

Vapor Deposition Polymerization of para-Xylylene Derivatives —Mechanism and Applications*

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Vapor deposition polymerization (VDP) of poly(p-xylylene) and its derivatives is discussed. The process, known as parylene technology, is a thin film vacuum deposition method, utilizing [2₂]-paracyclophanes as precursor compounds and it is approximately forty years old. Today, thanks to its applications in miniature electromechanical systems (MEMS) and all organic semiconductor (AOS) technologies, it is a subject of a strong renewed scientific interest.

The emphasis of this review is put on the mechanism of parylene deposition as well as on this process' applications. As far as the deposition mechanism is concerned it is discussed in terms of both chemical reactions and physical phases and phenomena involved. The occurrence of two different mechanisms, of which the solid phase addition polymerization takes place at temperatures below monomer melting point, is particularly stressed. The diversity of parylene uses, both present and future, is also discussed with an attention on the development of future biomedical, MEMS and AOS applications.

1. Introduction

Vapor deposition polymerization (VDP) processes belong to the category of chemical vapour deposition (CVD), but in contrast to typical CVD technologies, usually yielding thin inorganic oxide carbide or nitride films, they produce coatings of high molecular weight organic polymers. The technology of poly(p-xylylene) and related films, commonly recognized as parylene coatings, is the best known case of a VDP process. Xylylene polymers possess a number of useful properties, ranging from high mechanical strength and low friction coefficient to excellent barrier behavior and extraordinary chemical resistance. Since, in addition, the process is relatively simple to handle, easy to integrate with other vacuum technologies, with the resulting coatings being characterized by uniform thickness and extraordinary penetration abilities, it has found numerous applications in various areas of life and technology. Apart from that, a broad field of application of these materials in microtechnology has been emerging since the beginning of the twenty first century. Today, various types of MEMS devices, ranging from microfluidic valves, peristaltic pumps and miniaturized gas chromatography columns to free standing cantilevers and micromirrors, are produced with parylene films as a basic material. It is due to the MEMS applications of these films, as well as to their broad biomedical use, that the future of parylene technology appears to be well secured.

2. The advance of parylene technology

Parylene technology has very strong foundations in modern chemistry. The development of quantum theory and its methods of approximate solutions of many-body

wave equations allowed one to calculate electronic structure of various hypothetical compounds. Among these compounds was p-quinodimethane, also known as p-xylylene^{1,2}. Quantum mechanical calculations showed that its ground state had a quinoid form (**Fig. 1a**), while the first excited state possessed a diradical structure (**Fig. 1b**)².

Thermodynamically, the compound should be stable thanks to its high resonance energy of 38 kcal/mole¹. Yet, at the same time, it should be extremely reactive due to a large amount of free valence and a small energy difference between the ground and the first excited states, amounting to 12 kcal/mole².

Experimental work entirely confirmed theoretical predictions, and it was also in the same experiments where the process of vapor deposition of poly(p-xylylene) was discovered³. P-xylylene was formed in the gas phase as a pyrolysis product of p-xylene and thin films of poly(p-xylylene) were deposited on the reactor inner walls at room and lower temperatures³.

Due to its low efficiency and high pyrolysis temperature, the original route to poly(p-xylylene) is unsuitable for commercial applications. Low efficiency leads to large quantities of by-products, making the entire process unclean. One of these by-products is a cyclic p-xylylene dimer of a very peculiar geometry, which today is used as a clean and economical source of deposition of poly(p-xylylene). Chemical structure of di-para-xylylene, also known as [2₂](1,4)-cyclophane, is presented in **Fig. 2a**, while **Fig. 2b** shows its geometry, comprised of two

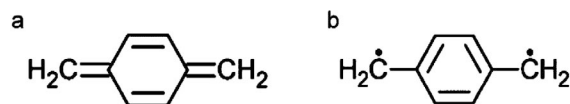


Fig. 1 Formulae of p-xylylene ground state (a) and first excited state (b).

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strained benzene rings, situated above one another⁴).

Di-p-xylylene is not only very stable under ambient conditions, but it also decomposes at relatively low pyrolysis temperatures (600–650°C, compared to 900–1000°C for p-xylene) with a quantitative formation of p-xylylene. Both these features enabled commercialization of the process, developed by W. F. Gorham of the Union Carbide Corporation (UCC)⁵ and known as Parylene technology. The name Parylene refers to coatings deposited from the dimers of the same trade name, supplied by the UCC and related enterprises, while the word parylene is commonly used to describe this group of polymers. For many years there have been three different dimers in a continuous supply: unsubstituted Parylene N, monochloro substituted (in the aromatic ring) Parylene C and dichloro substituted Parylene D. Today, there are many companies present on the market and many different trade-names are used with regard to poly(p-xylylene) products. One example is Japanese company Kishimoto, supplying such products as methylene substituted difluorinated dimer under the trade-name of diX F, and ring substituted amino derivatives under the names of diX A and diX AM. In general, the contemporary parylene market is divided between a few large companies, supplying everything from chemicals to deposition equipment and several dozen of those, who offer commercial deposition of polymer coatings using the parylene technology. A schematic block representation of this technology, together with the corresponding temperature and pressure values, is shown in Fig. 3.

As a chemical vapour deposition (CVD) process, parylene technology has several advantages over wet polymer coating methods. They are due to the fact that the deposition mechanism is controlled by the diffusion of gaseous molecules to the substrate surface. In this way there are no surface tension forces involved and the resulting film is conformal, i.e. it covers complicated and multi-faceted surfaces with a uniform thickness. The conformity

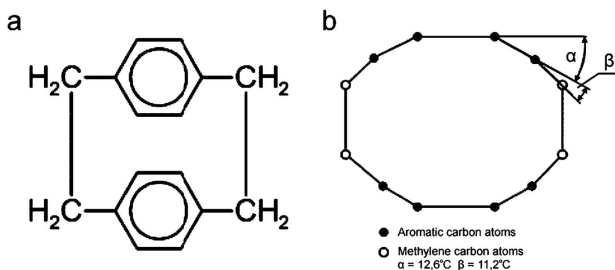


Fig. 2 Chemical structure of [2₂]paracyclophane (a) and its geometry (b).

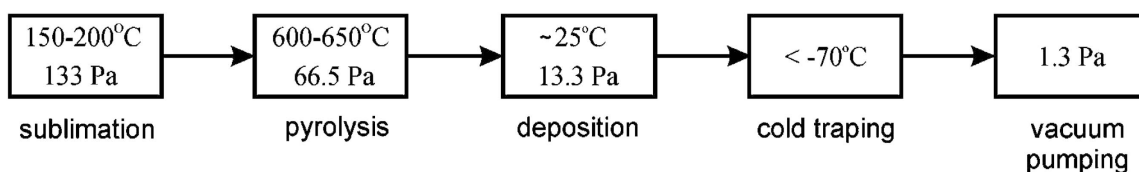


Fig. 3 Schematic representation of parylene process.

of parylene coating, as opposed to conventional wet polymer enamel deposition, is illustrated in Fig. 4.

Another extraordinary feature of the parylene process, resulting from the diffusion control, is its penetration ability. Figure 5 presents the results of narrow channels penetration tests for unsubstituted poly(p-xylylene), performed by Broer and Luijks⁶. As seen in the figure, parylene coating can penetrate hollows as narrow as 14 μm wide, and in the case of 56 μm wide channel polymer film thickness at the depth of 1 cm amounts to approximately 35% of its thickness at the channel's entrance⁶.

3. Deposition mechanism

From chemical point of view, parylene process is comprised of two stages, a stage of thermal decomposition of the dimer at elevated temperatures and that of polymerization at ambient or lower temperatures.

Theoretically, thermal cleavage of the dimer may proceed according to two different mechanisms. In order to initiate a polymerization process, it is not necessary to break both ethylene bridges in [2₂]paracyclophane. It would suffice to cleave only one of these bridges with the

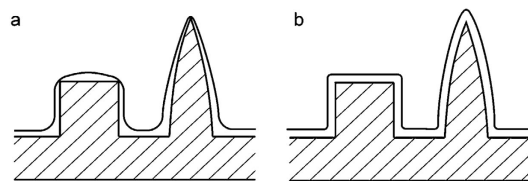


Fig. 4 Conformity of parylene deposition: wet polymer enamel coating (A) and parylene coating (B).

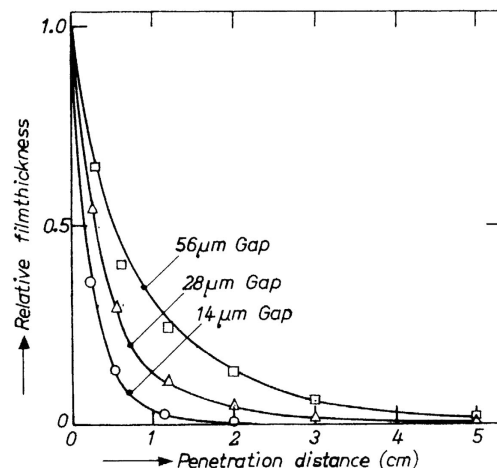


Fig. 5 Depths of Parylene N penetration of very narrow channels. After Broer and Luijks [6], with permission.

formation of a linear diradical dimer. However, in his pioneering work Gorham has demonstrated that both bridges undergo cleavage and two molecules of p-xylylene are formed during thermal decomposition of the cyclic dimer⁵. He pyrolysed mono-substituted²² paracyclophanes and studied the polymerization products. In the pyrolysis of acetyl-di-p-xylylene, for instance, he obtained two separate polymers: one deposited at 90°C and identified as poly(acetyl-p-xylylene) and the other, formed at 30°C and found to be pure poly(p-xylylene) [5]. The only rational explanation was that two monomer molecules must have been formed during thermal decomposition of the cyclic dimer. The course of that process is illustrated using schematic reactions, presented in **Fig. 6**.

As far as polymerization reaction is concerned, it consists of an initiation step and a propagation step. Initiation begins with two p-xylylene molecules forming a linear diradical dimer. Due to an excess of energy, however, this product is unstable. A notion prevails among parylene workers that it takes a formation of a diradical trimer, whose total energy is lower than the energy of three monomer molecules, to propagate a chain reaction^{7,8}. Under dynamic equilibrium conditions the concentration of linear trimer is extremely low and so is the frequency of initiation, which leads to a very high molecular weight of the polymer. Indeed, extraordinarily high values of molecular weight, exceeding 1000000, were postulated for parylene polymers on the basis of electron paramagnetic resonance (EPR) measurements⁹. Both reactions, chain initiation and chain propagation are schematically presented in **Fig. 7** below.

There are two features worth noting in the above scheme: one is an absence of molecules other than those of p-xylylene, and the second is a lack of a chain termination step. The first is a reason for a high purity of xylylene polymers—they are free of trace amounts of initiators that are typical for conventional polymers. The lack of termination step, on the other hand, indicates a formation of a living polymer. EPR measurements of xylylene polymers reveal, indeed, a presence of unpaired spins at substantial concentrations^{5,9,10}. A concentration of radi-

cal species in Parylene N, measured by Gorham, amounted to $5-10 \times 10^{-4}$ moles per mole of p-xylylene⁵. In the case of Parylene C it has been demonstrated that the decay pattern of EPR signal depends on whether it is recorded in the presence or in the absence of air⁹. Under vacuum, the decay progresses in accordance with second order kinetics and with the preservation of proton hyperfine splitting of the signal⁹. **Figure 8a** presents that pattern, while the concentration of unpaired spins in Parylene C as a function of time is shown in **Figure 8b**. The same results, computed in a second order kinetic co-ordinate system: $\ln c = f(t)$, are presented in the window. These data strongly indicate a post-deposition growth of polymer chains due to a recombination of macroradicals. The post-deposition polymerisation of xylylenes has also been demonstrated by measurements of the heat of reaction, which for both Parylene N and Parylene C keeps on evolving from the system long after the termination of deposition¹¹⁻¹³.

Physically, the cleavage of dimer molecules takes place in the gas phase and the chain growing reactions occur in the condensed phase, on a surface of the substrate. Diffusion of monomer molecules to the surface and their condensation on that surface play predominant role in the mechanism of the deposition/polymerization process under any deposition temperatures. Further behavior, however, strongly depends on whether that process takes place above or below melting point of the monomer.

Above its freezing point the monomer condenses as liquid, and the diffusion of its molecules towards the propagation sites, now continued in the liquid phase, is responsible for the growth of polymer chain. A comparison of a net flux of monomer molecules, necessary to produce typical rates of parylene deposition under these conditions, with that striking the substrate according to the kinetic theory of gases, shows the latter to be two-three orders of magnitude larger than the former¹⁴. This means that only one of several hundred collisions is effective, with the remaining molecules being re-evaporated back to the gas phase. These conditions produce a dynamic equilibrium, under which the growth of a pary-

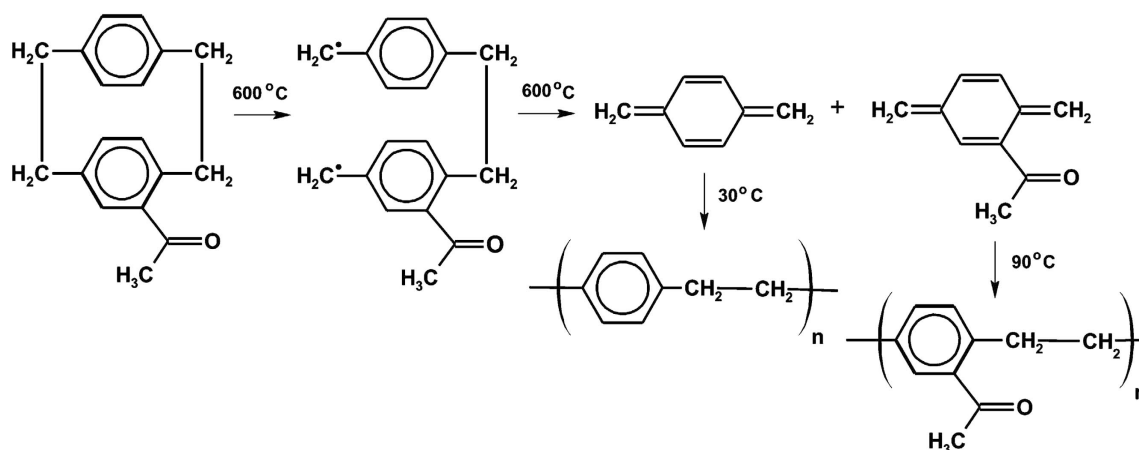


Fig. 6 Pyrolysis of acetyl-di-p-xylylene.

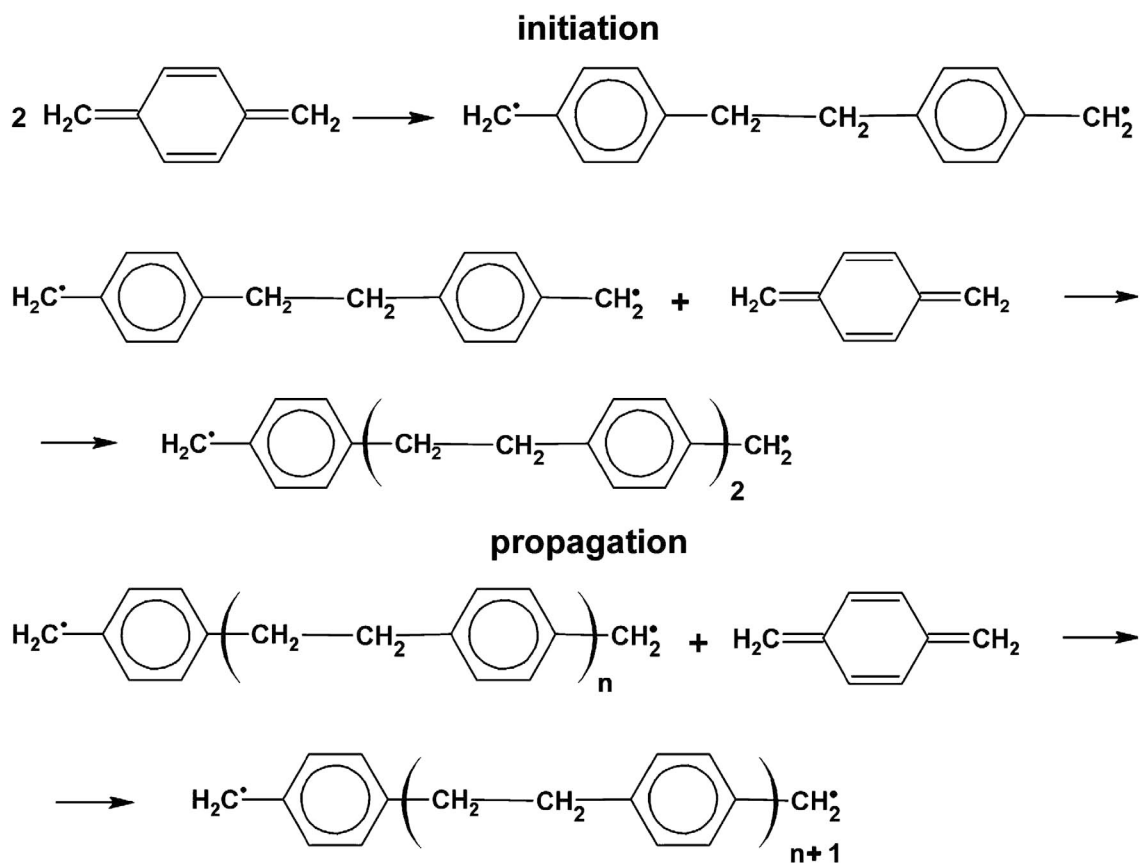


Fig. 7 Schematic representation of chain initiation and chain propagation reactions of p-xylylene.

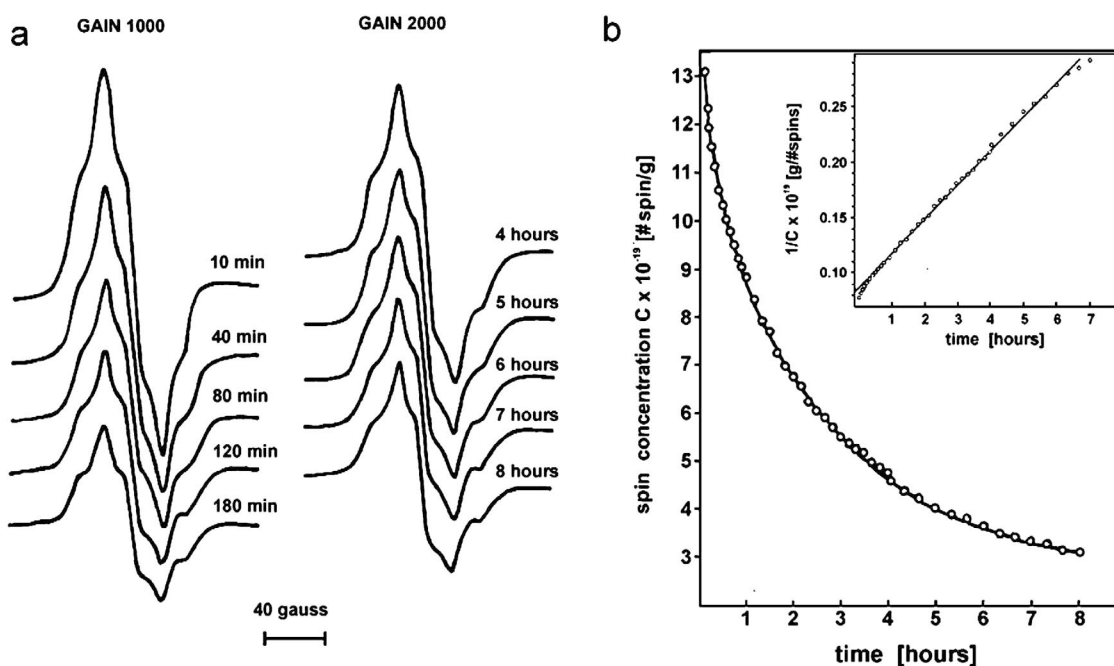


Fig. 8 A decay of the EPR signal (a) and the drop of unpaired spin concentration (b) in Parylene C recorded under vacuum. The window shows the same results presented in a co-ordinate system corresponding to the second order kinetics with respect to the radicals.

lene coating takes place. It is the rate of monomer consumption, controlled by the diffusion of its molecules towards the chain propagation sites, that governs the entire process.

At temperatures below its freezing point, the

monomer condenses as a crystalline solid. Results of thermal measurements during Parylene N and Parylene C deposition at very low temperatures indicate that freezing point of p-xylylene is located in the vicinity of -73°C^{13} , while that of chloro-p-xylylene nears -65

$^{\circ}\text{C}^{12}$). The same results, together with those obtained by Treiber et al.¹¹, strongly indicate an existence at low temperatures of two exothermic phenomena, substantially differing with their kinetics^{12,13}. These results were obtained by means of a specially constructed substrate-sensor, which not only enabled deposition at temperatures between -160°C and ambient, but also allowed one to record quick temperature changes¹².

A series of temperature recordings of the substrate-sensor for the deposition of Parylene C at different initial temperatures is presented in Fig. 9. It is evident from these plots that, at low temperatures, the process is accompanied by two separate heat effects with very different rates. One of them, present at any deposition temperature, consists in a continuous and relatively slow heat transfer to the sensor and it is indicated by a shift of the baseline towards higher temperatures.

The other heat effect, accompanying parylene deposition at low temperatures, is comprised of powerful and very quick heat shots, supplied to the sensor and represented in Fig. 9 by sharp temperature spikes. As seen in the figure, the spikes are observed only below certain threshold temperature, always lower than monomer melting point. They also are the more abundant, the lower is the initial temperature. An increase of a number of spikes is always accompanied by a decrease of the value of the baseline shift, as if both of these thermal effects, the slow and the quick, remained in a competition with one another. A width of the temperature range between the monomer melting point and the threshold temperature, within which no heat spikes are observed, strongly depends on the rate of dimer evaporation-the lower is

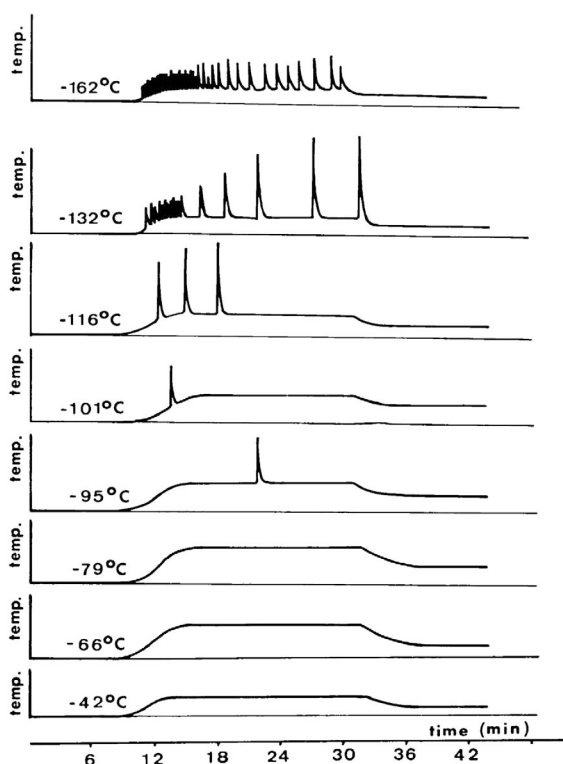


Fig. 9 Plots of substrate temperature recorded during the deposition of Parylene C at different initial temperatures.

that rate, the farther apart from melting point is the threshold temperature^{12,13}.

As shown above, a slow chain propagation process continues after termination of the deposition process. In certain cases, however, the quick evolution of heat, indicated by a temperature spike, is also recorded in a post-deposition phase of the process¹³. Figure 10 shows recordings of substrate temperature changes during Parylene N deposition at -116°C and -104.5°C , with both temperatures remaining well below the monomer freezing point (equal approximately -73°C)¹³.

As seen in the figure, the quick heat exchange at low deposition temperatures either takes place directly during the deposition (in that case usually in the form of multiple heat shots) or it occurs as one very large heat spike after the deposition has been terminated and the substrate temperature begins to rise.

The following is an interpretation of the observed heat effects. The continuous and relatively slow stream of heat, supplied to the sensor during entire deposition process, constitutes thermal manifestation of all those phenomena, which are connected to the transfer of mass and heat from regions of higher temperature to regions of lower temperature as well as of diffusion controlled exothermic processes. The three most important of all these phenomena, jointly contributing to the shift of the baseline, are: cooling monomer molecules, their condensation and diffusion controlled chain propagation reaction^{12,13}.

The presence of heat spikes, on the other hand, which is always observed below the freezing point, is interpreted as the evidence of very fast chain propagation reaction taking place within the crystalline film of the monomer, known as solid phase addition polymerization¹⁵. A careful observation of the film during its deposition onto the substrate/sensor allows one to notice a sudden change of the transparency as well as a shrinkage of the material, accompanying the heat spike. The strongest argument for the above interpretation, however, comes from the microscopic observations of the resulting films. A series of SEM micrographs of Parylene C films, deposited at the initial temperature of

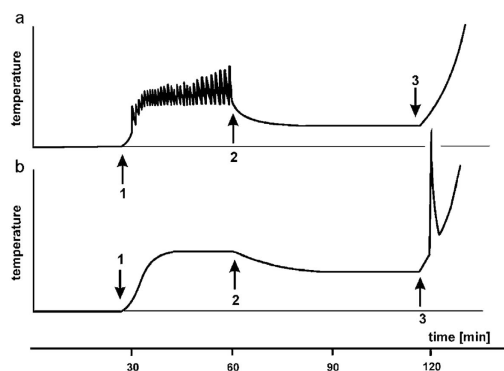


Fig. 10 Recordings of substrate temperature changes during Parylene N deposition at -116°C (a) and -104.5°C (b). The arrows indicate: beginning of deposition (1), end of deposition (2) beginning of heating the substrate (3).

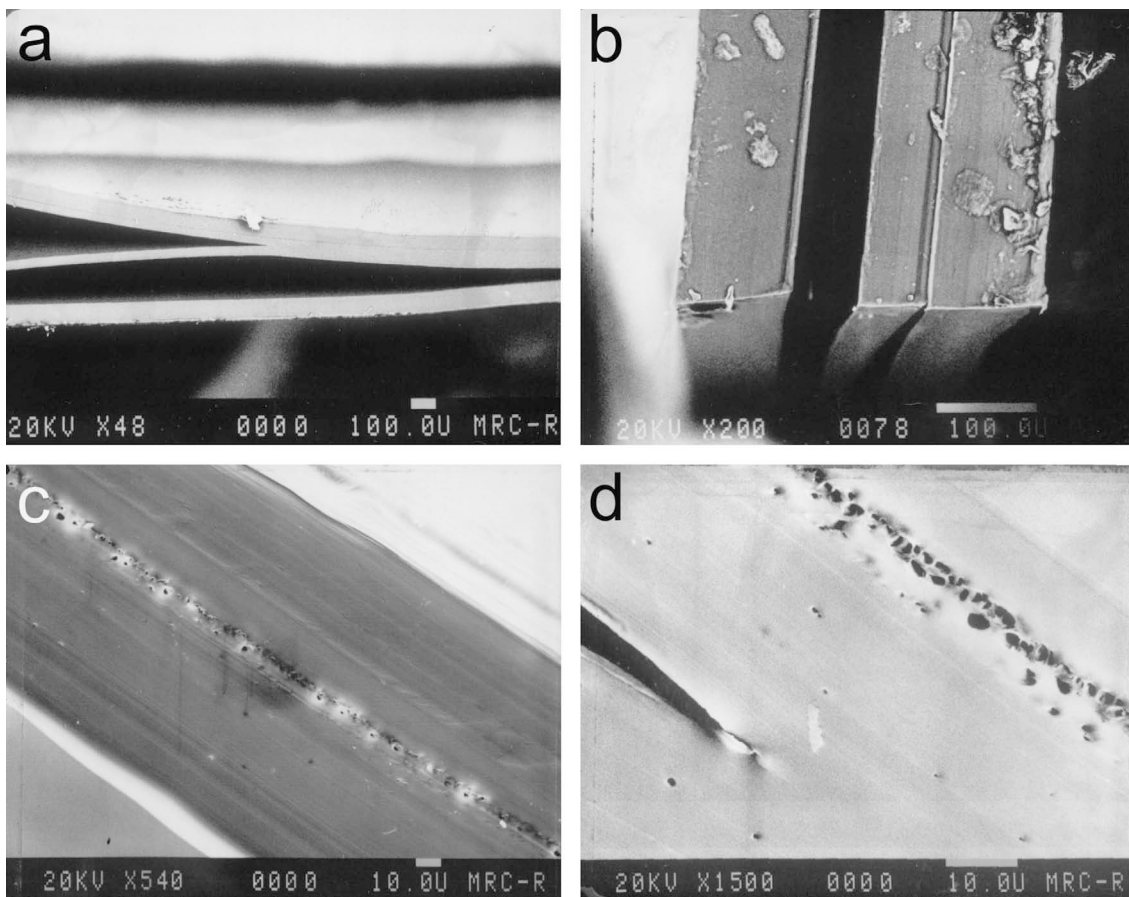


Fig. 11 Scanning electron micrographs of Parylene C films deposited at initial temperature of -141°C .

-141°C , is presented in Fig. 11.

As seen in the micrographs, polymer films obtained under these conditions clearly possess a multilayer structure. In many cases the layers are completely separated from each other, as seen in Fig. 11 a and b. There are, however, instances where the layer boundary is marked by perforation (see Fig. 11 c, d). In these cases, although the boundary line is still quite evident, there is no clear separation of the layers, which are tightly bridged along that line, apparently by the same material. This result suggests that both polymerization mechanisms and namely a quick, solid phase addition polymerization (responsible for separation of the layers), and a slow diffusion controlled chain propagation (leading to their partial integration), might take place either simultaneously or subsequently. In fact, Fig. 11 d presents both types of layer separation: one in the lower left corner and one in the upper right corner.

At temperatures below monomer freezing point, it is a crystalline film of p-xylylene that is deposited on the substrate. Although the diffusion of monomer molecules in this film is severely restricted, it appears to be to some extent possible, what is evidenced by the presence of diffusion controlled chain propagation reaction under these conditions. The analysis of thermal effects shows, however, that the lower is the deposition temperature, the less important this reaction becomes, with more and more monomer molecules being polymerized according to the solid phase addition polymerization mechanism.

This fact is very likely related to the degree of crystalline perfection of the monomer film. According to Bamfort and Eastmond¹⁵⁾, due to spatial reasons, the solid phase addition polymerization process is not possible in an ideal, defect-free crystalline lattice. To the contrary, for the process to start, a certain critical amount of the lattice defects is necessary. In the discussed case of parylene deposition, the number of lattice imperfections in the monomer crystalline layer is the higher, the farther (toward low temperatures) the substrate temperature departs from the monomer freezing point. This means that the probability of the solid phase addition polymerization should increase with the lowering of temperature, a tendency which is well documented in Fig. 9.

4. Applications

The most important feature of parylene technology is the VDP process itself. Many advantageous properties of the coatings result from the very way they are applied. Among others, these properties are: thickness uniformity, including sharp edges and trenches, very effective penetration, pinhole free deposition and low stress. Depositing poly(p-xylylenes) offers further benefits, stemming from the chemistry of the process. Since polymerization of xylylene and its derivatives requires no additional initiator and the process is practically quantitative, polymer layers of high purity result and they show a fairly stable dielectric behavior within a broad range of temperatures. A compactness of these layers and their

hydrophobicity makes them excellent materials forming a barrier against aqueous solutions of ionic species.

All the above features made parylene coatings very attractive in one of their major applications, namely that of electronic circuitry protection against external influence¹⁶). For over twenty years this application has been extensively used to preserve performance of printed circuit boards (PCB), operating under conditions of a corrosive environment. Another kind of circuitry coated with parylene films comprises hybrid circuits (HC), in which the coating offers an additional advantage of mechanical reinforcement of wire bonds. These bonds, made of very fine gold wires of a diameter of 25 μm or less, provide input/output connections of an integrated circuit with the rest of the device. Coating them (together with the entire HC) with parylene film markedly increases their tensile strength due to strengthening of the wires themselves and to reinforcement of their solder junctions. The penetrating power of the parylene is utilized in the HC assembly process in such a way that it allows one to coat the interior of the circuit using a 0.5–1 mm wide opening in the package¹⁷). Since parylene coatings won the US. Department of Defense certificate as insulating compound for coating printed circuits assemblies¹⁸), they have been extensively used to protect such assemblies in military hardware, particularly against seawater.

Apart from electronic circuits, many other objects are commercially encapsulated with parylene films. One such application, broadly used for commercial purposes, is an encapsulation of elastomer products in order to protect them against leakage of liquid additives, for instance plasticizers, from the bulk of the material. Coating rubber keys, constituting elements of communication gear keypads, makes a good example¹⁹).

When a conformal layer of an insulating material is used to coat a ferrite core, its winding window is maximized because, in contrast to coatings applied from solutions, no film broadening effect is observed in the inner corners of the core (see Fig. 4). For that purpose parylene is often applied to ferrite cores, particularly to those of small dimensions, where the number of windings is largely restricted²⁰). Rear earth permanent magnets are also often coated with parylene to prevent their corrosion²¹). In general, covering small objects, whether they are elastomer keys, ferrite cores or magnets, with parylene films is effectively realized in tumbler type reactors with large numbers of items being deposited at the same time²²).

The conformity of xylylene polymers makes them suitable for the purpose of sealing a variety of other objects, ranging from archeology and museum artifacts²³) to books and documents^{24,25}). In the field of conservation, an application of parylene coatings to protect paper is the most advanced one. Once again, the extraordinary penetration ability of parylene process plays to its advantage by making it possible to apply protective coating to the entire book, without a need to unbind it²⁴). The most spectacular, however, use of this process in the field of conservation is the coating of newspapers and docu-

ments recovered from the wreck of "Titanic"²⁵).

As a biomaterial, parylene has been defined by the US Pharmacopeia as Class VI plastic. It has been subjected to and passed a number of US Food and Drug Administration and International Organization for Standardization biological tests. As a result, biomedical technology makes a fast growing market for parylene industry. Lubricity enhancement by these polymers is utilized in coating such medical devices as catheters, mandrels, needles, cannulae, laproscopic tools or prosthetic components²⁶). Their dielectric and barrier properties enhance a use of these materials in pacemakers, pressure sensors and other implantable electronic circuits²⁷). A broadly investigated field of parylene biomedical application comprises brain probes-miniature recording or stimulating neurological electrodes^{28–30}

At the end of the twentieth century, a dynamic development of microelectromechanical systems (MEMS) technology opened a completely new area of applications for parylene films. Major advantages of these materials in microtechnology comprise: low deposition temperature, conformity, lack of stress, chemical inertness, low modulus, susceptibility to reactive ion etching and, last but not least, low costs. Examples of MEMS fabrication processes with integrated parylene technology make a long list, on which one can find fabrication of such devices as: microfluidic valves^{31,32}), peristaltic pump³³), miniaturized gas chromatography column³⁴), a flexible valve-actuated flapping wing³⁵), cantilever actuators³⁶), beam seismometer³⁷) and circular micromirrors³⁶).

A separate category is made by all organic semiconductor devices (AOS), in the development of which parylene plays an important role of a dielectric and insulating material. Encapsulation of organic light emitting diode (OLED)³⁸) and organic field effect transistor (OFET)³⁹) structures with parylene has been reported. Yasuda and Tsutsui used Parylene C to form a dielectric layer, separating the gate and the organic semiconductor (pentacene) layer of their OFET device and obtained the value of field effect mobility of 0.81 cm^2/Vs ⁴⁰). This result has been recognized as one of the best in the AOS technology. Thanks to the application of parylene film as gate dielectric, Pozdorov and co-workers were able to construct a OFET device directly on a monocrystal of rubrene⁴¹). In this device a Hall effect was also observed⁴²). Finally, a fabrication of the entire 48×48 pixels organic OLED display, controlled by OFET active matrix, where polycrystalline pentacene played the role of organic semiconductor and parylene was used as dielectric film, has been described by Zhou and co-workers⁴³).

While still finger-counted in 1999, the number of papers published in the area of parylene applications in both MEMS and AOS technologies now goes in hundreds and it remarkably increases every year.

5. Conclusions

The process of vacuum deposition polymerization of xylylene derivatives has been known and used in various fields for nearly forty years. It was its electronic and mili-

tary applications that for a long time stirred a scientific and industrial interest in these materials. Having finally come to a routine, at the end of the twentieth century parylene process found new areas of applications, of which that of MEMS technology is the most often practiced today. It is due to MEMS, AOS and biomedical applications, that parylene technology goes through a recent revival and appears to have very promising prospects for the future.

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