Structure-Property Relationship of Polynorborene derivatives

Boo-Gyo Shin, Jun Bok Shin, Swamkumar V. Mulpuri, Do Y. Yoon

Department of Chemistry, Seoul National University, Seoul, Korea
dyyoon@snu.ac.kr

Introduction
Vinyl-polyboronorene has good characteristics for the application in information technology devices, such as high optical transparency, good thermal stability up to 400 °C, a high glass transition temperature (Tg), a low moisture absorption, and a low dielectric constant. However, its poor solubility, mechanical brittleness, and low adhesion property need to be improved.1,2

Vinyl-polyboronorene with polar side groups could improve the solubility and adhesion properties at the same time. Because functional groups coordinate to catalyst metal, polymerization of functionalized boronorene is more difficult than that of norboronene. Moreover, the polymerization of endo-functionalized boronorenes becomes more difficult.3 Previously, functionalized polyboronorene with triethoxysilyl group showed good adhesion property by hydrolysis of ethoxy group followed by condensation reaction of hydroxy group to substrate.4

In this work, exo-norborene derivatives were selectively prepared for high polymerization yield. Polymerization was performed by Pd(II) late transition metal catalyst. Structure-property relationships of polynorborene derivatives were investigated by measuring the X-ray scattering, mechanical and electrical properties.

Experimental
All the experiments involving air- or moisture-sensitive compounds were performed using Schlenk or dry box techniques. The monomers and polymers were prepared according to the general scheme shown by Figure 1.

Norborene derivatives having ester group were prepared as follows:

- Norboronene-exo-2,3-dicarboxylic acid dibenzyl ester
- cis-5-Norborene-exo-2,3-dicarboxylic acid ethanol ester

cis-5-Norborene-exo-2,3-dicarboxylic acid hydrazide was rearranged to cis-5-norborene-exo-2,3-dicarboxylic acid hydrazide at 180 °C.5 Esterification of cis-5-norborene-exo-2,3-dicarboxylic acid hydrazide with benzyl alcohol in toluene yielded product.

Norbornene derivatives having other group were prepared as follows:

- 2,3-Dipropoxymethyl-norborene
- cis-5-Norborene-exo-2,3-dicarboxylic acid dibenzyl ester
- Norboronene-exo-2,3-dicarboxylic acid dibenzyl ester
- Norboronene-exo-2,3-dicarboxylic acid dibenzyl ester was dissolved in chlorobenzene. Catalyst solution was added through syringe filter. The solution was stirred at room temperature under argon. After 3 days, the solution was precipitated in excess methanol. Polymer was filtered and dried. To remove catalyst, polymer was dissolved and stirred in THF under hydrogen balloon. After Celite filtering, concentrated polymer solution was precipitated in excess methanol. Filtering and drying yielded polymer product.

Measurements
Thermal gravimetric analysis (TGA) was performed at 10 °C/min heating rate up to 700 °C. Dynamic mechanical analysis (DMA) was performed at 3 °C/min heating rate and 1 Hz frequency, in dual-cantilever mode up to 350 °C. X-ray scattering was measured using a small-angle X-ray scattering apparatus with general area detector system (Bruker). Data were collected 2θ = 40° as 2θ. Reflective index of spin-coated polymers on Si-wafer was measured using thin film analyzer (Fimetrics™).

Results and discussion
Pd(II) catalyst selectively polymerizes exo-nomer in exo-exo-nomer mixture.3 Norbornene derivatives derived by Diels-Alder reaction are exo- and endo-mixture. For high polymerization yield, pure exo-intermediate was synthesized by rearrangement and recrystallization of cis-5-norborene-exo-2,3-dicarboxylic acid hydrazide.5 Monomers were prepared from exo-norborene hydrazide and exo-dihydronorborene intermediate by esterification or Sn2 reaction of exo-intermediate. Monomers were polymerized by Pd(II) catalyst in chlorobenzene.

Figure 1. Scheme for preparing polynorborene derivatives

TGA thermogram showed that polymers are thermally stable up to 300 °C. Tg was measured by DMA as loss modulus peak; DSC was not sensitive to detect Tg of polynorborene derivatives. Tg is decreased as side-chain becomes bulkier. Modulus measured by nanodenter is decreased as the side-chain length is increased. These results show that side-chains act as plasticizer in polymer glass. Reflective index is decreased from 1.52 to 1.49, as the alkyl chain length is increased. Reflective index with benzyl group (1.57) is higher than alkyl group. Polymers are soluble in general organic solvents, except methanol (very polar solvent) and hexane (very nonpolar solvent).

Conclusions
Pure exo-norborene derivatives as monomers were prepared for high yield polymerization. Monomers were polymerized by Pd(II) catalyst without catalyst. The polymers have good solubility in general organic solvents, are thermally stable up to 300 °C, and Tg can be controlled by the side-chain group. Important physical properties for information technology application such as dielectric characteristics and coefficient of thermal expansion, and their structure-property relationship will be discussed.

References