

## Imide-Containing Ladder Polyphenylsilsesquioxanes with High Thermal Stability and Thermoplastic Properties

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**ABSTRACT:** This work reports for the first time the synthesis of ladder polyphenylsilsesquioxanes containing imide building blocks as parts of the main parallel chains. The ladder structure of the synthesized polymers was documented by means of small angle X-ray scattering (SAXS) measurements. The obtained ladder polymers exhibit stability with respect to decomposition up to temperatures as high as 460°C; additionally, they have melting points far below their decomposition temperatures, which make them interesting candidate materials for thermoplastic processing. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40085.

**KEYWORDS:** polyimides; thermoplastics; inorganic polymers; thermal properties

Received 5 July 2013; accepted 20 October 2013

DOI: 10.1002/app.40085

### INTRODUCTION

Polysilsesquioxanes are silicon-containing polymers with the formula  $(\text{RSiO}_{3/2})_n$  where R can be hydrogen, alkyl, or aryl groups.<sup>1–5</sup> Currently, four classes of polysilsesquioxane structures are known: amorphous, ladder, cube, and open cube. The ladder polysilsesquioxanes consist of two linear syndiotactic molecular chains that are linked periodically by siloxane units, Si—O—Si.<sup>5–7</sup> Their structure has been studied using X-ray methods. These studies revealed that the distance between the parallel chains is about 12.5 Å; whereas the monomer length (repeating intrachain distance) is about 5 Å.<sup>7–10</sup> These dimensions relate the appearance of two reflexes in their X-Ray diffractograms, at  $2\theta$  values of 6.5°–8° and 18°–20°, respectively.<sup>7–9</sup> Depending on the side groups attached to the Si-atoms of the main parallel chains, the interchain distance can however vary. On the other hand, ladder polysilsesquioxanes have been also studied by <sup>29</sup>Si-NMR spectroscopy. These studies revealed that the siloxane unit present in the parallel main chains (T3 unit) is characterized by a broad signal at –80 ppm.<sup>11</sup>

The ladder architecture of these materials leads to interesting properties. They have been shown to present high thermo-oxidative stability up to temperatures of 400–500°C,<sup>6,8</sup> high glass transition temperatures,<sup>12</sup> and high chemical stability. Thus, these polymeric compounds are currently used as coating materials<sup>13</sup> and insulators<sup>12</sup> for high temperature applications.

Ladder polysilsesquioxanes with different side groups have been developed in order to introduce new properties. Thus, by add-

ing perfluorated side groups, it is possible to obtain hydrophobic coating materials.<sup>14</sup> Furthermore, it is also possible to have side groups with reactive functionalities, such as in aminopropylsilsesquioxanes, which allow the ladder structures for further reactions.<sup>15</sup>

Polyphenylsilsesquioxanes have been intensively studied among polysilsesquioxanes. These polymers were first described in 1960 by von Braun.<sup>5,11</sup> Typically, they are obtained by hydrolysis and further polycondensation of tri-functional monomers like Ph-SiX<sub>3</sub>, with X being chlorine, alkoxide or acetate groups. By using these methods, special care needs to be taken regarding the purity of the reagents and the synthesis conditions. Examples of these synthesis conditions are a strict control of the reagents concentration,<sup>5</sup> removal of products or side products during the reaction,<sup>5,8</sup> and the use of base catalysts.<sup>8</sup> Otherwise, no ladder structures are obtained.<sup>8</sup> The need for performing the synthesis of polyphenylsilsesquioxanes under strict conditions implies high production costs, which hinder a broader use of polymers with ladder structure in large amounts. Thus, it is necessary to develop alternative synthesis methods that allow an easier and cost-effective production of polyphenylsilsesquioxanes with ladder structure.

Polyphenylsilsesquioxanes became of technical interest as some of them show a melting point below their degradation temperature,<sup>12</sup> thus allowing for their thermoplastic processing. The combination of high thermal stability and thermoplastic properties is unusual to be present in the same material, making

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polyphenylsilsequioxanes interesting candidates for the mass production of structural components for high temperature applications.

We have shown recently that it is possible to tailor the thermal properties of linear silicon-containing polyimides by adjusting the composition and structure of the building blocks of the imide unit.<sup>16</sup> Therefore, it can be expected that by introducing imide units into the molecular structure of ladder polyphenylsilsequioxanes, it is possible to influence the properties of these polymers in order to expand their application spectrum and improve their process-ability without sacrificing their high thermal stability. Thus, the aim of this work is to demonstrate that with our preparative method it is possible to produce different ladder polyphenylsilsequioxanes in high yields. Furthermore, we emphasize within this study that it is possible to tailor their properties by adjusting the molecular structure of the ladder polymers in order to target specific thermal profiles.

## EXPERIMENTAL

### Materials

All reagents and solvents were purchased from Sigma Aldrich (Munich, Germany). THF and hexane were dried under argon atmosphere using Na/K alloy; whereas dimethylacetamide (DMAc) was purchased anhydrous and used as-received. The other reactants were used as-purchased, without further purifi-

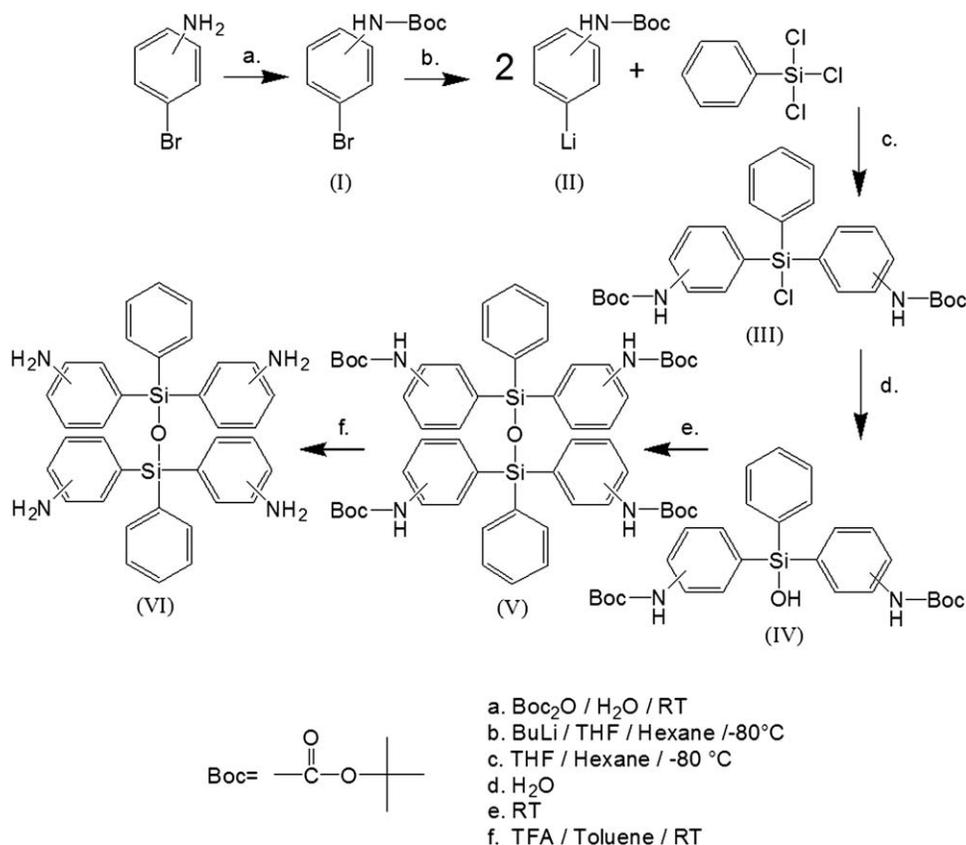
cation. All reactions were carried out under inert gas atmosphere, unless otherwise stated.

### Characterization

<sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded on a Bruker DRX 500 MHz spectrometer. All NMR samples were prepared in THF-d<sup>8</sup>. The FTIR measurements were carried out on a Perkin Elmer 1600 spectrometer using KBr pellets. The mass spectrometry characterization was performed on a Bruker Franzen Esquire LC mass spectrometer by using the electrospray ionization (ESI) technique. Simultaneous thermal analysis (STA) (i.e., thermogravimetric analysis coupled with differential thermal analysis, TGA/DTA) was performed on a Netzsch STA 449C Jupiter with a heating rate of 10°C/min under argon and oxygen atmospheres using a gas flow of 25 mL/min. The melting points of the polymers were determined from the STA data. The SAXS measurements of non-oriented samples were performed at the BESSY  $\mu$ Spot Beamline (7T-WLS71- $\mu$ Spot) in Berlin with the support of the Helmholtz-Zentrum Berlin for Materials and Energy under the umbrella of the projects 2009\_1\_80923 and 2009\_1\_81145. The measurements were carried out by Dr. Ivo Zizak, BESSY  $\mu$ Spot beamline.

### Synthesis of the Monomers

**1,1,3,3-Tetra-(4-aminophenyl)-1,3-diphenyldisiloxane and 1,1,3,3-Tetra-(3-aminophenyl)-1,3-diphenyldisiloxane.** The synthesis of the Si-based tetraamines as building blocks for the ladder



**Figure 1.** Synthesis method used to produce the Si-based tetraamines as monomeric building blocks for the ladder polyphenylsilsequioxanes.

polyphenylsilsesquioxanes consisted of six steps, which are summarized in Figure 1.

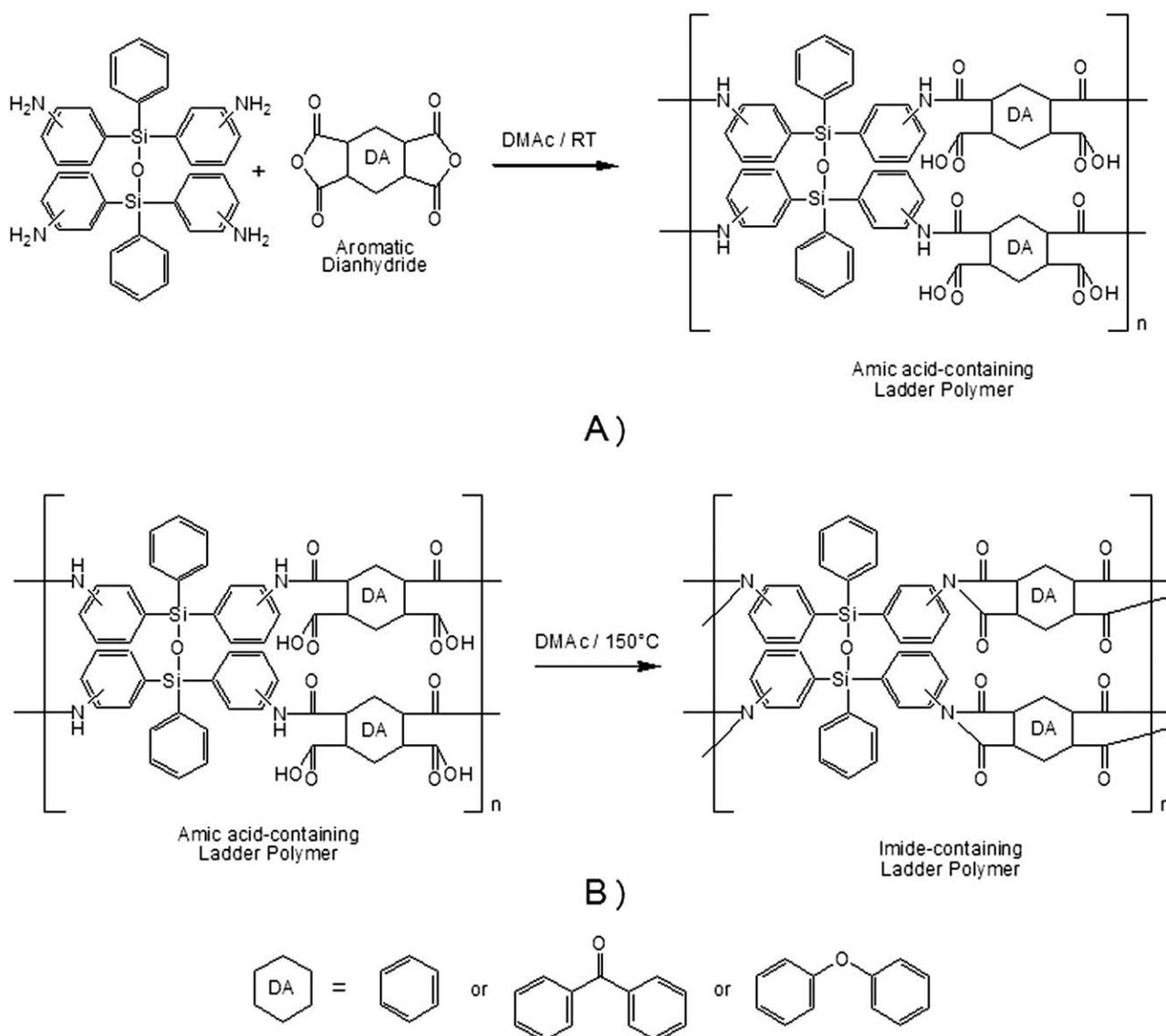
The first step was the protection of the amino group of the starting compound bromoaniline *via* its conversion into a *tert*-butyl carbamate (Boc) group. Thus, 20 g (0.116 mol) of either *p*-bromoaniline or *m*-bromoaniline were dispersed in 234 mL of water. Subsequently, di-*tert*-butyl dicarbonate was melted at 80°C and added dropwise to the stirred suspension of bromoaniline. The mixture was stirred at ambient temperature for 24 h. The resulting solid (I) was filtered, washed several times with water and dried at 80°C for 12 h.

The second step consisted in the lithiation of I. 15 g of I were dissolved in 350 mL of THF. Separately, 23.5 mL of a solution of butyl lithium (BuLi) in hexane was diluted in 150 mL of hexane and added dropwise to the stirred THF solution of I at -80°C. The reacting mixture was stirred for five hours at

-80°C in order to produce II. Since II is only stable at temperatures below -50°C, it was used for the next step without further purification and characterization.

In the next step, II was reacted with trichloro phenylsilane. Thus, 50 mL of a solution of trichloro phenylsilane in Hexane (0.46 mol/L) was added dropwise to the solution of II at -80°C. The molar ratio between II and trichloro phenylsilane was 2 to 1. The mixture was stirred for 5 h at -80°C in order to obtain III. The solvents were removed under reduced pressure ( $10^{-2}$  mbar).

The fourth step involved the hydrolysis of compound III, which was rinsed three times with each 150 mL of water at room temperature, leading to the formation of IV. Since the silanol groups of IV are reactive, they underwent condensation reactions and thus IV converted into V, which was dried at 80°C for 3 h.



**Figure 2.** Synthesis of the imide-containing ladder polyphenylsilsesquioxanes: (A) Polymerization of the Si-based tetraamines (B) Imidization reaction.

The last step was the removal of the carbamate protecting groups present in **V**. Thus, 0.014 mol of **V** were dissolved in 45 mL of toluene. Thereafter, 0.07 mol of trifluoroacetic acid (TFA) were added dropwise to this solution. The mixture was stirred at ambient temperature for 3 h. Toluene was subsequently removed under reduced pressure and the resulting solid **VI** was rinsed with a 0.5M NaOH solution until pH 7, washed three times with water and dried at 50°C for 12 h.

*1,1,3,3-Tetra-(4-aminophenyl)-1,3-diphenyldisiloxane*.  $^1\text{H-NMR}$  (500 MHz, THF- $d_8$ ,  $\delta$ ): 6.7 (d, 8H, -NH $_2$ ), 7.16 (d, 14H, Phenyl CH), 7.72 (s, 12H, Phenyl CH);  $^{13}\text{C-NMR}$  (500MHz, THF- $d_8$ ,  $\delta$ ): 109 (Phenyl CH), 116 (Phenyl CH), 128 (Phenyl CH), 132 (Phenyl CH), 134 (Phenyl C-Si-), 147 (Phenyl C-NH $_2$ );  $^{29}\text{Si-NMR}$  (500MHz, THF- $d_8$ ,  $\delta$ ): -80; IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ )=3600 (m, -NH $_2$ ); 3385 (s, -NH $_2$ ); 1430 (s, Si-C Phenyl); 1130 (s, Si-C Phenyl); 1068 (s, Si-O); 700 (s, Si-C Phenyl).

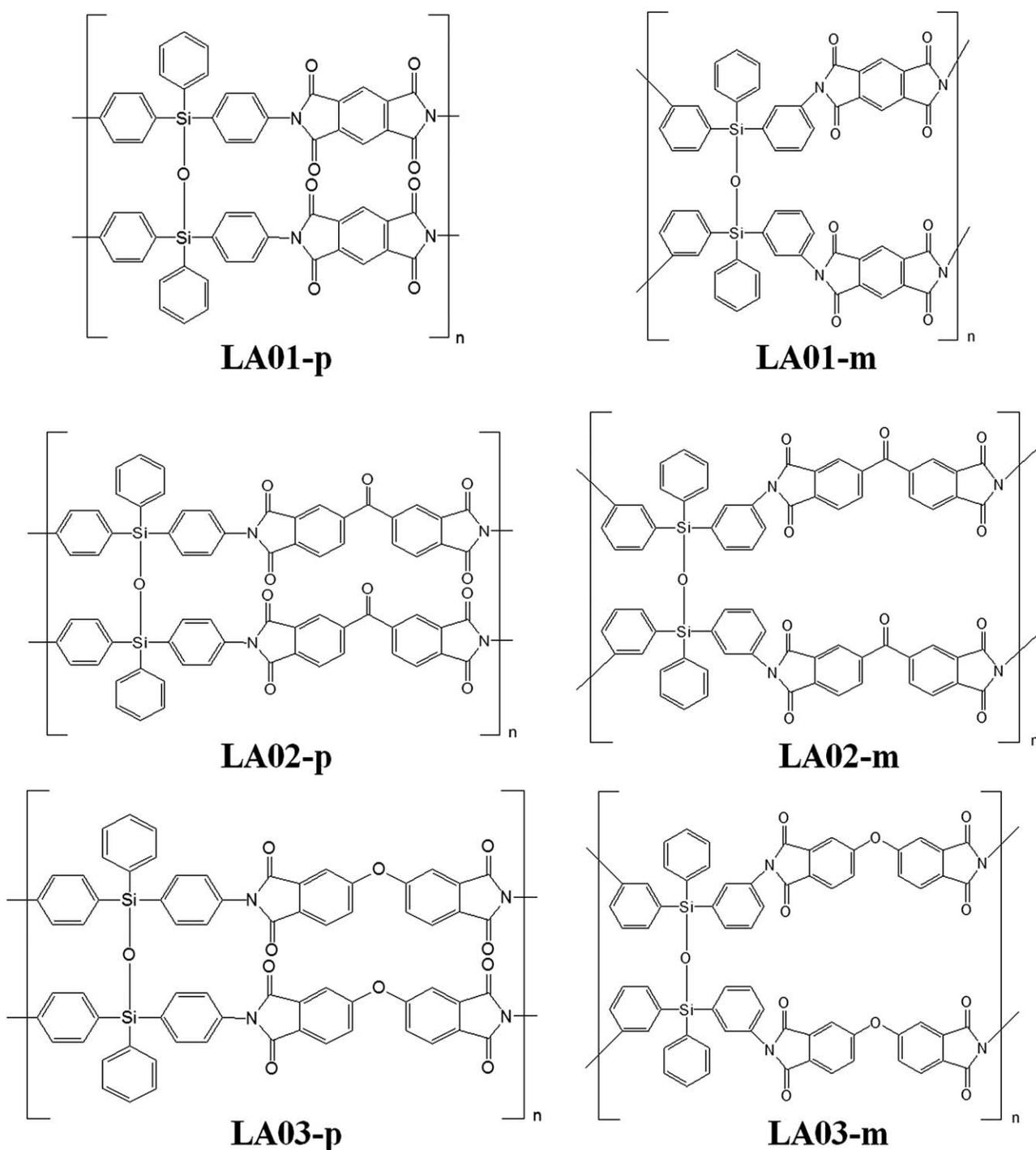
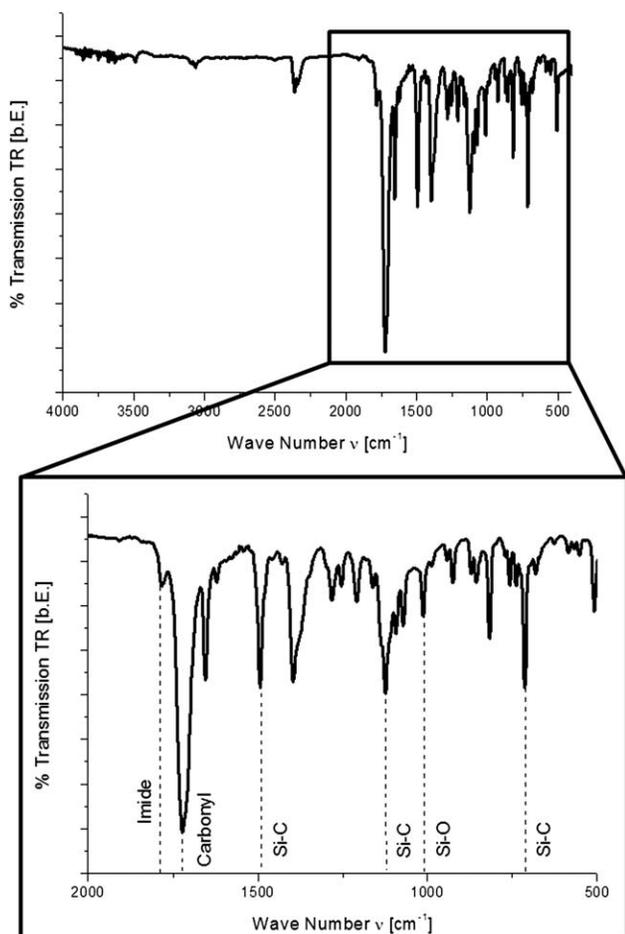


Figure 3. Obtained imide-containing ladder polyphenylsilsesquioxanes.

*1,1,3,3-Tetra-(3-aminophenyl)-1,3-diphenyldisiloxane.*  $^1\text{H}$  NMR (500MHz, THF- $d^8$ ,  $\delta$ ): 6.42 (d, 8H,  $-\text{NH}_2$ ), 6.57 (d, 8H, Phenyl CH), 6.70 (s, 8H, Phenyl CH), 6.79 (t, 10H, Phenyl CH);  $^{13}\text{C}$ -NMR (500 MHz, THF- $d^8$ ,  $\delta$ ): 114 (Phenyl CH), 118 (Phenyl CH), 120 (Phenyl CH), 123 (Phenyl C-Si-), 127 (Phenyl CH), 130 (Phenyl CH), 134 (Phenyl CH), 149 (Phenyl C- $\text{NH}_2$ );  $^{29}\text{Si}$  NMR (500MHz, THF- $d^8$ ,  $\delta$ ): -80; IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3399 (m,  $-\text{NH}_2$ ); 3071 (s,  $-\text{NH}_2$ ); 1432 (s, Si-C Phenyl); 1135 (s, Si-C Phenyl); 1068 (s, Si-O); 691 (s, Si-C Phenyl).

**Synthesis of the Imide Containing Ladder Polyphenylsilsesquioxanes.** The silicon containing tetraamine is reacted with the corresponding dianhydride [benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA), pyromellitic dianhydride, and 4,4'-oxydiphthalic anhydride (OPDA)], as shown in Figure 2(A)]. For this aim, 0.004 mol of the obtained Si-based tetraamine were dissolved in 14 mL of anhydrous DMAc. A stoichiometric amount of dianhydride was added subsequently to the solution. The polymerization was carried out using low concentrations of the tetraamine- and dianhydride-based solutions in order to avoid cross-linking reactions between the growing ladder molecules. The mixture was stirred for 24 h at ambient temperature



**Figure 4.** FTIR-Spectrum of LA02-p:  $\nu$  ( $\text{cm}^{-1}$ ) = 1781 (m, Imide); 1720 (s,  $-\text{C}=\text{O}$ ); 1491 (m, Si-C Phenyl); 1120 (m, Si-C Phenyl); 1012 (m, Si-O); 710 (s, Si-C Phenyl).

in order to obtain the corresponding amic acid-containing ladder polyphenylsilsesquioxanes.

The conversion of the amic acid units into imide units was carried out thermally. The amic acid solutions were thermally treated at  $150^\circ\text{C}$  for 12 h. This reaction is schematically shown in Figure 2(B). In some cases, the polymer precipitated and was rinsed three times with DMAc and dried at  $180^\circ\text{C}$ . For the imide-containing ladder polyphenylsilsesquioxanes that did not precipitate, water was added to the DMAc solution in order to precipitate the polymer. Finally, the obtained solids were rinsed with water and dried at  $80^\circ\text{C}$  for 12 h.

## RESULTS AND DISCUSSION

### Synthesis of the Monomers

The intermediates and end products of the synthesis procedure shown in Figure 1 were characterized through different spectroscopic methods. The results of these studies point out that the desired monomers were obtained. For further information about these results, please refer to the supplementary information.

The results of the spectroscopic characterization point out that only two chlorine atoms of the trichloro phenylsilane reacted with the lithiated intermediate **II**. This behavior might be a consequence of the steric hindrance of the two Boc-protected aniline-based substituents which have already reacted with the trichloro phenylsilane.

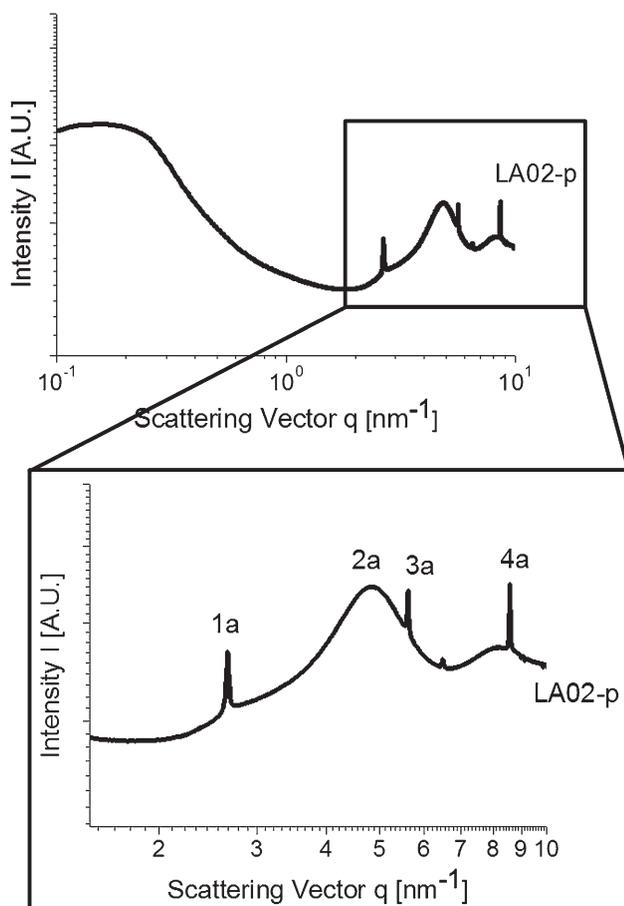
Since water is a smaller molecule than the Boc-protected aniline group, it can reach the chlorine atom, leading to the formation of a silanol group. Due to the high reactivity of the produced silanol groups, they became siloxane units in spite of steric hindrance. Thus, the removal of the Boc-protecting groups leads to Si-based tetraamines that can be used for the synthesis of imide-containing ladder polyphenylsilsesquioxanes. The overall yield of the monomer synthesis amounts 75% in weight.

### Synthesis of the Imide-Containing Ladder Polyphenylsilsesquioxanes

The molecular structure of the obtained imide-containing ladder polymers and their nomenclature adopted in this study are shown in Figure 3.

The results of the FTIR characterization (please refer to the Supporting Information) point out the presence of the imide groups after thermal treating of the polymerization products. Figure 4 shows the FTIR spectrum obtained for the compound LA02-p. In this spectrum, an absorption band at  $1781\text{ cm}^{-1}$  was assigned to the imide groups beside that of the carbonyl groups at  $1720\text{ cm}^{-1}$ . Furthermore, this spectrum shows the occurrence of absorption bands at  $1491$  and  $1012\text{ cm}^{-1}$ , which correspond to Si-C and Si-O bondings, respectively.

Additionally, the FTIR results show that the presence of primary amines ( $-\text{NH}_2$ ) in the polymer is low. This feature supports the presence of a ladder structure in the polymers. In a high cross-linked material, a high amount of primary amines (absorption bands between  $3700$  and  $330\text{ cm}^{-1}$ ) can be expected since the ladder structure is not continuous. On the contrary, by having a minimal or no cross-linking reaction between ladder molecules,

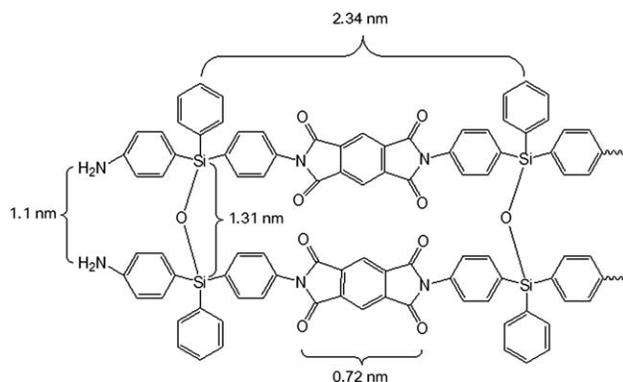


**Figure 5.** SAXS scattering curve obtained for the LA02-p ladder polymer.

the only primary amines present in the polyimides shall be the ones at the chain's ends. Since the intensity of the bands in the primary amine region observed for the polymers is low, it can be expected that the few amine groups present in the polymer are the ones located at the chain's ends.

In order to attain further information about the structure of the synthesized polymers, LA01-p was studied by using SAXS. The obtained scattering diagram is shown in Figure 5. Three sharp reflexes at  $2.68 \text{ nm}^{-1}$ ,  $5.68 \text{ nm}^{-1}$ , and  $8.62 \text{ nm}^{-1}$  and a broad reflex at  $4.78 \text{ nm}^{-1}$  have been analyzed. The scattering vectors were converted to the corresponding length using the Bragg-equation.

The obtained lengths are shown in Table I. Based on these results, the molecular structure shown in Figure 6 was proposed, showing features which are characteristic for polysilsesquioxane-based ladder polymers.<sup>8–10</sup> Furthermore, it is



**Figure 6.** Proposed structure of the LA01-p ladder polymer based on the SAXS data.

worth noting that the length calculated for the broad reflex at  $q = 4.78 \text{ nm}^{-1}$  (1.31 nm) is similar to the distance between parallel chains (1.25 nm) that was previously obtained for similar ladder polymers.<sup>7–10</sup> An additional result that supports the presence of a ladder structure in our polymer is the  $^{29}\text{Si}$ -NMR signal ( $-80 \text{ ppm}$ ) which exhibits a similar chemical shift as those of other ladder polysilsesquioxanes reported in the literature.<sup>11</sup>

#### Thermal Properties of the Polymers

The thermal properties and the solubility in DMAc of the obtained ladder polymers are summarized in Table II. Obviously, the used dianhydride for the synthesis of the polysilsesquioxane-ladder polymers has a strong influence on their properties. Only the BTDA- and OPDA-based polymers show a melting point; whereas the pyromellitic-dianhydride-based polysilsesquioxanes do not melt. This behavior is thought to be a consequence of the degree of mobility that the building blocks of the ladder polymer can achieve due to the structural characteristics of the dianhydride present in their structure. Since the pyromellitic dianhydride is composed of an aromatic ring (i.e., a rigid unit), the segments of the ladder polymer cannot move so freely; as it is the case, for the polymers synthesized using BTDA and OPDA.

Furthermore, BTDA and OPDA contain a carbonyl and an ether group, respectively, in their molecular structure. These groups are more flexible than that of the phenyl ring,<sup>17</sup> allowing the segment chains of the BTDA and OPDA based materials for moving more freely than those of the polymers based on pyromellitic dianhydride.

Furthermore, the use of a *p*- or *m*-isomer influences strongly the thermal properties of the resulting polymer.<sup>18,19</sup> The *m*-isomer containing materials show lower melting points and degradation

**Table I.** Structural Characteristics of the LA01-p Ladder Polymer Obtained from the Scattering Vector  $q$

Reflex	Scattering Vector $q$ [ $\text{nm}^{-1}$ ]	Length [nm]	Solubility in DMAc
1a	2.68	2.34	Distance between neighboring Si-atoms in the same chain
2a	4.78	1.31	Distance between parallel chains
3a	5.68	1.1	Distance between parallel chains
4a	8.62	0.72	Distance between Oxygen atoms

**Table II.** Thermal Properties and Solubility in DMAc of the Obtained Imide-Containing Ladder Polyphenylsilsesquioxanes<sup>a</sup>

Ladder polymer	Melting point (°C)	Degradation temperature (°C)	Solubility in DMAc
LA01-p	No melting	421	Not soluble
LA01-m	No melting	400	Not soluble
LA02-p	405	460	Not soluble
LA02-m	200	361	Soluble
LA03-p	235	358	Soluble
LA03-m	200	323	Soluble

<sup>a</sup>The degradation temperature and melting point were determined using thermogravimetric analysis (TGA) coupled with differential thermal analysis (DTA).

temperatures. This behavior might be a consequence of the conformations that the polymer chains can adopt depending on the isomer present in their structure. Since the position of the amino groups with respect to each other in the *p*-isomer is always the same (despite of the rotation of the phenyl rings), only a straight conformation can be present. This characteristic leads to a higher symmetry than that found in the *m*-isomer based polymers. In the latter one, the position of the amine groups with respect to each other can change during the polymerization due to the rotation of the phenyl rings, making the construction of symmetry more difficult along the polymer chains.

The degree of mobility and the symmetry of the polymer chains have also a strong influence on the solubility of the obtained ladder polymers. Flexible chains can reaccommodate themselves in order to be easily solvated by the DMAc molecules. Additionally, a less symmetric chain hinders the construction of crystalline structures, making the interaction of the polymer with the solvent easier. Since LA02-m material cannot easily build symmetric conformations (due to the *m*-isomer of its imide-based building block) and LA03-polymers (both *m*- and *p*-isomers) have a high degree of chain mobility due to the OPDA-based units, they are consequently soluble in DMAc.

On the other hand, it can be obtained from Table II that the polysilsesquioxanes based on BTDA and OPDA exhibit signifi-

cantly higher degradation temperatures than their melting points. This feature may allow for the thermoplastic processing of these imide-containing ladder polyphenylsilsesquioxanes. The thermal properties of LA02-p are shown in Figure 7. It can be seen that an endothermic process (melting point) takes place at 405°C; whereas at temperatures exceeding 460°C decomposition of the polymer starts. Until 460°C, no exothermic process and weight loss (degradation) are observed. Thus, this difference between the melting point and degradation temperature of the polysilsesquioxane LA02-p allows for its thermoplastic processing within a specific temperature range, which is called thermoplastic processing window and is shown in Figure 7.

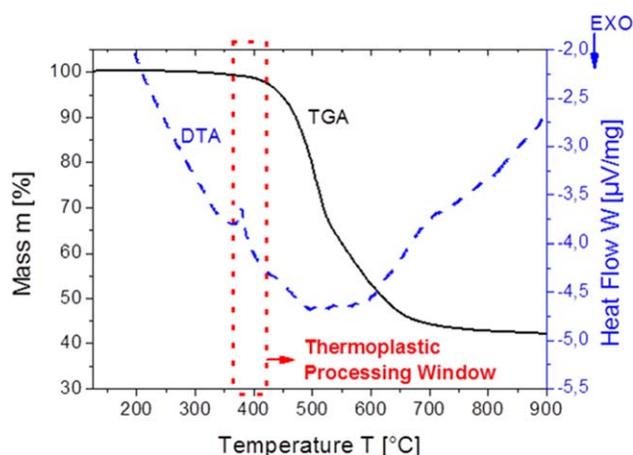
An additional feature that supports the presence of a ladder structure in the polymers synthesized within the present study is the comparison of their melting points with those that we previously obtained for similar Si-based linear polyimides.<sup>16</sup> A linear polymer synthesized from BTDA and a siloxane-containing diamine (*p*-isomer) exhibited a melting point of 390°C,<sup>16</sup> whereas the analogous ladder polymer based on BTDA and the siloxane tetraamine (*p*-isomer), which has been synthesized in the present work, exhibits a melting point of 405°C.

Furthermore, the linear polymers based on OPDA and siloxane based diamines (*p*- and *m*-isomers) with melting points of 190°C and 170°C, respectively,<sup>16</sup> show the same tendency by comparing them with the ladder polymers based on the OPDA and the siloxane tetraamines (*p*- and *m*-isomers) with melting points of 235°C and 200°C, respectively. These results reveal that the imide-containing ladder polyphenylsilsesquioxanes present higher melting points than their linear counterparts.

## CONCLUSIONS

This study presents a high yield synthesis method which allows the production of isomer pure (*p*- or *m*-) Si-based tetraamines that can be used as building blocks for the production of imide-containing ladder polyphenylsilsesquioxanes. The presence of a ladder structure within the polymers was substantiated by SAXS measurements.

The results obtained regarding the thermal properties of the synthesized materials pointed out that it is possible to tailor the melting point and degradation temperature of the imide-containing ladder polyphenylsilsesquioxanes by using different aromatic dianhydrides and isomers of the Si-based tetraamines.



**Figure 7.** TGA/DTA of the synthesized ladder polymer LA02-p. [Color figure can be viewed in the online issue, which is available at [www.wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

Furthermore, these results show that the synthesized polymers reveal a high thermal stability (degradation temperature between 320°C-460°C, depending on the material) and that some of them have potential to be processed using thermoplastic methods, since they exhibit melting points significantly below their degradation temperature.

#### ACKNOWLEDGMENTS

R.R. thanks the Fonds der Chemische Industrie for continuous financial support.

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