Synthesis of Thermotropic Liquid Crystalline Polyimides with Siloxane Linkages

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Thermotropic liquid crystalline (LC) semi-aliphatic polyimides have been developed from 3,3′,4,4′-tetracarboxybiphenyl dianhydride (BPDA) and diamines containing siloxane spacer units. These polyimides exhibited high thermal stability and lower transition temperature compared to the corresponding polyimides containing alkyl or oxyethylene spacer units.

The development of electronics is currently accelerated toward integration, miniaturization, and high functionalization. Under the current situation, both conductors and insulating materials in ICs have been packaged as dense as possible, and it is highly desirable to develop new polymeric materials which can release generated heat effectively, while maintaining electrically insulating functions. Organic materials are used in many semiconductors as electric insulators; however they are also thermal insulators. Therefore, the development of low dielectric and thermoconductive polymers is a challenging topic at the present time. Thermal conductive media depends on materials; free electrons for metals whereas lattice vibrations, defined as "phonon,"[1,2] for ceramics and organic materials. To increase phonon conductivity, highly oriented polymers, that is, LC polymers are powerful candidates. Among them, there are established studies on segmented LC polymers which possess rigid rod as well as flexible spacer units.[3,4]

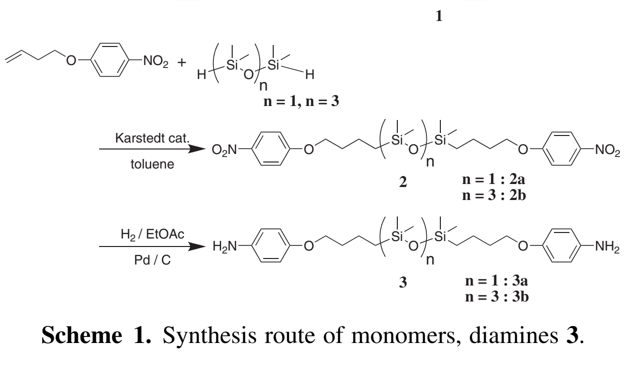
Aromatic polyimides are high-performance polymeric materials that have been widely used in the aerospace, electronics, and microelectronic industries because of their outstanding thermal and chemical stabilities, mechanical properties, electrical properties, and radiation resistance.[5,6] Thermoconductive polymers for insulators are required to have relatively low phase transition temperature and low elastic modulus. Therefore, polyimides with flexible chains are good candidates. Very few LC polyimides with sequences of methylene or ethylene oxide units have been reported. Watanabe and co-workers reported pioneering researches on thermotropic LC polyimides from 4,4″-terphenyltetracarboxylic dianhydride and aliphatic diamines with methylene spacer units (8–12).[7–9] The LC temperatures ranged from 144 to 249 °C depending on the number of methylene units. In this case, the specially designed dianhydride was used. Recently, Eastmond and co-workers used a common dianhydride, 3,3′,4,4′-tetracarboxybiphenyl dianhydride (BPDA), and reported the segmented polyimides based on BPDA and α,ω-bis(4-aminophenoxy)oxyethylene units. The resulting polyimides exhibited liquid crystallinity (smectic A) at temperatures decreasing from 352, 301, 256, to 243 °C with increasing spacer units (3, 4, 5, and 6), respectively.[10] These temperatures are relatively lower than those of the polyimides based on BPDA and diamines with methylene spacer units (>350 °C).[11] Therefore, more flexible oxymethylene units seem to be favorable rather than methylene units to lower transition temperatures.

In virtual electronics applications, further decrease of fabrication temperatures are required to avoid oxidation of copper wires inside ICs. It should be mentioned that there has been no example of LC fabrication temperature less than 243 °C among polyimide-based thermotropic liquid crystalline materials derived from commercially available BPDA. As siloxane units are well known to be highly flexible, the introduction of siloxane linkages to a polyimide main-chain should decrease LC transition temperatures. In addition, siloxane linkages are also responsible for thermal stability. In this communication, we describe the first synthesis of new polyimides derived from BPDA and diamines containing siloxane spacer units and their thermotropic LC behaviors.

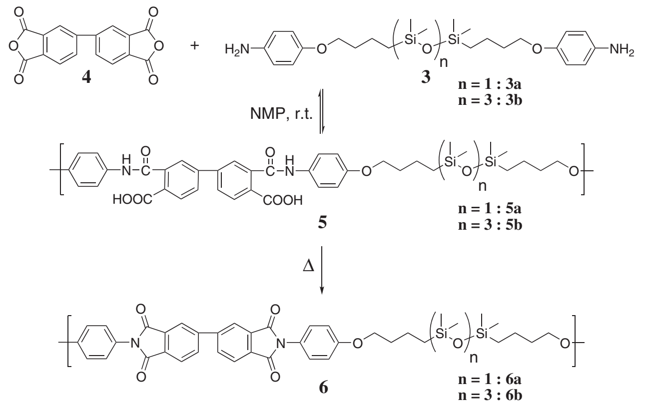
Diamines **3** containing siloxane linkages were prepared from *p*-nitrophenol in three steps as shown in Scheme 1. Reaction of *p*-nitrophenol with 4-bromo-1-butene in the presence of potassium carbonate in acetonitrile yielded 4-(3-butenyloxy)-nitrobenzene, (**1**). Hydrosilylation of compound **1** with 1,1,3,3-tetramethyldisiloxane or 1,1,3,3,5,5,7,7-octamethyltetrasiloxane in the presence of Karstedt's catalyst gave compounds **2**, which were hydrogenated to monomer diamines **3** (see Supporting Information[12]).

LC polyimides **6** shown in Scheme 2 were prepared by using a two-step polycondensation procedure. BPDA (**4**) reacted with diamines **3** at room temperature in *N*-methyl pyrrolidone (NMP) to produce poly(amic acid)s (PAAs) **5** with high inherent viscosities in the range of 1.1–1.4 dL g^{-1}. Then, PI films were obtained by thermal imidization of PAAs cast on glass substrates under nitrogen, followed by immersion in warm water. Successful thermal conversion was confirmed by the FT-IR spectra. The characteristic absorptions which originated from the imide moiety were observed at around 1770, 1712, and 1389 cm^{-1}. Self-standing and opaque yellow films with low elasticity were obtained.

Thermal properties such as 5% wight loss temperature and transition temperature were measured by TGA and DSC under



Scheme 1. Synthesis route of monomers, diamines **3**.



Scheme 2. Synthesis route of LC polyimides **6**.

Table 1. Thermal transition temperatures of polyimides[a]

T_x/°C[b]	6a	6b	ΔH_x/J g^{-1} [b]	6a	6b
T_m1	253	222	ΔH_m1	15.3	31.9
T_m2	264	268	ΔH_m2	2.8	2.3
T_m3	335	—	ΔH_m3	10.1	—
T_c1	325	254	ΔH_c1	10.1	2.0
T_c2	236	216	ΔH_c2	15.3	4.5
T_c3	—	203	ΔH_c3	—	24.4

[a] All determined by DSC at a second heating or cooling rate of 10 °C min^{-1}. **5a**: $\eta_{inh} = 1.07$ [dL/g], **5b**: $\eta_{inh} = 1.43$ [dL/g]. Inherent viscosities were measured at 30 °C in NMP at a PAA **5** concentration of 0.5 g dL^{-1}. [b] Transition temperature. T_m: peak top temperature of endotherm peak, T_c: peak top temperature of exotherm peak, ΔH_m: endotherm enthalpy, ΔH_c: exothermo enthalpy.

nitrogen, respectively (Table 1). Both polyimides **6** showed high thermal stability with 5% weight loss temperature over 440 °C. The DSC traces of polyimides **6** are shown in Figure 1. Three endotherm peaks on heating and two exotherm peaks on cooling were observed in polyimide **6a**, while two endotherm peaks on heating and three exotherm peaks on cooling in polyimides **6b**. These transition phases in these polyimides correspond to crystal, liquid crystal, and isotropic phases, and thermal transitions are summarized in Table 1. All polyimides **6** have high thermal stability and lower transition temperatures compared to polyimides containing alkylene or oxyethylene spacer units having the same numbers of atoms. Moreover, the transition temperature decreased with increasing siloxane sequence length because of increasing flexibility of the main chains.

Liquid crystallinity of polyimide **6** was supported by optical microscopy. In the case of polyimide **6b**, the fluidity and birefringence were observed above the first melting point (T_m1), and LC–isotropic transition was observed at the second endothermic temperature (T_m2). The optical micrographs of each polyimide annealed at 320 or 240 °C for 10 min are shown in Figure 2. The clear fan-shaped textures were assigned to smectic LC. The detailed characterization of the crystal and LC phases by X-ray diffraction and measurement of thermal conductivity are in progress.

In conclusion, we have developed new LC semialiphatic polyimides containing siloxane spacer units. They showed lower transition temperature compared to polyimides containing alkyl or oxyethylene spacer units. We expect that these polyimides will exhibit relatively high thermal conductivity, and can be used as insulators in electronics fields.

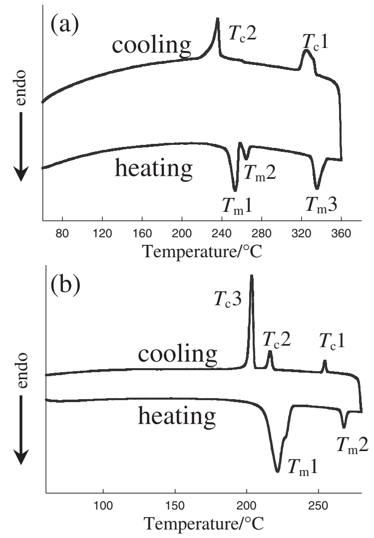


Figure 1. DSC traces for polyimides **6**: (a) **6a** and (b) **6b**.

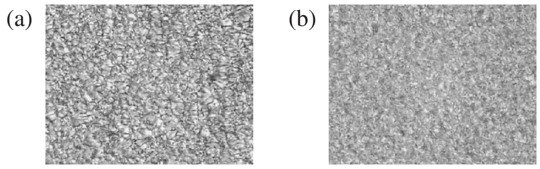


Figure 2. Polarized optical micrographs of polyimides **6**: (a) polyimide **6a** at 320 °C and (b) polyimide **6b** at 240 °C (×400).

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) June 13, 2009; doi:10.1246/cl.2009.716