Thermally Stable and Transparent Polyketones Having 1,3-Adamantanedimethylene Moiety

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We report herein semi-aromatic polyketones having a 1,3-adamantanedimethylene moiety, which consists of a hard alicyclic adamantane-1,3-diyl unit and flexible methylene ones, in a main chain. The polymers enable us to obtain thermally stable, transparent, and flexible films. Notably, the resulting films exhibit low birefringence that is hardly achieved by conventional transparent (colorless) polyimides. We believe that these are applicable to a component for curved, bendable, and foldable displays.

Keywords: Polyketone, Thermal stability, Transparency, Birefringence, Flexibility

1. Introduction

Thermally stable and transparent polymers have much attention due to their potential to be applied for optics, electronics, and medical materials [1]. Flexible transparent films are currently required for curved, bendable, and foldable displays [2]. Colorless polyimides are widely studied to realize both transparency and thermal stability, simultaneously [3-6] as materials for these applications. However, their optical properties remain to be improved such as transmittance, yellowness index, and birefringence [2]. Maeyama and co-workers reported thermally stable transparent polyketones prepared from an electron-rich arene such as 2,2'-dimethoxybiphenyl (1) and 1,4-cyclohexanedicarboxylic acid (2b) via direct polycondensation [7]. The resulting colorless polyketone powder exhibited glass transition temperature ($T_g$) above 200 °C measured by differential scanning calorimetry (DSC). However, making it into a self-standing film could not be achieved due to its limited solubility and flexibility.

In this study, we designed polyketones having 1,3-adamantanedimethylene moiety (poly 1-2a, 1-2a/1-2b, and 1-2a/1-2c), which consists of hard alicyclic adamantane-1,3-diyl unit and flexible methylene ones, in a main chain to improve its solubility, flexibility, thermal stability, and transparency (see, in Scheme 1). We then prepared self-standing films from the polyketones and evaluated its thermal, optical, and mechanical properties.

2. Experimental

2.1. Reagents

2,2'-Dimethoxybiphenyl was purchased from Alfa Aesar. 1,3-Adamantanedicarboxylic acid was purchased from Chongqing Maohuan Chemical Co., Ltd. 1,4-Cyclohexanedicarboxylic acid was purchased from Nikko Rica Corporation. Decahydronaphthalene-2,6-diyl dicarboxylic acid was provided by New Japan Chemical Co., Ltd. Phosphorus (V) oxide and methanesulfonic acid were purchased from FUJIFILM Wako Pure Chemical Corporation. All reagents were used without further purification.

2.2. Synthesis of the polyketones (Scheme 1)

The polyketones were prepared according to the previous report [7]. 2,2'-Dimethoxybiphenyl (1) was allowed to react with 1,3-adamantanedicarboxylic acid (2a) in P$_2$O$_5$-CH$_3$SO$_3$H (MsOH) [8] at 60 °C for 40 h as shown in Scheme 1. The resulting viscous reaction mixture was poured into water to
remove the reaction media affording poly 1-2a as colorless powder. The copolymer poly 1-2a/1-2b and 1-2a/1-2c were obtained similarly using 1 and 2a with the corresponding acid 2b or 2c. Molecular mass of the resulting polyketones was measured by SEC (Tosoh HLC-8320 equipped with TSKgel SuperMultipore HZ-M) using tetrahydrofuran (THF) as an eluent, based on polystyrene as a standard.

2.3. Preparation of the films
A polyketone film was obtained as follows. Poly 1-2a was dissolved in 1-methyl-2-pyrrolidone (NMP), and resulting solution was coated on a glass plate or a silicon wafer. Then, the whole was heated for 3 min at 120 °C, and then for 60 min at 200 °C to obtain a dry polyketone film (10 µm thick) on a substrate. This was dipped into water to isolate a transparent self-standing film of poly 1-2a.

2.4. Instruments and measurements
Transmittance of the polyketone films was measured by UV-visible spectroscopy (JASCO V-570 UV-visible spectrophotometer) on a glass substrate from 300 nm to 800 nm. The measured values were obtained at 400 nm, and corrected in certain film thickness (10 µm). Refractive index and birefringence of the films were measured according to prism-coupling method (Metricon 2010M prism coupler) on a silicon substrate using a 633 nm beam. Glass transition temperature ($T_g$) of the films was calculated by dynamic mechanical analysis (DMA, Rheometrics RSA-II). It was defined as a temperature at the peak in its loss tangent between 25 °C to 300 °C. Decomposition temperature ($T_d$) was estimated using the polyketone powder by thermo-gravimetric analysis (TGA, Hitachi High-Technologies EXSTAR 6000) at downturn in its temperature-mass curve from 50 °C to 500 °C. Storage modulus of the films was measured by DMA (Rheometrics RSA-II) at 25 °C. Flexibility was evaluated, in this study, according to Mandrel bend testing method referred to ASTM D 522 using a Gardner type Mandrel bending tester (YASUDA SEIKI No. 550). Bend radius denoted minimum radius without causing cracks on the film.

3. Results and discussion
The polyketones were synthesized using an electron rich aromatic compound (arene) and an alicyclic dicarboxylic acid as a monomer, respectively, via direct polycondensation reaction in $P_2O_5$-MsOH as a catalyst and medium [7]. We selected 2,2’-dimethoxybiphenyl (1) as the arene, since we expected that resulting polymers would exhibit thermal stability, transparency, and solubility due to its distorted structure [7]. We then selected 1,3-adamantanedicarboxylic acid (2a) as the acid, since we also expected that resulting polymers would exhibit thermal stability, transparency, and solubility due to its cage structure. And moreover, two methylene units of 2a would contribute to flexibility of a film obtained from the resulting polymer. Poly 1-2a was synthesized according to the Scheme as colorless powder. Number average molecular mass ($M_n$) and mass average molecular mass ($M_w$) of the resulting polyketone were 23000 and 100000, respectively. Poly 1-2a was soluble in NMP and the resulting solution was able to be cast on a substrate with a common method such as bar coating, spin coating, and dip coating. The isolated self-standing film of poly 1-2a was colorless and flexible as shown in Fig. 1.
We confirmed the transparency of poly 1-2a by UV-visible spectroscopy as shown in Fig. 2. Transmittance of the film is more than 95% over 380 nm. Then we evaluated optical, thermal, and mechanical properties of poly 1-2a as listed in Table 1. We note that poly 1-2a exhibits not only excellent transparency (95%) but also low birefringence (0.001). Poly 1-2a shows resistance on thermal decomposition ($T_d$) at less than 440 °C, although relatively low $T_g$ (182 °C) remains to be improved. As mentioned above, the film of poly 1-2a is flexible, that is supported by the result of its low modulus (0.9 GPa) and low bend radius (3 mm). We emphasize that the novel polyketone poly 1-2a has excellent optical properties as low birefringence consisting with flexibility and thermal stability.

We have mentioned that polyketone poly 1-2a shows excellent properties. However, its relatively low $T_g$ seems to be improved for further applications. Maeyama and coworkers found that 1,4-cyclohexanedicarboxylic acid (2b) was applied with the arene 1 to give a polyketone with relatively high $T_g$ measured by DSC [7]. This result suggests that a cyclic structure, without flexible methylene units, might contribute to an increase in $T_g$. However, the methylenes would positively contribute to the flexibility of the resulting film as described above. We next investigated copolymers consisting of 2a and a cyclic acid 2b or 2c [9] to satisfy this contradictory effect.

Table 1. Optical, thermal, and mechanical properties of a polyketone poly 1-2a.

| Items                        | poly 1-2a |
|------------------------------|-----------|
| Transmittance at 400 nm (%T) [%] | >95       |
| Refractive index [-]         | 1.614     |
| Birefringence [-]            | 0.001     |
| Glass transition temp. ($T_g$) [°C] | 182       |
| Decomposition temp. ($T_d$) [°C] | 440       |
| Storage modulus at 25 °C [GPa] | 0.9       |
| Bend radius [mm]             | 3         |

*The transmittance was corrected in 10 µm thickness.*

Copolymers of polyketones, poly 1-2a/1-2b and poly 1-2a/1-2c, were synthesized similarly as poly 1-2a by replacing the monomer 2a partially with 2b or 2c as shown in the Scheme 1. The $M_n$ and $M_w$ of the colorless polyketones were 11000 and 28000 for poly 1-2a/1-2b (m : n = 50 : 50), 10000 and 37000 for poly 1-2a/1-2c (m : n = 50 : 50), and 9000 and 33000 for poly 1-2a/1-2c (m : n = 25 : 75), respectively.

Table 2 shows optical, thermal, and mechanical properties of the copolymers. Poly 1-2a/1-2b prepared from 2a and 2b with the molar ratio of 1 : 1 showed higher $T_g$ (209 °C) compared with that of the homopolymer poly 1-2a. We also found that this modification hardly affected its optical and mechanical properties as transmittance (>95%) and bend radius (3 mm), respectively. Unfortunately, we obtained insoluble product by increasing in the content of 2b to the copolymer for higher $T_g$. We then replaced the acid 2b with decahydronaphthalene-2,6-diyl dicarboxylic acid (2c) from poly 1-2a/1-2b to improve $T_g$ (in the Scheme 1). The resulting polyketone poly 1-2a/1-2c (m : n = 50 : 50) exhibited higher $T_g$ (218 °C) as shown in Table 2. We obtained soluble copolymer poly 1-2a/1-2c by increasing in the content of 2c from 1 : 1 to 1 : 4 in contrast to...
poly 1-2a/1-2b. The polyketone poly 1-2a/1-2c (m : n = 25 : 75) exhibited the highest $T_g$ (238 °C) among the polymers in this study, maintaining its transmittance (>95%) and bend radius (3 mm) as shown in Table 2. We also found that poly 1-2a/1-2c exhibited slightly higher $T_d$ (445 °C or 448 °C) compared with poly 1-2a (440 °C). Thus, fused aliphatic bicyclic structure in the polyketone might contribute to the improvement of the thermal stability ($T_g$ and $T_d$).

Table 2. Properties of polyketones poly 1-2a, poly 1-2a/1-2b, and 1-2a/1-2c.

| Polyketones         | %T [%]a | $T_g$ [°C]b | $T_d$ [°C]c | Bend radius [mm] |
|---------------------|---------|-------------|-------------|-----------------|
| poly 1-2a           | >95     | 182         | 440         | 3               |
| poly 1-2a/1-2b      | >95     | 209         | 440         | 3               |
| (m : n = 50 : 50)    |         |             |             |                 |
| poly 1-2a/1-2c      | >95     | 218         | 448         | 3               |
| (m : n = 50 : 50)    |         |             |             |                 |
| poly 1-2a/1-2c      | >95     | 238         | 445         | 3               |
| (m : n = 25 : 75)    |         |             |             |                 |

a %T; transmittance at 400 nm (corrected in 10 µm thickness), b $T_g$; glass transition temperature, c $T_d$; decomposition temperature.

4. Conclusion

A film prepared from a semi-aromatic polyketone having 1,3-adamantanedi methane moiety (poly 1-2a) showed excellent thermal stability, transparency, and flexibility. The film also exhibited remarkable low birefringence that is hardly achieved by conventional transparent (colorless) polyimides. Glass transition temperature ($T_g$) of poly 1-2a was improved up to 238 °C by replacing its 1,3-adamantanedi methane moiety partially with decahydronaphthalene-2,6-diyl one. Resulting film has potential for a component of curved, bendable, and foldable displays. Further study on evaluation of their practical properties and improvement of their thermal, optical, and mechanical ones is in progress.

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