Alicyclic polyimides - a colorless and thermally stable polymer for opto-electronic devices

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Abstract. Alicyclic polyimides were prepared from polyalicyclic monomers using a two-step method. Light absorption of polyimides was elucidated from quantum chemistry. The alicyclic polyimide films were colorless, and the transparencies in the visible region were over 85%. The semi-aromatic polyimide films had an average refractive index range of 1.599 to 1.617, and that of a full-alicyclic polyimide was 1.522. The birefringencies were nearly zero. Semi-aromatic polyimides were soluble in aprotic polar solvents like DMAc. However, the non-aromatic (full-alicyclic) polyimides were insoluble except sulfuric acid. All the alicyclic polyimides have the 5 % weight loss temperatures in nitrogen over 450 °C, and 400 °C in air. They possess glass transition temperatures over 280 °C. The alicyclic polyimide films have a tensile modulus range of 1.3-3.0 GPa, and a tensile strength range of 38-145 MPa. Especially semi-aromatic polyimide films display high strength. They have an elongation at break range 5-30 %. All the polyimides exhibited amorphous patterns and broad dispersive peaks of diffraction around at 16° (2θ).

Keywords: Alicyclic polyimides, colorless, thermally stable, opto-electronic devices, flexible organic substrates.

1. Introduction
Aromatic polyimides are often insoluble and intractable in their fully imidized form, thus presenting serious processing difficulties. Much endeavor has been focused on synthesizing tractable and processable polyimides with no reasonable sacrifice of their own excellent properties [1]. One of the success strategies is to incorporate pendant alkyl and phenyl groups [2] or fluorine [3], bromine [4], unsymmetrical [5] and heterocyclic units [6] in the polymer backbone. Most of aromatic polyimides intensely absorb visible light and are colored reddish yellow or pale yellow, so they can be hardly used in areas where absence of coloration is an important requirement. By now the origin of the coloration is known to be caused by their highly conjugated structures and charge-transfer (CT) between the diamine (donor) and the dianhydride (acceptor) moieties. The first mention of CT in aromatic polyimides was made by Dine-Hart et al in 1971 [7]. Kotov et al. confirmed the occurrence of CT in aromatic polyimides in a study of the UV-VIS spectra of several poly(pyromellitimide)s and their model compounds [8]. The first example of colorless polyimides prepared from hexafluoroisopropylidene-bridged diamine and dianhydride was reported as a patent by Rogers about 45 years ago [9]. St. Clair et al. focused much attention on colorless polyimides from the viewpoint of
the potential applications on space components such as multilayer insulation blankets, solar cell, and thermal control coating systems [10]. They demonstrated that polyimides containing the hexafluorosopropylidene group exhibited high transparency in the visible region. Many other examples have been reported where dianhydrides with a biphenyl structure, sulfone linked diamines and fluorinated monomers were employed [11].

Recently, soluble and colorless polyimides using monomers with alicyclic structures, so-called "alicyclic polyimides" have been reported. The introduction of an alicyclic unit into the polyimide backbone would facilitate less polymer-polymer interaction and enhance the solubility in organic solvents. The lack of color is generally associated with the absence or inhibition of intramolecular CT interactions. These polyimides show excellent thermal stability and the high-temperature stability can also be explained by the introduction of an alicyclic structure, which would foster less probability of main chain scission because of the presence of multibonds and would increase main chain rigidity. Alicyclic polyimides have attracted much attention in recent years because of their potential applications including use as liquid crystal orientation layers, flexible solar cell substrates, organic EL substrates, light guide and low dielectric materials [12].

This article deals with the alicyclic polyimides consisting of each alicyclic dianhydride or alicyclic diamines and those of the both.

2. Experimental

2.1. Reagents and monomer synthesis

Bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic dianhydrides was prepared as follows: bismethoxycarbonylation of commercial endo-type nadic anhydride with carbon monoxide in methanol in the presence of catalytic amount of 5 % Pd-C and stoichiometric amounts of CuCl2 afforded the tetramethyl ester. The dianhydrides having different configurations (BHDAdx and BHDAxx) were obtained from the ester by an acid- and a base-catalyzed hydrolyses followed by dehydration ring-closure [13]. Cyclopentane-1,2,3,4-tetracarboxylic 1,2,3,4-dianhydride (CpDA) was prepared from cis,cis,cis,cis- 1,2,3,4-cyclopentanetetracarboxylic acid by thermal dehydration reaction then sublimation at 170-190 °C. Bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic dianhydrides with 2-endoc, 3-endoc, 5-exo, 6-exo-configuration (BODAdx) and its all-exo isomer (BODAxx) were synthesized according to our previous paper [14]. Two kinds of tetracyclic tercarboxylic dianhydrides, (4arH,8ach)-decahydro- 1t,4r:5c,8c-dimethanophthaline-2t,3t,6c,7c-tetracarboxylic 2,3:6,7-dianhydride (DNDAxx) [15] and the 2c,3c,6c,7c-tetracarboxylic 2,3:6,7-dianhydride (DNDAdx) [16], were prepared according to the previous report. An alicyclic dianhydride having a spiro carbon atom, 5-endocarboxymethylbicyclo[2.2.1]-heptane-2-exo,3-exo,5-exo-triacetic acid 2,3:5,5-dianhydride (BSDA) was prepared according to the literature [17]. 5-(2,5-Dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (MCTC, Epiclon® B-4400) was supplied from Dainippon Ink & Chemicals Incorporation, Japan.

Bis(aminomethyl)bicyclo[2.2.1]heptane (BBH) was donated by Mitsui Chemical Co. Ltd, and used without further purification. BBH consists of four isomers; 2-exo,5-exo- (30 wt%), 2-endoc,5-exo- (35 wt%), 2-exo,6-exo- (20 wt%), 2-endoc,6-exo- (15 wt%). 4,4’-Methylenebis(2-methylcyclohexylamine) (MCHM) were purchased from Aldrich Chemical Co. Inc. and Tokyo Kasei Kogyo Co. Ltd., respectively, and used as received. N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), 1,3-dimethyl-2-imidazolinone (DMI), and hexamethylphosphoramide (HMPA) were fractionally distilled over CaH2 under reduced pressure and stored over molecular sieve 4A.

2.2. General polymerization and film preparation

In a 30 mL three necked flask containing DMAc was placed the diamine (purified by sublimation) while a slow stream of nitrogen was maintained. The tetracarboxylic dianhydride was added into the solution and the mixture was stirred mechanically for 2 days in a nitrogen stream. The resulting
poly(amic acid) solutions were cast onto glass plates. The polyimide films were obtained by heating the plates in vacuum.

2.3. Measurements
The $^1$H and $^{13}$C NMR spectra were obtained using a JEOL JNM-LA500 spectrometer. The proton signal in the $^1$H NMR spectrum were assigned in the H,H, C,H-COSY, and NOESY (elimination of J correlation) spectra. Infrared spectra were recorded using a JASCO VALOR III and a JASCO FT/IR 460 PLUS Fourier transform spectrometers. UV-VIS spectra of the polyimide films were recorded on a JASCO V-570 UV/VIS/NIR spectrophotometer. Film thickness and refractive were measured by a Metricon model PC-2010 prism coupler at room temperature in open air. The birefringence of sample films was evaluated by means of ellipsometry. Thermal analyses were carried out using Seiko Instruments SSC 5200-TG/DTA 220 at a heating rate of 10 K/min in a nitrogen atmosphere or in open air. Thermomechanical analyses (TMA) were done using 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 10 K/min air. The mechanical properties were examined at room temperature in open air using Seiko Instruments TMA/SS 100 at a drawing rate of 1 mm/min; the sample size (film) was 3 mm long, 2 mm wide, and about 20 $\mu$m thick. The wide-angle X-ray diffraction measurements (WAXD) were performed on a Rigaku Rint 2500 X-ray diffractometer with graphite monochromated Cu $K\alpha$ radiation and a 12 kW (40 kV, 300 mA) rotating anode generator. Inherent viscosities ($\eta_{inh}$) were measured with an Ostwald viscometer in a 0.5 g/dL solution of poly(amic acid) at 30 °C.

2.4. Molecular orbital calculations
MO calculations were done with an IBM ThinkPad X31 personal computer (CPU:Pentium M processor 1400MHz). The structures of model compounds for the polyimides were geometrically optimized using AM1 in a software package of WinMOPAC Ver. 3 (Fujitsu Ltd.) which was transplanted from MOPAC2000. The electron absorption wavelengths were calculated based on the semi-empirical INSO/S Hamiltonian with configuration interaction (CI) wavefunctions in a software package of MOS-F Ver. 4.2 (Fujitsu Ltd.). In the excited state expressions of all electronic states (20 x 20 = 400 states) are included; they are generated by singly exciting all electrons in the 20 highest occupied MOs to the 20 lowest unoccupied MOs with respect to the ground state [18].

3. Results and discussion
3.1. Polymer synthesis
The structures of monomers used in the present study are illustrated in figure 1 along with their abbreviations. Alicyclic polyimides were prepared via two steps: the first step includes the poly(amic acid) formation at room temperature, and as the second step, the viscous polymer solutions are deposited onto the glass substrates and thermally cyclodehydrated at elevated temperature to yield the corresponding polyimide. The dianhydrides with a bicyclooctane structure, BODAdx and BODAxx, were less reactive than those with the bicycloheptane structure, BHDAdx and BHDAxx, due to the smaller strain of the ring structure. Therefore, even during the first polymerization step, a higher temperature was needed in order to obtain high molecular weight poly(amic acid)s which could be converted to the polyimides with film formability after the thermal cyclodehydration processing.

For polycondensations of an aromatic diamine with aromatic or aliphatic dianhydrides, the addition order of the monomers does not play a significant role, although higher molecular weights are obtained for many poly(amic acid)s when the anhydride is added to the diamine rather than the reverse addition. However, in the reaction using an aliphatic diamine with a polyalicyclic structure such as BBH, the order of addition becomes significant. A viscous poly(amic acid) solution was obtained only when BBH was slowly added to the the dianhydride solution. A precipitate developed when adding the dianhydride to the BBH solution. The result can be explained by salt formation [19]. That is, in the latter case, the carbonyl group of poly(amic acid) that was produced by the reaction between the
diamine and the dianhydride is easily reacted with an excess of the free diamine to form the salt. Semi-aromatic poly(amic acid)s have an inherent viscosity ($\eta_{inh}$) range of 1.00-0.53 dL/g (0.5 g/dL, 30 °C), and the flexible and free-standing polyimide films were obtained after thermal curing. The $\eta_{inh}$'s of the non-aromatic poly(amic acid)s were as low as 0.08-0.23 dL/g, however, they formed flexible films.

Figure 1. Structures and abbreviations of monomers for polyimide synthesis.

3.2. UV-VIS spectra of polyimide films and quantum chemical consideration

Figure 2. a) Absorption UV-VIS spectra of thin Kapton®-type PI(PMDA-DDE) films (1: ca. 1μm, 2: ca. 0.1 μm) formed on quartz plates [19]. b) The effect of pressure on the light transparency of 7.5 μm thick Kapton® film [21].

The absorption UV-VIS spectra of the Kapton®-type polyimide PI(PMDA-DDE) films formed on quartz plates using a spin-coating technique were determined and are shown in figure 2a. PI(PMDA-DDE) denotes the polyimide obtained from dianhydride PMDA and diamine DDE. The weak absorption is observed around 400 nm as a shoulder, and the peak is considered to the observed $\lambda_{max}$ of the polyimide. In 1970, at first Bikson directed scientific eye to discoloration aromatic polyimides [20]. Dine-Hart and Kotov reported that the coloration is caused by charge transfer complex [7, 8].
However, it has still not been confirmed whether the CT occurs intermolecularly or intramolecularly. Figure 2b shows the effect of pressure on the light transparency of 7.5 μm thick Kapton® film [21]. Reversible spectral change within 120 kBar is considered to be caused by an intermolecular CT.

**Figure 3.** The structure of a model compound M(PMDE-DDE) for Kapton® polyimide and the calculated light absorption spectrum of the model.

Light absorption of aromatic polyimides was elucidated from quantum chemistry that is using the MO calculations for the model compound. The structures were geometrically optimized by means of an AM1 method in MOPAC2000 and the MOs in the ground and excited states for the optimized structures were calculated using INDO/S method in MOS-F software. Figure 3 shows the structure of a model compound M(PMDE-DDE) for Kapton® polyimide and the calculated light absorption spectrum of the model. The calculated λmax is 392 nm, this value is in good agreement with the observed one around 400 nm. The wave function of the first excited state corresponding to 392 nm light absorption for the model, |Φe⟩ is given in equation (1), where |ΨHOMO→LUMO⟩ is monoeexcited configuration state function. In this state an electron is excited from the HOMO to the LUMO. The CI coefficients of the first excited state indicate that HOMO-LUMO transition is the major electronic transition, and the calculated contribution of the first excited state is 48 % for the M(PMDA-DDE).

\[
|Φ_{e,PMDA-\text{DDE}}⟩ = 0.691\left|\Psi_{\text{HOMO→LUMO}}\right⟩ - 0.567\left|Ψ_{\text{HOMO-2→LUMO}}\right⟩ - 0.238\left|Ψ_{\text{HOMO-1→LUMO}}\right⟩
\]

(1)

The difference in electron density between the ground and the first excited states was calculated and is illustrated in figure 4. The dark-gray area corresponds to regions of increased electron density in the excited state, while the light gray one corresponds to depleted regions from the ground state. From both the MOs and the charge difference maps, it is found that the benzene ring derived from the diamine DDE acts as an electron donor, and that the five-membered imide and benzene rings derived from the dianhydride PMDA act as electron-withdrawing groups. Therefore, the first excited state is characterized by a strong intramolecular CT.

**Figure 4.** Difference in electron density between the ground state and the first excited states.

**Table 1.** INDO/S calculated electronic properties of PI model compounds.
Figure 5. Transmission UV-VIS spectra of free-standing polyimide films.

Similarly, the calculated $\lambda_{\text{max}}$'s and configuration state functions of various kinds of model compounds were estimated, and results are summarized in Table 1. Semi-aromatic polyimide model M(PMDA-DCHM) obtained from an aromatic dianhydride and an alicyclic diamine has a $\lambda_{\text{max}}$ at 366nm in UV area. The HOMO-12 denotes the twelfth orbital below HOMO. The HOMO-12 and the LUMO correspond to a non-bonding and a $\pi^*$ orbital, respectively, therefore the main contributing transition is assigned to the n-$\pi^*$ transition. From both the MOs and the difference electron density between the ground and the first excited states, the first excited state is attributable to light-induced polarization in the five-membered imide ring. The other semi-aromatic polyimide model obtained from an alicyclic dianhydride and an aromatic diamine M(BHDA-DDE) has a $\lambda_{\text{max}}$ at 330nm in UV area. Non-aromatic (full-alicyclic) polyimide shows a $\lambda_{\text{max}}$ at 327 nm.
The transmission UV-VIS spectra of free-standing polyimide films are shown in figure 5 compared with calculated \( \lambda_{\text{max}} \). The semi-aromatic polyimide films exhibit a cut-off wavelength around 300 nm and are colorless, whereas an aromatic Kapton-type polyimide PI(PMDA-DDE) has a \( \lambda_{\text{max}} \) at 400 nm. A cut-off wavelength is defined here as the point where the transmittance becomes less than 1% in the spectrum. The cut-off wave lengths of full-alicyclic polyimides were observed at 234 nm and the films were entirely colorless. The order in cut-off wavelength of the polyimide films is essentially the same as obtained for calculated \( \lambda_{\text{max}} \) of their model compounds.

3.3. Refractive index, birefringence, and optically estimated dielectric constant

The dielectric constant of the material at optical frequencies can be estimated roughly from the refractive index \( n \) according to Maxwell’s equation \( \varepsilon = n^2 \). The \( \varepsilon \) of polyimide around 10 GHz is evaluated to be \( \varepsilon = 1.1n^2 \), including an additional contribution of approximately 10% from the orientation and ionic polarization [22]. Refractive index, birefringence, and optically estimated dielectric constant of free-standing polyimide films are summarized in table 2 together with transparency and glass-transition temperatures. Transparency in the visible region was evaluated by averaging the transmittances in the range from 400 to 780 nm in the UV-VIS spectrum. An average refractive index was calculated following the equation, \( n_{\text{av}} = (2n_{\text{TE}} + n_{\text{TV}})/3 \), where \( n_{\text{TE}} \) and \( n_{\text{TV}} \) indicate the in-plane and out-of-plane refractive indices of the sample polyimide films, respectively. Birefringence \( \Delta n \), the difference between in-plain and out-of-plain refractive indices gives information on the three dimensional structure of polymer, spatial arrangement of the structure units to contribute to a refractive index, e.g. imide groups and benzene rings. The \( n_{\text{av}} \) of the full-alicyclic polyimide film PI(BHDA-BBH) is as low as 1.52, which translates into a dielectric constant of 2.55. The decreasing aromatic character of the polyimide diminishes the refractive index as exemplified by the comparison of semi-aromatic and aromatic polyimide in agreement with one generalization that aromatic polymers possess high refractive indices. Aromatic polyimides exhibit a large birefringence which indicated the preference of the polymer chains to orient in the plane of the film. The negligibly small birefringence in semi- and non-aromatic (full-alicyclic) polyimides implies that the polymer chains are randomly oriented in the film due to a weak polymer-polymer interaction.

### Table 2. Film thickness, optical properties, and glass transition temperatures of polyimide film.

| polyimide       | \( d (\mu\text{m})^a \) | \( T(\%)^b \) | \( n_{\text{TE}}^c \) | \( n_{\text{TM}}^d \) | \( n_{\text{AV}}^e \) | \( \Delta n^f \) | \( \varepsilon^g \) | \( T_g(\text{C})^h \) |
|-----------------|-------------------------|--------------|----------------------|----------------------|----------------------|------------------|------------------|------------------|
| PI(BODA-BDE)    | 4.6                     | 94           | 1.605                | 1.588                | 1.599                | 0.017            | 2.81             | 383              |
| PI(BODA-BAB)    | 14.7                    | 92           | 1.615                | 1.615                | 1.615                | 0.000            | 2.87             | 211              |
| PI(BODAx-BDE)   | 13.1                    | 86           | 1.605                | 1.588                | 1.600                | 0.017            | 2.82             | 385              |
| PI(BODAx-BAB)   | 11.3                    | 90           | 1.617                | 1.617                | 1.617                | 0.000            | 2.88             | 225              |
| PI(DNDAx-BAB)   | 12.3                    | 90           | 1.607                | 1.594                | 1.603                | 0.013            | 2.83             | 257              |
| PI(BSDA-BAB)    | 11.8                    | 86           | 1.616                | 1.601                | 1.611                | 0.015            | 2.85             | 227              |
| PI(BHDAx-BBH)   | 14.8                    | ND\(^1\)     | 1.522                | 1.522                | 1.522                | 0.000            | 2.55             | 297              |
| PI(PMDA-DDE)\(^j\) | 6.2                     | 67           | 1.715                | 1.636                | 1.688                | 0.079            | 3.13             | ND\(^1\) |

\(^a\)Film thickness. \(^b\)Average transmittance in the visible region (400-780 nm). \(^c\)The in-plane refractive indices. \(^d\)The out-of-plane refractive indices. \(^e\)Average refractive index, \( n_{\text{AV}} = (2n_{\text{TE}} + n_{\text{TV}})/3 \). \(^f\)Optical anisotropy (birefringence); \( \Delta n = n_{\text{TE}} - n_{\text{TM}} \). \(^g\)Optically estimated dielectric constant; \( \varepsilon = 1.10n_{\text{AV}}^2 \). \(^h\)The glass transition temperature by TMA. \(^1\)Not determined. \(^j\)By Nae et al.

3.4. Qualitative solubility of alicyclic polyimides

The qualitative solubility of the alicyclic polyimide films is shown in table 3. The introduction of polyalicyclic structure as a dianhydride or a diamine unit improved the solubility of the polyimides with retention of excellent thermal stability due to the maltibond and rigidity of the polyalicyclic structure. Semi-aromatic polyimides, I and II series, are soluble in aprotic polar solvents like DMAc, however all the full-alicyclic polyimide films are insoluble except sulfuric acid.
Table 3. Qualitative solubility of alicyclic polyimides.

| solvent                      | la | lb | lc | lla | lla | llb | llc |
|------------------------------|----|----|----|-----|-----|-----|-----|
| N-methyl-2-pyrrolidone       | vs | vs | vs | s   | sw  | i   | i   |
| N,N-dimethylecapramide       | vs | vs | vs | s   | sw  | i   | i   |
| 1,3-dimethyl-2-imidazolinone | s  | vs | s  | s   | sw  | sw  | i   |
| dimethyl sulfoxide           | s  | vs | s  | i   | sw  | sw  | i   |
| pyridine                     | s  | vs | vs | vs  | sw  | i   | i   |
| m-cresol                     | s  | ND | vs | vs  | sw  | i   | i   |
| chloroform                   | i  | i  | vs | vs  | i   | i   | i   |
| dioxane                      | i  | i  | s  | i   | i   | i   | i   |
| benzene                      | i  | i  | i  | i   | i   | i   | i   |
| hexene                       | i  | i  | i  | i   | i   | i   | i   |
| sulfuric acid                | vs | vs | vs | vs  | s   | s   | s   |

vs: soluble at r.t.; s: soluble on heating, sw: swelling, i: insoluble even on heating; ND: not determined.

3.5. Thermal properties of alicyclic polyimides

The thermogravimetric analysis (TGA) of polymer films was done at a heating rate of 10 K per minute in nitrogen atmosphere. TGA profiles of the representative alicyclic polyimide films are displayed along with that of polyethylene in figure 6. Full-alicyclic polyimide PI(DNDA-BBH) has good thermal stability with no significant weight-loss up to approximately 350 °C, and the 5 % weight loss temperature, T5, is 459 °C. T5 of semi-aromatic polyimide PI(DNDA-DDE) is as high as 514 °C, which is comparable to that of an aromatic polyimide. The 5 % weight loss temperatures in nitrogen and air and the glass transition temperature of alicyclic polyimides were measured and the results are summarized in table 4 along with Kapton type polyimide PI(PMDA-DDE). All the alicyclic polyimides have the 5 % weight loss temperatures in nitrogen over 450 °C, and 400 °C in air. They possess glass transition temperatures over 280 °C. The degradation of polymers in an inert atmosphere is caused by homolytic C-C bond scission. If the polymer backbone consists of a single-chain like that of poly(ethylene), the scission results in direct decreasing of the molecular weight. In most cases, volatile compounds are produced and released as a decomposed gas. On the other hand, in the case of step-ladder type polymers bearing double strands like the alicyclic polyimides, even if the C-C bond scission occurs, it does not lead to a significant decrease in the molecular weight or to the production of volatile compounds. The introduction of a polyalicyclic structure into the polymer backbone would facilitate less polymer-polymer interaction and increased main chain rigidity, and, additionally possibly less probability of main chain scission because of having multibonds.
3.6. Mechanical properties
Mechanical properties of alicyclic polyimide films were examined at room temperature, and the results are listed in table 5. The polyimide films have a tensile modulus range of 1.3-3.0 GPa, and a tensile strength range of 38-145 MPa. They have an elongation at break range 5-30%. The full-alcyclic polyimide film PI(BHDA expand-BBH) possessed a tensile modulus of 2.1 GPa and a tensile strength of 52 MPa, and these values can compete in terms of strength with those of a commercial polycarbonate (PC) [23].

Table 4. Qualitative solubility of alicyclic polyimides.

| Polymer         | Tg/N2(°C)  | Tg/air(°C) | Tg(°C)  |
|-----------------|------------|------------|---------|
| ![Polymer a](image1) | 515        | 490        | 429     |
| ![Polymer b](image2) | 514        | 470        | 404     |
| ![Polymer c](image3) | 448        | 406        | 282     |
| ![Polymer d](image4) | 455        | 411        | 297     |
| ![Polymer e](image5) | 459        | 416        | 340     |
| Polyethylene    | 367        | 352        | 135     |

* in N2, ** in air 5% weight loss temperature ³ by TMA

Figure 6. TGA Profiles of alicyclic polyimides [16].
Table 5. Mechanical properties of alicyclic polyimide films.

| polymer | TM(GPa) | TS(MPa) | EB(%) |
|---------|---------|---------|-------|
| ![Polymer Structure] | 3.5 | 160 | 40 |
| ![Polymer Structure] | 1.3 | 145 | 15 |
| ![Polymer Structure] | 2.0 | 96 | 11 |
| ![Polymer Structure] | 2.3 | 112 | 30 |
| ![Polymer Structure] | 3.0 | 115 | 5 |
| ![Polymer Structure] | 1.6 | 84 | 6 |
| ![Polymer Structure] | 2.1 | 52 | 6 |
| ![Polymer Structure] | 1.3 | 38 | 11 |

* a Tensile modulus  b Tensile strength  c Elongation at break

3.7. *Reflection WAXD analysis of alicyclic polyimide films*

The crystallinity of the full-alicyclic polyimide films was examined by wide angle X-ray diffractions (WAXD). All polyimides exhibited amorphous patterns and broad dispersive peaks of diffraction around at 16° (2θ). This observation is quite reasonable because the presence of polyalicyclic (bicyclic) structure decrease the intermolecular force between the polymer chains with a consequent decrease in crystallinity.

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