Low Temperature Film-fabrication Methods for Hardly Soluble Alicyclic Polyimides with High Tg

Toshihiko MATSUMOTO(松本 利彦) [1], Hiroki OZAWA [1], Tomohiro MIZUTA [1],
Eriko ISHIGURO [1], and Shinichi KOMATSU [2]

[1] *Dept. of Life Sci. & Sustainable Chem., Faculty of Eng., Tokyo Polytechnic University*
1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan
[2] *Specialty Chem. & Mater Com, JX Nippon Oil & Energy Co.,*
8 Chidoricho, Nakaku, Yokohama, Kanagawa 231-0815, Japan

Abstract: An alicyclic dianhydride having cyclopentanone bis-spironorbornane structure (CpODA) was polycondensated with aromatic diamines at room temperature in various kinds of polar solvents to give poly(amic acid)s having an inherent viscosity (η_{inh}) range of 1.47-0.54 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. A novel technique "precipitation chemical imidization method" can be applicable to some polyimides which were precipitated in the imidizatition medium but soluble in chloroform. The homogeneous chloroform solutions gave highly transparent polyimide films only by drying at 80 °C under vacuum. All the polyimide films possessed excellent thermal stability and Tg 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 $\lambda_{cut\text{-}off}$ 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 method and a precipitation chemical imidization methods had outstanding optical properties (T_{vis}: >88 %, $\lambda_{cut\text{-}off}$: 278 nm) due to the low temperature film-fabrication.
Keywords: Alicyclic Polyimides, Colorless Polyimides, High Tg, Low CTE, Combined Chemical and Thermal Imidization, Precipitation Chemical Imidization, Low Temperature Film-fabrication

1. Introduction

In recent years, alicyclic polyimides prepared from polyalicyclic dianhydrides and aromatic diamines have much attention because of their high-temperature stability and transparency in the visible region. The authors reported the alicyclic polyimides synthesized from the dianhydrides with alkanone bis-spironorbornane structure.[1,2] These polyimides possessed the glass transition temperatures (Tg) in the range of 300-350 °C. The films exhibited cutoffs at wavelengths shorter than 290 nm. Transparency in the visible region (400-780 nm) of each polyimide film was over 85%. The high Tg is presumed to be 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 number-averaged molecular weight of PI(CpODA+3,4'-DDE) obtained by curing the reprecipitated poly(amic acid) at 300 °C for 1 h under vacuum was 4×10^4, whereas the value increased more than three times on heating at 350 °C for an additional 30 min. This result implied that the post-polymerization took place over the Tg (333 °C). The preparation of a flexible and tough polyimide film requires a high temperature imidization process.[3] However, when the colorless polyimide film is cured at temperature higher than 250 °C, the transparency is decreased with an increase in curing temperature.[4] Usually a chemical imidization is carried in the solution using a mixture of a dehydration agent and a base catalyst. However, the method is inapplicable to the synthesis of 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 two novel techniques, "a combined chemical and thermal imidization method" and "precipitation chemical imidization method" in low temperature film-fabrication of hardly soluble alicyclic polyimides with high Tg.

2. Results and Discussion

A combined chemical and thermal imidization method is schematically illustrated in **Figure 1**.[3] In the first step, the poly(amic acid) was partially, about 30%, imidized using a chemical imidization technique at room temperature for 16 h, which gave a homogeneous solution. In the second step, the solution was cast, then cured at 200 °C to give a flexible film. In spite of low-temperature cure under Tg, the imidization ratio reached to 100 % . This method was verified under various conditions. The results are summarized in **Table 1**. Only when a combination of trifluoroacetic anhydride (TFAA) and trimethylamine (TEA) was used, flexible film was given even by low-temperature imidization at 200 °C. When using acetic anhydride and TEA at the first step, a flexible film was obtained only when cured at 350 °C in the second step. The chemical imidiztion conditions affected definitely quality of the polyimide films. SEC profiles of PI(CpODA+3,4'-DDE) prepared using different methods are shown in **Figure 2**. As stated in thermal method, the molecular weight increases with an increase of imidization temperature due to the post-polymerization. Similarly, in the combined method high temperature cure of the second step enhance the molecular weight. Because the partial imidization suppress the degradation of poly(amic acid) and the free diamine can undergo the post-polymerization with anhydride moiety at high temperature.

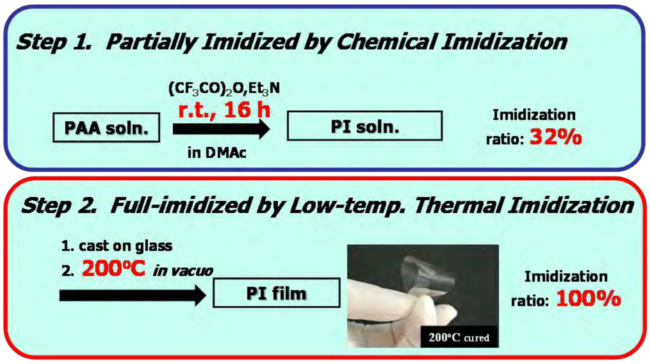
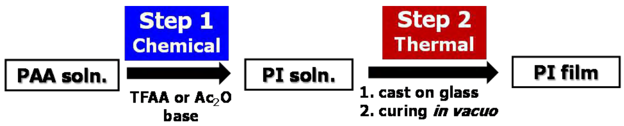


Figure 1. Schematic illustration of a combined chemical and thermal imididation method.

Table 1. Verification of a combined chemical and thermal imididation method under various condition.



Step 1 a)						Step 2		
anhydride (mmol)	base (mmol)	temp. (°C)	time (h)	state	I.R. b) (%)	film / cure temp. 200 °C	300 °C	350 °C
TFAA (0.6)	TEA (1)	r.t.	16	homo	32	*flexible*	*flexible*	*flexible*
TFAA (2)	TEA (2)	r.t.	23	homo	40	*flexible*	*flexible*	*flexible*
TFAA (2)	TEA (2)	70	1	ppt	96	—	—	—
TFAA (0.6)	Py (1)	r.t.	19	homo	<ND>	brittle	brittle	brittle
Ac_2O (0.6)	TEA (1)	r.t.	16	homo	<ND>	brittle	brittle	*flexible*
Ac_2O (0.6)	Py (1)	r.t.	15	gel	<ND>	—	—	—

a) CpODA=1.0 mmol, 3,4'-DDE=1.0 mmol, in DMAc. b) by ^{1}H-NMR.

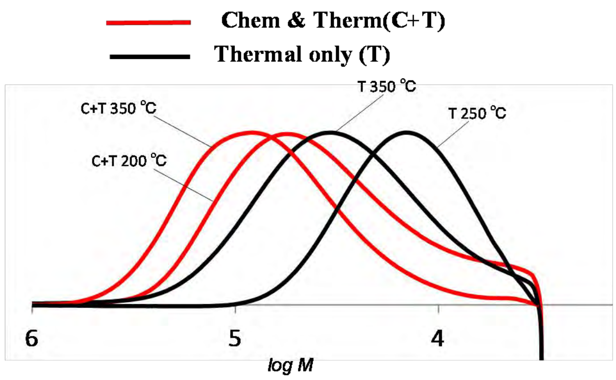


Figure 2. SEC Profiles of PI(CpODA+3,4'-DDE) prepared by different methods.

The second method for low temperature imidization, "precipitation chemical imidization" is schematically shown in **Figure 3** together with SEC profiles of PI(CpODA+3,4'-DDE) polyimide films prepared using precipitation chemical imidization. As described above, CpODA-based polyimides were precipitated in conventional chemical imidization. As it happens, we found that the precipitates were soluble in halogenated organic solvents such as chloroform and dichloromethane. The chloroform solution of polyimide was cast on the glass plate, then cured in vacuo. The three SEC have almost the same shape and maximum peak position. This implied that high molecular weight was fixed due to suppression or inhibition of depolymerization of the poly(amic acid) by precipitation chemical imidization and that the post-polymerization did not undergo due to the absence of free amino group.

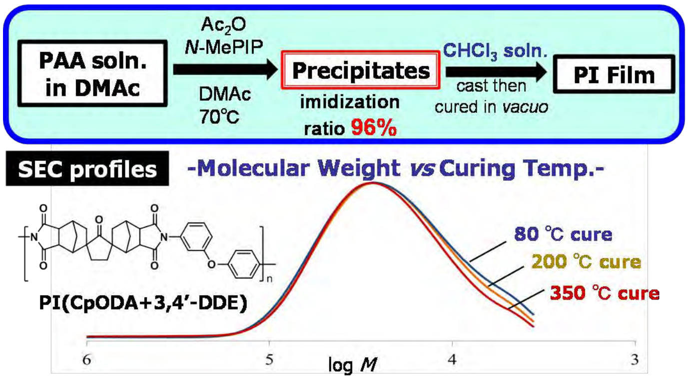


Figure 3. Schematic illustration of a precipitation chemical imididation method and the SEC profiles.

The thermal properties of the polyimide films are summarized in **Table 2**. The symbols "C", "C+T" and "T" denote a chemical, a combined chemical and thermal, and a thermal imidization methods, respectively. The 5 % weight-loss temperatures measured in nitrogen are over about 460 °C and the decomposition temperature are in a range from 480 to 500 °C. Introduction of multibond in polyalicyclic unit resulted in less probability of main chain scission. The polyimides have Tgs over 330 °C. The high Tg is due to a dipole-dipole interaction between the keto groups of the polymer chains as well as to a development of rigid polyalicyclic units. In-plane CTE were measured using TMA. 4,4'-DABA polyimide film possessed a much lower value, which is comparable to copper foil. 4,4'-DABA contains an amide-linkage having a planar structure and give a rod-like nature to the polyimide backbone.

Table 2. Thermal properties of CpODA-based polyimide films prepared by three different methods.

method	diamine	(℃)	(℃)	(℃)	(ppm/K)
C	*m*-Tol	456	475	345	38
	3,4'-DDE	478	488	329	48
C+T	4,4'-DABA	472	495	>400	24[g)]
	3,4'-DDE	472	488	331	54
T	4,4'-DABA	481	501	>400	17
	3,4'-DDE	467	483	333	57
	4,4'-DDE	468	488	354	49
	1,3-BAB[h)]	487	496	290[e)]	56

[a)]C : chemical imidization(80 ℃), C+T : combined chemical and thermal imidization(200 ℃), T : thermal imidization(300-350 ℃). [b)]5 % weight-loss and [c)]decomposition temperatures in N_2 at 10 K/min. [d)]measured by TMA in air at 10 K/min. [e)]by DSC. [f)]coefficient of thermal expansion(100-200 ℃) measured by TMA in air or [g)]N_2 . [h)] by Kimura

The transmission Uv-vis spectra of the polyimide films are shown in **Figure 4**. The averaged transmittance in the visible region (T_{vis}, 400-780 nm) and the cut-off wavelength ($\lambda_{cut\text{-}off}$, the wavelength where the light transmittance becomes below 1%) are listed in **Table 3**. The polyimide films exhibited cut-off wavelength shorter than 336 nm, and the T_{vis} value of each polyimide film is over 84%. Especially, the films prepared by a precipitation chemical method and a combined method exhibited outstanding optical property, T_{vis} over 88% and 86%, due to the low temperature film fabrication.

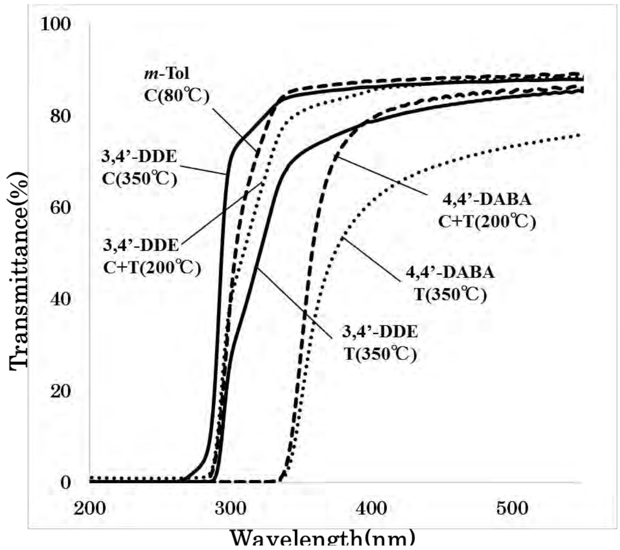


Figure 4. Transmission Uv-vis spectra of the polyimide films fabricated by three different methods.

Table 3. The averaged transmittance in the visible region and the cut-off wavelength.

method	diamine	T_{vis} [a] (%)	$\lambda_{cut\text{-}off}$ [b] (nm)
C	*m* -Tol	89	285
	3,4'-DDE	88	268
C+T	4,4'-DABA	86	334
	3,4'-DDE	88	278
T	4,4'-DABA	84	337
	3,4'-DDE	85	289
	4,4'-DDE	86	290

[a]averaged transmittance in visible region(400-780nm).b)wavelength at 1% transmittance.

3. Conclusions

The alicyclic dianhydride having cyclopentanone bis-spironorbornane structure (CpODA) was polycondensated with aromatic diamines at room temperature. Poly(amic acid)s possessed an inherent viscosity (η_{inh}) range of 1.47-0.54 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. All the polyimide films prepared in this study possessed excellent thermal stability and had a T5 range and Td ranges of 487-459 ^{o}C and 501-475 ^{o}C, respectively. Most of the polyimides had Tg's over 330 ^{o}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 $\lambda_{cut\text{-}off}$ 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 precipitation chemical and a combined chemical and thermal methods had outstanding optical properties (T_{vis}: 88 %, $\lambda_{cut\text{-}off}$: 278 nm). These colorless polyimide films may be a promising candidate for the substrate of flexible optoelectronic devices.

References

[1]. T. Matsumoto, E. Ishiguro, S. Nakagawa and R. Kimura, *J. Photopolymer Sci. & Technol.*, **26** (2013) 361.

[2]. R. Kimura and T. Matsumoto, *Kobunshi Ronbunshu*, **68** (2011) 127.

[3]. T. Matsumoto, E. Ishiguro and S. Komatsu, *J. Photopolymer Sci. & Technol.*, **27** (2014) 167.

[4]. T. Matsumoto and T. Kurosaki, *Macromolecules*, **30** (1997) 993.