices include ocular implants, implantable cardiac defibrillators, neurostimulator pulse generators, RFID implants, transdermal drug delivery devices, digital dental imaging equipment, cochlear implants, ingestible sensors/transmitters, and implantable radiation dosimeters. Parylenes' suitability and bioacceptability encourage researchers to explore their role in biosensors, biochips and other active electronic devices for medical applications [2, 3, 4].

During the past several years, Parylene polymers have been considered an integral part of medical devices by many biomedical engineering researchers as electronic devices are made of Parylene through MEMS technology [5, 6, 7, 8]. Parylenes have drawn considerable attention as structural materials for microfluidic devices because of their exceptional properties such as stress-free truly conformal deposition, chemical inertness, bioacceptability and optical transparency. Examples of such developments include mass flow controller (consisting of an

NSTI-Nanotech 2007, www.nsti.org, ISBN 1420061836 Vol. 2, 2007

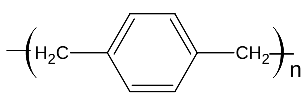
electrostatically actuated microvalve) [3, 9, 10], Parylene micro-nozzle for electrospray [12], Parylene flapping wing [12], Parylene electrophoretic channel and electrostatic actuators [13]. Such advancements in Parylenes, coupled with existing coating capabilities, will enhance the role of micro and nano electronics in many medical applications.

This paper provides an overview of Parylene's attributes and their impacts on nanoelectronic devices and also highlights its use in making nano and meso structured hollow spheres and tubes for variety of applications.

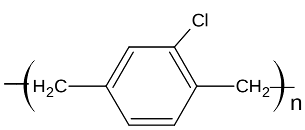
2 PARYLENE POLYMERS

Parylene is the generic name for members of a unique polymer series. The Parylenes (xylylene polymers) have been classified as thermoplastic polymers that are formed on substrate surfaces using vacuum deposition polymerization. They are polycrystalline and linear in nature, and possess useful dielectric and barrier properties per unit thickness. They are also chemically inert and form thin layer coatings without pinholes.

Parylene N



Parylene C



Parylene HT

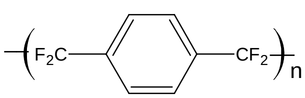


Figure 1: Parylene variants for nanotechnology applications.

Parylenes are applied to substrates in a vacuum chamber and have certain similarities with vacuum metallizing. Unlike vacuum metallization, however, which is conducted at pressures of 10^{-5} torr or below, the Parylenes are formed at around 0.1 torr. Under these conditions, the mean free path of the gas molecules in the deposition chamber is in the order of 0.1cm. As a result, all sides of an object to be coated are uniformly impinged by the gaseous monomer, providing a high degree of conformability [1, 14].

Vacuum deposition polymerization begins with the vaporization of a Parylene dimer. The dimer vapor is pyrolytically cleaved at temperatures of 600 to 750^{o}C to form a reactive monomer vapor. The reactive monomer vapor is then transferred to a deposition chamber where the substrates are located. In the deposition chamber, the reactive monomer vapor spontaneously condenses onto the substrates to form a Parylene coating. There is no liquid phase in the deposition process, and substrate temperatures remain near ambient.

Although Parylene research and development efforts during the past four decades have resulted in several Parylene types, only two of them, Parylene N and C, have found wide commercial application in medical fields to date. Properties of Parylene N and C are described extensively in the literature [1,18]. The recent commercial availability of Parylene HT has now added many additional advantages for medical electronics applications. Parylene HT possesses unique properties compared to all existing Parylenes and other vapor phase coatings and is able to meet the requirements of better dielectric capabilities, higher temperature integrity and mechanical processing of dynamic medical nanoelectronics. The chemical structures of Parylene N, C and Parylene HT are shown in Figure. 1

Parylene HT can easily be applied on nano devices, nanoelectronics and other nano parts for high performance and reliability. It provides excellent corrosion, solvent, acid, moisture, and UV resistance. It can also help manage the stiction issues of nano and micro devices. Its very low dielectric constant, low coefficient of friction, high dielectric strength make it ideal for protecting parts that are exposed to high temperature, saline and corrosive environments. In addition to enhancing components' overall reliability, it is also suitable for contamination control, dry film lubrication and as an interlayer dielectric in manufacturing high density and high-speed integrated circuits.

3 AS NANO & MESO STRUCTURED MATERIALS

Parylene has been considered as nano and meso structured material [15, 19]. Parylene hollow fibers with inner diameter from 50 nm to 20 microns were successfully developed using TUFT-process (TUFT = Tubes by fiber templates). Such structures are suitable as separation and storage media, as dielectrics, in medicine, electronics, catalysis, osmosis and optics.

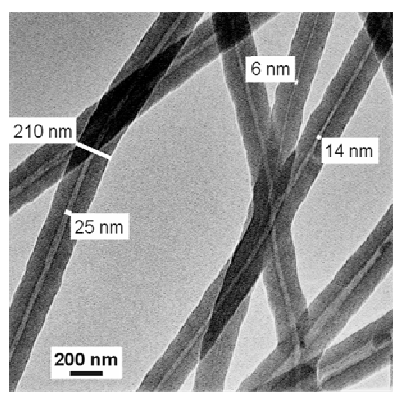


Figure 2: Parylene Nanotubes

Examples also include, but not limited to controlled release of drug delivery systems, sensors, separation technology (gases, particle filtration, bacteria etc.) and electronics (piezoelectric shaping, nanoperistaltic pumps etc.).

The nano spheres and particles were also made from Parylene using vapor phase polymerization processes involving scaffold, foaming, spraying and various types of chemical reactions (patented pending). Examples of nano and meso structured are shown in Figure 2-4.

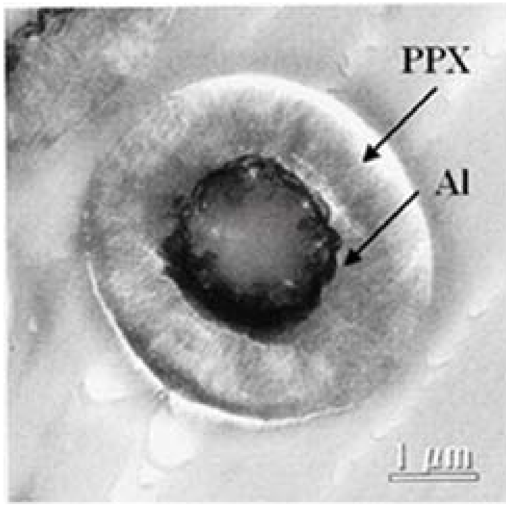


Figure 3: Parylene nanotube with Al lining

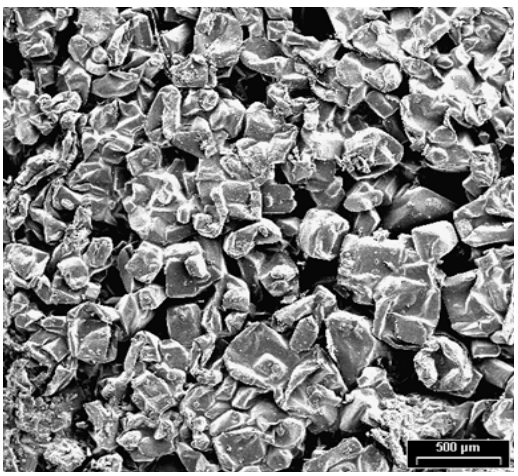


Figure 4: Parylene Hollow-spheres or structures

4 AS PROTECTIVE COATINGS FOR NANO DEVICES AND SURFACES

Because of the unique characteristics, Parylene coatings have been used for performance and long-term reliability of many miniaturized parts and electronic components that include pressure and temperature sensors, PCB's, MEM's, variety of micro and optoelectronic devices, fuel cell components and nano-electronic parts. Parylenes offer solutions to many existing protective, packaging and reliability challenges of nanotechnology in part because of its excellent electrical & mechanical properties, chemical inertness and long-term thermal stability. In addition, Parylene truly conforms to the parts due to its molecular level deposition characteristics. The most common attributes that impact nanotechnology applications include biostability, bioacceptability, controlled thickness down to angstroms level, chemical inertness, nano and micro-encapsulation capabilities, superior chemical, electrical and moisture barrier, corrosion resistance, contamination control and dry-film lubricity. Some key properties are briefly described below.

4.1 Biostability and Bioacceptability

Parylenes N, C and Parylene HT® comply with the biological testing requirements for ISO-10993. Testing includes cytotoxicity, sensitization, intracutaneous reactivity, acute systemic toxicity, implantation (1, 12 and 26 weeks for C; 1 and 12 weeks for N and Parylene HT), and hemocompatability. In vitro tissue culture studies show that human cell types readily proliferate on Parylene C coated surfaces to produce thin, adherent layers of morphologically normal tissue [16]. Culture studies using diploid WI-38 embryonic human lung cells have demonstrated that Parylene C coatings are highly compatible[22]. Successful in vivo growth studies [17] and compatibility of Parylene C with experimental circulatory assist devices have also been reported [20].

4.2 Barrier and Chemical Inertness

The bulk barrier properties of Parylenes are among the best of organic polymer coatings. Their excellent moisture and chemical barrier attributes are well suited for medical devices and electronic components. Generally applied much thinner than any other polymeric coatings, Parylene provides a pinhole-free barrier to protect against body fluids as well as moisture, chemicals and common gases. Parylene coatings resist chemical attack from organic solvents, inorganic reagents, and acids. At temperatures below 150^{o}C, Parylenes resist all attempts to dissolve them.

4.3 Dielectric Properties

Parylenes have excellent dielectric properties. Their high dielectric strength is attributable to the fact that they can be formed as thin, continuous films free from defects and the fillers commonly found in conventional coatings, both of which tend to reduce dielectric strength. Parylene HT has the lowest dielectric constant and dissipation factor among industry standard coatings, enabling it to transfer electrical signals without absorption or loss. The dielectric constant and dielectric losses are unaffected by moisture absorption and the low dielectric constant for Parylene in the gigahertz frequency range is often of great interest to designers of high frequency devices.

4.4 Thermal Stability

For some nanoelectronics, harsh operating environments range may be from –40° C to more than 300° C, making coating stability critical to the trouble-free life of such electronics. In oxygen-free atmospheres or in the vacuum of space, the continuous service temperature projections exceed 200^{o}C for both Parylene N and C. Parylene HT has ability to resist thermal oxidation up to 450^{o}C both in oxygen and

NSTI-Nanotech 2007, www.nsti.org, ISBN 1420061836 Vol. 2, 2007

oxygen-free atmospheres. Parylene HT has shown to survive continuous exposure to 350°C in air without any adverse property change for more than 1000 hours. The excellent thermal oxidative stability of Parylene HT in both air and inert environments is due to the stable carbon-fluorine bond in the polymer chain

4.5 Dry Lubricity

Parylenes possess excellent dry-film lubricity characteristics. The coefficients of friction (COF) for Parylenes HT, N and C, as measured by ASTM D 1894, are 0.15, 0.25 and 0.29, respectively, for static observations.

4.6 Corrosion Control

Parylenes successfully control corrosion of many electronic assemblies and substrates in a variety of application conditions. Since the actual corrosive environment changes from day to day (or faster), most testing experiments are designed to expose samples to various environmental stresses that promotes corrosion.

4.7 Stress

Another property which may be very important is the total stress applied by coatings on the nano surfaces. The stress values for Parylene N were found to be compressive in nature while polyimide exhibits stresses in the tensile mode [21]. Parylene N, which can achieve a 10 µm thickness in one layer, offers reduction in stress of 54% and 50% compared to two and four layered polyimide films, respectively.

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