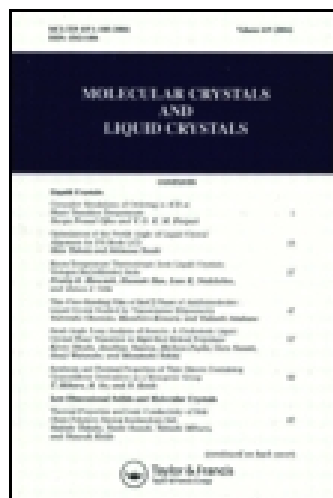


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### Design of Multilayered Polymeric Dielectric Insulators for Advanced Microelectronics Packaging

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## DESIGN OF MULTILAYERED POLYMERIC DIELECTRIC INSULATORS FOR ADVANCED MICROELECTRONICS PACKAGING

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**Abstract** 2,2-Bis[4-((4-fluorophenyl)buta-1,3-diyne)phenoxyphenyl]hexafluoropropane and co-polymer of 1,4-bis(4-fluorophenyl)buta-1,3-diyne and hexafluorobisphenol-A were prepared for the use as photosensitive multilayered polymeric dielectric insulators. The prepared materials turned out to be stable at high temperatures as well as thermally or photochemically curable. It was found that the mechanical properties of cross-linked products by thermal or photochemical curing of the prepared diacetylenic materials were much more improved in comparison with those of cured poly(triethynylbenzene)(PTEB).

### INTRODUCTION

There has been considerable interest by the microelectronics industry<sup>1</sup> in design of multilayered polymeric dielectric insulators to further enhance performances of the next generation of packages. The photosensitive polyimides derived from pyromellitic dianhydride and 4,4'-oxydianiline were developed in the 1970's and find use in industry due to their ability to greatly reduce the number of processing steps.<sup>2</sup> During the past 15 years some progress has been made in the design of improved high temperature polyimides with development of a) polyimides that are more readily processible, b) polyimide blends which reduce the dielectric constant, and c) with more rod-like polyimides which control the coefficient of thermal expansion. However, a number of critical problems still remain with these polyimides, for example, poor interlayer adhesion, relatively high dielectric

constants, anisotropic swelling in solvents such as NMP, and tendency to pick up moisture.<sup>3</sup>

Hay prepared high molecular weight diacetylene polymers by the oxidative coupling of *m*-diethynylbenzene. These polymers reportedly underwent exothermic decomposition upon heating above 180 °C to give insoluble materials.<sup>4</sup> Wegner reported that certain diacetylenes could be polymerized by ultraviolet radiation.<sup>5</sup>

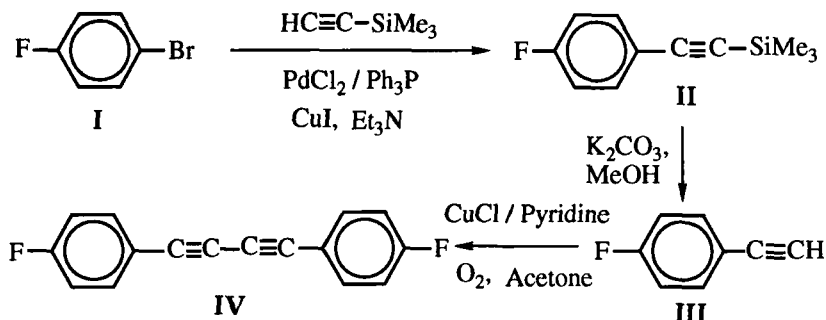
Recently, Economy reported the preparation of low molecular weight poly(triethynylbenzene)(PTEB) oligomer by the oxidative coupling of 1,3,5-triethynylbenzene with phenylacetylene as a capping agent.<sup>6</sup> This oligomer displayed excellent planarizability, and could be thermally cross-linked into a film with low dielectric constant, and good interlayer adhesion as compared to polyimides. Unfortunately, the PTEB had one shortcoming, namely its brittleness (elongation at break < 2%) which probably was due to the high degree of cross-linking.<sup>7</sup>

We wish to report the synthesis and properties of co-polymer consisting of photosensitive diacetylenic derivative and a flexible toughening group, which greatly reduces the brittleness problem.

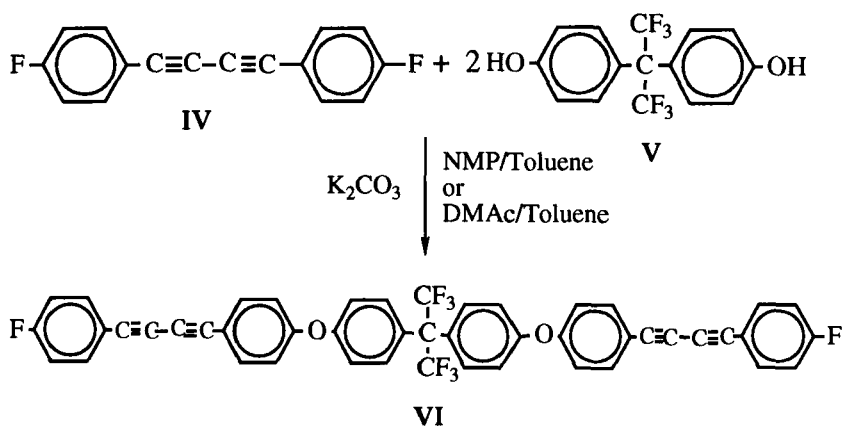
## RESULTS AND DISCUSSION

The synthesis of monomer 1,4-bis(4-fluorophenyl)buta-1,3-diyne(IV) from commercially available 1-bromo-4-fluorobenzene(I) is outlined in Scheme I. The synthesis of 1-ethynyl-4-fluorobenzene(III) involves two steps: (1) displacement of I with trimethylsilylacetylene, and (2) the subsequent cleavage of the trimethylsilyl protecting group to III.<sup>8</sup> Trimethylsilylacetylene was easily displaced with a properly activated arylbromide I in the presence of palladium(II)chloride, triphenylphosphine, copper(I)iodide and triethylamine in high yield,<sup>9</sup> in which bromide group, not fluoride, was selectively substituted with trimethylsilylacetyl group. The cleavage of trimethylsilyl protecting group was done in 100% yield by the treatment with a weak base such as potassium carbonate. Diacetylenic monomer IV was then prepared by a Glaser oxidative coupling reaction of III in the presence of a catalytic amount of copper(I)chloride and pyridine with bubbling oxygen gas through reaction mixture.

## Scheme I



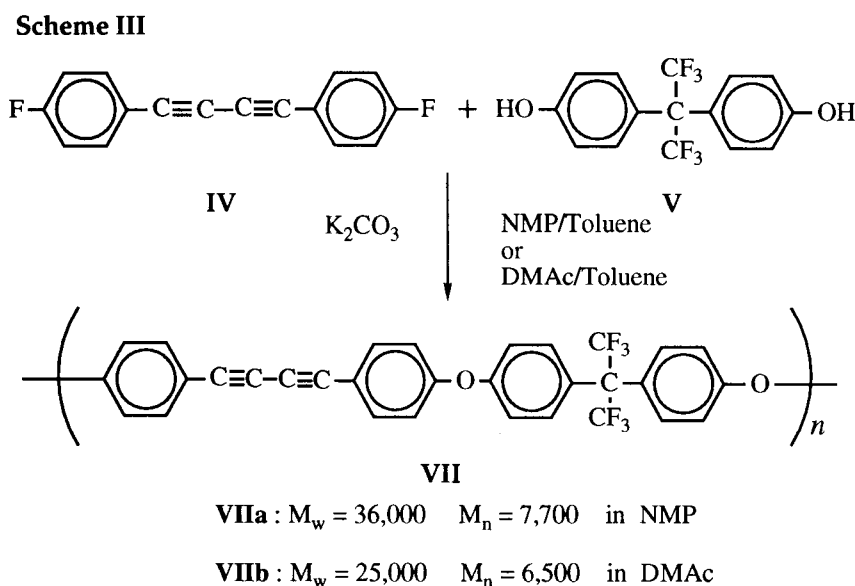
## Scheme II



The reaction between 1 mol of IV and 2 mol of hexafluorobisphenol-A (V) was carried out in *N*-methyl-2-pyrrolidone (NMP)/toluene solvent mixture in the presence of  $\text{K}_2\text{CO}_3$  (Scheme II). Toluene was used to remove the water generated upon heating to 150 °C by azeotrope using a Dean-Stark trap. After dehydration, the toluene was removed through the Dean-Stark trap and the reaction mixture was heated to 180 °C. It was found that one fluorine group of IV was displaced with V to yield 2,2-Bis[4-((4-fluorophenyl)buta-1,3-diyne)phenoxy]hexafluoropropane (VI) in quantitative way through aromatic nucleophilic substitution reaction.<sup>10</sup>

The reaction between 1 mol of IV and 1 mol of V gave co-polymer consisting of photosensitive diacetylenic IV and a toughening group V in similar way of reaction condition of VI by aromatic nucleophilic

substitution polymerization reaction<sup>11</sup>(Scheme III). The copolymerization reactions were carried out in NMP/toluene or *N,N*-dimethylacetamide (DMAc) as solvent mixture in the presence of  $K_2CO_3$  by conventional procedure.<sup>12,13</sup> The monomers **IV** and **V** were polymerized in NMP to yield polymer **VIIa** whose  $M_w/M_n$  equals 36,000/7,700, whereas the same monomers polymerized in DMAc resulted in polymer **VIIb** whose  $M_w/M_n$  equals 25,000/6,500.



The thermal stabilities of **VI** and **VIIa** in a nitrogen atmosphere were determined by thermogravimetric analysis (TGA) (Figure 1). In the case of **VI** it was stable up to 300 °C. Between 300 and 450 °C the sample loses only 3% of initial weight. Rapid weight loss of 31% of the initial sample weight occurs between 450 and 650 °C. Between 650 and 1000 °C an additional 5% weight loss occurs. A black residue amounting to 61% of the initial weight remains when the sample is heated up to 1000 °C. The similar pattern of TGA were observed in polymers **VIIa** and **VIIb**. Differential scanning calorimetry (DSC) trace of **VI** shows a large broad exotherm centered at 290 °C in the range of 200-350 °C, whereas DSC of **VIIa** plots a large exotherm centered at 320 °C in the range of 250-350 °C (Figure 2). DSC of **VIIb** showed similar pattern with **VIIa**.

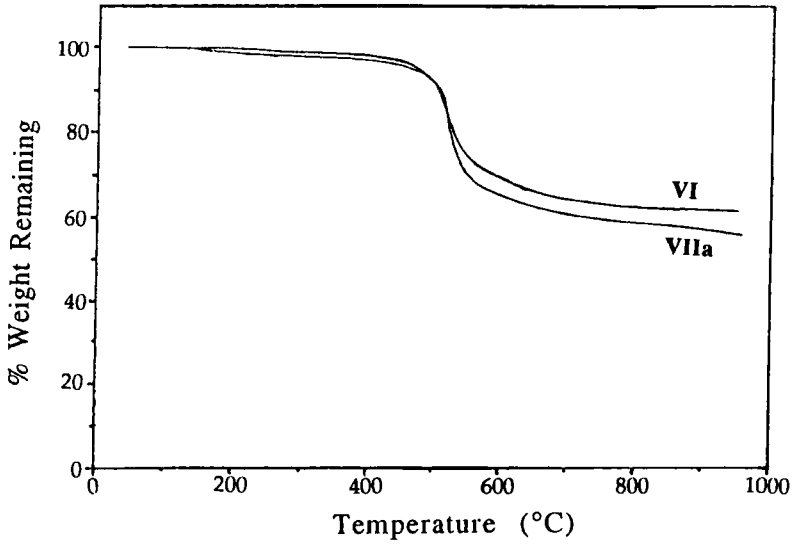


FIGURE 1 Thermal gravimetric analysis (TGA) traces of VI, VIIa.

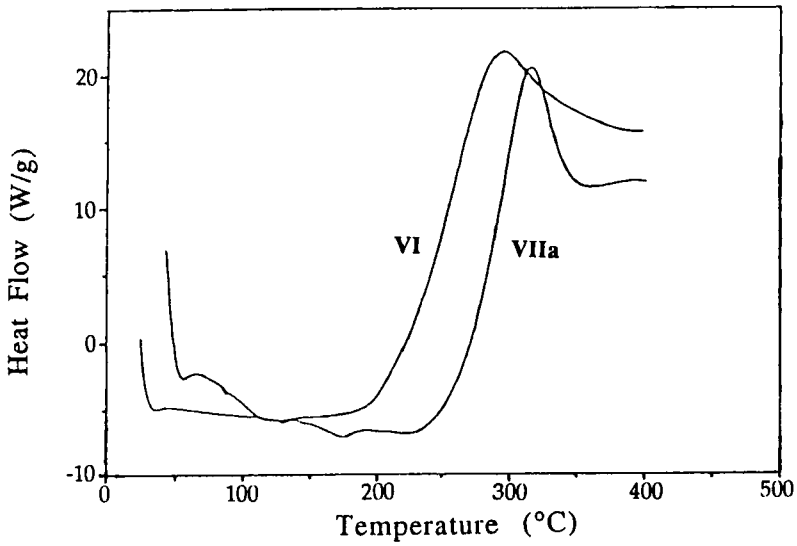


FIGURE 2 Differential scanning calorimetry (DSC) traces of VI, VIIa.

Both exotherm peaks probably result from the cross-linking of the diacetylene group to form fused polycyclic aromatic materials via [1,2]-addition, [1,4]-addition, or [2+4] cycloaddition reactions.

The copolymers absorb at 316 nm (molar absorptivities are 9670 and 2381 L/(mol·cm) for VIIa and VIIb, respectively) with band in the range of 290-360 nm which is attributed to the  $\pi$  system of diacetylenes (Figure 3).

The results of DSC and UV spectra indicate that these new materials can be cured by thermal or photochemical processes. VI and VII are soluble in most ethereal, aromatic, and halocarbon solvents. However, the thermally cured materials are not soluble in any solvents.

The mechanical properties of thermally cured films of VI, VIIa are summarized in Table 1. The elongation at break, tensile strength, and tensile modulus of the cured film of VIIa was 6.0%, 18 MPa, and 307 MPa, respectively. Tensile strength and tensile modulus could be increased by further curing process. The elongation at break of VIIa is much improved when compared with the less than 2% of PTEB. As might be expected, the flexible toughening group such as hexafluorobisphenol-A plays an important role in reducing the brittleness problem. Furthermore, the dielectric constants of VI, VIIa, and VIIb have been measured as 2.7-2.9

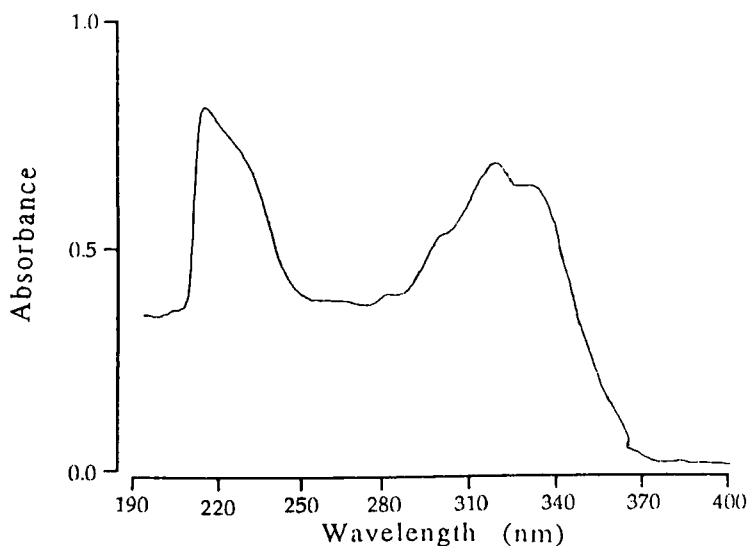


FIGURE 3 UV absorption spectrum of VIIa.



**TABLE 1** Mechanical Properties of Cured Films\* of VI, VII

Polymer	Elongation at Break(%)	Tensile Strength (MPa)	Tensile Modulus (MPa)
<b>VI</b>	3.2	10	308
<b>VIIa</b>	6.0	18	307

\* Films were prepared at 300 °C and thermally cured for 1-2 min at 300 °C under argon atmosphere.

**TABLE 2** Dielectric Properties of VIa,\* VIb,\* VIIa, VIIb

Materials	Dielectric constant, k'	Thickness(Å)
<b>VIa</b>	2.76	145
<b>VIb</b>	2.67	149
<b>VIIa</b>	2.93	203
<b>VIIb</b>	2.86	103

\* **VIa**: VI prepared in NMP; **VIb**: VI prepared in DMAc.

(Table 2), which are much lower than those of polyimides, 3.4-3.8.<sup>1,2</sup> These polymers appear inert to moisture. Research in this class of diacetylene copolymeric materials is being continued to evaluate the photochemical curing of these systems.

## **EXPERIMENTAL**

All chemicals were purchased from Aldrich Chemicals Inc., and (4,4'-hexafluoroisopropylidene)diphenol (hexafluorobisphenol-A) was used without further purification. *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) were distilled from CaH<sub>2</sub>.

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE 300 spectrometer. Chemical shifts were measured

using tetramethylsilane as internal standard or the solvent as standard. IR spectra were recorded by a Perkin-Elmer series 1600 FTIR spectrophotometer. UV/vis spectra were recorded on a Perkin-Elmer Lambda 3 UV/vis spectrophotometer

Elemental analyses were performed by the Microanalytical Laboratory at University of Illinois at Urbana-Champaign. Low resolution mass spectra were measured on Finnigan Mat CH5 mass spectrometer by EI ionization at 70 eV. High resolution mass spectra were measured on VG 70-VSE mass spectrometer by EI ionization at 70 eV using perfluorokerosene-H as standard.

Molecular weights were performed in tetrahydrofuran (flow rate 1.0 cm<sup>3</sup>/min) using a Waters System; 510 HPLC pump, 410 differential refractometer, and ultrastragel linear column. Calibration curve was obtained using polystyrene standard samples; 1.5M, 9.5K, 19.75K, 1.8K.

Thermogravimetric analyses (TGA) of the polymers were performed on DuPont Hi-Res TGA 2950 thermal analyzer, and differential scanning calorimetric analyses (DSC) were performed on DuPont DSC 2910 or DSC 10 thermal analyzer.

Mechanical properties were determined on an Instron Model materials tester with a crosshead speed of 10.0 mm/min. Films for specimens were prepared by hot pressing at 300 °C for 1-2 min under argon atmosphere.

**1-Fluoro-4-[(trimethylsilyl)ethynyl]benzene (II).** In a 2-liter 3-neck flask, equipped with mechanical stirrer, condenser, Ar gas inlet, and heating mantle, 1-bromo-4-fluorobenzene (I) (72.0 g, 0.411 mol), triphenylphosphine (1.56 g, 5.95 mmol), ethynyltrimethylsilane (50.0 g, 0.509 mmol) and 800 ml of triethylamine were placed under an argon atmosphere. The mixture was warmed to 40 °C and then palladium(II)chloride (0.15 g, 1.2 mmol) and copper(I)iodide (0.13 g, 0.68 mmol) were added. The reaction mixture was heated to reflux overnight. The mixture was allowed to cool, the triethylaminehydrobromide salt was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was taken into dichloromethane (700 mL) and the solution was successively washed with 5% hydrochloric acid and water. The solution was dried over magnesium sulfate, filtered and the solvent was removed. The residue was distilled under reduced pressure. The colorless liquid, 72.1 g, 66-67 °C/0.11

mmHg, was obtained; yield 92%. Anal. Calcd for  $C_{11}H_{13}FSi$ : C, 68.70; H, 6.81; F, 9.88. Found: C, 68.63; H, 6.88; F 9.83.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  0.058 (s, 9H,  $CH_3$ ), 6.77 (t, 2H, aromatic CH,  $J = 8.7$  Hz), 7.23 (q, 2H, aromatic CH,  $J = 5.3, 7.4$  Hz).  $^{13}C$  NMR( $CDCl_3$ ):  $\delta$  -0.12, 93.74, 103.96, 115.29, 115.58, 119.22, 119.26, 133.78, 133.89, 160.87, 164.18. MS (m/e (relative intensity)): 194(3.1), 193(10.9), 192( $M^+$ , 64.9), 179(22.4), 178(68.8), 177( $M^+ - CH_3$ , 100), 161(10.3), 147(38.3), 123(21.5), 115(22.8), 88(33.6), 47(87.1). IR ( $cm^{-1}$ , neat)  $\nu$ : 3050, 2961, 2900, 2362, 2068, 1601, 1505, 1252, 1234, 1214, 1156, 1093, 869, 838, 767, 700.

**1-Ethynyl-4-fluorobenzene (III).** II (83.3 g, 0.438 mol) was dissolved in 300 mL of deoxygenated anhydrous methanol. Anhydrous potassium carbonate (3.03 g, 0.0219 mol) was added and the mixture was stirred for 4 h under argon purge. Solvent was distilled out. The residue was taken into dichloromethane (500 mL), and washed with a 5% sodium bicarbonate solution and water. After drying over magnesium sulfate and filtering the solvent was removed. The residue was distilled under reduced pressure. The colorless liquid, 43.2 g, 69-71 °C/7.9 mmHg, was obtained; yield 82%.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  3.04(s, 1H, acetylenic CH), 6.98(t, 2H, aromatic CH,  $J = 8.7$  Hz), 7.44(q, 2H, aromatic CH,  $J = 5.3, 8.5$  Hz).  $^{13}C$  NMR( $CDCl_3$ ):  $\delta$  77.0, 82.6, 115.4, 115.7, 118.1, 118.2, 133.9, 134.1, 161.0, 164.4. MS (m/e(relative intensity)): 121(8.5), 120( $M^+$ , 100), 100(9.5), 94(17.7), 74(15.0), 50(11.5). Exact Mass Calcd for  $C_8H_5F$ : 120.0375. Found: 120.0376. IR ( $cm^{-1}$ , neat)  $\nu$ : 3296, 3050, 2113, 1895, 1654, 1602, 1505, 1233, 1157, 1094, 1015, 837, 662, 619.

**1,4-Bis(4-fluorophenyl)-buta-1,3-diyne (IV)** In a 2-L 3-neck flask, equipped with heating mantle, addition funnel, mechanical stirrer, and condenser were placed copper(I)chloride (2.31 g, 23.3 mmol) and acetone (700 mL). The mixture was slowly heated to 30 °C. The addition funnel was charged with a solution of 40 mL of acetone and 40 mL of pyridine; and 40 mL of the acetone/pyridine mixture was added. The dark green solution was stirred for 10 min and III (28.1 g, 0.234 mol) was added. A small exotherm was noted. 40 mL of the mixture of the acetone/pyridine mixture was added. After 10 min of stirring, oxygen gas was bubbled through the reaction mixture. The heating mantle was used to maintain the reaction temperature at 35-40 °C for 6 h. The reaction work-up was conducted under yellow light conditions in order to prevent UV-induced cross-linking. The reaction mixture was added to a vigorously stirred solution of 33 mL of 12 N HCl in 1 L of methanol. The precipitated product was isolated by

decantation and washed with methanol. The crude product was redissolved in 600 mL of chloroform, washed with 10% aqueous HCl (3 x 100 mL), neutralized with water (2 x 100 mL), dried over magnesium-sulfate, and filtered. The chloroform solution was concentrated to 200 mL and recrystallized by the addition of methanol. The solid was filtered, washed with methanol and dried in vacuum. The white crystalline product, 20.0 g, mp 195-197 °C, was obtained; yield 72%. Anal. Calcd for C<sub>16</sub>H<sub>8</sub>F<sub>2</sub>: C, 80.66; H, 3.39; F, 15.95. Found: C, 80.57; H, 3.35; F, 15.94. Exact Mass Calcd for C<sub>16</sub>H<sub>8</sub>F<sub>2</sub>: 238.0594. Found: 238.0593. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.04 (t, 4H, J = 8.7 Hz), 7.51 (q, 4H, J = 5.4, 8.9 Hz). MS (m/e(relative intensity)): 240(1.5), 239(17.2), 238(M<sup>+</sup>, 100), 218(6.26), 168(4.3), 119(12.8). IR(cm<sup>-1</sup>, KBr pellet) v: 3101, 3070, 1887, 1639, 1595, 1502, 1464, 1404, 1227, 1159, 1093, 828, 696, 526.

**2,2-Bis[4-((4-fluorophenyl)buta-1,3-diyanyl)phenoxyphenyl]hexafluoropropane(VI).** In a 250 mL 3-neck flask, equipped with an argon inlet, stirring bar, Dean-Stark trap, and condenser, IV (4.77 g, 20.0 mmol), hexafluorobisphenol-A (3.36 g, 10.0 mmol), and 60 mL of NMP were placed under argon atmosphere. K<sub>2</sub>CO<sub>3</sub> (4.14 g, 30.0 mmol) and 40 mL of toluene were than added. The reaction mixture was heated until the toluene began to reflux. Water formed during the reaction was removed as an azeotrope with toluene over 4-5 h period. The reaction mixture was slowly raised to 180 °C. The reaction mixture was maintained at 180-190 °C for 24 h. During the initial formation of the phenoxide, a yellowish brown color developed, and as the refluxing proceeded, the color changed to dark brown. The product was extracted with 350 mL of chloroform, washed with 5% HCl solution 3 times to remove excess salts, neutralized with water, and dried over anhydrous magnesium sulfate. Most of the solvent was removed under reduced pressure and the product was precipitated with addition of methanol, filtered, and dried in a vacuum oven at room temperature. Brown solid product, 10.6 g, mp 155-156 °C, was obtained; yield 91%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.90-7.10(m), 7.30-7.60(m). Exact Mass Calcd for C<sub>47</sub>H<sub>24</sub>F<sub>8</sub>O<sub>2</sub>: 772.1649. Found: 772.1650. MS (m/e(relative intensity)): 774(15.5), 773(49.0), 772(M<sup>+</sup>, 93.8), 554(8.9), 386(29.2), 337(21.4), 282(15.7), 281(37.6), 123(59.9), 98(94.0), 73(47.6). IR(cm<sup>-1</sup>, KBr pellet) v: 3048, 1895, 1703, 1596, 1498, 1248, 1206, 1175, 1136, 1015, 968, 929, 854, 832, 736, 705, 528.

**Synthesis of Copolymers (VIIa, VIIb).** In a 250 mL 3-neck flask, equipped with an argon inlet, stirring bar, Dean-Stark trap, and condenser, IV (4.77 g, 20.0 mmol), hexafluorobisphenol-A (6.72 g, 20.0 mmol), and 60 mL of NMP were placed under argon atmosphere.  $K_2CO_3$  (4.14 g, 30.0 mmol) and 40 mL of toluene were then added. The reaction mixture was heated until the toluene began to reflux. Water formed during the reaction was removed as an azeotrope with toluene over 4-5 h period. The reaction mixture was slowly raised to 180 °C. The reaction mixture was maintained at 180-190 °C for 2-3 h. Polymerization was also carried out in DMAc using a similar procedure except that  $K_2CO_3$  (5.52 g, 40.0 mmol), 40 mL of DMAc, and 20 mL of toluene were used and the reaction temperature was 160 °C overnight. During the initial formation of the phenoxide, a yellowish brown color developed, and as the refluxing proceeded, the color changed to darkish brown. The polymer was isolated with 100 mL of methanol, washed with water/methanol 4-5 times to remove excess salts completely. The suspension was warmed with water/methanol, filtered, and dried in a vacuum oven at room temperature. In the case of NMP solvent, pale beige color polymer VIIa, 10.6 g, was obtained; yield 91%. Molecular weight:  $M_w = 36000$ ,  $M_n = 7700$ ,  $M_w/M_n = 4.7$ . UV in THF (molar absorbance)  $\lambda$ : 332(8970), 316(9670), 298(7410), 212(11388) in nm(L/(mol·cm)). In the case of DMAc solvent, a beige color polymer VIIb, 10.8 g, was obtained; yield 93%. Molecular weight:  $M_w = 25000$ ,  $M_n = 6500$ ,  $M_w/M_n = 3.8$ . UV in THF (molar absorbance)  $\lambda$ : 332(2065), 316(2381), 298(1935), 212(3088) in nm(L/(mol·cm)). Anal. Calcd for  $(C_{31}H_{16}F_6O_2)_n$ : C, 69.66; H, 3.02; F, 21.33. Found: C, 66.77; H, 3.19; F, 22.50.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.78 - 7.13(br m), 7.15 - 7.65(br m). IR( $cm^{-1}$ , KBr pellet)  $\nu$ : 3048, 2037, 1896, 1690, 1597, 1498, 1411, 1244, 1206, 1174, 1135, 1015, 968, 928, 831, 735, 704, 528. TGA of VIIa indicated stability to 300 °C, while between 300 and 450 °C the sample lost only 2% of initial weight. Rapid weight loss of 32% of the initial sample weight occurred between 450 and 650 °C. Between 650 and 1000 °C an additional 5% weight loss occurred. A black residue amounting to 61% of the initial weight remained when the sample was heated up to 1000 °C. TGA pattern of VIIb is similar with VIIa.

**Dielectric Measurement of Polymer.** Measuring the dielectric properties of these materials requires deposition of materials, characterization of film thickness, and capacitance measurement at various frequencies.

A) Sample preparation: A smooth metal was used as the substrate. The polymer film was spin coated onto this surface. NMP was used as the solvent for spin coating. The spin rate of the substrate was 4000 rpm. Two to eight mL were placed on the spinning substrate using a syringe. The sample was cross-linked by heating at 320 °C for 2-3 min in inert atmosphere. The thickness was then measured using ellipsometry. A grid of small gold circles was applied to the sample by sputtering gold through a mask. Dimensions of the gold pads were measured with a scanning electron microscope to determine pad area. A small part of the surface was then sanded to remove the gold grids and polymer film in that area. This sanding allowed electrical contact with the bottom metal.

B) Capacitance measurement: The capacitance versus frequency was recorded using a HP4284 high impedance meter. One probe from the machine was placed on one of the top gold pads. The other probe was placed on the sanded away region where the metal substrate was exposed. The capacitance was measured at different pads. This was done for averaging and to find regions where pinholes and other defects of the applied polymer were minimal. In polymer films under 400 Å thick pinholes and other defects allow the top pads to be in electrical contact with the metal substrate. This causes the device to act like a resistor rather than a capacitor. Reducing pad area decreases the probability of a defect occurring within the region of measurement. Measuring more pads increases the probability that a defect free device will be measured.

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### REFERENCES

1. D. S. Soane and Z. Martynenko, Polymers in Microelectronics Elsevier Science Publishers B. V., New York, 1989.
2. H. Ahne, H. Kruger, E. Pammer, and R. Rubner, Polyimides: Synthesis, Characterization, and Applications, K. L. Mittal, ed., Vol. II, Plenum Press, 1984.

3. J. Economy, Contem. Top. Plym. Sci. **5**, 351 (1984).
4. A. Hay, J. Poly. Sci. Part A-1, **7**, 1625 (1969).
5. G. Wegner, Z. Naturforsch. B, **24(7)**, 824 (1969).
6. D. J. Dawson, W. W. Fleming, J. R. Lyerla and J. Economy, ACS Symp. Ser., **282**, 63 (1985).
7. J. Economy, Makromol. Chem. Macromol. Symp., **33**, 223 (1990).
8. S. J. Havens, J. Polym. Sci., Polym. Chem. Ed., **22**, 3011 (1984).
9. R. F. Heck, Palladium Reagents in Organic Syntheses, Academic Press, San Diego, 1985.
10. J. March, Advanced Organic Chemistry, 3rd ed., John Wiley & Sons, New York, 1985, p. 576.
11. J. L. Hedrick, W. Volksen and D. K. Mohanty, J. Polym. Sci. Part A: Polym. Chem., **30**, 2085 (1992).
12. J. L. Hedrick, J. W. Labadie and T. P. Russell, Macromolecules **24**, 4559 (1991).
13. V. Percec, R. S. Clough, P. L. Rinaldi and V. E. Litman, Macromolecules **24**, 5889 (1991).