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Vapor Deposition Polymerization as a Route to Fluorinated Polymers

J. A. MOORE and CHI-I. LANC

18.1. INTRODUCTION

Microelectronics has become a dominant influence in our lives. This latest industrial revolution was originally driven by the need for very small and lightweight electronic circuits for military and aerospace applications. With the development of, first, the transistor and, later, the integrated circuit (IC), microelectronics has now grown into a multibillion dollar industry, and its applications are ubiquitous. Device miniaturization has brought us from small-scale (SSI), medium-scale (MSI), and large-scale (LSI) integration to very large-scale integration (VLSI) with 10^5 or more components per chip.

There are three main elements in the fabrication of computer chips: the integration of devices, the wiring (or the interconnects), and the packaging. Research has been going on intensively in all three areas to provide ever higher performance (speed) and density. Active research foci include the scaling of devices and the search for novel materials and processing technologies for interconnects and packaging. Because speed is now limited largely by packaging technology rather than state-of-the-art chip construction, the bottleneck to computer speed improvement resides in further developments of packaging schemes and materials. The development of new insulators for interconnects and packaging is one approach to increase the speed of pulse propagation.[1]

Advances in the speed and complexity of integrated circuits and multichip modules (MCMs) have created a demand for the development of high-density

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J. A. MOORE and CHI-I. LANG • Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590.

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interconnects with controlled impedance.[2] Compatibility with thin-film fabrication techniques; low-dielectric losses; good adhesion to a variety of substrate materials; and thermal, mechanical; and chemical stability have made polymer materials attractive choices as the interlayer dielectric (ILD). In its simplest form, the multilevel interconnect structure comprises a metal pattern on a substrate, a polymer layer on top with metalized vias, and a second metal pattern on top of the polymer.

As the operating frequencies of electronic devices enter the gigahertz range and as the dimensions of electronic devices approach the submicron level, dielectric media with low dielectric constants (< 3) become increasingly more important for the reduction of signal coupling among transmission lines. Therefore, there is a clear need to understand the chemistry of materials used in these applications to evaluate better their effects on the electrical and physical performance of devices. There is also a need to develop a new materials that address the problems and requirements of IC manufacturing.

Organic materials exhibit high bulk and surface resistivities. Table 18.1 presents a comparison of the bulk resistivities of some relevant materials. The response of a dielectric material to a suddenly imposed voltage can be quite complex. Polar groups become oriented and local environments and chain stiffness affect the rate of this conformational reorientation. A distribution of response times characterizes this process. Mobile ions also begin to migrate. The response generally outlasts the polar group orientation that accounts for the initial surge of current. This current dissipates quickly as the orientation process nears completion. The mobility of ions and other impurities gives rise to a pseudo-steady-state current dictated by the rate at which trapped ions become mobilized.

These postulated mechanisms[3] are consistent with the observed temperature dependence of the insulator dielectric properties. Arrhenius relations characterizing activated processes often govern the temperature dependence of resistivity. This behavior is clearly distinct from that of conductors, whose resistivity increases with temperature. In short, polymer response to an external field comprises both dipolar and ionic contributions. Table 18.2 gives values of dielectric strength for selected materials. Polymers are considered to possess

Table 18.1. Bulk Resistivity of Selected Materials

Resistivity range (ohm-cm)	Material
$10^{-6} - 10^{-3}$ (conductor)	Cu, Ag, Al, Ni
$10^{0} - 10^{8}$ (semiconductor)	Si, Ge, Se, CuO
$10^{10} - 10^{11}$ (insulator)	Urea-formaldehyde resin
$10^{13} - 10^{14}$	Polyethylene
$10^{14} - 10^{15}$	Ceramics
$10^{16} - 10^{17}$	Teflon

Table 18.2. Intrinsic Dielectric Strength (Breakdown Voltage)

Material	*V* (V/mil)
Sodium chloride	3,800
Minerall oil	5,000
Polyimide	8,000
Polyethylene	16,500
Poly(methyl methacrylate)	25,000

adequate strengths against breakdown in packaging application.[4] However, moisture absorption lowers the breakdown threshold.

For a material to be suitable as an interconnect dielectric, it should have a low dielectric constant and be able to withstand temperatures higher than the 500°C necessary for the subsequent heating steps without the evolution of volatile by-products. Other important considerations are compatibility with other materials; long-term thermal, chemical, and electrochemical stability; ease of fabrication; and low cost. SiO_2, which has a dielectric constant of 3.5–4.0, has been used as the interlayer dielectric material in the industry. Further breakthroughs in high-performance chips hinge critically on the development of new insulators with dielectric constants much lower than that of SiO_2. It is generally believed that to achieve such a low dielectric constant organic polymeric materials must be considered instead of the traditional inorganic materials. An examination of Table 18.3 points to some of the advantages and disadvantages of organic polymers over inorganic dielectrics.

Apart from new low-dielectric materials, a clean method to deposit the dielectric as a uniform film is also required. Owing to the way fabrication technology in the microelectronics industry has developed and because larger silicon wafers (> 8 in.) are being used (currently, the technical difficulty of

Table 18.3. Comparison of Properties between Polyimide and Selected Inorganic Dielectrics

Physical properties	Polyimide	SiO_2	Si_3N_4
Process temperature, ºC	300–350	350–450	700–900
Decomposition temperature, ºC	500	1710	1900
Dielectric strength, MV/cm	3–4	5–8	5–10
Volume resistivity, ohm-cm	1015–1016	> 1016	1014–1016
Dielectric constant	3.2–3.6	3.5–4.0	7–10
Expansion coefficient 10^{-6}/ºC	20–70	0.3–4.5	4
Thermal conductivity, W/cm – ºC	0.0017	0.021	0.12

controlling thin-film uniformity for larger wafers has been a challenging area for spin-coating), a methodology with the ability to deposit polymers with appropriate properties as conformal films from the gas phase would be a useful advance, yielding high purity, uniform films on larger wafers.

Organic polymers such as polyimides and poly(benzocyclobutenes) are applied by spin-coating, and these materials can planarize the underlying topography to provide a planar surface for the next metal deposition. Senturia *et al.*[5] reported that planarization between 48 and 69% can be achieved with a single coating of polyimide. The degree of planarization is determined by the ratio of the step height with the polyimide coating to the initial step height of the metal pattern.

While these organic dielectrics have excellent planarizing properties, there are problems associated with their use: occasionally, polymer films are contaminated with solvent; polymer film curing processes are not complete; polymer films may be hygroscopic; and metal bubbling caused by water vapor trapped at the metal/polymer interface during high-temperature processing can, at times, be severe. Additionally, the nonuniformity when larger wafers are used is an unavoidable difficulty for the spin-coating technique. Among these problems, an important consideration is that of environmental safety, which strongly suggests that future technology should adopt a solvent-free process.

Although commercial materials such as DuPont's Vespel polyimide and Teflon AF, Union Carbide's Parylenes, or Dow's poly(benzocyclobutenes) have lower dielectric constants than inorganic insulators, some of these materials still fall short of certain requirements, such as thermal stability. For instance, Parylenes (*vide infra*), depending on the type, have dielectric constants ranging from 2.38 to 3.15, and Teflon AF has an even lower dielectric constant of 1.89 but poor thermal stability (360°C in air). However, VLSI interconnection and packaging applications also require high thermal stability of the films being used. A further consideration is that diffusion in and adhesion of metal to polymer films rely strongly on the thermal stability of the polymer film. For instance, Cu diffusion in Parylene-N starts at a temperature of 300–350°C, which corresponds roughly to the onset of thermal degradation. Adhesion failure between Cu and Parylene-N also starts at 300°C. The thickness of the film begins to shrink at 350°C while it is being annealed in nitrogen.[6]

The development of low-dielectric-constant materials as ILDs is crucial to achieve low power consumption, reduce signal delay, and minimize interconnect cross-talk for high-performance VLSI devices. In one of the multilevel interconnect process routes, metal lines (e.g., Al—Cu or Cu) are patterned through reactive ion etching, and then dielectric films are filled in the trenches formed between these lines. These trenches can have widths in the sub-0.5 μm range and aspect ratios greater than 3. Therefore, small gap-filling capability is also required for such dielectrics.

The main objective of the work to be described here is to design and synthesize new organic dielectric materials, and to develop new techniques to deposit these materials as thin, thermally stable films with very low dielectric constants, for use as ILDs. New dielectric materials must not only possess proper electrical, thermal, and mechanical properties but should also minimize or eliminate the use of solvents in this era of concern for environmental pollution.

A detailed consideration of the physical and chemical parameters that affect the magnitude of the dielectric constant of organic polymers as well as modulate thermal stabilities and mechanical properties' reveals that an ideal material for a low-dielectric-constant medium would be a rigid, (partially) fluorinated hydrocarbon polymer. Adding the requirements of good to excellent thermal stability leads to the narrower choice of rigid, perhaps lightly cross-linked, nonconjugated aromatic fluoropolymers. If we make the standards even more stringent, we would include a requirement of freedom from the need for solvents and a film-generation process that leads to conformal, dense films. One might say that the described task is an impossible one. However, we believe that we may have found a promising process in vapor deposition polymerization, as described in this brief overview of our work to date.

18.2. VAPOR DEPOSITION POLYMERIZATION

Chemical vapor deposition (CVD) is a process whereby a thin solid film is synthesized from the gaseous phase by a chemical reaction. It is this reactive process that distinguishes CVD from physical deposition processes, such as evaporation, sputtering, and sublimation.[8] This process is well known and is used to generate inorganic thin films of high purity and quality as well as form polyimides by a step-polymerization process.[9–11] Vapor deposition polymerization (VDP) is the method in which the chemical reaction in question is the polymerization of a reactive species generated in the gas phase by thermal (or radiative) activation.

18.2.1. Parylene N

The best developed example of a material produced by VDP is poly(*p*-xylylene) designated as Parylene-N by the Union Carbide Corporation. Poly(*p*-xylylene) was discovered by Szwarc[12] in 1957 and then commercialized by Gorham at Union Carbide.[13,14] (Scheme 1). Gorham has reported that di-*p*-xylylene is quantitatively cleaved by vacuum vapor-phase pyrolysis at 600°C to form two molecules of the reactive intermediate *p*-xylylene, which subsequently polymerizes on the cold substrate. In a system maintained at less than 1 Torr, *p*-xylylene spontaneously polymerizes on surfaces below 30°C to form

high-molecular-weight, linear poly-*p*-xylylene. The facile cleavage of di-*p*-xylylenes to *p*-xylylene is, in all probability, due to the high degree of steric strain in the dimeric species and to the comparatively stable nature of *p*-xylylene.

600°C
0.1 Torr
H_2C=⟨⟩=CH_2
di-p-xylylene
p-xylylene
< 30°C
poly-p-xylylene
(Parylene)

Scheme 1. Synthesis of Parylene.

The VDP process takes place in two stages that must be physically separated but temporally adjacent. Figure 18.1 is a schematic of typical Parylene deposition equipment and indicates the approximate process operating conditions.

The Parylene-N process has certain similarities with vacuum metalizing. The principal distinction is that truly conformal Parylene coatings are deposited even on complex, three-dimensional substrates, including on sharp points and into hidden or recessed areas. Vacuum metalizing, on the other hand, is a line-of-sight coating technology. Whatever areas of the substrate cannot be "seen" by the evaporation source are "shadowed" and remained uncoated. This evidence provides insight into the differences between the two processes.

The major drawback of poly(*p*-xylylene) is that it reverts to a monomer when thin films are heated above ca. 400°C and it cracks when the films are annealed at 300–350°C in nitrogen. During module assembly the chip-joining (soldering)

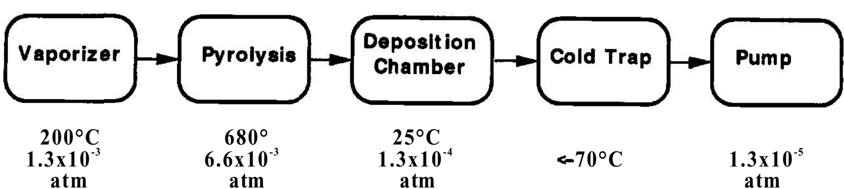


Figure 18.1. Parylene-N deposition apparatus.

process causes short exposure to temperatures between 300–450°C and therefore precludes use of this material under these conditions.

18.2.2. Parylene F

Although Parylene-N possesses an outstanding combination of physical, electrical, and chemical properties, the benzylic C—H bonds present are potential sites for thermal and oxidative degradation. It is well known that replacing a C—H bond with a C—F bond not only enhances the thermal stability of the resulting polymer, but also reduces the dielectric constant. Because incorporation of fluorine is known to impart thermal and oxidative stability, it became of interest to prepare poly(α,α,α′,α′-tetrafluoro- *p* -xylylene), Parylene-F Joesten[15] reported that the decomposition temperature of poly(tetrafluoro-*p*-xylylene) is ca. 530°C. Thus, it seemed that the fluorinated analog would satisfy many of the exacting requirements for utility as an on-chip dielectric medium.

The comparison of physical and chemical properties of Parylene-N and Parylene-F is shown in Table 18.4. Parylene-N is considerably less stable in air than in nitrogen as a result of oxidative degradation. However, the similarity between its behavior in air and in nitrogen suggests that Parylene-F has very good thermal oxidative stability, which is most likely the result of the high stability of the C—F bond, and provides evidence that oxidative attack starts at the benzylic C—H bonds in Parylene-N.[15]

Hertler[16] was the first to report the preparation of poly(tetrafluoro-*p*-xylylene) by a multistep synthesis as shown in Scheme 2. Pyrolysis (330°C, 0.025 Torr) of dibromotetrafluoro-*p*-xylene ($Br_2F_4C_8H_4$) over zinc led to deposition of the polymer film in a cold trap.

Table 18.4. Several Properties of Parylene-N and Parylene-F

Polymer	$-(CH_2-C_6H_4-CH_2)_n-$ Parylene N	$-(CF_2-C_6H_4-CF_2)_n-$ Parylene F
Decomposition	430°C in N_2	530°C in N_2
Temperature	300°C in air	450°C in air
Dielectric constant	2.65 ± 0.5	2.36 ± 0.5
UV stability	Stable in N_2	Stable in N_2
	Degraded in air	Stable in air

$BrF_2C-C_6H_4-CF_2Br$ —Zn, 330 °C / 0.025 Torr→ $F_2C{=}C_6H_4{=}CF_2$

α,α',dibromo-α,α,α',α'-teaafluoro-p-xylene α,α,α',α'-tetrafluoro-p-xylylene

—polymerize, cold trap, -78 °C→ $[-CF_2-C_6H_4-CF_2-]_n$

poly(α,α,α',α'-teuafluoro-p-xylene)
(Parylene F)

Scheme 2. Synthesis of poly(tetrafluoro-*p*-xylylene.

Fuqua and co-workers[17] tried to develop a much shorter route from α,α,α',α'-tetrafluoro-*p*-xylene to poly(tetrafluoro-*p*-xylylene) but were unsuccessful in generating a polymer because they conducted their pyrolyses at 820–925°C/3–5 Torr, and under those conditions instead of losing H_2 to form α,α,α',α'-tetrafluoro-*p*-xylylene, α,α,α',α'-tetrafluoro-*p*-xylene lost HF and underwent rearrangement to form β,β,*p*-trifluorostyrene [Eq. (l)].

(1) $HF_2C-C_6H_4-CF_2H$ —850-925 °C, 3-5 Torr→ $F-C_6H_4-CH{=}CF_2$

α,α,α',α'-teaafluoro-p-xylene β,β,p-trifluorostyrene

Chow and co-workers18 developed a multistep synthesis for the commercial production of α,α,α',α'-tetrafluoro- *p* -xylene that uses octafluoro[2.2]paracyclophane (PA-F dimer) as the precursor to polymer. PA-F dimer was cracked at 720–730°C and polymer was deposited on a substrate at –25 to –35°C [(Gorham method) Eq. (2)]. Chow[19] also attempted to pyrolyze $Br_2F_4C_8H_4$ at very high temperatures. The film that was deposited was of poor quality compared to that prepared from dimer.

(2) PA-F dimer —(Gorham Method)→ $[-CF_2-C_6H_4-CF_2-]_n$

PA-F dimer **Parylene-F**

In spite of its potential commercial utility, PA-F dimer has not been extensively used as a Parylene-F precursor because the only reported preparative methods for PA-F dimer involve pyrolysis of different precursors at very high temperatures 600–950°C and yields are very low. The conventional way of synthesizing PA-F dimer involves a pyrolysis process as shown in Eq. (3).

(3) $XF_2C{-}C_6H_4{-}CF_2X' \xrightarrow{\Delta}$ PA-F dimer

PA-F dimer

The special apparatus required for the synthesis makes laboratory preparation unattractive, while the required high temperatures make commercialization impracticable. In principle, any method that could generate α,α,α′,α′-tetrafluoro-*p*-xylylene would be a potential source of dimer.

Recently, Dolbie[20,21] reported a new, nonpyrolytic method for the synthesis of PA-F dimer [Eq. (4)]. This method allows easy laboratory preparation of gram quantities of PA-F dimer but still presents difficulties with regard to commercialization because of the high-dilution methodology that is required for a good yield of high-purity product.

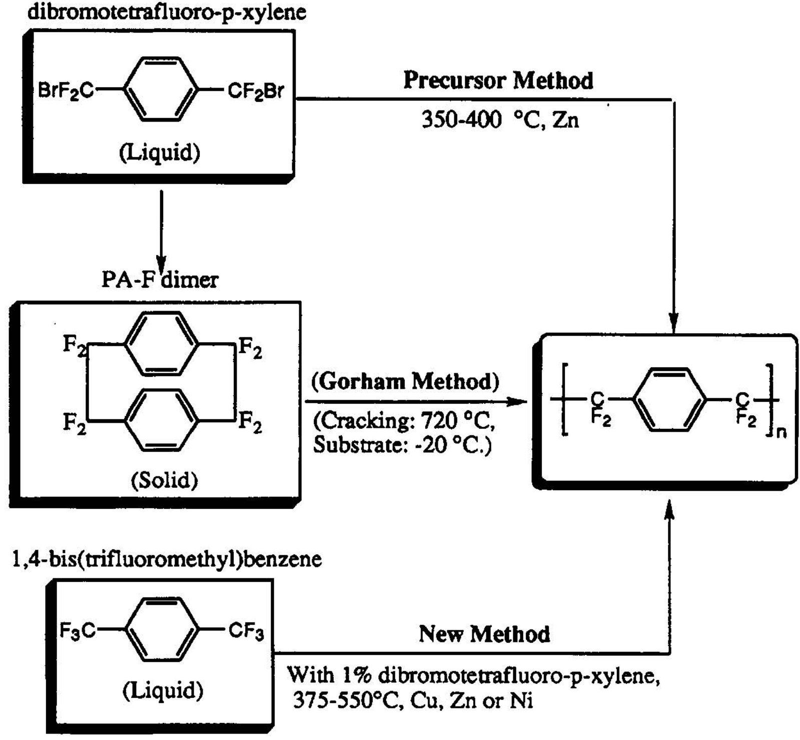
(4) $XF_2C{-}C_6H_4{-}CF_2X \xrightarrow{TiCl_4 / LiAlH_4}$ PA-P dimer

X = Br, or Cl **PA-P dimer**

One advantage of VDP is that it is compatible with the deposition of metal on silicon wafers. Cracking dimer does provide a clean and efficient process for depositing film but the main hindrance in producing PA-F thin films in large quantities by this method are the extremely high cost and the short supply of PA-F dimer. Therefore this situation provided the impetus to develop an alternative process to make PA-F film. In principle, a process that could generate α,α,α′,α′-tetrafluoro-*p*-xylylene directly from the vapor state in a conventional vacuum system would be a potential method for depositing poly(tetrafluoro-*p*-xylylene) film.

As noted above, the synthesis of dimer involved a complicated synthetic procedure and produced very low yields. Alternative routes for deposting poly-(tetrafluoro-*p*-xylylene) thin film were studied: the precursor method and a new

method (Scheme 3). “Parylene-F” is a trade name and is only used for material produced by the Gorham method from dimer. The polymer produced by any other process is called poly(tetrafluoro-*p*-xylylene).



Scheme 3. Different routes to poly(tetrafluoro-*p*-xylylene).

Three different techniques, the Gorham method, the precursor method, and a new method, were used to deposit polymer. Films ranging in thickness from 2000–8000Å were deposited. Thicker films could be deposited by using more source material or a longer reaction path. FTIR spectroscopy indicates that the films, as deposited, are essentially identical to those prepared by the conventional route. The average dielectric constant of the films deposited by this technique was 2.6 ± 0.1 (presursor method), while the value measured on films generated by cracking the dimer was 2.38 ± 0.5 (Gorham method). X-ray photoelectron spectroscopy (XPS) measurements of the as-deposited film from the precursor method revealed the presence of O (5.86–9.00 at.%), Zn (4.03 at.%), and Br (5.4 at.%) contaminants.[22] Annealing the films in nitrogen at 530°C for 30 min removed Br and and reduced the O and Zn levels to 3.63 and 3.23%, respectively.

Further improvements in the design of the apparatus and optimization of the deposition conditions are expected to remove the remaining discrepancies.

To simplify the synthetic effort required to deposit such films, attempts were made to deposit films by pyrolyzing tetrafluoro-*p*-xylene ($F_4C_8H_6$). Under similar reaction conditions, a polymer film was deposited that was different from poly(tetrafluoro-*p*-xylylene) as the FTIR spectrum indicates that it contains more hydrogen and less fluorine. Presumably HF is preferentially eliminated rather than H_2.

Attempts were made not only to find an alternative way to replace dimer and to deposit high-quality poly(tetrafluoro-*p*-xylylene) film, but also to eliminate the dibromide as the precursor because of the difficulty of synthesis. Therefore, the deposition of poly(tetrafluoro-*p*-xylylene) film by using hexafluoro-*p*-xylene as the precursor instead of dibromotetrafluoro-*p*-xylene was tried. However, no polymer film was deposited on the wafer. Effort was expanded and other metal reagents such as nickel or copper were used to react with 1,4-bis(trifluoromethyl)-benzene to generate $\alpha,\alpha,\alpha',\alpha'$-tetrafluoro-*p*-xylylene to deposit poly(tetrafluoro-*p*-xylylene) film. However, the result showed that no film was deposited, which was not unexpected, because a C—X bond that is weaker than C—F bonding might be necessary to initiate the formation of the desired intermediate.

Accidently, using hexafluoro-*p*-xylene with the contaminated copper wire obtained from the precursor method experiments, a polymer film was deposited on the silicon substrates. Obviously, some dibromotetrafluoro-*p*-xylene from the precursor method that adhered to, or reacted with, the metal could somehow initiate this VDP process. However, a complete explanation of these results is not yet available. As an extension of this discovery, commercially available 1,4-bis(trifluoromethyl)benzene in conjunction with a catalyst/initiator has proved to be a potential alternative by which to deposit poly(tetrafluoro-*p*-xylylene) film successfully.[23]

The copyrolysis of 1 wt% dibromotetrafluoro-*p*-xylylene with commercially available hexafluoro-*p*-xylene (Aldrich) with metals was examined and it was found that it was indeed possible to prepare films that were spectroscopically indistinguishable from those deposited from dimer. The PA-F films obtained are of excellent quality, having dielectric constants of 2.2–2.3 at 1 MHz and dissociation temperatures up to 530°C in N_2. A uniformity of better than 10% can be routinely achieved with a 0.5-µm-thick film on a 5-in. silicon wafer with no measurable impurities as determined by XPS. During a typical deposition, the precursor was maintained at 50°C, the reaction zone (a ceramic tube packed with Cu or Ni) was kept at 375–550°C, and the substrate was cooled to –10 to –20°C. The deposited film had an atomic composition, C : F : O = 66 : 33 : 1 ± 3 as determined by XPS. Except for 0, no impurities were detected. Within instrumental error, the film is stoichiometric. Poly(tetrafluoro-*p*-xylylene) has a theoretical composition of C : F = 2 : 1. Figure 18.2 illustrates the XPS of the binding energy

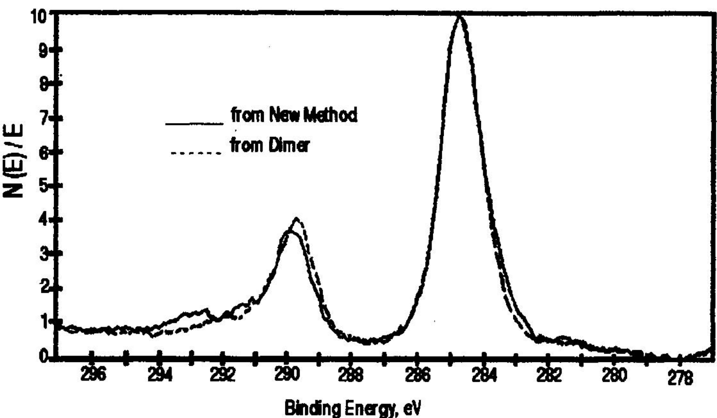


Figure 18.2. XPS of poly(tetrafluoro-*p*-xylylene) from the new method.

of C 1*s* electrons of poly(tetrafluoro-*p*-xylylene) deposited by the new method. The two peaks in the spectrum represent two groups of C atoms in different chemical environments, which correspond to the six C atoms of the benzene ring and the two CF_2 groups of the poly(tetrafluoro-*p*-xylylene) repeating unit. The stronger peak in Figure 18.2 is assigned to the Cl*s* binding energy of *C*=C and *C*—H, which have almost the same Cls binding energies of approximately 285 eV. The other peak in the spectrum is from the CF_2 group with a Cls binding energy of 290 eV.

A source of difficulty here remains the metal reagent used to generate the reactive intermediate. It became deactivated after the surface of the metal had been in contact with the dibromide precursor and hexafluoro-*p*-xylene, and the film growing process was interrupted as a result. An interesting result was observed during annealing of the polymer films from cracking dimer (Gorham method) and from the new method. Some 30% of the films deposited by the Gorham method developed cracks when the films were annealed at 510°C in nitrogen but no cracks were observed in any of the films deposited by the new method.

18.2.3. Poly(Benzocyclobutenes)

The use of cross-linked polymers as engineering materials has been extensive owing to their rigidity, strength, mechanical and thermal stability, and chemical resistance. Typically, these materials are synthesized using step-growth methods where polymer growth and cross-linking arise from the same chemical reaction.[24] These materials are usually processed as low-molecular-weight prepolymers because of the intractability of the final cross-linked material.

Another approach adopts a two-step process: processable prepolymers are synthesized, and then the prepolymers are cured to drive the polymerization reaction to higher conversions, initiating network formation. Chemically, this

scheme has the problem that complete conversion is rarely achieved and defects from unreacted chain ends and intramolecular cyclization are common.

18.2.3.1. Benzocyclobutene Chemistry

The Parylene family has very attractive properties for use as dielectric materials as was noted above, but their thermal stability at the temperatures used in the fabrication of electronic devices is less than optimum. When considering alternatives as possible precursors for VDP, the isomeric *ortho*-xylylene (*o*-quinodimethane) is a likely candidate (Scheme 4). This approach involves the thermolysis of benzocyclobutene derivatives to generate a reactive dieneoid intermediate (*o*-quinodimethane),

Benzocyclobutene
Δ
o-Quinodimethane
Diels-Alder
Spirodimer
Benzylic diradical
polymerization
cyclization
Poly(o-xylylene)
Dibenzocyclooctane

Scheme 4. Ring-opening reaction of benzocyclobutene.

which can then undergo a Diels–Alder reaction between two *o*-quinodimethane molecules, one as a diene and one as a dienophile, to yield an intermediate spirodimer. The spirodimer then fragments to give a benzylic diradical species, which may undergo intramolecular coupling to give dibenzocycloocta-1,5-diene (cyclo-di-*o*-xylylene) or oligomerize to provide poly(*o*-xylylene).[25,26] If two benzocyclobutene units are joined together, they should undergo polymerization upon heating to yield an insoluble, cross-linked system without evolving by-products.

18.2.3.2. Polymers Containing Benzocyclobutenes

In the late 1970s, Kirchhoff at Dow Chemical Company developed the use of benzocyclobutenes in polymer synthesis and modification. These efforts culminated in 1985 with the issuance of the first patent describing the use of benzocyclobutene in the synthesis of high-molecular-weight polymer.[27] Similar work that involved a thermosetting system based on Diels–Alder cycloaddition between terminal benzocyclobutene and alkyne groups,[28,29] was reported separately and independently by Tan and Arnold.[28] Since these initial discoveries, the field of benzocyclobutene polymers has expanded rapidly and benzocyclobutene chemistry constitutes the basis of a new and versatile approach to the synthesis of high-performance polymers for applications in the electronics and aerospace industries.[30]

The basic benzocyclobutene technology involves a family of thermally polymerizable monomers that contain one or more benzocyclobutene groups per molecule.[31–33] Depending on the degree and type of additional functionality, these monomers can be polymerized to yield either thermosetting or thermoplastic polymers. For monomers of the class that contains only benzocyclobutene moieties as reactive groups, the *o*-quinodimethane groups react rapidly with one another to give a highly cross-linked polymer.

Although the moisture insensitivity of poly(benzocyclobutenes) is superior to polyimides, unlike polyimide films, poly(benzocyclobutenes) are very sensitive to oxygen and must be cured in a nitrogen atmosphere. In general, the thermal stabilities of poly(bemcyclobutenes) are also lower than those of the polyimide family. If too much oxygen is incorporated during the cure cycle, several important properties are adversely affected, including dielectric constant, chemical resistance, and flexibility.[34] Introduction of fluorine would be expected to enhance thermal stability significantly.

(a) Poly(Octafluorobisbenzocyclobutene). To date, the systems reported have used R groups which are oligomeric and are, therefore, not volatile [Eq. (5)]. If, however, *R* were to be made small enough that the mass of the

(5)

monomer was close to that ofparacyclophane, it should be possible to use VDP to prepare polymers from such monomers (Figure 18.3).

Although the mass of the fluorinated benzocyclobutene analogue is significantly higher than that of the hydrocarbon it should be noted that the incorporation of fluorine often enhances the volatility of derivatives beyond the expected levels, e.g., tetrafluorobenzocyclobutene with a mass of 176 boils only 10° higher than *o*-xylene with a mass of 106 (153°C vs. 143°C).

Using a fluorinated benzocyclobutene-based monomer (Figure 18.4) should provide at least one advantage over the already promising properties of fluorinated poly(*p*-xylylene). All the desirable properties such as low dielectric constant and low affinity for water should remain but the thermal stability should be enhanced because of the cross-linking that would accompany the generation of these films. The synthesis and polymerization paths for poly(octafluorobisbenzocyclobutene) are depicted in Scheme 5.

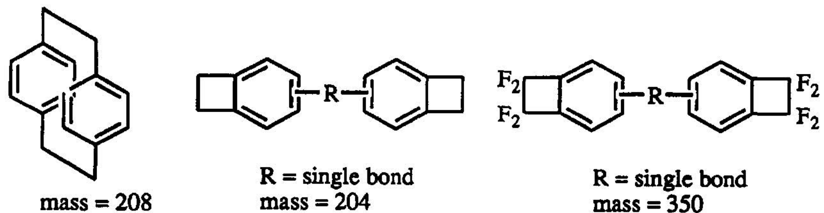


Figure 18.3. Di-*p*-xylelene variants based on benzocylobutene.

F_8-bis-Benzocyclobutene

Figure 18.4. Octafluorobisbenzocyclobutene.

Scheme 5. Synthesis of poly(octafluorobisbenzocyclobutene).

Initially the deposition conditions used for Parylene-F were used in attempts to deposit polymer film on glass or silicon substrates. Reaction temperature, pressure, and retention time of the fluorinated precursor in the reaction zone were varied from 600 to 850°C and from 0.25 to 760 Torr in packed and unpacked tubes, to no avail. The cure chemistry of these systems is primarily based upon the fact that under appropriate thermal conditions, the strained four-membered ring of benzocyclobutene undergoes an electrocyclic ring opening. The temperature at which such a concerted process occurs depends principally on the substitutents at the alicyclic, rather than on the aromatic positions. It has been reported by Kirchhoff[35] that an electron-donating substitutent at C_7 and/or C_8 will favor ring-opening, but electron-withdrawing groups at those positions will make the ring-opening energetically more demanding. 7,7′,8,8′-Octafluoro-4,4′-bis(1,2-dihydro-

benzocyclobutene) has four fluorine atoms on each ring and it might be expected that the reaction temperature would be higher than for an unfluorinated system. However, the electronic effect is so overwhelming that this compound did not polymerize or undergo Diels–Alder reactions with added dienes or dienophiles at the temperatures or conditions that were useful for benzocyclobutene.

(b) UV-Assisted Vapor Deposition Polyrnerization.[36] In this approach, a monomer is activated in the gas phase by UV radiation. Subsequently, the activated monomer polymerizes on the substrate. Despite the fact that octafluorobisbenzocyclobutene did not polymerize efficiently within a convenient temperature range, it was found that it was possible to activate it by UV irradiation in the vapor state or in solution [Eq. (6)]. A polymer was obtained as a film that was not soluble in common laboratory solvents.

(6)

7,7',8,8'-Octafluoro-4,4'-bis-(1,2-dihydrobenzocyclobutene) — UV → Poly(octafluorobenzocyclobutene)

The film that was obtained was very thin and it was not possible to grow thicker films. This result was most probably caused by absorption of the incident radiation by the film formed on the interior of the quartz reactor, thereby blocking the incoming UV light and preventing the activation of the monomer and continous polymerization. The UV absorption of the monomer and of polymer film reside in the same region. Figure 18.5 and 18.6 show the UV absorption spectra of the precursor and the polymer film as deposited on the quartz surface, respectively.

18.2.3.4. Properties of Poly(Octafluorobisbenzocyclobutene)

(a) Infrared Spectroscopy. The IR spectrum of poly(octafluorobenzocyclobutene) is the most informative in confirming the structure of the proposed polymer[37,38] at the present time. Figure 18.7 presents the IR spectrum of poly(octafluorobenzocyclobutene). The repeating unit of the polymer contains an absorption band attributable to a 1,2,4-trisubstituted phenyl pattern. The bands at 981–831 cm^{-1} are assigned to the bending of a lone hydrogen atom at the 3-position, and the bands at 905–757 cm^{-1} arise from the bending of two adjacent hydrogen atoms. Additionally, the ring deformation absorption of 1,2,4-trisub-

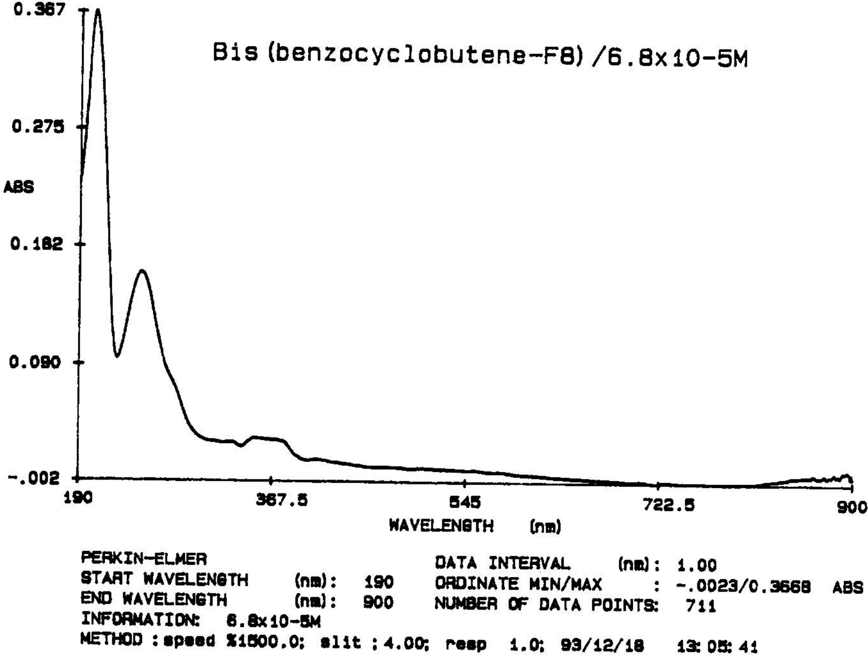


Figure 18.5. UV-absorption spectrum of 7,7′,8,8′-0ctafluoro4,4′-bis(1,2-dihydrobenzocyclobutene).

stituted benzene appears in the region of 756–697 cm^{-1}. An investigation of the polymeric structure by solid state NMR has not yet been successful because of the strong fluorine coupling, which complicates the ^{13}C spectrum.

(b) X-Ray Photoelectron Spectroscopy. The composition of the polymer obtained by photopolymerization, was studied by XPS. The chemical formula of the repeating unit of poly(octafluorobenzocyclobutene) is $C_{16}H_6F_8$; therefore, the theoretical ratio of different types of carbon atoms can be represented as the ratio of the areas of different binding energies is Cls electrons. Two types of Cls binding energies from XPS of the polymer (Figure 18.8) were expected to be observed, and the area ratio was expected to be C (*C*—C or C—H) : C (F—*C*—F) = 3 : 1. However, the results showed that the ratio of different Cls peaks of deposited polymer was not consistent with the theoretical value (Table 18.5).

By comparision of the calculated carbon ratios and those determined from XPS data, it can be seen that the number of fluorine atoms is lower than the theoretical value, and is approximately C (C—C or C—H): C (F—*C*—F + *C* — F) = 4: 1.

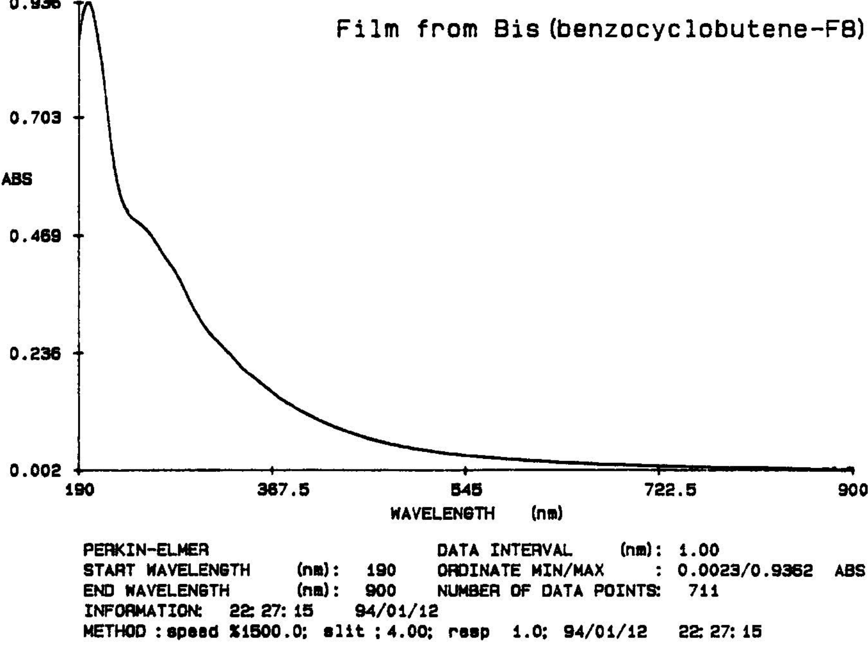


Figure 18.6. UV-absorption spectrum of a thin film of poly(fluorinatedbisbenzocyclobutene) as-deposited.

Ideally, there should be twelve carbon atoms with a Cls binding energy of 286 eV and four carbon atoms with an energy of ca. 291 eV for each repeating unit of the polymer. However, the XPS data showed that the defect structure of as-deposited film was best described as roughly eight carbon atoms with Cl*s* at 286.26 eV (*C*—C and *C*—H), and tail to high binding energy because of the presence of carbon atoms bearing only one fluorine atom [Cls at 288.27 (*C*—F)] and a small tail at the end of the spectrum [C2*s* at 291.57eV (F—*C*—F)]. Obviously some of the fluorine atoms on the aliphatic linkages were missing from the polymer structure. This deficit might be caused by fluorine atoms of *C*—F

Table 18.5. The XPS Results of Poly(Octafluorobisbenzocyclobutene) from UV-Assisted Polymerization

Parameter	*C*—C and *C*—H (C1*s*)	*C*—F (Cl*s*)	F—*C*—F (C1*s*)
Peak position (eV)	286.26	288.27	291.57
Area	3820	524	365
% of total area	81.12	11.13	7.75

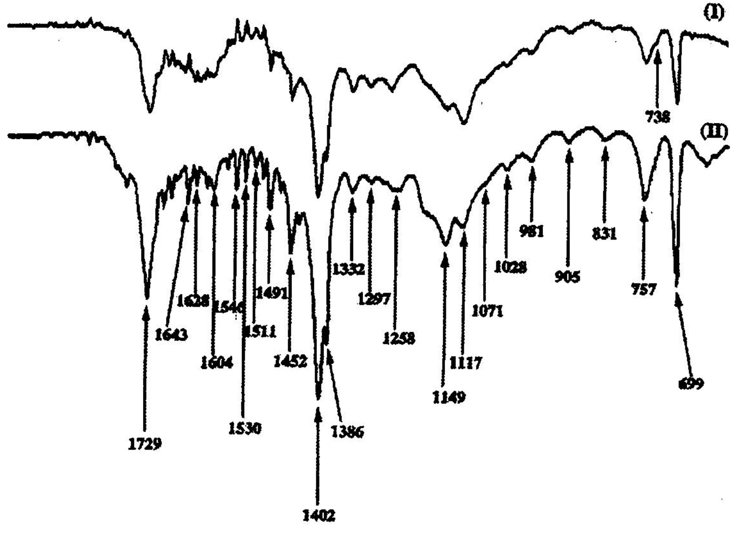


Figure 18.7. IR spectrum of poly(octafluorobisbenzocyclobutene).

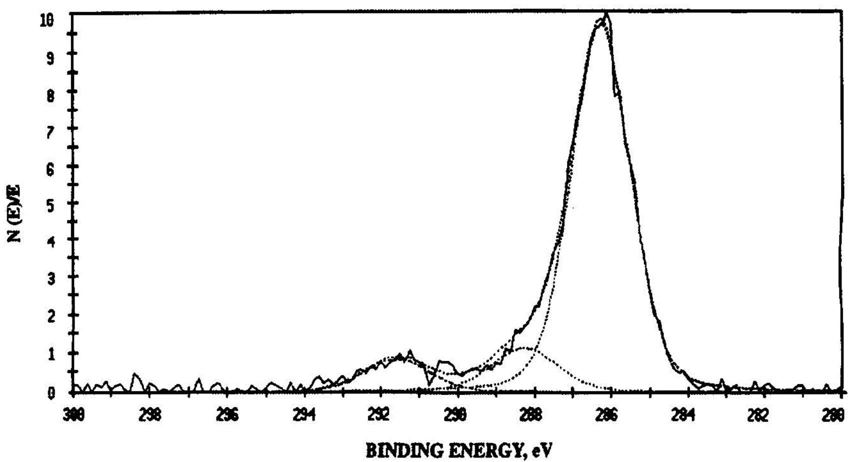


Figure 18.8. XPS of poly(octafluorobisbenzocyclobutene).

bonds being replaced by hydrogen atoms during photopolymerization by an, as yet, unclarified process or by reaction of the fluoropolymer with the quartz substrate to form Si-F bonds. These and other possibilities are under investigation.

(c) Thermal Stability. The thermal stability of films of the polymer as reported here is given as the temperatures of 5 and 10% sample weight loss. The thermal stability of the polymer synthesized by photopolymerization was only 268°C (5% TGA weight loss) in nitrogen and 314°C (10% TGA weight loss) as shown in Figure 18.9.

(d) Dielectric Constant. While this work was in progress, there was an independent effort by Kudo *et al.*[39] at the Fujitsu Research Center (Japan) to fluorinate poly(bisbenzocyclobutene) by using an NF_3 plasma. The hydrocarbon polymer poly(bisbenzocyclobutene) was dissolved in an organic solvent, spin-coated onto a silicon wafer, and cured to cross-link the polymer. The cross-linked film was then exposed to an NF_3 plasma in a microwave downstream plasma system to fluorinate the aliphatic C—H bonds as an approach to poly(octafluoro-benzocyclobutene) [Eq. (7)].

H_2 H_2 H_2 H_2 n $\xrightarrow{NF_3}$ F_2 F_2 F_2 F_2 n

Poly(bis-benzocyclobutene) Poly(octafluombenzocyclobutene)

(7)

Before fluorination, the dielectric constant of poly(bisbenzocyclobutene) was 2.8, and this value was reduced to 2.1 after plasma treatment. No data were reported in the paper on characterization of structure or properties, except for the dielectric constant of the modified poly(bisbenzocyclobutene). The authors did report that the thermal stability of fluorinated poly(vinylidenefluoride) was inferior to the original poly(vinylidenefluoride) when treated in a similar way. One of the probable reasons for the low thermal stability is that the NF_3 plasma degraded the polymer. According to their results, the thickness of fluorinated poly(bisbenzo-cyclobutene) was reduced by 30%. The same phenomenon was observed for other hydrocarbon polymers subjected to the NF_3 plasma process. A remaining question is whether plasma treatment can modify more than a thin surface layer of the cured polymer? Additionally, one of the side products generated was hydrogen fluoride, which is a serious drawback to this approach.

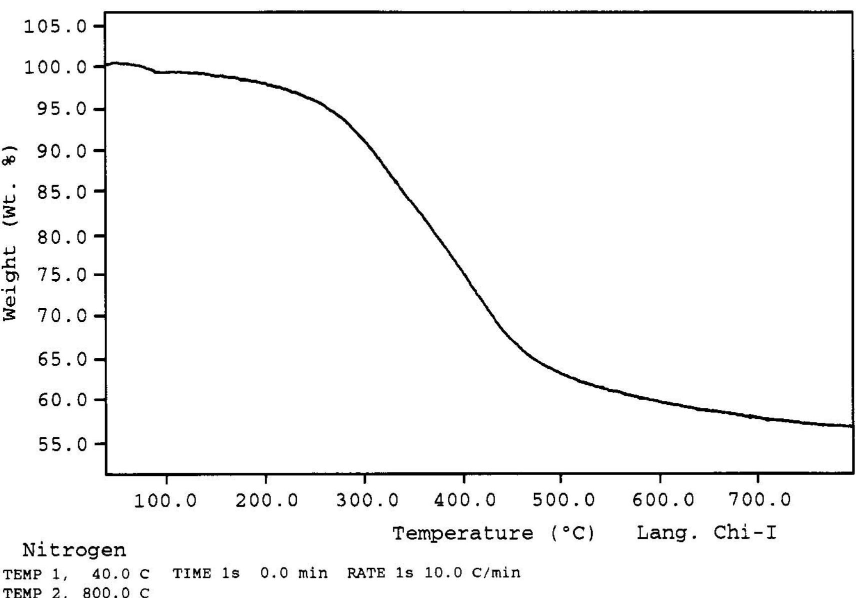


Figure 18.9. Thermogravimetric anlaysis of poly(octafluorobisbenzocyclobutene) in nitrogen.

Although we were unable to grow thicker films of poly(octafluorobenzocyclobutene), 7,7′,8,8′-octafluoro4,4′-bis(1,2-dihydrobenzocyclobutene) appears to be a promising compound, which may eventually lead to poly(octafluorobenzocyclobutene) under the proper experimental conditions. A different reactor geometry and the use of intense laser sources could prove to be a promising way to grow thicker films.

18.2.4. Polynaphthalenes

The formation of C—C bonds between aromatic rings is an important step in many organic syntheses and can be accomplished by chemical, photochemical, or electrochemical means. As was noted earlier, fundamental considerations of the parameters for a dielectric which must be dealt with in designing a thermally stable, low-dielectric-constant polymer naturally lead one to consider rigid-rod, nonconjugated aromatic polymers containing no "lossy" functional groups. A structure such as poly(naphthalene) is a likely candidate.

Poly(naphthalene) is chemically similar to poly(*p*-phenylene), which is an insoluble, infusible, low-molecular-weight polymer, all attributes that preclude application in thin-film form in microelectronics. Although these materials possess several very desirable properties, such as high glass transition tempera-

ture, insolubility, infusibility, resistance to oxidation, radiation, and thermal degradation,[46] the synthesis of rigid-rod macromolecules via conventional synthetic methods has been an ongoing problem because the poor solubility of these aromatic polymers has resulted in low molecular weight and poor processability.

Poly(naphtha;ene) is an insoluble material that precipitates as an oligomer as synthesized by classical methods. The first route to poly(naphthalene) was the direct polymerization, in 1965, of naphthalene using a technique developed by Kovacic and others.[41] The process is known as oxidative cationic polymerization and was conducted in *o*-dichlorobenzene with a catalyst such as ferric-chloride–water or aluminum-chloride–cupric-chloride. Another way to synthesize polynaphthalene is to use nickel-catalyzed polycondensation of Grignard reagents derived from dibromonophthalenes by Sato and co-workers.[42] Additionally, Banning and Jones[43] used a Grignard coupling reaction[44] to synthesize poly(1,4-naphthalene), poly(1 5-naphthalene), poly(2,6-naphthalene), and poly(2,7-naphthalene) (Figure 18.10). These polymers are generally obtained as powders of low molecular weight.

There are a few reports of poly(naphthalene) thin films. Yoshino and co-workers.[45] used electrochemical polymerization to obtain poly(2,6-naphthalene) film from a solution of naphthalene and nitrobenzene with a composite electrolyte of copper(II) chloride and lithium hexafluoroarsenate. Zotti and co-workers[46] prepared poly(1,4-naphthalene) film by anionic coupling of naphthalene on. platinum or glassy carbon electrodes with tetrabutylammonium tetrafluoroborate as an electrolyte in anhydrous acetonitrile and 1,2-dichloroethane. Recently, Hara and Toshima[47] prepared a purple-colored poly(1 ,4-naphthalene) film by electrochemical polymerization of naphthalene using a mixed electrolyte of aluminum chloride and cuprous chloride. Although the film was contaminated with the electrolyte, the polymer had very high thermal stability (decomposition temperature of 546°C). The only catalyst-free poly(naphthalene) which utilized a unique chemistry, Bergman's cycloaromatization, was obtained by Tour and co-workers recently (vide infra).

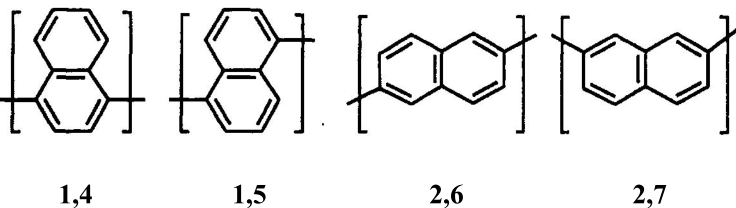


Figure 18.10. Structural variants of poly(naphthalene).

18.2.4.1. Bergman's Cycloaromatization

In the nearly 1970s, Bergman and co-workers[48,49] postulated that cis-hex-2-ene, 1,5-diyne (A) upon thermolysis would undergo a thermal rearrangement to the benzene 1,4-diradical intermediate (or, 1,4-dehydrobenzene, B), which could revert to starting material or collapse to the rearrangement product (C) [Eq. (8)].

(8)

A B C

Numerous synthetic and mechanistic studies were done to investigate this reaction further, and a variety of enediynes have been thermalized in the presence of radical traps such as 1,4-cyclohexadiene. Even though large excesses of radical traps were employed, the yields of the substituted benzenes were often moderate at best. Most important of all, Tour *et al.*[50] demonstrated that 1,4-naphthalene diradicals generated in solution couple to eventually form a polymer [Eq. (9)].

(9)

Pd(0), CuI Pd(0), CuI

Tour's work showed that polymerization is still a preferred process even though large excesses of radical traps (1,4-cyclohexadiene) were employed. They obtained poly(1,4-naphthalene) only as an insoluble brown powder by polymerization of 1,2-diethynylbenzene in benzene solution. This route appears to be an attractive approach to a new dielectric medium:

1. It requires no catalysts or reagents other than heat for the polymerization.
2. Heteroatomic coupling sites such as halogen are not necessary in the polymerization process, and all atoms present in the monomer are also present in the polymer.
3. The monomers can be readily synthesized by Pd/Cu coupling with a variety of substitution patterns.

By carefully adapting the unique chemistry of Bergman's cycloaromatization, it seemed possible to synthesize the rigid-rod polymer as a thin film of high quality and high purity.

18.2.4.2. Poly(Naphthalene) and Poly(Tetrafluoronaphthalene)

Scheme 6 outlines the stepwise synthesis of poly(naphthalene) and poly-(tetrafluoronaphthalene).

A_4-C$_6$-Br, Br → CuI $(Ph_3P)_2PdCl_2$, Argon → HC≡CSi(CH)$_3$, 75-80 °C →

A=H 1,2-Dibromobenzene
A=F 1,2-Dibromotetrafluorobenzene

A_4-C$_6$(C≡CSi(CH$_3$)$_3$)$_2$ (A=H, A=F) → KOH, MeOH / H_2O, room temp. → A_4-C$_6$(C≡CH)$_2$ (A=H, A=F)

→ [A_4-naphthalene diradical] (A=H, A=F)

→ polymerization → poly(naphthalene), A_4, n (A=H, A=F)

Scheme 6. Synthesis of poly(naphthalene) and poly(tetrafluoronaphthalene).

(a) Solution Polymerization. The thermal reactivities of these two diacetylenes were dramatically different when the polymerization was carried out in diphenyl ether under a nitrogen atmosphere. Aromatic solvents are expected to be unreactive toward free radical hydrogen atom abstraction and indeed, proved to be almost completely inert toward the intermediates produced during the reaction.

Powdery PNT-N was obtained when the unfluorinated compound was refluxed in diphenyl ether solution. When the temperature was raised to 196°C for 24 h, the amount of solid increased with time and there was no observable change in the appearance ofthe solid. However, in the case ofPNT-F, a black solid formed suddenly between 120– 150°C, and no additional solid formed even when the temperature was increased to 190°C. Apparently the fluorinated derivative reacts much more rapidly and exothermically than the hydrocarbon analogue. Care should be exercised when heating such compounds in sealed glass tubes.

(b) Vapor Deposition Polymerization. A schematic drawing of the VDP apparatus used for the preparation of PNT-N and PNT-F thin films in this work is shown in Figure 18.11. The unit consists of four sections: a source vessel with a needle valve, a vapor introduction channel, a Pyrex or quartz tube containing silicon substrates, recycling traps, and a pumping system. 1,2-Diethynylbenzene or tetrafluoro-1,2-diethynylbenzene can be easily and safely polymerized in the deposition apparatus described. It should be carefully noted that polyacetylenic compounds are reactive materials and can be exothermically converted to graphite upon heating. In closed systems, the pressure increase generated because of the amount of heat liberated when graphite is formed can be significant. Proper shielding should be utilized at all times.

Poly(naphthalene) and poly(tetrafluoronaphthalene) were synthesized by vaporizing the appropriate precursor *in vacuo* and transporting the vapor into a hot chamber maintained at 150–400°C. In the high-temperature zone, the

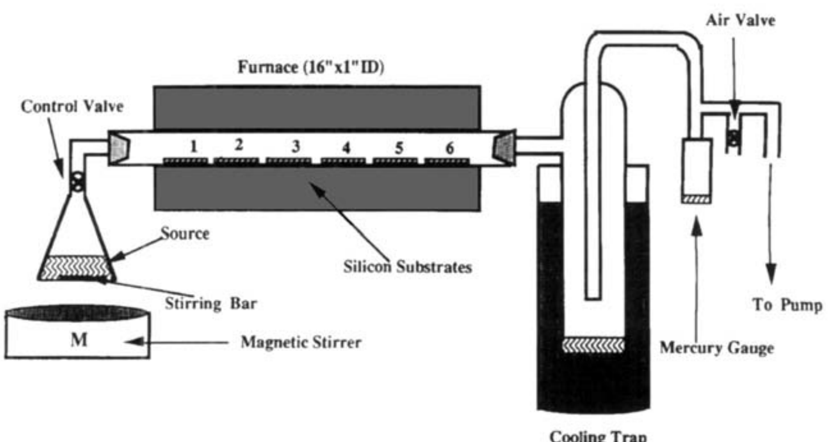


Figure 18.11. The VDP system for the deposition of PNT-N and PNT-F films.

monomer forms the intermediate and subsequently condenses and polymerizes on the substrate. The VDP was monitored by following the pressure changes accompanying the beginning of the reaction. The vapors of the monomers caused an increase in the pressure, which returned to the initial base vacuum of the system when the reaction reached completion.

The temperature distribution of the furnace of the VDP reactor is uneven, and the temperatures at positions 1, 2 and 5, 6 are lower than the temperatures at position 3, 4. For PNT-N, the film was concentrated on positions 3, 4, 5 (see Figure 18.11) and for PNT-F film, the film was concentrated at positions 2, 3, 4. This phenomenon indicates that the fluorinated compound required a lower temperature than the unfluorinated one to be polymerized. Approximately, the temperatures of positions 1 and 6, 3 and 4, and 2 and 5 are the same, and the temperature gradient is 3, 4 > 2, 5 > 1, 6. The deposition temperature is reported as the temperature at positions 3 and 4.

The diethynylbenzene analogues, depending on their individual properties, can be evaporated or sublimed into the reaction zone. The lower limit of the deposition temperature for poly(naphthalene) (PNT-N) was explored, and it was observed that deposition began at a substrate temperature somewhere in range of 150–200°C. A summary of the poly(naphthalene) and poly(tetrafluoronaphthalene) deposition conditions described here is given in Table 18.6.

From the analysis of different depositions of PNT-N films, it can be concluded that the beginning of the VDP process is of particular importance because it affects the adherence of the film to the substrate. The best results were obtained by maintaining the substrate at the desired deposition temperature for an extended time (approximately 2 h) before starting the actual deposition. The heater is also kept on at the end of the deposition while evacuating the chamber to the base vacuum during cooling to avoid contaminating the film.

Table 18.6. Deposition Conditions for Poly(Naphthalene) and Poly(Tetrafluoronaphthalene)

Polymer	Poly(naphthalene)	Poly(tetrafluoronaphthalene)
Source material	(I,2-diethynylbenzene)	(1,2-diethynyltetrafluorobenzene)
Base vacuum	0.2–0.25 Torr	0.2–0.25 Torr
Deposition pressure	0.5–1 Torr	0.5–1 Torr
Deposition temperature	350°C	350°C
Substrate temperature	350°C	350°C
Deposition rate	0.1–0).5Å/s	0.3–1.0Ås
Thickness	0.5–4 μm	0.5–2 μm
Dissociation temperature	570°C in N_2	590°C in N_2
Dielectric constant	2.2–2.3	2.1–2.2

18.2.4.3. Properties of PNT-N and PNT-F Films

The properties of PNT-N and PNT-F were measured on films deposited under the conditions reported in Table 18.6. The films, generated by vapor deposition on hot surfaces such as glass or silicon substrates as previously described, are not soluble in common laboratory solvents. The best film was obtained in the absence of oxygen. Film that was deposited in an oxygen-rich ambient exhibited lower thermal stability and poor adhesion.

(a) X-Ray Powder Diffraction. The X-ray powder diffractogram showed that the PNT-N and PNT-F films deposited by the VDP process at 0.45 Torr are slightly crystalline (Figure 18.12). The vertical axis is the intensity and the horizontal axis is the diffraction angle.

When argon was used as a carrier gas to deposit PNT-N film at 10 Torr, amorphous PNT-N film was obtained but the mechanical properties of the film as deposited were inferior to the film deposited at 0.45 Torr without a carrier gas.

(b) Thermal Stability. One of the most important properties of a good dielectric material is thermal stability. The thermal stability of PNT can be very different depending on the polymerization process. According to Tour's[50] work, a brown powder of PNT-N was obtained in benzene solution in a pressure tube. The thermal stability of the PNT-N obtained was reported to be 500°C. Using the procedure described by Tour, we obtained a brown powder with a thermal stability of 420°C. We also polymerized o-diethynyl benzene under an argon atmosphere in diphenyl ether solution, to give a material with a thermal stability of 460°C. All

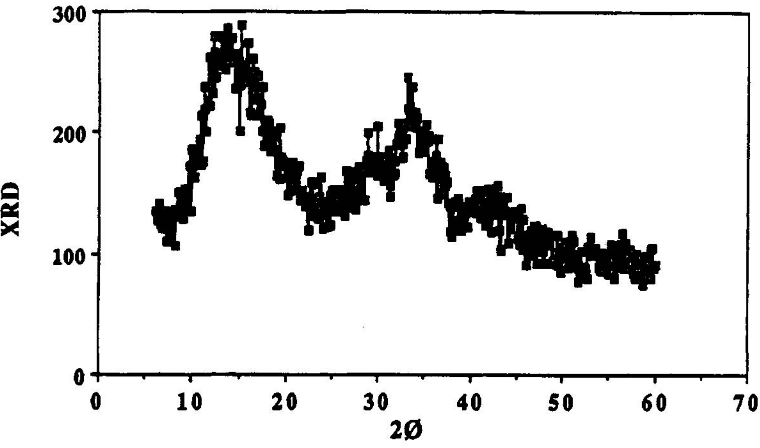


Figure 18.12. X-ray diffractogram of PNT-N film deposited by VDP.

the samples of PNT-N obtained from solution polymerizations were obtained as insoluble brown powders. The thermal stability of PNT-N film obtained by Hara[47] using an electrochemical reaction was reported to be 546°C. The thermal stability measurements of PNT-N and PNT-F films from the VDP process at 0.45 Torr are presented in Figure 18.13.

The thermal stability of PNT from different polymerization methods is presented in Table 18.7. It appears that the colored (dark brown) but transparent PNT-N film synthesized by VDP is the cleanest film among the polynaphthalenes from other polymerization processes that have been reported. These PNT-N films from VDP also have very low dielectric constants in comparison to poly(tetra-fluoro-*p*-xylylene) films. PNT-N and PNT-F films have higher dissociation temperatures (>570°C) and better thermal stability (>530°C), and no film cracking was observed until PNT-F was annealed at 600°C in nitrogen. Table 18.8 presents a summary of the different properties of PNT-N and PNT-F prepared by the VDP process.

It appears that the main reasons for the high thermal stability of PNT-N and PNT-F arise from their inherent rigid-rod polymer structure and the high aromatic content of the repeating unit. However, the fact that the thermal stability of PNT-F is higher than PNT-N might be the result of strong intermolecular interaction between chains because of dipole–dipole interactions.

Although there is no consistent explanation of the relationship between organic polymer morphology and electrical properties,[51] amorphous structures are generally preferred over a crystalline structure. An experiment was conducted to study the structure of the film deposited using an inert carrier gas. The PNT-N

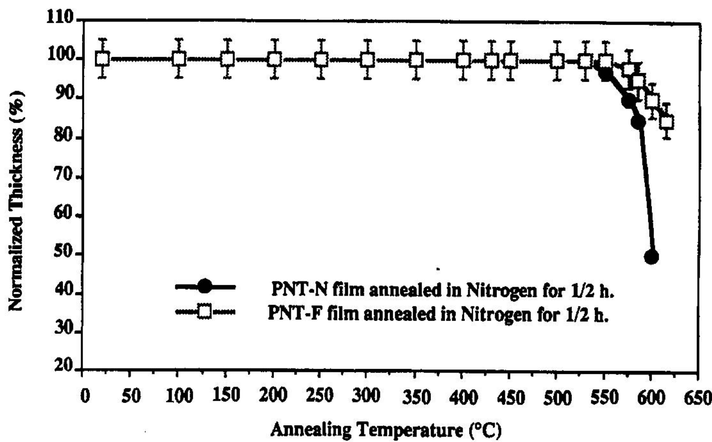


Figure 18.13. Thermal stability of PNT-N and PNT-F films.

Table 18.7. Thermal Stabilities of PNT from Different Polymerization Processes

Method	Thermal stability	T50%	Color
Benzene solution/170°C[50]	500°C (10% weight loss) (N_2)	>900°C	Brown powder
Electrochemical reaction[47]	546°C	NA	Purple film
Benzene solution/170°C (this work)	420°C (10% weight loss) (N_2)	>900°C	Brown powder
Diphenyl ether/200°C (this work)	460°C (10% weight loss) (N_2)	>900°C	Black powder
CVD 350°C/0.4 Torr (this work)	570°C (N_2)	NA	Transparent film

Table 18.8. Properties of PNT and PNT-F Prepared by the CVD Process

Polymer	PNT-N	PNT-F
Dielectric constant	2.4±0.1	2.2 ± 0.1
Electric breakdown	3 x 10^7 v/m	5 x 10^7 V/m
structure	Semicrystalline	Semicrystalline
Dissociation temperature (°C)	570°C in (N_2)	590°C in N_2
Cracks	No cracks at 570°C in N_2	No cracks at 600°C in N_2

films, as-deposited, were amorphous in the presence of an inert vaporous diluent in the VDP process. However, this deposition condition might not be preferred because the films deposited with argon as a carrier gas did not adhere well to silicon substrates.

(c) IR Spectra of PNT-N At the present time the IR spectra are most informative in confirming the structure of the proposed polymers. These polymers show characteristic absorption bands in the 760–940cm^{-1} and the 1300–1600 cm^{-1} regions. The IR spectra of PNT-N from three different polymerization processes are collected in Figure 18.14. The top spectrum is PNT-N (powder) from solution polymerization using diphenyl ether as the solvent. The middle spectrum is PNT-N (powder) from solution polymerization in a pressure tube with benzene as the solvent, and the bottom spectrum is PNT-N (thin film) from the VDP process. Basically, these three spectra are superimposable with slight differences among them. In the literature, there are different versions of IR characterizations of the poly(1,4-naphthalene) structure. Unfortunately, they are not exactly consistent with one another. The shoulder above 3000 cm^{-1} comes from the C—H stretching vibration. According to Tour's[50] analysis, bands at 1595 and 878 cm^{-1} (two adjacent H atoms) and 754 cm^{-1} (four adjacent H atoms) are characteristic for a 1,4-disubstituted naphthalene unit. These bands were also observed in the IR spectra of PNT-N. However, there is a very interesting peak at 699 cm^{-1} which was reported only by

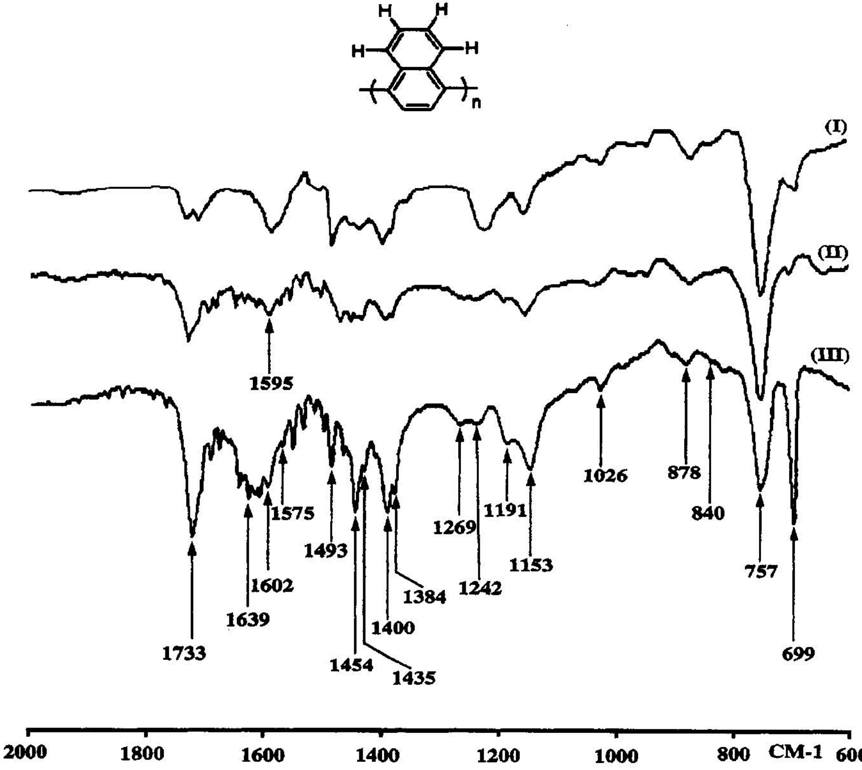


Figure 18.14. IR spectra of PNT-N from different polymerization processes.

Banning,[43] who synthesized 1,4-naphthalene oligomer using a Grignard coupling reaction with 1,4-dibromonaphthalene as the starting material. The IR spectra of PNT-N prepared in this work all have this absorption at 699 cm^{-1}. Films collected from different VDP reactions always exhibit this specific absorption, between 696–699 cm^{-1}.

(d) IR Spectra ofPNT-F For PNT-F, the IR spectrum also showed a strong absorption at 757–760 cm^{-1} and 699–700 cm^{-1}. Therefore it is reasonable to believe that the 699 and 757 cm^{-1} bands might be important indications of 1,4 linkages for polynaphthalene analogues. Figure 18.15 shows the IR spectrum of PNT-F prepared by two different polymerization processes. The top spectrum was prepared in diphenyl ether solution, and the bottom from a polymer film prepared by the VDP process.

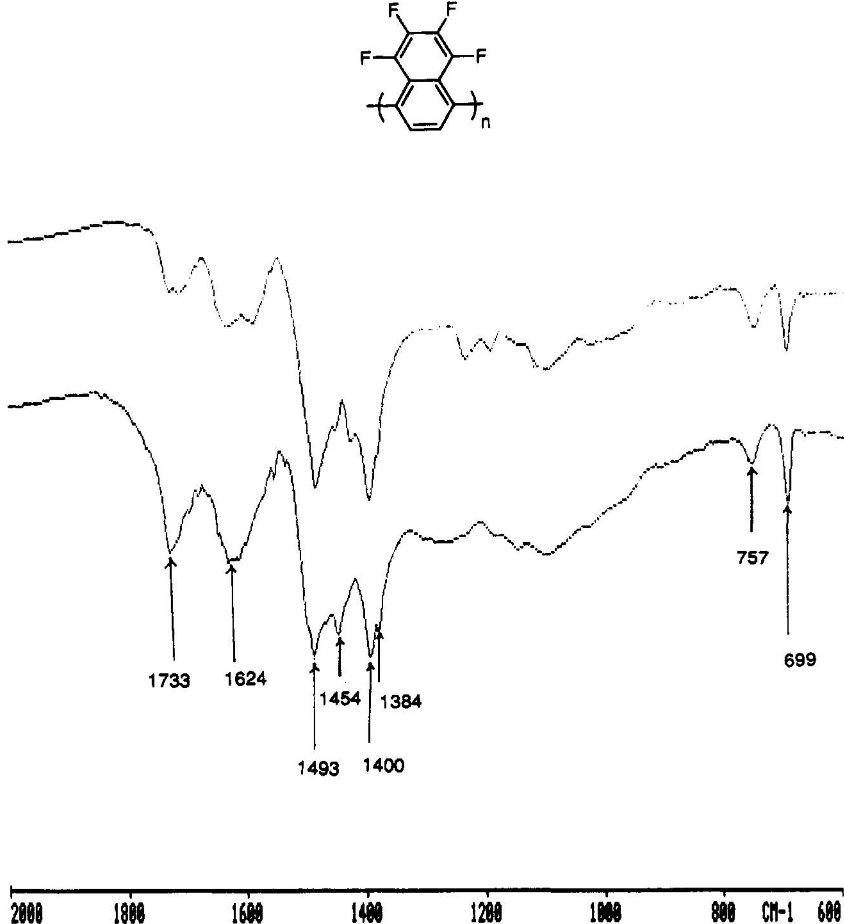


Figure 18.15. IR spectra of PNT-F from different polymerization processes.

(e) Solid State NMR Spectrum ofPNT-N The brown powder of PNT-N that was prepared by solution polymerization in benzene was investigated using magic-angle cross-polarization (CPMAS) ^{13}C-NMR spectroscopy (Figure 18.16). The area ratio of the peaks for hydrogen-substituted carbon atoms and quaternary carbon atoms was ca. 55 : 45 (curve fit), which approximately corresponds to a hydrogen/carbon ratio of C : H= 10 : 5.5.

(f) Solid State NMR Spectrum of PNT-N. The attempts to study PNT-F were not successful because the complicated coupling pattern between carbon and fluorine atoms makes the analysis too difficult to accomplish at this time.

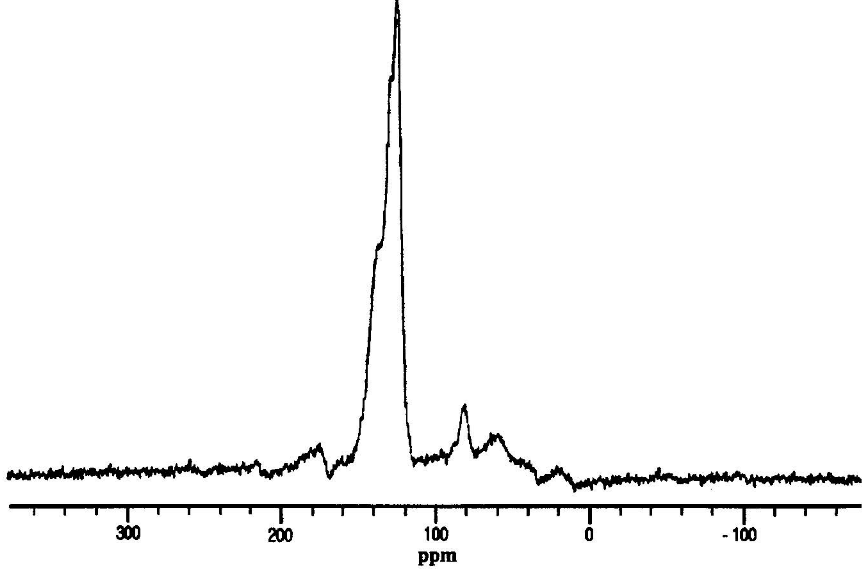


Figure 18.16. Solid State ^{13}C-NMR spectrum of PNT-N prepared by solution polymerization in benzene.

(g) X-Ray Photoelectron Spectroscopy. The shifts in Cl*s* levels for oxygen-containing structural features in terms of the number of carbon–oxygen bonds are given below[52]:

$$O{=}C\!\begin{smallmatrix} O \\ O \end{smallmatrix} > O{=}C{-}O > C{=}O \sim O{-}C{-}O > C{-}O$$

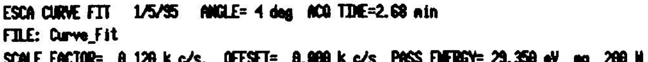
~290.6 eV ~289.0 eV ~ 287.9 eV ~286.6 eV

The reference binding energy for carbon not attached to oxygen (e.g., in polyethylene) is 285.0 eV and the primary substituent effect of oxygen can be described in terms of a simple additive model. The shift in binding energy of Cl*s* core level electron, subsequent to replacing carbon or hydrogen by oxygen is ca. ~ 1.5 eV per carbon–oxygen bond. This value is only half the shift induced by fluorine.

(h) XPS of PNT-N. We were able to link the XPS data to the thermal stability and dielectric constant of the deposited films. Because of the structural simplicity of PNT-N and PNT-F films the assignment of the signals is straightforward in the light of the foregoing discussion, in which it was noted that the primary shift

induced by oxygen is ca. 1.5 eV per carbon–oxygen bond and roughly additive. PNT-N does not provide an easily interpretable spectrum because only C—C and C—H atoms exist in the polymer and their Cl*s* binding energies are indistinguishable or extremely difficult to assign. The XPS spectra of the PNT-N films, however, clearly showed that these films contain defect structures, which apparently result from the incorporation of oxygen atoms into the polymer. Ideally, there should be only one Cl*s* peak at ca. 285 eV (*C*—C and *C*—H) for a defect-free PNT-N film. However, two to three different types of carbon atoms were observed, depending on the concentration of the incorporated oxygen atoms. Oxygen-incorporation was observed from the additional Cl*s* peaks at ca. 286.5 eV (*C*—O) and at ca. 287.9eV (O—C—O or C═O) in the XPS spectra. The low thermal stabilities and high dielectric constants of these films also confirmed these defects, indirectly.

It is apparent that VDP of PNT-N is sensitive to the presence of oxygen and, perhaps, moisture, as would be expected if the growing chain ends bear unpaired electrons. The higher the incorporated oxygen concentration as detected by XPS, the higher the dielectric constant. When both the —C══O and —C—O peaks were detected in XPS spectra, the incorporated oxygen contents in the films were usually higher than 12%. If only a —C—O peak was observed, approximately 5–8% oxygen was incorporated.



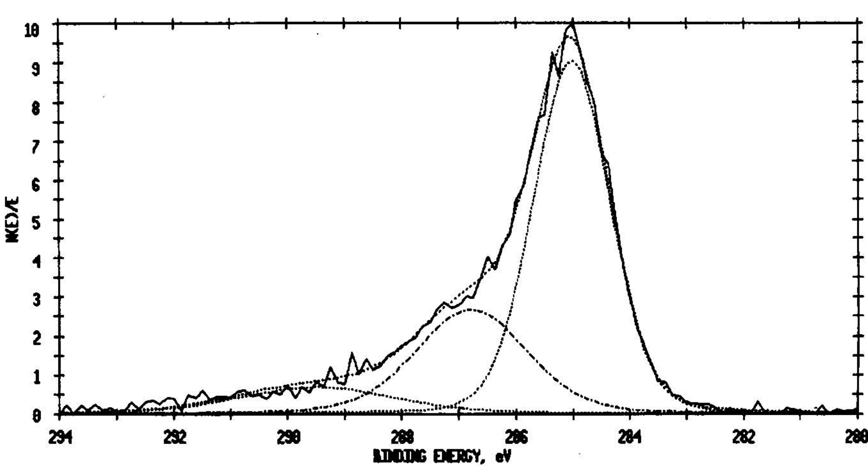


Figure 18.17. XPS spectrum of PNT-F film.

Figure 18.18. Several possible defect structures in PNT-F film.

(i) XPS ofPNT-F. Figure 18.17 presents the XPS spectrum of C1*s* binding energy ofthe PNT-F sample made by VDP. The three broad peaks in the spectrum represent three groups of C atoms from different chemical environments, which correspond to the six carbon atoms of the backbone ring (*C*—C and C—H have almost the same Cls binding energy, approximately 285 eV), oxygenated carbon atoms of the naphthalene ring (*C*—O) and fluorinated carbon atoms (*C*—F). In Figure 18.16, the strongest group of peaks in the spectrum is assigned to the C atoms of *C*—C and *C*—H of the backbone ring, and the medium group ofpeaks is assigned to the C atoms of *C*—O. The smallest group of peaks in the spectrum is assigned to the *C*—F groups. Table 18.9 gives the XPS data for this PNT-F film.

The expected chemical formula of each repeating unit is ($C_{10}H_2F_4$), with a calculated ratio of C (*C*—C and *C*—H) : C (*C*—F) = 6 : 4. Thus, there should be six carbon atoms (*C*—C and *C*—H) with Cl*s* binding energy of 285.03 eV and four carbon atoms (*C*—F) with Cl*s* binding energy of ca. 288 eV. However, the defect structure of the as-deposited film was clearly demonstrated by the extra peaks and the stoichiometry of C atoms (the corresponding area) from the XPS analysis. Relatively, there are six carbon atoms with Cl*s* binding energy of 285.03 eV, and the Cl*s* spectrum possesses a tail to high binding energy owing to the presence of predominantly carbon singly bonded to oxygen, C 1*s* 286.79 eV, and a small tail at the end of spectrum with Cl*s*, 289.5 eV from C—F bonding. It seems that some fluorine atoms on the aromatic ring may have been replaced by the C—*OH* bond and, perhaps, further converted to diphenyl ether linkages during the deposition process. Several speculative defect structures are illustrated in Figure 18.18. The oxygen atoms within the polymer structure or formed as end

Table 18.9. XPS Results for PNT-F

Parameter	*C*—C and *C*—H (CI*s*)	*C*—O (CI*s*)	*C*—F (CI*s*)
Peak position (eV)	285.03	286.19	289.50
Area	1971	867	331
% of total area	62.20	21.36	10.44

Table 18.10. XPS Results for “Improved” PNT-F Film

Parameter	*C*—C and *C*—H (CI*s*)	*C*—F (C1*s*)
Peak position (eV)	285.57	281.66
Area	1584	1123
% of total area	58.81	41.49

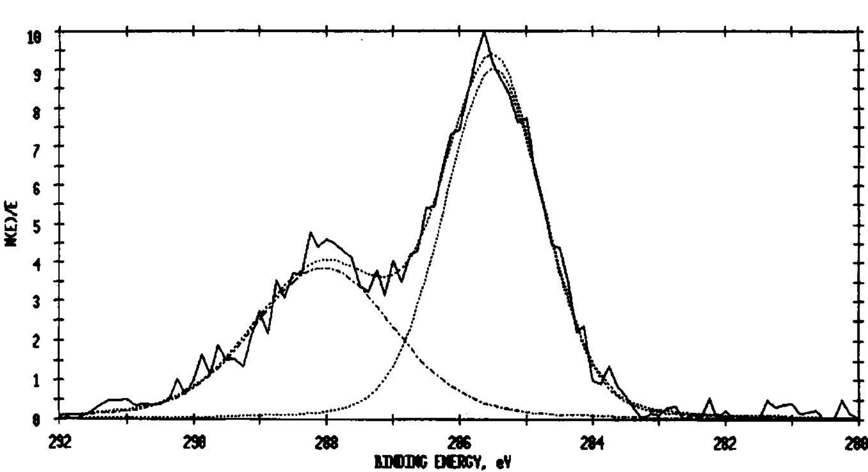


Figure 18.19. XPS spectrum of “improved” PNT-F film.

Table 18.11. Properties of Thin Films Prepared by VDP

Film	PA-N	PA-F	Teflon	Teflon AF	PNT-N	PNT-F	Bis(BCB-F8)
Film deposition	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor
Source material	Dimer (solid)	Precursor (liquid)	Polymer (solid)	Polymer (solid)	Precursor (liquid)	Precursor (solid)	Precursor (solid)
Toxicity of source material	No	Hazardous	Hazardous	Hazardous	—	—	—
Dielectric constant	260 ± 0.1	2.2–2.3	2.1	1.93	2.4±0.1	2.3 ±0.1	2.0–2.1
Electric break-down	2 x 10_7 V/mil	5 x 10_7 V/miI	5 x 10_7 V/miI	5 x 10_7 V/mil	3 x 10_7 V/miI	5 x 10_7 V/miI (best)	NA
Hardness (Gpa)	0.2	—	—	0.5	3.1 (R. #1) 1.6 (R. #2)	3.8 (R. #I)	—
Dissociation T(ºC)	430°C in N_2	530°C in N_2	320°C in air	360°C in air	570°C in N_2	590ºC in N_2)	—
Thickness vs. annealing temperature	No change to 350°C in N_2	No change to 500°C in N_2	—	—	No change to 530°C in N_2	—	—
Structure as deposited	Crystalline	Crystalline/ amorphous	Crystalline/ amorphous	Amorphous	Microcrystalline/ amorphous	Mcirocrystalline/ amorphous	Cross-linked
Cracks	Yes (annealing at 300ºC in N_2)	No (annealing at 510°C in N_2)	—	Yes –15°C in air 250°C in N_2	No (annealing at 570°C in N_2)	No (annealing at 600°C in N_2)	No

groups could have resulted from reactions with H_2O or O_2 during the deposition or upon exposure of the films to air. A compelling explanation of how the *C*—O defects were incorporated into the PNT-F film is not clear at present, but these oxygen-based defects will cause a higher dielectric constant and a lower thermal stability.

In a subsequent experiment, the quality of the deposited PNT-F film was greatly improved by taking pains to prevent atmospheric contamination, yielding a carbon atom ratio (calculated from the area of the binding energy peaks), C (*C*—C and *C*—H) : C (*C*—F) = 59 : 41, where the theoretical ratio is 60 : 40 (Figure 18.19). The deposited PNT-F film had a very low dielectric constant (2.1 –2.2) and high thermal stability (590°C in nitrogen). Table 18.10 shows the XPS results for the improved film.

18.3. CONCLUSIONS

An overview of the properties of the materials we are studying is presented in Table 18.11. The objective of this work was to find new approaches to the problem of generating new media with low dielectric constants and high thermal stabilities for use as interlayer dielectrics in microelectronic interconnection applications. We have been partially successful in this quest but there is still much more work to be done. The materials we have been able to deposit remain to be characterized in full detail, which includes not only elucidating their molecular structure but also measuring the panoply of physical properties necessary for practical applications.

VDP also provides a route for the synthesis of thin films without the use of toxic solvents, an opportunity not to be overlooked in this era of increased environmental watchfulness. There remains, however, the challenge of preparing potential source materials useful in this methodology. The amazingly productive field of Organic Chemistry will most certainly be able to meet this challenge.

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