

Synthesis and Characterization of Novel Polyimides Containing Bulky Trimethylsilylphenyl Group

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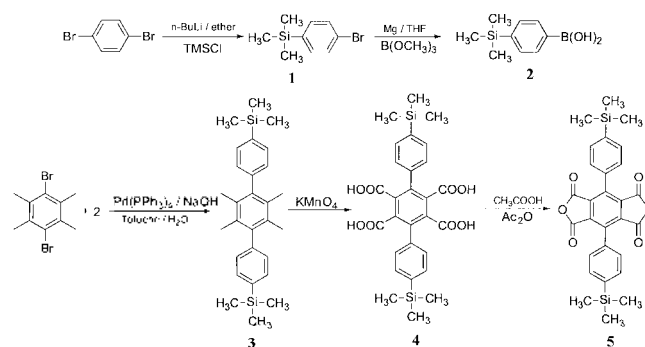
Aromatic polyimides possess outstanding thermal, mechanical and electrical properties as well as excellent chemical resistance. A large number of new polyimides with unique properties have been introduced for various industrial and consumer product applications since their commercialization in the beginning of the 1960s.¹⁻⁵ One of the directions in the development of new polyimides is the synthesis and study of extended rod or rigid rodlike aromatic polyimides because such polyimides have potential as materials for thermally stable high modulus, high-strength fibers, as materials with low thermal expansion coefficient (TEC) for packaging materials in microelectronic applications, or as materials for gas separation membranes. In general, rodlike polymers, due to strong enthalpy interactions and the minimal increase in conformational entropy associated with their dissolution or melting, are basically intractable or only processable under extreme conditions.⁶ To overcome these difficulties, structural modifications of the polymer backbone, such as the addition of bulky lateral substituents, flexible alkyl side chains, noncoplanar biphenylene moieties, and kinked comonomer have been utilized to modify the polymer properties, either by lowering the interchain interactions or by reducing the stiffness of the polymer backbone.⁷⁻⁹

It is known that the interesting features of silicon containing polymers are high thermal stability, gas permeabilities, weather resistance, insulating properties, and so on.^{10,11} Recently, many studies have been reported that polymers containing trimethylsilyl derivatives has excellent gas permeability.¹²⁻¹⁷

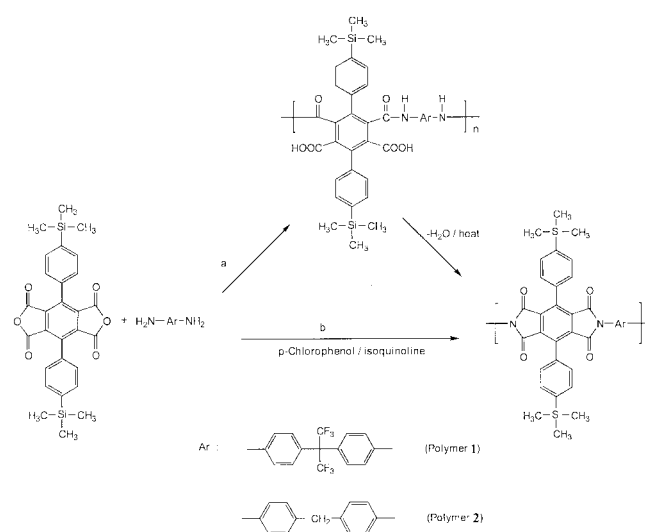
Soluble polyimides containing bulky and flexible trimethylsilyl offer particular promise in gas separation membrane application due to their superior mechanical property, high permeability and permselectivity. Thus, we tried to synthesize new polyimides containing bulky *p*-trimethylsilylphenyl group, which is expected to give good solubility and good physical properties. In this paper, we report the synthesis and characterization of new soluble polyimides derived from new pyromellitic dianhydride with bulky *p*-trimethylsilylphenyl group and conventional aromatic diamines.

Monomer synthesis. The synthetic route of the monomer is shown in Scheme 1. 1,4-dibromodurene (**1**) was obtained by bromination of durene. The obtained 1,4-dibromodurene was silylated for the synthesis of *p*-trimethylsilylbromobenzene (**2**) which was reacted with trimethylborate by Grignard

reaction to generate *p*-trimethylsilylbenzeneboronic acid (**3**). 1,4-Bis(4'-trimethylsilylphenyl)durene (**4**) was obtained by Suzuki coupling reaction of *p*-trimethylsilylbenzeneboronic acid (**3**) and 1,4-dibromo durene (**1**). 1,4-Bis(4'-trimethylsilylphenyl)pyromellitic dianhydride (BTPD) (**5**) was obtained by oxidation and dehydration of 1,4-bis(4'-trimethylsilylphenyl)durene (**4**). The yields in each steps were very high. The obtained 1,4-bis(4'-trimethylsilylphenyl)pyromellitic dianhydride (**5**) is confirmed by ¹H-NMR and FT-IR analyses. The proton peaks of trimethylsilyl and aromatic ring appeared at 0.3 ppm and 7.2-7.5 ppm, respectively. In the FT-IR spectrum, instead of the broad acid peak disappeared, character-



Scheme 1



Scheme 2

istic carbonyl group of dianhydride peak appeared at 1790 cm^{-1} and 1870 cm^{-1} .

Polymer synthesis. There are two major methods for the preparation of polyimides (Scheme 2). One procedure involves two steps and proceeds *via* poly(amic acids) intermediate. The other is a one-step solution polymerization. The one step method has some advantages over the two-step method. Polyimides in bulk are more easily produced, and polyimides with higher crystallinity can be more readily obtained.¹⁸ The one step method is also useful for unreactive diamines and dianhydrides which can not form high molecular weight polyamic acids by the two step method.^{19,20} The disadvantage of the one step method is that insoluble polyimides can not form high molecular weight polyimides because of premature precipitation. We tried two major methods. When polyimides were synthesized by the conventional two step procedure involving a ring-opening polyaddition and subsequent thermal cyclodehydration, the polymer molecular weight was not enough for preparing of the free stand film. It may be suggested that dianhydride is deactivated by steric hindrance of trimethylsilylphenyl. Otherwise, the one-step polymerization at high temperature, as shown in synthetic route b, resulted in high viscosity. BTPD and diamines were reacted in *p*-chlorophenol with 2% (w/w) isoquinoline as a catalysts and a polymer concentration around 5% (w/w). After the first part of the reaction was proceeded at 60 °C for 2 h, the temperature was raised slowly up to 250 °C and maintained at that temperature for 5 h. The water formed during imidization was removed continuously with a stream of nitrogen. After polymerization, *p*-chlorophenol added to the reaction mixture, and the reaction mixture precipitated into methanol. The polymer was filtered and washed with methanol several times. The yields of polymerization were 87-90%. The results of the polymerization are summarized in Table 1. The high molecular weight polyimides with high inherent viscosities of 0.89-1.06 dL/g were obtained. The elemental analysis values agreed quite well with the calculated values for the proposed structure of polyimides. The IR spectra of the polymers also supported the formation of polyimides. The characteristic absorption bands of the imide ring appeared near 1780 (asym C=O str), 1720 (sym C=O str), 1390 (C-N str), and 745 cm^{-1} (imide ring deformation).

The solubility of polyimides was tested in various solvents. Owing to bulky and flexible trimethylsilylphenyl group, the synthesized polyimides were amorphous and sol-

uble in a number of common organic solvents such as *m*-cresol, NMP and *p*-chlorophenol. The thermal properties of the polyimides were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA thermograms showed that the 5% weight losses in nitrogen were 500-510 °C, 20% at 530-550 °C, and 35% at 600-620 °C. Thermal transitions (T_g) of polyimide **1** and polyimide **2** were investigated by DSC in 275 °C and 307 °C, respectively. The results of the TGA and DSC analyses showed the general excellent thermal stability of the polyimides.

The tensile properties of the polyimide films were studied. The films had tensile strength of 58-72 MPa, elongation at break of 5.64-6.93%, and tensile modulus of 1.7-1.5 Gpa. From the above results, the new synthesized polyimides containing bulky and flexible substituents by one-step method have good solubility, and good thermal and mechanical property. Now we are progressing the study of gas separation properties of new polyimides.

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Table 1. The Results of Elemental Analysis and Viscosities of Polymers

Polymer	Diamine	Elemental Analysis (%)			η_{inh}^c	
			C	H		N
Polymer 1 (C ₄₃ H ₃₃ N ₂ O ₄ F ₆ Si ₂)	6FDA ^a	Cal.	63.5	4.2	3.45	1.06
		Found	62.7	4.12	3.61	
Polymer 2 (C ₄₁ H ₃₆ N ₂ O ₄ Si ₂)	MDA ^b	Cal.	72.78	5.33	4.14	0.89
		Found	72.59	5.21	4.06	

^a4,4'-(hexafluoroisopropylidene)dianiline. ^b4,4'-methylenedianiline.
^c0.05 g/dL in DMAc at 30 °C