CHEMISTRY OF
MATERIALS
Communication

Chem. Mater. **2010,** *22,* 3823–3825 3823
DOI:10.1021/cm1010746

Silicon-Containing Polyimide-Based Polymers with High Temperature Stability

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Received April 17, 2010
Revised Manuscript Received June 10, 2010

In the field of advanced polymers, polyimides are known as having excellent thermal stability with respect to decomposition. Furthermore, they show good mechanical properties and are chemically stable against oxidation.[1] Usually, polyimides are synthesized by reacting a diamide with an aromatic dianhydride in order to produce a polyamic acid that is thermally or chemically treated to obtain the polyimide.[2,3]

The physical and chemical properties of polyimides are strongly determined by their molecular structure. Therefore, the chemical and structural characteristics, such as isomeric configuration and functional groups present in the dianhydride and diamine components, have a strong effect on the properties of the final polyimide.[4] Keeping this feature in mind, different monomers have been developed such as Si-containing diamines[5,6] in order to obtain polyimides with a certain profile regarding their thermal and mechanical properties.[7−11]

One of the current challenges in the development of polyimides with improved thermal stability is to produce isomerically pure aromatic Si-containing diamines. Common nitration reactions are stereochemically not selective,[12] thus leading to mixtures of isomers, which makes it difficult to control and to tailor the properties of the obtained polyimides. Therefore, it is important to develop new synthetic strategies to obtain isomerically pure Si-based diamines.

Here, we report on the synthesis of novel Si-containing polyimides and on the characterization of their thermal properties. The synthesis was performed in three steps: (i) monomer synthesis, (ii) polymerization, and (iii) thermal treatment. In the first step a method to synthesize isomerically pure diamino silanes and diamino siloxanes in high yields starting from bromoaniline was developed. Via reaction of the obtained monomers with different aromatic dianhydrides (step ii) novel silicon-containing polyamilic acid-based compounds were obtained and converted by a final heat treatment (step iii) into polyimides with excellent high-temperature stability.

The method used to obtain the isomeric pure Si-containing diamines is described in Scheme 1. In a first step, the amino group of bromoaniline, that is, either *para* or *meta* isomer, was protected via reaction with ditert-butyl dicarbonate in order to obtain compound **I** (Scheme 1). Subsequently, the bromine substituent in **I** was replaced by lithium through reaction with BuLi at −80 °C, leading to compound **II** (Scheme 1). The corresponding organosilicon compound, that is, either dichlorodiphenyl silane or 1,3-dichloro-tetraphenyldisiloxane, was reacted with **II** at this temperature to give the product **III**. In a final step, the protecting group attached to the amino group was removed by using trifluoroacetic acid forming the corresponding diamino silane or diamino siloxane derivatives **IV** (Scheme 1).

Using this procedure, the monomers shown in Figure 1 were obtained with yields of approximately 75−76 wt %. By reacting the obtained silicon-based diamines with different aromatic dianhydrides, that is, benzophenone-3,3′4,4′-tetracarboxylic dianhydride (BPDA), pyromellitic dianhydride, and 4,4′-oxidiphtalic anhydride (OPDA), polyimides with high temperature stability were synthesized. Thus, the prepared diamines were first dissolved in an aprotic dipolar solvent, such as dimethyl acetamide (DMAc) or N-methyl pyrrolydone (NMP). Subsequently, the dianhydride was added in solid form to the diamine solution in order to obtain a polyamic acid. Finally, the solved polyamic acid was thermally treated in an oil bath for 12 h at 150 °C to give the polyimide materials.

The molecular structure of the synthesized polyimides is shown in Figure 1; their thermal properties and solubility in dimethyl acetamide are summarized in Table 1. As can be seen from Table 1, the anhydride used has a strong influence on the thermal properties of the final polyimide. Both silane- and siloxane-containing polyimides based on BPDA and OPDA were found to melt, whereas those based on pyromellitic dianhydride do not melt. However, the anhydride used is not the only factor that determines the properties of the final polyimide. The thermal properties and solubility also depend on the

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Published on Web 06/15/2010

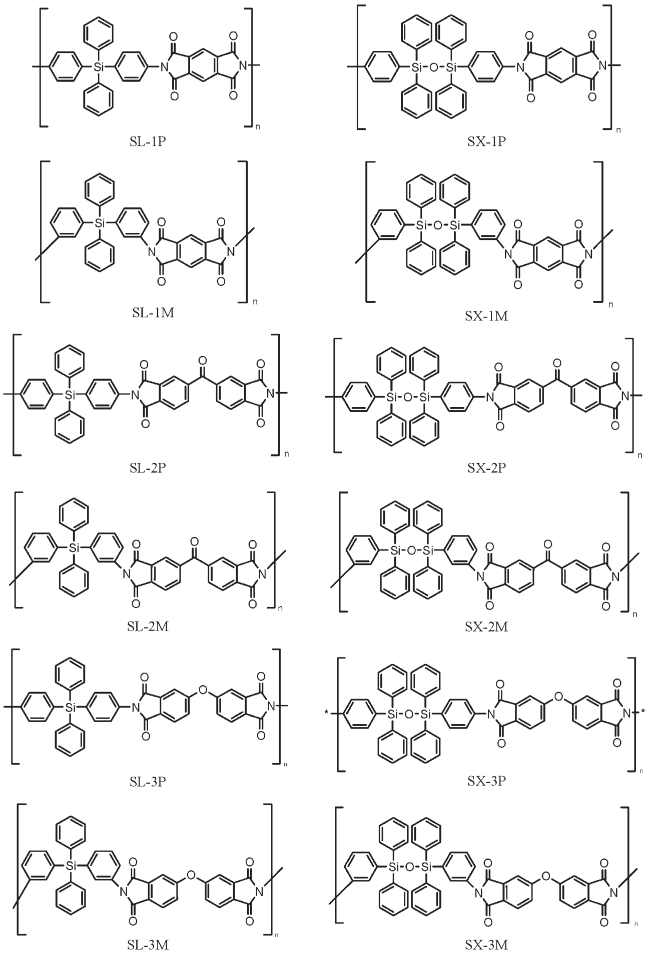

Figure 1. Si-containing polyimides obtained via reactions of silicon-containing diamine monomers with dianhydrides, followed by a thermally induced polyimidation step.

Scheme 1. Synthetic Method Used for the Synthesis of Si-Containing Diamines (*para* or *meta* isomer)

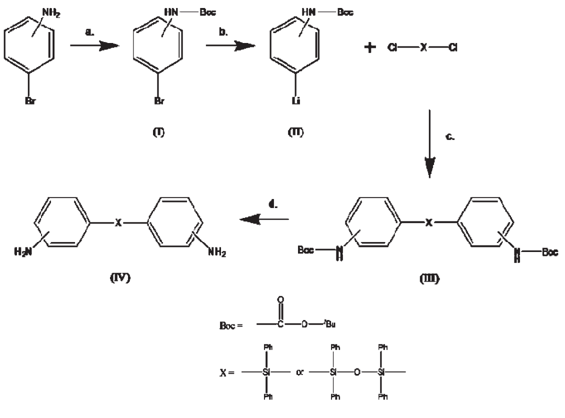

Table 1. Thermal Properties and Solubility in DMAc of the Obtained Si-Containing Polyimides[a]

polyimide	melting point [°C]	degradation temperature [°C]	solubility in DMAc
SL-1P	none	330	insoluble
SL-1M	none	400	insoluble
SL-2P	398	460	insoluble
SL-2M	190	343	soluble
SL-3P	160	336	soluble
SL-3M	140	279	soluble
SX-1P	none	421	insoluble
SX-1M	none	392	insoluble
SX-2P	390	457	insoluble
SX-2M	183	361	soluble
SX-3P	190	358	soluble
SX-3M	170	323	soluble
poly(imide siloxane)s[15,16]	none	460−500	insoluble
Kapton[14]	none	570	insoluble

[a] The degradation temperature was analysed by TGA studies.

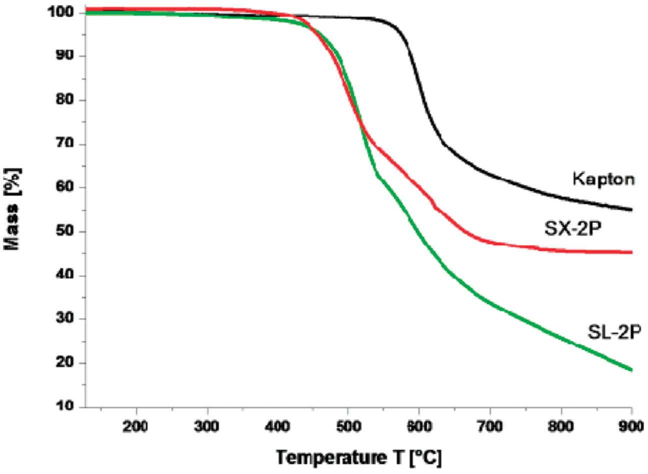

Figure 2. TGA curves of Kapton (commercially available polyimide from Du Pont), SX-2P, and SL-2P in argon atmosphere.

isomer of the silicon-containing diamine. Polyimides based on the same dianhydride presented differences in their melting points, degradation temperatures, and solubility depending on the diamine isomer used for their synthesis. Polyimides synthesized from the *para* isomer of bromoaniline show higher melting points and tend to have higher degradation temperatures if compared with those based on the *meta* isomer of bromoaniline. Furthermore, the *meta* isomer of the polyimides based on BPDA were found to be soluble in DMAc, whereas the corresponding *para* isomeric polyimides were insoluble. These features have to be discussed in terms of the different configurations that the polyimides can achieve depending on the starting isomer of the bromoaniline. Thus, a reason for the lower melting points and degradation temperatures with respect to that of the analogous *para* isomers might be the effect of the steric hindrance for the meta-isomers which could restrict polymerization to some extent and yield lower molecular weight products compared with those derived from *para* isomers. This was also observed for aromatic copolyimides, where the meta isomers exhibited glass transition and decomposition temperatures which were lower than those of analogous *para* isomers.[13]

This study presents a synthetic approach which allows for modifying and tailoring the properties of silicon-containing polyimides by using appropriate dianhydride

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and suitable isomers of silicon-containing diamines. Our method reported in this communication enables the synthesis of isomerically pure Si-containing diamines (silane- and siloxane-based) in high yields that can be used as starting compounds for the production of polyimides with high temperature stability.

Comparing the results regarding the decomposition temperature of the obtained Si-containing polyimides (see Table 1, Figure 2) with those of some commercially available carbon-based polyimides[14] or of poly(imide siloxane) block copolymers,[15] one can conclude that Si-containing polyimides exhibit a thermal stability similar to that of poly(imide siloxane) copolymers and slightly lower than that of carbon-based polyimide.

However, silicon-containing polyimides present two main advantages compared with other polyimide materials: (i) since they are meltable (below their degradation temperature), it is possible to shape them as thermoplastics, making their processability easier; (ii) their polymeric structure does not allow for microphase separation, as, for example, it is the case for poly(imide siloxane) block copolymers.[16] These characteristics make the obtained silicon-based polyimides promising materials for the production of complex shaped plastic parts for high temperature applications.

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

Supporting Information Available: Description of the synthesis of the polyimides, NMR and IR spectroscopy, mass spectrometry, and elemental analysis results (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.