Structure-Property Relationship of Polynorbornene derivatives

Boo-Gyo Shin, Jin Bok Shin, Syamkumar V. Mulpuri, Do Y. Yoon*

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

Introduction

Vinyl-polynorbornene has good characteristics for the application in information technology devices, such as high optical transparency, good thermal stability up to 400 ℃, a high glass transition temperature (T_g), 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-polynorbornene 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 norbornene is more difficult than that of norbornene. Moreover, the polymerization of endo-functionalized norbornenes becomes more difficult.[3] Previously, functionalized polynorbornene 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-norbornene derivatives were selectively prepared for high polymerization yield. Polymerization was performed by Pd(II) late transition metal catalyst. Structure-property relationships of polynorbornene 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.

Norbornene derivatives having ester group were prepared as follows:

Norbornene-exo-2,3-dicarboxylic acid dibenzyl ester

cis-5-Norbornene-endo-2,3-dicarboxylic anhydride was rearranged to cis-5-norbornene-exo-2,3-dicarboxylic anhydride at 180 ℃.[5] Esterification of cis-5-norbornene-exo-2,3-dicarboxylic anhydride with benzyl alcohol in toluene yielded product.

Norbornene derivatives having ether group were prepared as follows:

2,3-Di(propoxymethyl)-norbornene

cis-5-Norbornene-exo-2,3-dicarboxylic anhydride was reduced to norbornene-exo-2,3-dimethanol by $LiAlH_4$ in THF solution. S_N2 reaction of norbornene-exo-2,3-dimethanol, bromopropane, and NaH as a base yielded product.

Polymerization reactions were carried out as follows:

Poly(norbornene-exo-2,3-dicarboxylic acid dibenzyl ester)

Norbornene-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 ℃/min heating rate up to 700 ℃. Dynamic mechanical analysis (DMA) was performed at 3 ℃/min heating rate and 1 Hz frequency, in dual-caltilever mode up to 350 ℃. X-ray scattering was measured using a small-angle X-ray scattering apparatus with general area detector system, (Bruker). Data were collected 2° ~40° as 2 theta. Refractive index of spin-coated polymers on Si-wafer was measured using thin film analyzer (Filmetrics™).

Results and discussion

Pd(II) catalyst selectively polymerizes exo-monomer in exo-, endo-monomer 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-norbornene-endo-2,3-dicarboxylic anhydride.[5] Monomers were prepared from exo-norbornene anhydride and exo-dihydroxynorbornene intermediate by esterification or S_N2 reaction of exo-intermediate. Monomers were polymerized by Pd(II) catalyst in chlorobenzene.

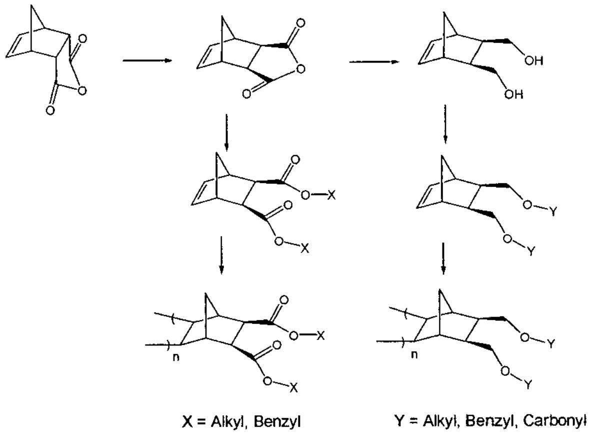

Figure 1. Scheme for preparing polynorbornene derivatives

TGA thermogram showed that polymers are thermally stable up to 300 ℃. T_g was measured by DMA as loss modulus peak; DSC was not sensitive to detect T_g of polynorbornene derivatives. T_g is decreased as side-chain becomes bulkier. Modulus measured by nanoindenter is decreased as the side-chain length is increased. These results show that side-chains act as plasticizer in polymer glass.

Refractive index is decreased from 1.52 to 1.49, as the alkyl chain length is increased. Refractive 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-norbornene derivatives as monomers were prepared for high yield polymerization. Monomers were polymerized by Pd(II) catalyst without cocatalyst. The polymers have good solubility in general organic solvents, are thermally stable up to 300 ℃, and T_g 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

[1] C. Janiak, and P. G. Lassahn, Macromol. Rapid Commun., 22, 479, (2001)

[2] B.G. Shin, M.S. Jang, D.Y. Yoon, and W. Heitz, Macromol. Rapid Commun.,25, 728, (2004)

[3] B. S. Heinz, W. Heitz, S. A. Krügel, F. Raubacher, and J. H. Wendorff, Acta Polym., 48, 385 (1997).

[4] N.R. Grove, P.A. Kohl, S.A.B. Allen, S. Jayaraman, and R. Shick, J. of Polymer Sci., Part B., 37, 3003, (1999)

[5] D. Craig, J. Am. Chem. Soc., 73, 4889 (1951).