Novel High Tg Low Dielectric Constant Coil-Shaped Polymer

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This paper reports that the novel high Tg low dielectric constant polymer with highly rigid coil-shaped main-chain structure was obtained for interlayer dielectric applications in microelectronics. The low dielectric constant of the polymer was induced by it that the coil-shaped main-chain structure with a bulky side-chain out of the main-chain. The coil-shaped structure leads to decrease packing density and increase free volume. The polymer was exhibited low dielectric constant (2.31) without pore. The glass transition temperature of the polymer is higher than 400°C. TGA shows that the polymer was heat stable higher than 350°C under nitrogen flow. The elastic modulus of the polymer is 4.3 GPa. The film is able to be prepared with lower temperature (at solvent boiling point). The polymer prepared is novel poly(norbornene imide) containing bulky fluorinated aryl unit in side-chain. We confirmed that the fluorinated poly(norbornene imide) displays a coil-shaped a main-chain polymer structure by molecular simulation. The syntheses of the fluorinated poly(norbornene imide) are described in this paper.

Keywords: poly(norbornene imide), dielectric constant, high glass transition temperature, elastic modulus

1. Introduction

Continuing improvement of the very large scale integration of microelectronic circuits has reached the point where multi-layer metallization and the interlayer dielectric have become the limiting factors in process integration and device performance. The major improvements in performance of microelectronics come from device size miniaturization, which leads to faster device speeds, higher device packing density, and more functions on a chip. As the devices scale to smaller feature sizes, the transistor operating speed is increased, yet the line-to-line capacitance and resistance of the metal lines increase. As a result, the resistance-capacitance (RC) delay caused by interconnect tends to limit the chip performance [1].

A new generation of low dielectric constant materials is required to achieve the advantages in high speed and low cross talk noise. Besides the dielectric constant, the second most important requirement for new interlayer dielectric is thermal stability [2]. An annealing step is necessary to ensure void free and lower resistance copper deposition as metal lines. Since this step is performed at temperatures in the range 400-450°C. Most high temperature dense polymers have been suggested for use of interlayer dielectrics [1]. This includes aromatic polyimides [3-5], poly(aryl ether)s [6], heteroaromatic polymers [7,8], poly(norbornene) [9,10], amorphous C:F [11], inorganic-organic hybrids [12], and fluorinated silica glass [13]. Moreover, since the dielectric constant of gases is not much different from that of vacuum(k0=1), the incorporation of free space or pores has been suggested as an attractive approach to decrease the dielectric constant of the polymer films for requirement lower dielectric constant. A submolecular level free space by using bulky groups such as fluorenyl in the repeating units of polymers decreases packing density. Increment constructed free volume for calculation of dielectric constants indicates that the bulky groups should result in lower dielectric constants [14]. Foamed films with pores in the 10 nm range

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have been successfully demonstrated to exhibit quite low dielectric constant [15,16]. However, since the cohesion of pores in the polymer induces to decrease an elastic modulus of the polymer and increased dielectric constant due to water absorption into the pores. There are great hopes that the dielectric constant of the dense polymer is as low as possible.

Recently it was reported that synthesis and simulation of novel poly(norbornene imides) obtained via vinylic polymerization of exo aryl-nadimides using a Pd(II) catalyst [17]. The poly(norbornene imides) have highly rigid yet densely coil-shaped main-chain polymer structure with a bulky side-chain imide unit out of the main-chain. This rigidity causes a high glass transition temperature excess to 370ºC and the temperature of initial decomposition as high as 470ºC. There is no report on the dielectric constant and mechanical properties of poly(norbornene imide).

We expect the poly(norbornene imides) are one of the new generation low dielectric candidates due to good thermal properties and the coil-shaped main-chain polymer structure with a bulky side-chain imide unit out of the main-chain which may lead to decrease packing density and increase free volume. This paper reports the synthesis and characterization of the novel poly(norbornene imide) containing small polarizability fluorinated aryl or alicyclic unit side-chain with an expectation of low dielectric constant. We think the fluorinated poly(norbornene imide) maintain good thermal properties and have suitable mechanical properties due to highly rigid main-chain structure.

2. Experimental Section  
2.1 Materials and syntheses

Before use chlorobenzene, Nitrogen gas was bubbled through it over night due to getting rid of moisture and oxygen gas in it. Fluorinated aryl amines (Wako chemical), Silver tetrafluoroborate, silver tetrafluorantimonate and silver tetrafluorophosphate were used as received (Wako chemical).

Exo-Nadic anhydride

Exo-norbornene 2,3-dicarboxy anhydride (exo-nadic anhydride) was prepared from commercially available endo-nadic anhydride (wako) by thermal isomerization according to the procedure of Caster and Calderon [18]. For this purpose, endo-nadic anhydride(100g, 0.61mol) was heated under nitrogen atmosphere in a three-neck flask at 200ºC for 6h. Contents were cooled to 120ºC and toluene(100ml) was added. The colorless needle crystals obtained on cooling were recrystallized from toluene (yield 32.8%, m.p. 143-144ºC), in agreement with literature.

Exo-N-[3,5-bis(trifluoromethyl)phenyl] nadimide (NI-A)

Exo-nadic anhydride (6.85g, 41mmol) was dissolved in glacial acetic acid (20% w/v) in a three-necked flask. The solution was stirred using a magnetic stirrer and nitrogen was bubbled through it. A stoichiometric amount of 3,5-bis(trifluorooro- methyl)aniline (41mmol) was added in the solution. The temperature raised to 120ºC and the solution was refluxed for 8h. The content was cooled and added to water (600 ml) to pale yellow precipitate N-fluorinated aryl nadimide. The crude product was dried and recrystallized using ethylacetate. The colorless needle crystals were collected.

Yield:68%, m.p.:128-129ºC
IR:3116, 3074, 2962, 2892 cm⁻¹ (CH), 1709 cm⁻¹ (imide C=O)
1H-NMR(ppm):1.46 (d, 1H, J=9.9Hz, H-CH), 1.63 (d, 1H, J=9.9Hz, H-CH), 2.91 (s, 2H, CH), 3.44 (s, 2H, CH), 6.38 (s, 2H, CH=CH), 7.85 (s, 2H, Ar-H), 7.89 (s, 1H, Ar-H)

Syntheses of Other N-substitute nadimides was performed similarly as above NI-A other than the amine.

Exo-N-(4-trifluoromethylphenyl) nadimide (NI-B)
Yield:68%, m.p.:202-204ºC
IR:3112, 3081, 2989, 2888 cm⁻¹ (CH), 1708 cm⁻¹ (imide C=O)
1H-NMR(ppm):1.46 (d, 1H, J=9.9Hz, H-CH), 1.63 (d, 1H, J=9.9Hz, H-CH), 2.89 (s, 2H, CH), 3.43 (s, 2H, CH), 6.37 (s, 2H, CH=CH), 7.55 (q, 4H, Ar-H)

Exo-N-(3-fluoro-4-trifluoromethylphenyl) nadimide (NI-C)
Yield:77%, m.p.:152-153ºC
IR:3097, 2997, 2962, 2889 cm⁻¹ (CH), 1709 cm⁻¹ (imide C=O)
1H-NMR(ppm):1.43 (d, 1H, J=10.2Hz, H-CH), 1.65 (d, 1H, J=10.2Hz, H-CH), 2.89 (s, 2H, CH), 3.42 (s, 2H, CH), 6.37 (s, 2H, CH=CH), 7.31-7.38 (m, 2H, Ar-H), 7.46 (s, 1H, Ar-H)
Exo-N-(pentafluorophenyl)imidide (N-I-D)
Yield: 67%, m.p.: 124-125°C
IR: 3074, 3001, 2958, 2885 cm\(^{-1}\) (CH), 1728 cm\(^{-1}\)
(Imide C=O)
H-NMR (ppm): 1.57 (d, 1H, J=9.8Hz, H-CH), 1.66 (d, 1H, J=9.8Hz, H-CH), 2.96 (s, 2H, CH), 3.42 (s, 2H, CH), 6.36

Exo-N-[3-fluoro-4-{3,5-bis(trifluoromethyl)phenoxy}phenyl]imidide (N-I-E)
Yield: 73%, m.p.: 148-149°C
IR: 3074, 3008, 2966, 2885 cm\(^{-1}\) (CH), 1693 cm\(^{-1}\)
(Imide C=O)
H-NMR (ppm): 1.46 (d, 1H, J=10.0Hz, H-CH), 1.67 (d, 1H, J=10.0Hz, H-CH), 2.89 (s, 2H, CH), 3.43 (s, 2H, CH), 6.37 (s, 2H, CH=CH), 7.22-7.34 (m, 3H, Ar-H), 7.41 (s, 1H, Ar-H), 7.62 (s, 1H, Ar-H)

Exo-N-[3-trifluoromethyl-4-{3,5-bis(trifluoromethyl)phenoxy}phenyl]imidide (N-I-F)
Yield: 68%, m.p.: 176-178°C
IR: 3108, 3074, 2993, 2889 cm\(^{-1}\) (CH), 1705 cm\(^{-1}\)
(Imide C=O)
H-NMR (ppm): 1.46 (d, 1H, J=10.0Hz, H-CH), 1.67 (d, 1H, J=10.0Hz, H-CH), 2.91 (s, 2H, CH), 3.44 (s, 2H, CH), 6.38 (s, 2H, CH=CH), 7.07-7.73 (m, 6H, Ar-H)

Exo-N-[2,4-bis{3,5-bis(trifluoromethyl)phenoxy}phenyl]imidide (N-I-G)
Yield: 87%, m.p.: 49-51°C
IR: 3070, 2993, 2885 cm\(^{-1}\) (CH), 1712 cm\(^{-1}\)
(Imide C=O)
H-NMR (ppm): 1.48-1.64 (m, 2H, CH\(_2\)), 2.81-2.95 (m, 2H, CH), 3.30-3.40 (m, 2H, CH), 6.32 (s, 2H, CH=CH), 6.62-6.70 (m, 1H, Ar-H), 7.47-7.51 (m, 4H, Ar-H), 7.65 (s, 1H, Ar-H)

Exo-N-(adamantyl)imidide (N-I-H)
Yield: 46%, m.p.: 159-160°C
IR: 2989, 2912, 2881, 2854 cm\(^{-1}\) (CH), 1689 cm\(^{-1}\)
(Imide C=O)
H-NMR (ppm): 1.31 (d, 1H, J=9.3Hz, H-CH), 1.45 (d, 1H, J=9.3Hz, H-CH), 1.66 (d, 3H, J=12.1Hz, H-CH), 1.74 (d, 3H, J=12.1Hz, H-CH), 2.11 (s, 3H, CH), 2.48 (s, 6H, CH\(^2\)), 2.64 (s, 2H, CH), 3.22 (s, 2H, CH), 6.17 (s, 2H, CH=CH)

Scheme 1:
\[
\begin{align*}
\text{Scheme 2:} & \\
PdCl\_2 + HCl & \xrightarrow{\Delta} H\text{PdCl}_4 & \xrightarrow{\text{MeOH}} & \text{Pd catalyst} + 2\text{AgCl} \\
\text{chlorobenzene} + AgX & \rightarrow & 2 \left\{ \begin{array}{c} 
\text{MeO} \\
Pd^+ \cdot X^- 
\end{array} \right\} & \xrightarrow{2\text{AgCl}} \\
\end{align*}
\]
Pd(II) catalysts
The precursors of the catalyst were prepared according to the literature [19,20]. The preparation of the final catalyst is also described [21].

Vinyl polymerization of N-substitute nadimides
For a monomer/catalyst mole ratio of 50, a mixture of the palladium chloride dimer (0.21g, 0.40mmol), AgBF4 (0.25g, 1.28mmol) and chlorobenzene were stirred for 15 min at room temperature. The solution of the yellow catalyst was filtered off to remove a precipitate and added to the N-substitute nadimide (40mmol) and chlorobenzene as a condition of 0.24mol/l. The solution was allowed to stir for 36h at room temperature. The polymer was precipitated from the solution. The polymer was recovered from filtration and dried under vacuo.

2.2 Measurement by IR, NMR and GPC
The IR spectra were recorded on a FT-IR spectrophotometer type FT-720 (Horiba). 1H-NMR spectra were recorded on a FT-NMR EX 270 (JEOL) with a frequency range of 270Hz. Gel permeation chromatography (GPC) was performed using Model 510 (Waters) with column (KF-802, KF-803, KF-804L (Toso). The detector was a differential refractometer. The eluent was THF with a 0.8ml/min flow rate. The calculation of molecular weight is based on the standard PS.

2.3 Measurement of dielectric constant
The coating polymer solutions (33wt%) dissolved in 2-heptanone were coated on Al substrate with a spinner to obtain 2μm thickness. Heat treatment was carried out at 80°C for 2min on a hot plate, and 250°C for 1h under nitrogen atmosphere in a convection oven successively. The electrode for dielectric measurements was prepared by vacuum deposition of 2cm diameter upper Al electrodes on the spin-coated polymer layer/Al (MIM structure). The capacitance, C, and dissipation factor, tanδ, of the films were measured by a LCR meter 4284A (YHP) at 1kHz. The dielectric constant, k, of the films was calculated by the formula of parallel plate capacitor:

\[ k = \frac{C \times t}{(k_0 \times A)} \]  (1)

Where C is the capacitance of the MIM element, t is the thickness of the dielectric layer, A is the area of the upper Al electrode and \( k_0(8.854 \times 10^{-12} \text{ F/m}) \) is the space permeability.

2.4 Thermal properties
The coating solutions were dropped into aluminum cells which are used for thermal gravimetric analysis (TGA) and for calorimetric analysis (DSC) measurement and baked under 250°C for 1h under nitrogen atmosphere. TGA was determined by TGA-50 (Shimadzu) at 350°C for 1h. 1% weight loss temperature was determined by TGA with heating from r.t. to 500°C (heating rate: 10°C/min) under nitrogen flow. Calorimetric analysis was done by DSC-50 (Shimadzu) with heating from r.t. to 400°C (heating rate: 10°C/min) under nitrogen flow.

2.5 Mechanical properties
The elastic modulus of the polymer films (1μm) on silicon wafer were measured by Nanoindentater XP (Toyo/MTS).

2.6 Simulation on the chain conformation
We calculated simulation on the chain conformation of the polymer by MM2 method using WinMOPAC 3.0 (Fujitsu).

3. Results and Discussion
3.1 Syntheses of monomers and polymers
N-substitute nadimides (monomer) shown in tab.1 were prepared by reacting fluorinated aryl amines or adamantly amine with exo-nadic anhydride using glacial acetic acid as a solvent. A typical preparation is described in Scheme 1 and 2.

<table>
<thead>
<tr>
<th>Tab.1 Structures of monomer</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono mer</td>
<td>R</td>
<td>Mono mer</td>
</tr>
<tr>
<td>NI-A</td>
<td><img src="https://via.placeholder.com/150" alt="Image" /></td>
<td>NI-E</td>
</tr>
<tr>
<td>NI-B</td>
<td><img src="https://via.placeholder.com/150" alt="Image" /></td>
<td>NI-F</td>
</tr>
<tr>
<td>NI-C</td>
<td><img src="https://via.placeholder.com/150" alt="Image" /></td>
<td>NI-G</td>
</tr>
<tr>
<td>NI-D</td>
<td><img src="https://via.placeholder.com/150" alt="Image" /></td>
<td>NI-H</td>
</tr>
</tbody>
</table>
The nadimides were polymerized using Pd catalyst.

The Mw was found to be higher in the condition as follow: monomer concentration (0.5mol/l), polymerization temperature (r.t.), catalyst anion (SbF₆⁻) (Tab.2). The maximum Mw value 60000 was obtained in the above condition.

Tab.2 Effect of different condition

<table>
<thead>
<tr>
<th>Monomer concentration (mol/l)</th>
<th>Temp. (°C)</th>
<th>Catalyst</th>
<th>Anion: X</th>
<th>Molecular weight (Mw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24 r.t.</td>
<td>BF₄⁻</td>
<td>25000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50 r.t.</td>
<td>BF₄⁻</td>
<td>30000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.75 r.t.</td>
<td>BF₄⁻</td>
<td>28000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50 50</td>
<td>BF₄⁻</td>
<td>28000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50 r.t.</td>
<td>PF₆⁻</td>
<td>13000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50 r.t.</td>
<td>SbF₆⁻</td>
<td>60000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Monomer : NI-A, Pd cat./Monomer=1/50, Time 24h

Under similar conditions of polymerization using a various nadimides, NI-E was found to give higher Mw compared to the others. The polydispersity index (Mw/Mn) was of the order 1.20 to 1.47 (Tab.3).

Tab.3 Result of vinyl polymerization at various monomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Mw</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI-A</td>
<td>25000</td>
<td>17000</td>
<td>1.47</td>
<td>46</td>
</tr>
<tr>
<td>NI-B</td>
<td>19000</td>
<td>14000</td>
<td>1.36</td>
<td>78</td>
</tr>
<tr>
<td>NI-C</td>
<td>11000</td>
<td>8500</td>
<td>1.29</td>
<td>76</td>
</tr>
<tr>
<td>NI-D</td>
<td>22000</td>
<td>18000</td>
<td>1.22</td>
<td>72</td>
</tr>
<tr>
<td>NI-E</td>
<td>49000</td>
<td>36000</td>
<td>1.36</td>
<td>49</td>
</tr>
<tr>
<td>NI-F</td>
<td>10000</td>
<td>7800</td>
<td>1.28</td>
<td>40</td>
</tr>
<tr>
<td>NI-G</td>
<td>24000</td>
<td>20000</td>
<td>1.20</td>
<td>23</td>
</tr>
<tr>
<td>NI-H</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>95</td>
</tr>
</tbody>
</table>

Pd cat./Monomer=1/50, Time 24h, Temp. r.t., Catalyst anion:BF₄⁻

*Data was not obtained because the polymer from NI-H was insoluble in any organic solvent.

In IR spectra of the polymers, sharp absorption bands were around 1700cm⁻¹ due to imide C=O. The IR spectrum of the polymer from NI-A (pNI-A) is shown in Fig.1.

In ¹H-NMR spectra of the polymers, olefinic protons (around δ=6.4) signals were disappeared due to its polymerization.

Fig.1 IR spectrum of p(NI-A) film on Si wafer after heat treatment at 250 °C for 1h

The polymers from all monomers expect pNI-H were good solubility in ketones as acetone and 2-heptanone, but poor solubility in esters, ethers and amides solvent. The pNI-H was poor solubility in a variety of solvent. We did not obtain some properties of pNI-H.

The polymer film is able to be prepared with lower temperature just to remove casting solvent, because the polymer has no ring closure reaction like general polyimides.

3.2 Dielectric constant

The dielectric constants of the polymers are shown in tab.4. The range of the dielectric constant was from 2.31 to 2.65 with the different imide side-chain structures (R shown tab.1). The pNI-A containing 3,5-bis(trifluoromethyl)phenyl unit with symmetry structure, that induces to cancel out polarization of the substituted unit, was the lowest dielectric constant in the evaluated polymers. However pNI-D containing perfluorophenyl unit with symmetry structure like pNI-A had dielectric constant of 2.62 higher by 0.3 than that of pNI-A. Both pNI-A and pNI-D fluorine contents are about 30wt%, but large difference dielectric constant of the both polymers. The difference is about 0.3. This result is thought to be by bulky 3,5-bis(trifluoro methyl)phenyl unit of side-chain in order to lead to decrease packing density and increase larger free volume than perfluorophenyl unit.

3.3 Thermal properties and mechanical property

Thermal properties are shown in tab.5. DSC shows that the every polymers except for NI-G have high glass transition temperature (Tg) at
higher than 378°C. TGA shows that the polymers except the pNI-G were heat stable higher than 350°C under nitrogen flow. Only pNI-G had poor thermal stability and its melting point was at 276°C.

Tab.4 Dielectric constant at 1kHz of the various polymers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>K</th>
<th>tanδ</th>
<th>Content of fluorine (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI-A</td>
<td>2.31</td>
<td>0.0042</td>
<td>30.4</td>
</tr>
<tr>
<td>NI-B</td>
<td>2.50</td>
<td>0.0062</td>
<td>18.5</td>
</tr>
<tr>
<td>NI-C</td>
<td>2.65</td>
<td>0.0055</td>
<td>23.4</td>
</tr>
<tr>
<td>NI-D</td>
<td>2.62</td>
<td>0.0055</td>
<td>28.9</td>
</tr>
<tr>
<td>NI-E</td>
<td>2.46</td>
<td>0.00161</td>
<td>27.4</td>
</tr>
<tr>
<td>NI-F</td>
<td>2.32</td>
<td>0.0064</td>
<td>31.9</td>
</tr>
<tr>
<td>NI-G</td>
<td>2.37</td>
<td>0.0036</td>
<td>32.8</td>
</tr>
</tbody>
</table>

We think that the polymer except of the pNI-G has high thermal stability due to rigid coil-main structure. On the other hand, we thought that pNI-G had high thermal stability. But it did not have good thermal stability. Reason of the poor heat stability is due to the large bulky side-chain. The large bulky side-chain might be to induce main-chain-scission of pNI-G.

We measured mechanical properties of pNI-A. The elastic modulus of NI-A was 4.3GPa by nanoindentation.

Tab.5 Glass transition temperature (Tg) and weight loss at 350°C for 1h and 1% weight loss temperature (Tdl) under nitrogen flow.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Tg (°C)</th>
<th>Weight loss at 350°C/1h(wt%)</th>
<th>Tdl (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NI-A</td>
<td>&gt;400</td>
<td>&lt;0.5</td>
<td>420</td>
</tr>
<tr>
<td>NI-B</td>
<td>&gt;400</td>
<td>&lt;0.5</td>
<td>443</td>
</tr>
<tr>
<td>NI-C</td>
<td>&gt;400</td>
<td>&lt;0.5</td>
<td>433</td>
</tr>
<tr>
<td>NI-D</td>
<td>378</td>
<td>&lt;0.5</td>
<td>420</td>
</tr>
<tr>
<td>NI-E</td>
<td>&gt;400</td>
<td>&lt;0.5</td>
<td>416</td>
</tr>
<tr>
<td>NI-F</td>
<td>&gt;400</td>
<td>&lt;0.5</td>
<td>413</td>
</tr>
<tr>
<td>NI-G</td>
<td>-*</td>
<td>10</td>
<td>281</td>
</tr>
</tbody>
</table>

* NI-G has the melting point at 276°C

3.4 Simulation of polymer conformation

We simulated the chain conformation of the pNI-A by MM2 method. The simulated result is shown in Fig.2. The simulated chain conformation looks like the coil-shaped main-chain polymer structure with a bulky side-chain imide unit out of the main-chain as we expected. We believe that the polymer has coil-shaped so it has large free volume. The large free volume endows its extremely low dielectric constant. From the calculated chain conformation, it was found that one cycle of the coil has 8 monomers (molecular weight is about 3000). The Mw of 25000 of the pNI-A corresponds to about 8 cycles of the coil.

Fig.2 Frame taken from simulation on the chain conformation of the pNI-A.

4. Conclusion

The novel high Tg low dielectric constant fluorinated poly(norbornene imide)s was obtained for interlayer dielectric applications in microelectronics. The low dielectric constant of the polymer was induced by it that the coil-shaped main-chain structure with a bulky and symmetry side-chain out of the main-chain. The coil-shaped structure leads (1) to decrease packing density and increase free volume and (2) to cancel out polarization of the substituted unit. Especially the polymer containing 3,5-bis(trifluoromethyl) phenyl unit induces to become the lowest dielectric constant because of its bulkiness and symmetry. The polymers have good thermal properties and suitable mechanical properties. The film is able to be prepared with lower temperature (just remove casting solvent). We hope the fluorinated poly (norbornene imide)s are one of the new generation low dielectric candidates.

5. Acknowledgments

We appreciate that the measurements of mechanical properties by nanoindentation were supported by Toyo and MTS.
References