Low Temperature Film-fabrication of Hardly Soluble Alicyclic Polyimides with High $T_g$ by a Combined Chemical and Thermal Imidization Method

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The alicyclic dianhydride having cyclopentanone bis-spironorbornane structure (CpODA) was polycondensated with aromatic diamines at room temperature to give poly(amic acid)s having an inherent viscosity ($\eta_{inh}$) range of 1.3-0.54 dL/g. The poly(amic acid)s were imidized by three methods. The imidization ratio of PI(CpODA+3,4’-DDE) reached 100% at 200 °C using a combined chemical and thermal imidization method. All the polyimide films possessed excellent thermal stability and most of the polyimides had $T_g$’s over 330 °C. The CTE value of thermally imidized PI(CpODA+4,4’-DABA) was as low as 15 ppm/K. The polyimide films exhibited $\lambda_{cut-off}$’s shorter than 336 nm, and the $T_{vis}$ value of each polyimide film was over 85%. Especially, PI(CpODA+3,4’-DDE) prepared by a combined chemical and thermal method had outstanding optical properties ($T_{vis}$:88 %, $\lambda_{cut-off}$’s:278 nm) due to the low temperature film-fabrication.

Keywords: alicyclic polyimides, colorless polyimides, high $T_g$, combined chemical and thermal imidization, low temperature film-fabrication

1. Introduction

In recent years, alicyclic polyimides derived from polyalicyclic dianhydrides and aromatic diamines have much attention because of their high-temperature stability and transparency in the visible region. Most recently we reported the alicyclic polyimides prepared from the dianhydrides with alkanone bis-spironorbornane structure.[1,2] These polyimides possessed the glass transition temperatures ($T_g$’s) in the range of 290-354 °C. The films exhibited cutoffs at wavelengths shorter than 290 nm. Transparency in the visible region (400-780 nm) of each polyimide film was around 85%. The high $T_g$ is due to a dipole-dipole interaction between the keto groups of the polymer chains as well as a development of rigid polyalicyclic units. The film quality and the polymerization degree of the polyimide were influenced strongly by imidization temperature. The polymerization degree of PI(ChODA+3,4’-DDE) (Fig. 1) obtained by curing the reprecipitated poly(amic acid) at 300 °C for 1 h under vacuum was 17, whereas the value increased six times on heating at 350 °C for an additional 30 min. This result means that the post-polymerization took place over the $T_g$ (335 °C). The preparation of a flexible and tough polyimide film requires a high temperature imidization process. However, when the colorless polyimide film is cured at temperature higher than 250 °C, the transparency is decreased with an increase in curing temperature.[3]
Fig. 1. The chemical structure of PI(ChODA+3,4'-DDE)

Usually a chemical imidization is carried in the solution using a mixture of a dehydration agent and a base catalyst. The method is however, inapplicable to hardly soluble or insoluble polyimides. Most of high Tg polymers are practically insoluble in organic solvents due to a strong interaction between polymer chains. In the present article, we will report a combined chemical and thermal imidization method in low temperature film-fabrication of hardly soluble alicyclic polyimides with high Tg.

2. Experimental

2.1. Materials

Norbornane-2-spiro-α-cyclopentanone-α’-spiro-2’-norbornane-5,5”,6,6”-tetracarboxylic di-anhydride (CpODA) was prepared according to the previous paper,[2] and heated at 170°C for 2h just prior to use. 1,3-Bis(4-aminophenoxy)benzene (1,3-BAB) and 2,2’-dimethyl-1,1’-biphenyl-4,4’-diamine (m-Tol) were supplied from Wakayama Seika Kogyo Co. Ltd. and purified using a vacuum-sublimation apparatus. 4,4’-Diaminodiphenyl ether (4,4’-DDE) was obtained from Wako Pure Chemical Industries, Ltd. and purified by sublimation. 3,4’-Diaminodiphenyl ether (3,4’-DDE) and 4,4’-diaminobenzanilide (4,4’-DABA) were purchased from Tokyo Chemical Industry Co. Ltd. and sublimed under reduced pressure. The other reagents were of commercial grade and used without further purification.

2.2. Polymerization process and polyimide film preparation

2.2.1. Synthesis of poly(amic acid)s from CpODA and aromatic diamines

A typical polymerization process is described below. In a 30-mL three-necked flask equipped with a mechanical stirrer were placed 3,4’-DDE (2.0 mmol) and 3 mL of DMAc. As a slow stream of dry nitrogen gas was maintained, the mixture was stirred until the diamine was entirely dissolved. The dianhydride CpODA (2.0 mmol) and an additional 2 mL of DMAc were added, and the mixture was stirred at a rate of 30-100 rpm for 24 h at room temperature.

2.2.2. Thermal imidization of poly(amic acid)

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 plate at 80°C for 2h, then at 350°C for 0.5 h under vacuum. The glass plate was immersed in boiling water to remove the free-standing film.

2.2.3. Combined chemical and thermal imidization method for the polyimide film-fabrication

To the remainder of the poly(amic acid) solution (ca. a half of the original amount) prepared as described above were added triethylamine (1.0 mmol) and trifluoroacetic anhydride (0.6 mmol), and the mixture was stirred magnetically for 18 h at room temperature. The solution was cast on a glass plate, and the plate was heated at 80°C for 2 h, then at the prescribed temperature for 1 h under vacuum.

2.3. Measurements

Inherent viscosities were measured in 0.5 g/dL DMAc solutions of poly(amic acid)s using an Ostwald viscometer at 30°C. The Infrared spectra were recorded using a JASCO 460 Plus Fourier transform spectrophotometer. UV-vis spectra of the free-standing polyimide films were recorded on a JASCO V-570 UV/vis/NIR spectrophotometer. The 1H- and 13C-NMR spectra were obtained using a JEOL JNM-LA 500 spectrometer. Thermal analyses were carried out using a Seiko SSC 5200-TG/DTA 220 instrument at a heating rate 10 K/min under nitrogen with a flow rate of 200 mL/min for the thermogravimetric analysis (TGA). The glass transition temperatures were determined using a Seiko TMA/SS100 thermomechanical analyzer equipped with a penetration probe of 1 mm diameter with an applied constant load of 10 g (stress, 0.125 MPa) at a heating rate of 10 K/min in air. The coefficient of thermal expansion (CTE) of the polyimide film (10 mm long, 3.5 mm wide and 10-20 μm thick) was measured in a temperature range of 40-240°C at a heating rate of 5 K/min on a Seiko TMA/SS100 instrument with a drawing load of 0.35 g in μm, namely 980 mN/mm², in air. The value was evaluated as an average with 100-200 °C for the film plane direction.
3. Results and Discussion

3.1. Polymer synthesis

All the aromatic diamines were purified by vacuum sublimation just prior to use in order to prepare polyimide film with the objective of obtaining maximum optical transparency. Polyimide films were synthesized and fabricated by an ordinary two-step and a combined chemical and thermal imidization methods. The synthetic route of polyimide, the chemical structures of monomers, and their abbreviations are shown in Scheme 1.

Scheme 1. The synthetic route of polyimide, the chemical structures of monomers, and their abbreviations.

Poly(amic acid)s possessed an inherent viscosity ($\eta_{inh}$) range of 1.3-0.54 dL/g and gave flexible and colorless films after cured at 250-350 °C in a thermal imidization method. In the IR spectrum of PI(CpODA+3,4'-DDE) film prepared by the thermal imidization technique, two characteristic peaks assigned to C=O stretching bands of the imide carbonyl groups were observed at 1776 ($\nu_{as}$) and 1718 ($\nu_{s}$) cm$^{-1}$, and the peak of keto carbonyl group of cyclopentanone appeared at 1706 cm$^{-1}$ as a shoulder beside the strong imide peak of 1718 cm$^{-1}$.

3.2. Chemical imidization

The PI(CpODA+3,4'-DDE) polyimide was prepared also by a chemical imidization method under various conditions. The precipitated and reprecipitated (in methanol) polyimides were dissolved in CDCl$_3$ and the $^1$H-NMR spectra were measured. The imidization ratio (I.R.) was estimated from the spectrum by following equation (1), where A and B represent the signal areas of amide and aromatic protons, respectively.

$$I.R. = \frac{(1 - 4A/B)}{} \times 100 \quad \cdots \cdots \cdots (1)$$

<table>
<thead>
<tr>
<th>run</th>
<th>anhydride (mmol)</th>
<th>base (mmol)</th>
<th>temp. (°C)</th>
<th>time (h)</th>
<th>state</th>
<th>I.R. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TFAA(0.6)</td>
<td>TEA(1)</td>
<td>r.t.</td>
<td>16</td>
<td>homogeneous</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>TFAA(0.6)</td>
<td>TEA(1)</td>
<td>70</td>
<td>1</td>
<td>precipitate</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>Ac$_2$O(0.6)</td>
<td>TEA(1)</td>
<td>r.t.</td>
<td>16</td>
<td>homogeneous</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>TFAA(0.6)</td>
<td>Py(1)</td>
<td>r.t.</td>
<td>19</td>
<td>homogeneous</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>Ac$_2$O(0.6)</td>
<td>Py(1)</td>
<td>r.t.</td>
<td>20</td>
<td>gelation</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Ac$_2$O(6)</td>
<td>NMeP$_2$(2)</td>
<td>70</td>
<td>1</td>
<td>precipitate</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 1. The imidization ratio (I.R.) of PI(CpODA+3,4'-DDE) prepared by a chemical imidization method a).

a) CpODA=1mmol, 3,4'-DDE=1mmol, 20 wt-% DMAc solution.

The polyimide precipitated as a white solid when the poly(amic acid) solution was heated at 70 °C for 1h together with dehydrate agents (runs 2 and 6). The I.R. of the precipitated polyimides are around 96 %. In the case of stirring the mixture at room temperature for 16-19 h (runs 1, 3 and 4), the reaction proceeded homogeneously except for the “Ac$_2$O+Py” system (run 5), and the polyimides had an I.R. range of 32-60 %.

3.3. Combined chemical and thermal imidization method for film fabrication at low temperature

It is known that the film quality and the polymerization degree of the polyimide are influenced strongly by the curing temperature in thermal imidization process.[3] High-temperature cure over Tg (331 °C, PI(CpODA+3,4'-DDE)) is required in order to obtain the flexible and tough polyimide films. However when the colorless film is heated at higher temperature than 300 °C for 1 h under reduced pressure, the film turns somewhat brown. The chemical imidization, which is a low-temperature method, is inapplicable to hardly soluble or practically insoluble polyimides like PI(CpODA+3,4'-DDE) as described in Introduction part. In the present article, we propose “a combined chemical and thermal imidization method” as a low temperature film-fabrication technique of hardly soluble alicyclic polyimides with high Tg, where the poly(amic acid) solution is partially imidized by treating with trifluoroacetic anhydride (TFAA) and triethylamine (TEA) at room temperature for 16 h
then curing at 80°C for 2 h and 200°C for 1 h under vacuum.

Fig. 2. 1H-NMR spectra and the imidization ratio of PI(CpODA+3,4'-DDE) films prepared by curing the poly(amic acid) at 200°C a) without a chemical procedure and b) after treating with trifluoroacetic anhydride and triethylamine (run 1).

The imidization ratio (R.I.) of the film prepared by only thermal imidization of the poly(amic acid) with curing at 200°C for 1 h is estimated to be 56% as can be seen from Fig. 2 a, and the film was fragile. However, the value reaches 100% using a combined chemical and thermal imidization method Fig 2 b and the resulting polyimide film was flexible and tough. It is of interest that the other combination of an anhydride and a base than “TFAA + TEA” gave no flexible films after curing at 200°C.

3.4. Properties of polyimides

3.4.1. Thermal stability

The 5% weight-loss (T5) and the decomposition (Td) temperatures were measured using TGA at a heating rate of 10 K/min under a nitrogen atmosphere and these results are summarized in Table 2. All the polyimide films prepared in this study possessed excellent thermal stability with no significant weight loss up to 400°C, and have a T5 and Td ranges of 487-459°C and 501-475°C, respectively. The glass transition temperature (Tg) was measured using a thermomechanical analyzer (TMA) with a penetration probe. The polyimides have Tg’s over 330°C except for the 1,3-BAB-based one. The high Tg is due to a dipole-dipole interaction between the keto groups of the polymer chains as well as a development of rigid polyalicyclic unit. The coefficient of thermal expansion (CTE) was measured as an average within 100-200°C for the film plane direction. The CTE value of PI(CpODA+4,4'-DABA) is as low as 15 ppm/K which is comparable to that of Cu (17 ppm/K), whereas most of the CpODA-based polyimide films show a CTE range 50-70 ppm/K of which values are nearly equal to other transparent flexible plastics such as polycarbonate. The diamine 4,4'-DABA contains an amide-linkage having a planar structure and may give a rod-like nature to the polyimide backbone.[4]

3.4.2. Averaged transmittance in visible region (Tvis) and cut-off wavelength (λcut-off)

The Uv-vis spectra of the polyimide films are shown in Fig. 3. The symbols “T” and “C+T” denote a thermal and a combined chemical and thermal imidization methods, respectively. Transparency in the visible region (Tvis) evaluated by averaging the transmittance in the range from 400 to 780 nm in the UV-vis spectrum and λcut-off’s (at the wavelength where the light transmittance becomes below 1%) are listed in Table 3. The polyimide films exhibited λcut-off’s shorter than 336 nm, and the Tvis value of each polyimide film is over 85%. Especially, PI(CpODA+3,4'-DDE) prepared by a combined chemical and thermal method has outstanding optical property (Tvis: 88%, λcut-off’s: 278 nm) due to the film-fabrication at low vacuum.
temperature.

Fig. 3. Transmission UV-vis spectra of the CpODA-based polyimide films (free-standing, ca. 15 µm thick). The symbols “T” and “C+T” denote a thermal and a combined chemical and thermal imidization methods, respectively.

Table 3. The averaged transmittance in visible region (T_{vis}) and the cutoff wavelength (λ_{cut-off}) at which the transmittance becomes below 1%.

<table>
<thead>
<tr>
<th>method a)</th>
<th>diamine</th>
<th>T_{vis} b) (%)</th>
<th>λ_{cut-off} c) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C+T</td>
<td>3,4'-DDE</td>
<td>88</td>
<td>278</td>
</tr>
<tr>
<td></td>
<td>3,4'-DDE</td>
<td>85</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td>4,4'-DABA</td>
<td>86</td>
<td>336</td>
</tr>
<tr>
<td>T</td>
<td>4,4'-DDE</td>
<td>86</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td>1,3-BAB</td>
<td>88</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td>m-Tol</td>
<td>87</td>
<td>292</td>
</tr>
</tbody>
</table>

a) T: thermal imidization, C+T: combined chemical and thermal imidization, b) averaged transmittance in visible region (400-780 nm), c) wavelength at 1 % transmittance.

4. Conclusion
The alicyclic dianhydride having cyclopentanone bis-spiroborornane structure (CpODA) was polycondensated with aromatic diamines at room temperature. Poly(amic acid)s possessed an inherent viscosity (η_{inh}) range of 1.3-0.54 dL/g. The poly(amic acid)s were imidized by three methods, that is a thermal, a chemical, and a combined chemical and thermal ones. The imidization ratio (I.R.) of PI(CpODA+3,4'-DDE) obtained as a white precipitate and a homogeneous solution on a chemical imidization was 96 % and 60-32 %, respectively, whereas that of the polyimide prepared by a thermal method with heating at 200 °C was 56 %. However, the I.R. value reached 100% using a combined chemical and thermal imidization method. All the polyimide films prepared in this study possessed excellent thermal stability and had a T_{5} range and T_{d} ranges of 487-459 °C and 501-475 °C, respectively. Most of the polyimides had T_{g}’s over 330 °C. The CTE value of thermally imidized PI(CpODA+4,4'-DABA) film was as low as 15 ppm/K which is comparable to that of Cu (17 ppm/K). The polyimide films exhibited λ_{cut-off}’s shorter than 336 nm, and the T_{vis} value of each polyimide film was over 85%. Especially, PI(CpODA+ 3,4'-DDE) film prepared by a combined chemical and thermal method had outstanding optical properties (T_{vis}: 88 %, λ_{cut-off}’s: 278 nm).

These colorless polyimide films may be a promising candidate for the substrate of flexible optoelectronic devices.

References