

Fully Aliphatic Polyimides Based on Alicyclic Monomers

Toshihiko MATSUMOTO

Department of Applied Chemistry, Tokyo Institute of Polytechnics

1583 Iiyama, Atsugi, Kanagawa 243-0297, Japan

Fax: +81-46-242-3000, e-mail: matumoto@chem.t-kougei.ac.jp

Abstract: Fully aliphatic polyimides were synthesized by polycondensations of four kinds of cycloaliphatic dianhydrides with a cycloaliphatic diamine **BBH** in HMPA. Although the inherent viscosities of the poly(amic acid) were low, the polymers gave the free-standing polyimide films after curing. The films were soluble in organic polar solvents such as DMAc and NMP. The films have good thermal stability with no significant weight loss up to 350°C and possess a T_g range from 210°C to 340°C. The full-aliphatic polyimide films exhibit cutoff's at a wavelength shorter than 235 nm and are colorless. The averaged refractive indices were 1.52-1.54 and the optical anisotropies were nearly zero. The dielectric constants that were estimated from the refractive index according to the modified Maxwell equation, $\epsilon = 1.1n^2$, were 2.55-2.73.

1. Introduction

Polyimides are classified into four distinct categories according to their chemical structures (**Figure 1**). Although aromatic polyimides have excellent thermal stability and mechanical properties, most of them including Kapton® are insoluble in organic solvents and strongly absorb visible light, and have relatively higher dielectric constants ϵ over 3.0. It is well known that low dielectric constant (low k) materials are indispensable to the drive to faster microprocessors.

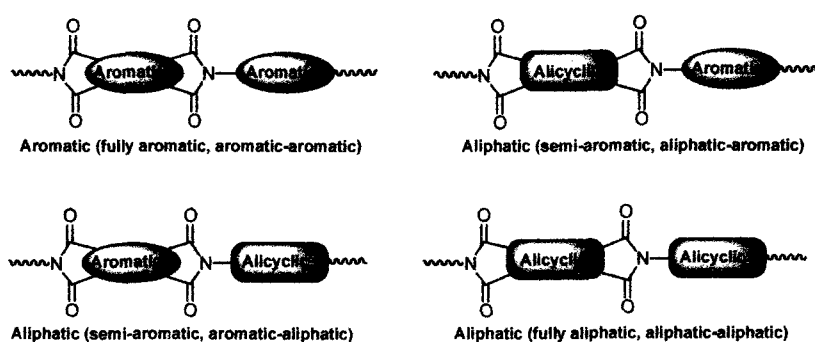


Figure 1 Four categories for polyimides classified according to the chemical structure.

Dielectric constant ϵ of the material can be estimated roughly from the averaged refractive index n according to the Maxwell's equation, $\epsilon = n^2$. Therefore, the low refractive index materials exhibit low ϵ . The ϵ around 1 MHz is evaluated to equal about 1.1 times n square including an additional contribution of approximately 10% from the infrared absorption, that is, $\epsilon = 1.1n^2$. [1] The refractive index n is expressed using Lorentz-Lorentz formula as described below, [2]

$$n = \frac{\sqrt{1 + 2K_p\phi}}{\sqrt{1 - K_p\phi}}$$

where K_p is polymer packing constant and ϕ is expressed as below.

$$\phi = \frac{4\pi\alpha}{3V_{\text{vdw}}}$$

In this equation, α and V_{vdw} mean the molecular polarizability and Van der Waals volume of a repeating unit of the polymer, respectively. As the n is a monotone increasing function with respect to the product of K_p and ϕ , these values need to be decreased these in order to obtain low n materials. There may be two approaches in the molecular design to high temperature low n materials. The first one is to lower polymer packing constant K_p , which implies lowering the density of the polymers with nano size porosity. IBM group at Almaden Research Center has successfully achieved to prepare the thermally stable and low density material, organosilicates with nanoporosity.[3] The second approach is to lower ϕ , which means increasing Van der Waals volume of the molecule and decreasing α . Introduction of bulky substituents and twisted or bended linkage into the polymer leads us increasing Van der Waals volume, and to lower n . It is known to be much effective for decreasing α to introduce fluorine atoms in aromatic polymers.[4] Another way to decrease α is excluding benzene rings in high temperature polymers. We have calculated averaged molecular polarizabilities α 's of polyimide models using a semi-empirical molecular orbital method (MOPAC2000/AM1 and MOS-F/INDO/S). The results are illustrated in **Figure 2**.

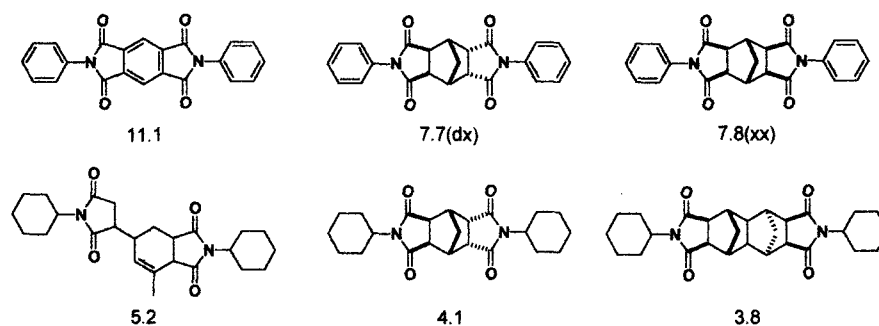


Figure 2 Averaged molecular polarizability α for polyimide models (unit: 10^{-24} cm³ at 0.2eV).
(Geometry optimization: MOPAC2000/AM1 Polarizability a: MOS-F/CNDO/2)

The decreasing aromatic character of the polyimide diminishes the α . Therefore it is expected that full-aliphatic polyimides might have low refractive indices, and it agrees one generation that aromatic polymers possess high refractive indices. In this article, the synthesis and the properties of full-aliphatic polyimides will be discussed.

2. Experimental

2.1. Materials

5-(2,5-Dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexen-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*-tetracarboxylic 2,3:5,6-dianhydride (**BHDAdx**) and (4*arH*,8*acH*)-decahydro-1*t*,4*t*:5*c*,8*c*-dimethanonaphthalene-2*c*,3*c*,6*c*,7*c*-tetracarboxylic 2,3:6,7-dianhydride (**DNDAdx**) were synthesized according to the previous literatures.[4,5] 2,5(6)-bis(aminomethyl)bicyclo[2.2.1]heptane (**BBH**) was 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 VALOR III Fourier transform spectrometer. UV-Vis spectra of the polyimide film were recorded on a Jasco V-570 UV/VIS/NIR spectrophotometer. 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. Film thickness and refractive index were measured by a Metricon Model PC-2010 prism coupler (Thin Film Thickness/Refractive Index Measurement System) at room temperature in open air. The measurements were made at a wavelength of 632.8 nm (He-Ne laser). A prism 6561 designated 200-P-4 with a refractive index of 2.1677 at the He-Ne wavelength was used for the experiments. Using parallel (TE) and perpendicularly (TM) polarized laser light, the in-plane (*n*TE) and out-of-plane (*n*TM) refractive indices of the sample films were determined. Thermal analyses were carried out using a Seiko SSC 5200-TG/DTA 220 instrument at a heating rate of 10 K/min in a nitrogen atmosphere or in air for the thermogravimetric analysis (TGA). Thermomechanical analyses (TMA) were done using a Seiko Instruments TMA/SS 100 equipped with a penetration probe of 1.0 mm diameter and using an applied constant load of 10 g (stress, 0.125 MPa) 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.

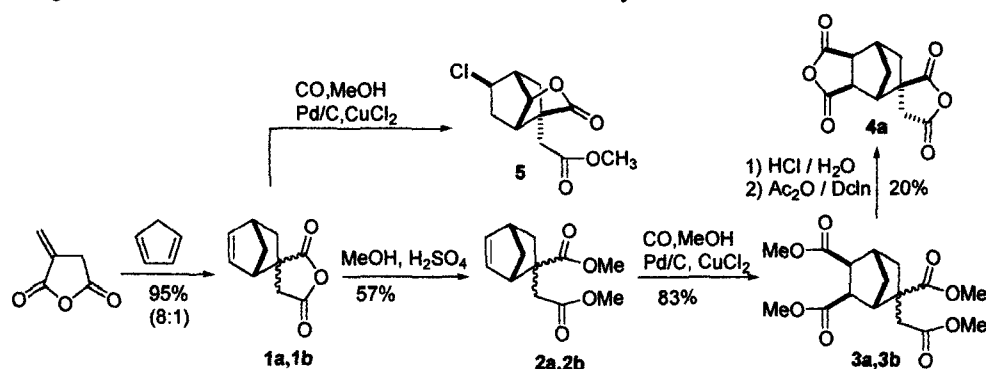
2.4. General Polymerization Procedure and Film Preparation of Polyimide

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

The synthetic route to 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 is illustrated in **Scheme 1**. 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-*endo*-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,[6] 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,[7] 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(mol/mol)). The dianhydride **4a** (**BSDA**) was isolated by sublimation, although isolation of the isomer **4b** has not been successful yet.



Scheme 1 Synthetic route to bicyclo[2.2.1]heptanetetracarboxylic dianhydride with spiro structure.

3.2. Polymer Synthesis

The structures and abbreviations of monomers used in this study are illustrated in **Figure 3**.

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. 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 basicity of primary aliphatic diamines is about a million times higher than that of aromatic diamines. The difference influences the polymerization behavior as Dr. Volksen pointed out.[8]

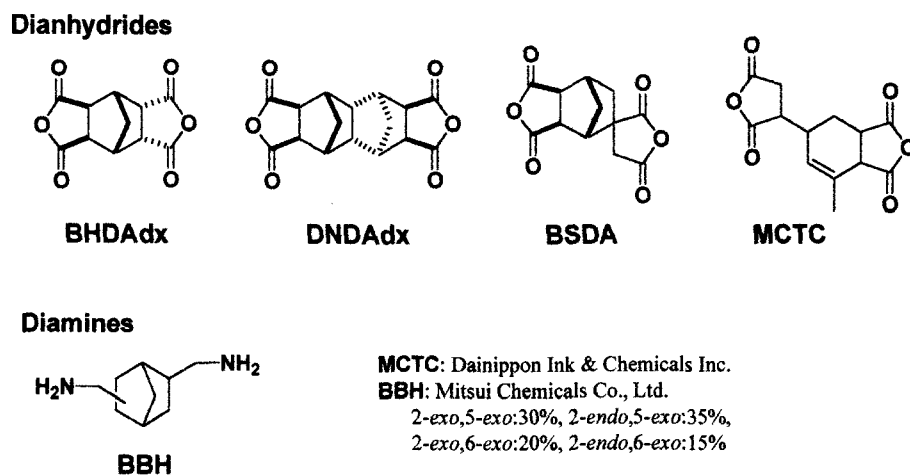


Figure 3 The structures and abbreviations of cycloaliphatic monomers for fully aliphatic polyimides.

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 possessed 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.

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

monomers	η_{inh} (dL/g) of poly(amic acid) ^a	film quality of polyimide
BHDA-BBH	0.21	free-standing & tough
DNDAdx-BBH	0.36	free-standing
BSDA-BBH	0.22	somewhat brittle
MCTC-BBH	0.20	free-standing

^a inherent viscosity of poly(amic acid), 0.5 g/dL HMPA solution at 30°C.

3.3. Properties of Polyimides

In the IR spectrum of PI(**DNDAdx-BBH**) film (**Figure 4**), 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.

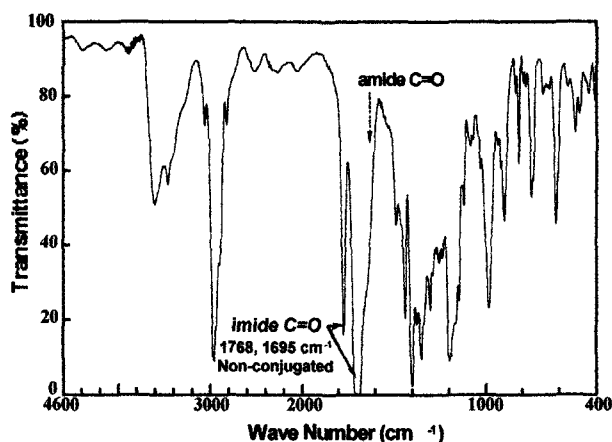


Figure 4. IR spectrum of PI(DNDAdx-BBH) film.

The qualitative solubility of the full-aliphatic polyimide films is shown in **Table 2**. All of these polyimides are soluble in polar solvent such as HMPA and DMAc.

Table 2. Qualitative solubility of fully aliphatic polyimides from cycloaliphatic monomers ^a.

solvent	dianhydrides			
	BHDAdx	DNDAdx	BSDA	MCTC
hexamethylphosphoramide	+	+	+	+
<i>N,N</i> -dimethylacetamide	++	++	++	++
<i>N</i> -methyl-2-pyrrolidone	++	++	++	++
1,3-dimethyl-2-imidazolinone	++	++	++	+
dimethyl sulfoxide	++	++	++	+
<i>m</i> -cresol	ND ^b	ND ^b	++	+
acetone				

^a ++: soluble at r.t., +: soluble on heating, -: insoluble even on heating. ^b Not determined.

The thermogravimetric analyses of polymer films were done at a heating rate of 10K/min. The representative profile of DNDAdx-BBH polyimide film is shown in **Figure 5** as a solid black line, together with the differential TG curve. The polyimide has a good thermal stability with no significant weight loss up to approximately 400°C and the 5% weight-loss temperature (T_5) is 459°C. The TGA curves of a semi-aromatic polyimide DNDAx-DDE(4,4'-diaminodiphenyl ether) and polyethylene as another example of full-aliphatic polymers are also illustrated in the figure as gray lines. Although the T_5 of a semi-aroma polyimide is as high as 514°C, the weight-loss of polyethylene starts around 250°C and the T_5 is 367°C. **Figure 6** shows a thermomechanical profile of the DNDAdx-BBH polyimide film using probe penetration method. The penetration increases with temperature much more significantly above T_g , so the intersection of extrapolations of

the two slopes can yield the mechanically determined T_g . The T_g of the polyimide is 340°C. The results along with the T_g 's measured in nitrogen and in air are summarized in **Table 3**. The full-aliphatic polyimides prepared in this study have the T_g 's over 200°C, especially those of cycloaliphatic polyimides are 250°C. The higher T_g is caused by the introduction of cycloaliphatic or polycyclic structures which results in an increase in the polymer main chain rigidity. The T_g 's in N_2 are over 420°C and in air around 410°C.

The high-temperature stability of the alicyclic polyimides would be explained by their chemical structure. The degradation of polymers in an inert atmosphere is known to be aroused from homolytic C-C bond scission rather than C-H bond scission. When the polymer backbone is made from single-chain like polyethylene, the bond scission results in fatal decreasing in the molecular weight. In almost cases, volatile compounds are produced and released as the decomposed gas. On the other hand, in the case of step-ladder type polymers like **DNDAdx-DDE** polyimide, even if the C-C bond scission occurs at any points of the polymer chain, it does not immediately lead to a significant decrease in the molecular weight or to the production of volatile compounds. In other words, the introduction of the multibonds facilitates less probability of main chain scission. Furthermore, even if the C-C bond scissions happen, the produced carbon radicals recombine at once each other unless the species don't remove or are not released as gas. Although an ideal structure of thermal stable polymers may ladder-type, the synthesis of structurally perfect polymers are extremely difficult. A more ideal structure of non-aromatic polymers with high thermal stability is diamond where the C-C bonds expand three-dimensionally. Diamond is said to be stable over 1000°C in an inert atmosphere, although in air it burns at the temperature. However, we cannot fabricate it as fibers or self-standing films. Practically, in order to enhance the thermal stability of polymers, one of the breakthroughs is to introduce C-C multibonds into the polymer backbone without sacrificing the good fabrication.

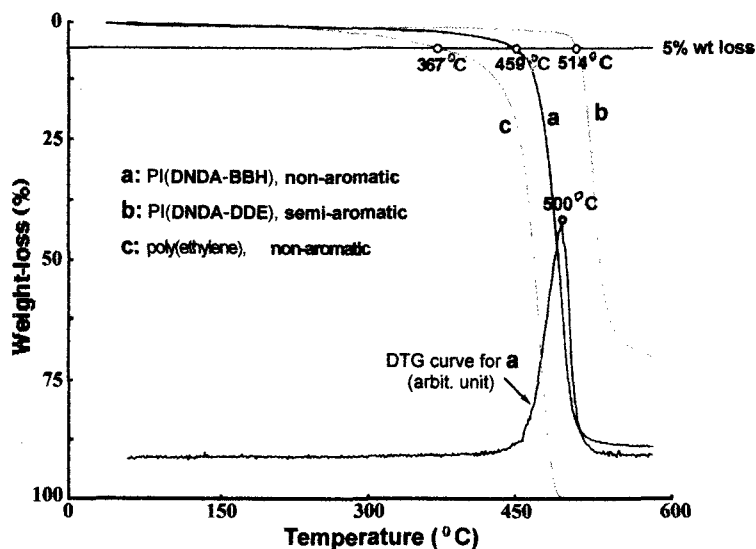


Figure 5. TGA profiles of polyimide films along with polyethylene.
(measured at a heating rate of 10 K/min in N_2)

Table 3. Thermal properties of fully aliphatic polyimides from cycloaliphatic monomers ^a.

polyimides	$T_5(^{\circ}\text{C})^a$		$T_g(^{\circ}\text{C})^b$
	in N_2	in air	
BHDAdx-BBH	455	411	297
DNDAdx-BBH	459	416	340
BSDA-BBH	422	ND	253
MCTC-BBH	424	ND	209
DNDAdx-DDE	514	470	404

^a 5% Weight loss temperatures measured by TGA (10 K/min). ^b Measured by TMA in air (10 K/min).

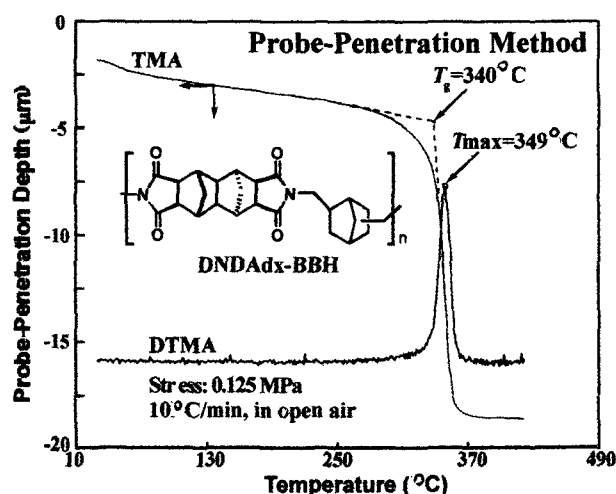


Figure 6. TMA profile of the **DNDAdx-BBH** polyimide film using probe penetration method.

The transmission UV-vis spectra of the free-standing polyimide films are shown in **Figure 7** along with a semi-aromatic polyimide, **DNDAdx-BAB**(1,3-bis(4-aminophenoxy)benzene), and aromatic polyimides, **BPDA-DDE** and **PMDA-DDE**. The full-aliphatic polyimide exhibit cutoff's at 235 nm, although a small absorption around 280 nm due to the carbonyl $n-\pi^*$ can be observed.

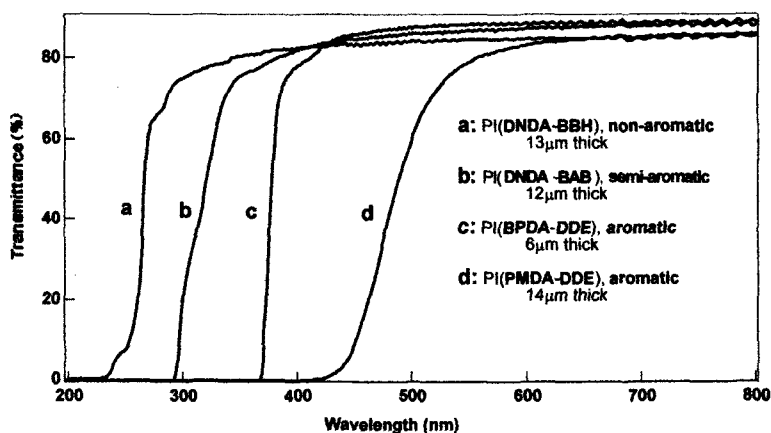


Figure 7. UV-visible spectra for free-standing films of non-aromatic (fully aliphatic), semi-aromatic, and aromatic polyimides.

The refractive index of the free-standing polyimide film was determined by an *m*-line method. The results are listed in **Table 4** along with those of an aromatic and semi-aromatic polyimides for comparative purpose. An averaged refractive index n_{AV} was calculated using this equation from the in-plane and the out-of-plane indices. The optical anisotropy Δn is given as the difference between the in-plane and the out-of-plane indices. The n_{AV} of **BHDAdx-BBH** film is as low as 1.522 and is comparable to poly(ethylene). The value of another full-aliphatic polyimide **MCTC-BBH** is 1.542. The decreasing aromatic character of the polyimide diminished the refractive index as exemplified by the comparison of this series, in agreement with one generation that aromatic polymers possess high refractive indices due to their high molecular polarizability α . The Δn 's of the full-aliphatic polyimides synthesized in this study are nearly zero. The negligibly small anisotropy in the polyimides implies that polymer chains are randomly oriented in the film, and it may be caused by the nature of the "co-polyimide" stereochemistry because the cycloaliphatic diamine **BBH** used here is a not single compound but a mixture of four isomers as stated above. The ϵ around 1 MHz was optically estimated from the refractive index using the equation $\epsilon = 1.1n^2$. [1,8] The refractive indices of 1.522 and 1.542 for **BHDAdx-BBH** and **MCTC-BBH** translate into ϵ 's of 2.55 and 2.73, respectively, whereas ϵ 's are 2.81-2.87 for the semi-aromatic polyimides and 3.13 for an aromatic polyimide **PMDA-DDE**.

Table 4. Optical properties and dielectric constant of polyimide films ^a.

polyimides	category	n_{av} ^b	Δn ^c	$\epsilon(\text{opt.})$ ^b
BHDAdx-BBH	non-aromatic	1.522	0.000	2.55
MCTC-BBH	non-aromatic	1.542	0.000	2.73
BSDA-BAB	semi-aromatic	1.611	0.015	2.85
DNDAdx-BAB	semi-aromatic	1.603	0.013	2.83
PMDA-DDE	aromatic	1.688	0.079	3.13

^a *m*-Line method. ^b Averaged refractive index, $n_{AV} = (2n_{TE} + n_{TM})/3$.

^c Birefringency, $\Delta n = n_{TE} - n_{TM}$. ^d Optically estimated, $\epsilon = 1.1n_{AV}^2$.

4. Conclusions

As an occlusion, exclusion of benzene rings in polyimides lowers molecular polarizability and leads us to the low refractive index materials. Polycondensations of four kinds of aliphatic dianhydrides with an aliphatic 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 low, the resulting full-aliphatic polyimide films were free-standing. The films were soluble in organic polar solvents such as DMAc and NMP. The films have good thermal stability with no significant weight loss up to 350°C and possess a T_g range from 210°C to 340°C. The full-aliphatic polyimide films exhibit cutoff's at a wavelength shorter than 235 nm and are entirely colorless. The averaged refractive indices were about 1.52-1.54 and the optical anisotropies were nearly zero. These values translated into an epsilon of 2.55-2.73. The full-aliphatic polyimides may be of interest for microelectronics or opto-electronics applications.

Acknowledgments

The author acknowledges Dr. C. Feger at T. J. Watson Research Center, IBM, for measuring the refractive index and Dr. Volksen at Almaden Research Center, IBM for his excellent comments. This work was partly supported by a Grant-in-Aid for Scientific Research (No. 12650890) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1. a) Boese, D.; Lee, H.; Yoon, D. Y.; Swalen, J. D.; Rabolt, J. *J. Polym. Sci., Part B: Polym. Phys.*, **1992**, *30*, 1321. b) Herminghaus, S.; Boese, D.; Yoon, D. Y.; Smith, B. A. *Appl. Phys. Lett.*, **1991**, *59*, 1043. 2. a) Ando, S. *Kobunshi Ronbunshu*, **1994**, *51*, 251. b) Slonimskii, G.; Askadskii, A.; Kitaigorodskii, A. *Polym. Sci. USSR*, **1970**, *A12*, 556.
3. Nguyen, C.; Hawker, C. J.; Miller, R. D.; Huang, E.; Hedrick J. L.; Gauderon, R.; Hilbon, J. G. *Macromolecules*, **2000**, *33*, 4281.
4. a) Hougham, G.; Tesoro, G.; Shaw, I. *Macromolecules*, **1994**, *27*, 3642. b) Cassidy, P. E. *J. Macromol. Sci. Rev. Macromol. Chem., Phys.*, **1994**, *34*, 1.
5. a) Yamada, M.; Kusama M.; Matsumoto, T.; Kurosaki, T. *J. Org. Chem.*, **1992**, *57*, 6075. b) Matsumoto, T.; Kurosaki, T. *Macromolecules*, **1995**, *28*, 5684.
6. Matsumoto, T. *Macromolecules*, **1999**, *32*, 4933.
7. James, D. E.; Stille, J. K. *J. Am. Chem. Soc.*, **1976**, *98*, 1810.
8. Volksen, W.; Cha, H. J.; Sanchez, M. I.; Yoon, D.Y. *React. Funct. Polym.*, **1996**, *30*, 61.