Synthesis of Fully Alicyclic Polyimides from 2,5(6)-Bis(aminomethyl)bicyclo[2.2.1]heptane

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Bicyclo[2.2.1]heptane-2-exo,3-exo,5-exo-tricarboxyl-5-endo-acetic dianhydride (4a, BSDA) and its 5-endo-carboxyl-5-exo-acetic isomer (4b) with an alicyclic and spiro structure were prepared from a Diels-Alder adduct of itaconic anhydride with cyclopentadiene via three steps. Fully alicyclic polyimides were synthesized by polycondensations of an alicyclic diamine, 2,5(6)-bis(aminomethyl)bicyclo[2.2.1]heptane (BBH) with four kinds of cycloaliphatic dianhydrides including BSDA in HMPA. Although inherent viscosities of the poly(amic acid) were somewhat low, the polymer solutions gave the free-standing polyimide films after curing. The films were soluble in organic polar solvents such as DMAc and NMP.

Keywords: aliphatic, alicyclic, cycloaliphatic, soluble, polyimides

1. Introduction

Polyimides are classified into four distinct categories according to their chemical structures (Figure 1), aromatic polyimides, two types of semi-aromatic polyimides, and non-aromatic (fully aliphatic) polyimides. Fully aliphatic polyimides have attracted much attention in recent years because of their potential applications including low dielectric materials.[1] Wu et al. have firstly prepared these polyimides in 1962 from bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic 2:3:5:6-dianhydride derivatives and aliphatic diamine with a straight chain.[2] Recently, Volkson et al and Li et al have independently reported the synthesis of a fully alicyclic polyimide, which are derived from aliphatic monomers, using 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and 1,1-bis(4-aminocyclohexyl)methane and investigated the optical properties.[1,3] Seino et al synthesized fully alicyclic polyimides by a one-step polycondensation of bicyclo[2.2.2]octane-1,2,5,6-tetracarboxylic dianhydride with adamantane-based aliphatic diamines.[4]

In polycondensations of an aliphatic diamine with aromatic or aliphatic dianhydrides, a precipitate appears in the initial stage of the polymerization. The nature can be explained by salt formation as illustrated in Figure 2. The basicity of primary aliphatic diamines (pK_b=3.4) such as cyclohexylamine is about a million times higher than that of aromatic ones (pK_b=9.4) like aniline, and the difference affects strongly the polymerization behavior. In order to avoid the salt formation, Oishi et al used isolated or in-situ synthesized N,N'-disilylated aliphatic diamines instead of free diamines.[5,6]

In this article, the synthesis of fully alicyclic
polyimides from 2,5(6)-bis(aminomethyl)bicyclo[2.2.1]heptane, the characterization, and the solubility as well as the dianhydride synthesis will be discussed.

2. Experimental

2.1. Materials

5-(2,5-Dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (MCTC, Epiclon® B-4400) was obtained from Dainippon Ink & Chemicals Incorporation, Japan. Bicyclo[2.2.1]-heptane-2-endo,3-endo,5-exo,6-exo-tetraacrylic acid, 2,3:5,6-dianhydride (BHDAdx) and (4arH,8acH)-decahydro-t,4t:5c,8c-dimethanonaphthalene-2c,3c,6c,7c-tetracarboxylic 2,3:6,7-dianhydride (DNADAdx) were synthesized according to our previous literatures.[7-9] 2,5(6)-Bis(aminomethyl)bicyclo[2.2.1]heptane (BBH) was kindly supplied from Mitsui Chemicals Co. Ltd. Japan as a mixture of four isomers, 2,5-, 2,6-position and endo, exo-isomers. Itaconic anhydride was purchased from Tokyo Kasei Kogyo Co. Ltd. Japan and used without further purification. Cyclopentadiene was prepared by thermal decomposition (retro Diels-Alder reaction) of dicyclopentadiene at 180°C which was obtained from Maruzen Petrochemical Co., Ltd. Hexamethylphosphoramide (HMPA) and N,N-dimethylacetamide (DMAc) were fractionally distilled over CaH₂ under reduced pressure and stored over molecular sieves 4A.

2.2. Measurement

Infrared spectra were recorded using a JASCO VARIOR III Fourier transform spectrometer. The ¹H and ¹³C NMR spectra were obtained using a JEOL JNM-LA500 spectrometer. The proton signals were assigned in the H,H, C,H-COSY, and NOESY (elimination of J correlation) spectra. Melting points were measured using a Seiko Exster 6000/DSC-220 instrument at a heating rate of 10 K/min in air. Inherent viscosities were measured with an Ostwald viscometer in a 0.5 g/dL DMAc solution of poly(amic acid) at 30°C.

2.4. General Polymerization Procedure and Film Preparation of Polyimide

In a 30 mL three-necked flask equipped with a mechanical stirrer were placed the dianhydride (2.00 mmol) and 3 mL of HMPA. As a slow stream of nitrogen gas was maintained, the mixture was stirred...
until the anhydride was entirely dissolved. BBH (2.00 mmol) and an additional 2 mL of HMPA were then added into the clear solution. The flask was heated at 60°C, and the solution was stirred for 2 days. An aliquot of the polymerization solution containing poly(amic acid) was cast on a glass plate using a doctor blade. The polyimide film was prepared by heating the glass plate at 80°C for 2 h and then at 250°C for 2 h under vacuum. After curing, the glass plate was immersed in boiling water to facilitate removal of the free-standing polyimide film.

3. Results and Discussion

3.1. Synthesis of BSDA

We have already reported briefly the synthetic method of bicyclo[2.2.1]heptane-2-exo,3-exo,5-exo-tricarboxyl-5-endo-acetic dianhydride (4a, BSDA) and its 5-endo-carboxyl-5-exo-acetic isomer (4b) with a polyalicyclic and spiro structure (Scheme 1).[10] Here, the details including the IR and NMR spectral data are described. A Diels-Alder reaction between itaconic anhydride and cyclopentadiene afforded the adducts in high yield. Judging from the 1H- and 13C-NMR spectra, the adducts were easily found to be a mixture of bicyclo[2.2.1]hept-5-ene-3-exo-carboxyl-3-endo-acetic anhydride (1a) and its endo-exo isomer (1b), and it was also revealed that the molar ratio of 1a and 1b was 8:1 from the integral areas of the proton signals. At first, tetramethyl bicyclo[2.2.1]heptane-2-exo,3-exo,5-exo-tricarboxyl-5-end acetate (3a) and its 5-endo,5-exo isomer (3b) were expected to form directly by the Pd-catalyzed methoxycarbonylation of 1a and 1b. However, this attempt, the direct bismethoxycarbonylation, was unsuccessful and a five-membered lactone (5) was produced predominantly. The anhydrides (1a and 1b) were esterified with methanol in the presence of a catalytic amount of concentrated sulfuric acid to give the corresponding dimethyl esters, 2a and 2b. According to the same method as reported previously,[10] a mixture of 2a and 2b was allowed to react with methanol and carbon monoxide and converted into the tetramethyl esters, 3a and 3b. James and Stille reported that, in the Pd-catalyzed bismethoxycarbonylation of norbornene, the two methoxycarbonyl groups were introduced with exo configuration.[11] Therefore, the stereochemistry of the methoxycarbonyl groups introduced into 2a and 2b was anticipated to be 2-exo and 3-exo. The tetramethyl esters were hydrolysed in aqueous hydrochloric acid, and then the resulting tetracarboxylic acids were, with no isolation, derived into the corresponding dianhydrides, 4a and 4b, by heating in acetic anhydride containing decahydronaphthalene (decalin). The dehydrated products could be confirmed to consist of two isomers by NMR spectroscopy (4a:4b=4:1). The dianhydride 4a (BSDA) was isolated by sublimation, although isolation of the isomer 4b has not been successful yet. The H,H-cosy spectrum of BSDA measured in DMSO-d6 is shown in Figure 3, where three long
range W couplings are observed. **BSDA**: mp 164.2°C (by DSC, 10K/min). \(^1\)H-NMR \(\delta\) (DMSO-d\(_6\)): 1.28 (1H, dd, \(J_{7,6}=2.7\) (W-coupling), \(J_{7,7}=11.9\), H-7), 1.71 (1H, dd, \(J_{6,6}=13.4\), \(J_{6,7}=2.7\) (W-coupling)), \(H'\)-6), 2.18 (1H, dd, \(J_{6,6}=13.4\), \(J_{6,1}=4.0\), H-6), 2.18 (1H, d, \(J_{7,7}=11.9\), H',7), 2.73 (1H, \(J_{1,6}=4.0\), H-1), 3.01 (1H, d, \(J_{H,8}=18.6\), H-8), 3.08 (1H, s, H-4), 3.20 (1H, d, \(J_{2,3}=7.3\), H-2), 3.31 (1H, d, \(J_{3,2}=7.3\), H-3), 3.35 (1H, \(J_{H,8}=18.6\), H'-8). \(^{13}\)C-NMR \(\delta\) (DMSO-d\(_6\)): 40.9(C-8), 42.2(C-6), 43.3(C-1), 47.9(C-7), 50.3(C-5), 51.8(C-4), 133.5(C-3), 141.8(C-2), 169.9(C-9), 177.4(C-10). IR(KBr): 2987, 1858, 1779, 1224, 1069, 1005, 993, 962, 919, 788, 736, 601 cm\(^{-1}\). Anal. Calcd for C\(_{12}\)H\(_{10}\)O\(_6\): C, 57.61; H, 4.03. Found: C, 57.32 H, 4.05. The atom labeling used here is same as in Figure 3.

### 3.2 Polymer Synthesis

The structures and abbreviations of monomers used in this study are illustrated in Figure 4. When using aliphatic diamines for polyimide synthesis, a special care must be paid to the monomer addition order and the solvent. If the dianhydride is added to the DMAc solution containing BBH, a precipitate develops immediately. The phenomenon can be explained by the insoluble salt formation as described above. A carboxyl group of amic acid once formed is easily reacted with an excess amount of the free diamine to produce the salt. In polycondensations of an aromatic diamine with the dianhydrides, the addition order of the monomers does not strongly affect the polymerization behavior. However, in the reaction using an aliphatic diamine, the addition order becomes significantly important. The difference in basicity between primary aliphatic diamines and aromatic diamines influences the polymerization behavior. A viscous poly(amic acid) solution was obtained when BBH was slowly added to the HMPA solution of the dianhydride. The homogeneous solution was stirred at 60°C for 2 days in nitrogen atmosphere, and an aliquot of the resulting polycondensation solution was cast on a glass plate, then the glass plate was heated under vacuum at 80°C and 250°C for each 2 hours to give the polyimide film.
The results are listed in Table 1. The poly(amic acid)s possess an inherent viscosity range from 0.20 to 0.36. In spite of the low inherent viscosities, the solutions gave the polyimide as free-standing films except for the BSDA-BBH polymer. The post-polymerization might occur on curing and lead to high molecular polyimides.

3.3. Properties of Polyimides

In the IR spectrum of PI(DNDAdx-BBH) film (Figure 5), strong absorptions at 1768 and 1695 cm⁻¹ assigned to the imide carbonyl appear, and they are 10-20 cm⁻¹ lower than those of an aromatic polyimide. A very small absorption assigned to amide-carbonyl was observed as a shoulder. Nonconjugation of the imide carbonyl group due to the absence of an aromatic ring causes the absorption shifts. The qualitative solubility of the fully alicyclic polyimide films is shown in Table 2. All of these polyimides are soluble in polar solvent such as HMPA and DMAc. Introduction of polyalicyclic units into the polymer backbone would facilitate less polymer-polymer interaction and enhance the solubility in organic solvents.

4. Conclusions

Polycondensations of four kinds of alicyclic dianhydrides with an alicyclic diamine BBH were carried out in HMPA, where the monomer addition order becomes significantly important. Although the inherent viscosities of the poly(amic acid) were

Table 1. Inherent viscosities of poly(amic acid)s and film quality of the polyimide.

<table>
<thead>
<tr>
<th>monomers</th>
<th>( \eta_{inh} ) (dL/g)</th>
<th>polyimide film</th>
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<tbody>
<tr>
<td>BHDA-BBH</td>
<td>0.21</td>
<td>free-standing &amp; tough</td>
</tr>
<tr>
<td>DNDAdx-BBH</td>
<td>0.36</td>
<td>free-standing</td>
</tr>
<tr>
<td>BSDA-BBH</td>
<td>0.22</td>
<td>somewhat brittle</td>
</tr>
<tr>
<td>MCTC-BBH</td>
<td>0.20</td>
<td>free-standing</td>
</tr>
</tbody>
</table>

*Inherent viscosity of poly(amic acid), 0.5 g/dL HMPA solution at 30°C.
somewhat low, the resulting fully-alicyclic polyimide formed free-standing films. In the IR spectrum of polyimide film, strong absorptions at 1768 and 1695 cm\(^{-1}\) assigned to the imide carbonyl appear, and they are 10-20 cm\(^{-1}\) lower than those of an aromatic polyimide. Nonconjugation of the imide carbonyl group due to the absence of an aromatic ring causes the absorption shifts. The polyimide films were soluble in organic polar solvents such as DMAc and NMP.

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**References**


