Synthesis of Wholly Alicyclic Polyimides from *N*-Silylated Alicyclic Diamines

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A synthetic method to give wholly aliphatic polyimides with high molecular weights has been developed. The polymerization of cyclobutanetetracarboxylic dianhydride **(CBDA)** with 5-trimethylsilylamino-*N*-trimethylsilyl-1,3,3-trimethylcyclohexanemethylamine **(NSD-1)** or 2,5(2,6)-bis(*N*- trimethylsilylaminomethyl)bicyclo[2.2.1]heptane **(NSD-2)** was carried out in polar aprotic solvents at room temperature, giving poly(amic acid trimethylsilyl ester)s **(PATSEs)** as precursor polymers which were hydrolyzed to poly(amic acid)s **(PAAs)** with inherent viscosities up to 0.74 dL g^{-1}. Both polyimide precursors were readily converted to the corresponding polyimides by thermal treatment.

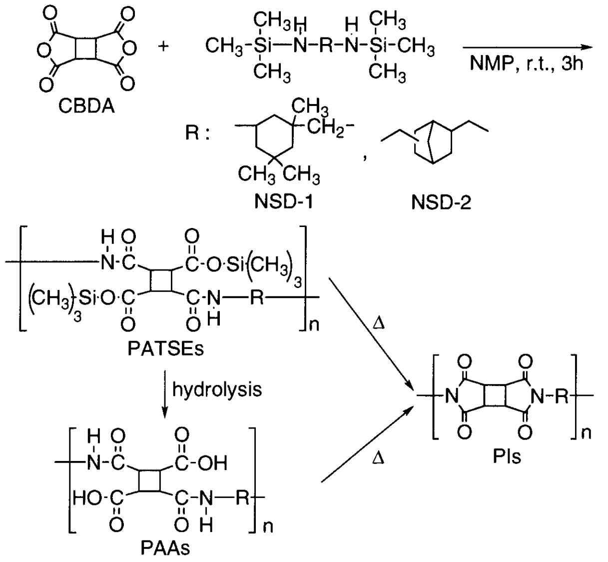
Polyimides (**PIs**) are widely used in microelectronics packaging as buffer coats, α-ray shielding and passivation films, because of their excellent thermal, chemical, mechanical and electrical properties.[1] Recently, aliphatic and alicyclic **PIs** have been interested in the applications as optoelectronics and interlayer dielectric materials, because of the better colorless transparency and the low dielectric constant.[2,3] They hardly form inter- or intramolecular charge transfer complexes, which increase the dielectric constant and lower the transparency. Furthermore, alicyclic structures are effective to decrease a molecular density due to their bulkiness, giving **PIs** with a low dielectric constant.

Generally speaking, the reaction of dicarboxylic anhydrides with highly basic diamines such as aliphatic and alicyclic diamines first provides an amic acid and then a free amine forms a carboxylic acid salt with carboxyl group of amic acid due to its high basicity. In the polymerization, the salt formation inhibits the formation of high molecular weight **PAA**. Sometimes, solution imidization and acid-chloride methods are available as previously reported.[4,5] Furthermore, we reported the synthesis of **PIs** from *N*-silylated aromatic diamines and aromatic tetracarboxylic dianhydrides.[6] For extension of this work, we were interested in this method for a synthesis of wholly alicyclic **PIs.**

In this paper, we describe the successful synthesis of wholly alicyclic **PIs** with relatively high molecular weights by the polymerization of **CBDA** with *N*-silylated alicyclic diamines.

As alicyclic diamines, 5-amino-1,3,3-trimethylcyclohexanemethylamine and 2,5(2,6)-bis(aminomethyl)bicyclo-[2.2.1]heptane were selected and silylated with trimethylsilyl chloride in the presence of triethylamine in toluene.

The ring-opening polyaddition of **CBDA** with *N*-silylated diamines, **NSD-1** and **NSD-2** was carried out in various solvents at room temperature for 3 h (Scheme 1). Polymerizations proceeded in homogeneous state without salt formation, giving poly(amic acid trimethylsilyl ester)s (**PATSEs**), which were converted to the corresponding **PAAs** by hydrolysis. The inherent viscosities of **PAAs** obtained reached up to 0.74 dL g^{-1}. These results are summarized in Table 1.



Scheme 1. Synthesis of Wholly Alicyclic Polyimides from *N*-Silylated Alicyclic Diamines

Table 1. Synthesis of wholly alicyclic poly(amic-acid) (PAA)[a]

Polymer	Diamine	Solvent	Yield %	Inherent viscosity[b] dL g^{-1}
PAA-1	NSD-1	NMP	100	0.73
PAA-2	NSD-2	NMP	91	0.58
PAA-3	NSD-1	DMAc	94	0.74
PAA-4	NSD-2	DMAc	84	0.46
PAA-5	NSD-1	DMSO	98	0.53
PAA-6	NSD-2	DMSO	84	0.50
PAA-7	NSD-1	THF	97	0.39
PAA-8	NSD-2	THF	67	0.30

[a]Polymerization was carried out with 1.0 mmol of each monomer (CBDA and diamine) in the solvent at room temperature for 3 h under nitrogen. Monomer concentration: 30 wt%. [b]Measured at a concentration of 0.5 g dL^{-1} in NMP at 30 °C.

Polymers were confirmed to be the corresponding **PATSEs** and **PAAs** by IR spectroscopy and elemental analysis. The IR spectra of **PATSEs** showed characteristic amide and silyl ester absorptions at 1654 and 1716 cm^{-1}. On the other hand, two characteristic amide, carboxyl, and hydroxyl group absorptions at 1654,1720, and 3200-3700 cm^{-1}, were observed for **PAAs** (Figure 1). **PATSEs** were soluble in tetrahydrofuran (**THF**),

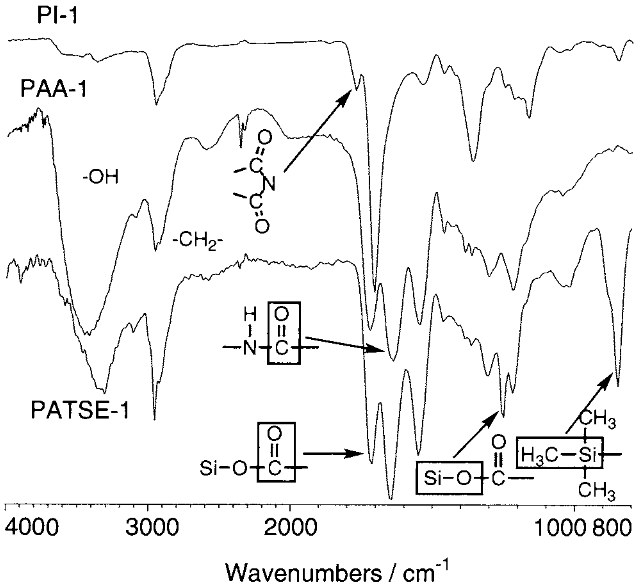


Figure 1. Change of IR spectra in PATSE-1, PAA-1 and PI-1 films.

chloroform, and polar aprotic solvents such as 1-methyl-2-pyrrolidinone (**NMP**), *N*,*N*-dimethylacetamide (**DMAc**) and dimethyl sulfoxide (**DMSO**) at room temperature. On the other hand, **PAAs** were only soluble in polar aprotic solvents.

These polyimide precursors were readily converted to the corresponding **PIs** by thermal treatment. The traces of thermogravimetric analysis for **PAA-1** and the corresponding polyimide (**PI-1)** are shown in Figure 2. The rapid weight loss for **PAA-1** was observed at 200-350 °C. In this range, the weight loss was 9.6% which is in good agreement with the value of weight loss (9.8%) calculated from the elimination of water due to the imidization. A 10% weight loss in nitrogen for **PI-1** was 420 °C. This result shows the thermal stability is lower than that of aromatic **PIs**, whereas it is enough for microelectronics uses.

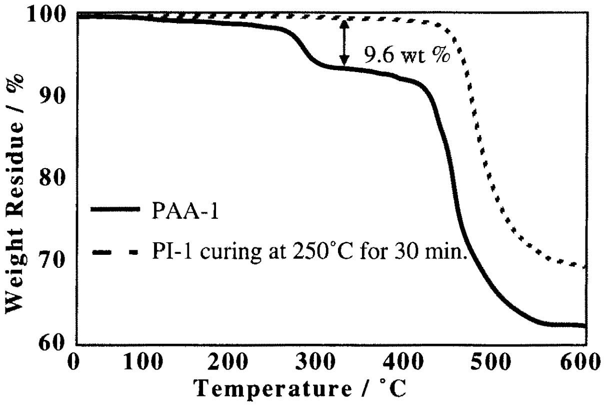


Figure 2. TG traces of PAA-1 and PI-1 under nitrogen.

The IR spectrum of thermally treated **PAA-1** film (250 °C for 30 min), is shown in Figure 1. Where characteristic imide absorptions at 1780 and 1720 cm^{-1} were appeared and the absorption due to the carboxylic acid groups at around 3300 cm^{-1} was completely disappeared. The solubility of alicyclic **PIs** were low and they were only soluble in *m*-cresol and sulfuric acid.

In summary, the wholly alicyclic **PIs** were successfully prepared by *N*-silylated diamine method. This method will provide a potentially efficient route for the synthesis of aliphatic **PIs**.

References and Notes

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