

Synthesis of a new diamine and its effect on the residual stress of colorless polyimide

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Abstract—A new diamine was designed and synthesized to improve the flexibility of colorless polyimides by reducing residual stress. Four variations of colorless polyimides with the same dianhydride (4,4'-(hexafluoroisopropylidene)-diphthalic) and four different diamines (bis[4-(3-aminophenoxy)-phenyl] sulfone, bis(3-aminophenyl) sulfone, 2,2'-bis(trifluoromethyl)benzidine, and 2,2-bis(4-aminophenyl)-hexafluoropropane) were used. A series of colorless polyimides were prepared by adding the new diamine. The carbon and ether bonds between the benzene rings of the new diamine affected the flexibility and optical properties of colorless polyimide. The synthesis of the new diamine was confirmed by NMR measurements. Furthermore, the decrease in residual stress at room temperature and the glass transition temperature was confirmed. The effect of the new diamine was most evident for polyimide with a bulky and rigid structure. Though a slight yellow color appears because of the broken charge transfer complex balance, controlling the content of the new diamine will allow application of polyimides in flexible display.

Keywords: Colorless Polyimide, Residual Stress, New Diamine

INTRODUCTION

Flexible displays are attracting interest in various applications, including wearable devices, flexible smartphones and flexible TVs [1]. To assemble a flexible display requires developing a flexible substrate, as well as display and process technologies. Most importantly, development of flexible materials to replace the glass used in planar displays is necessary [2]. Such materials require high flexibility, durability, and transparency. Polyimide (PI) is considered the most suitable polymer to fulfill these requirements [3].

Generally, aromatic PIs are known for their exceptional performance in terms of their excellent thermal and chemical resistances, mechanical properties, and electronic properties [4]. PIs were produced by NASA in the 1970s for application to the aerospace industry and have ever since been used in various other industries [5]. Their use in the display industry is limited because of their yellow color, which is caused by the formation of charge transfer complex (CTC) between an electron-donating group (EDG) and electron-withdrawing group (EWG). Although, this limitation was overcome by the development of colorless PIs that contain fluorine or sulfone groups in the monomer, such colorless PIs exhibit notable drawback, i.e., high residual stress caused by the bulky and rigid backbone [6-8]. The high residual stress caused by the modulus between the PI and the substrate produces poor-quality interlayer devices. The residual stress also leads to delamination and cracks at the PI/substrate interlayer or within the PI [9]. Notably, a decrease in the residual stress is reflective of an improvement in the flexibility of the PI. Therefore, we must reduce the residual

stress in order to apply colorless PIs to the interlayer device in the flexible display industry.

We examined the PI backbone to develop suitable strategies for reducing the residual stress. We expected that the flexible backbone would act as a linkage in the bulk PI and reduce the residual stress. Therefore, we synthesized a new diamine with a flexible structure and applied it to colorless PIs. Measurements performed with a thin film stress analyzer revealed that the new diamine reduced the residual stress and thus improved the reliability of colorless PIs. The resulting colorless PI containing the new diamine can be applied in various industries, including the flexible display industry.

EXPERIMENTAL

1. Materials

α,α' -Dibromo-*m*-xylene and 3-nitrophenol were purchased from Tokyo Chemical Industry Co. Bis[4-(3-aminophenoxy)-phenyl] sulfone (mBAPS), bis(3-aminophenyl) sulfone (APS), 2,2'-bis(trifluoromethyl)benzidine (TFDB), 2,2-bis(4-aminophenyl)-hexafluoropropane (6FPD) as a diamine, and 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride as a dianhydride were purchased from Tokyo Chemical industry Co. *N,N*-dimethyl acetamide (DMAc) and *N,N*-dimethyl formamide (DMF) were purchased from Duksan Pure Chemicals Co. Hydrazine monohydrate was purchased from Sigma-Aldrich. All reagents were used as-received without further purification.

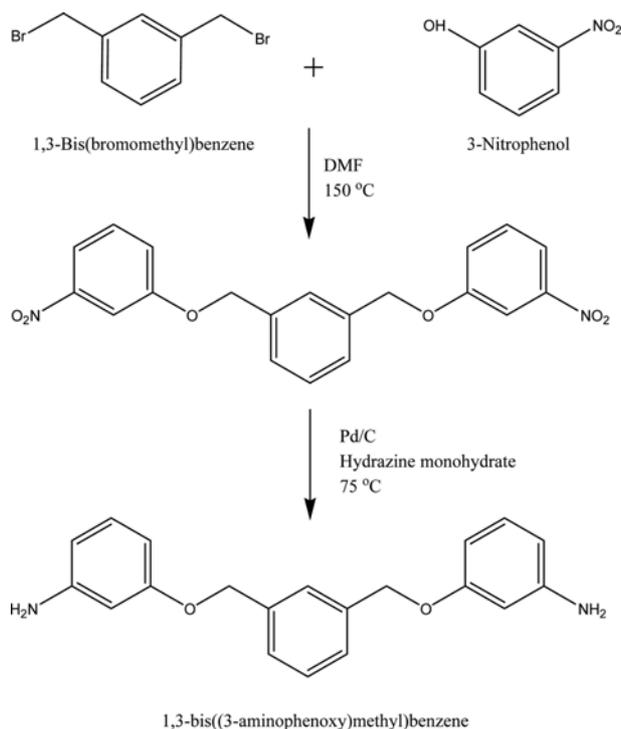
2. Synthesis of 1,3-Bis((3-aminophenoxy)methyl)benzene (NDA)

α,α' -Dibromo-*m*-xylene, 3-nitrophenol, and potassium carbonate were dissolved in DMF in a round flask with stirring. After 30 min of stirring at 25 °C, the solution was heated to 150 °C for 9 h and stirred at room temperature for 12 h under nitrogen. The ob-

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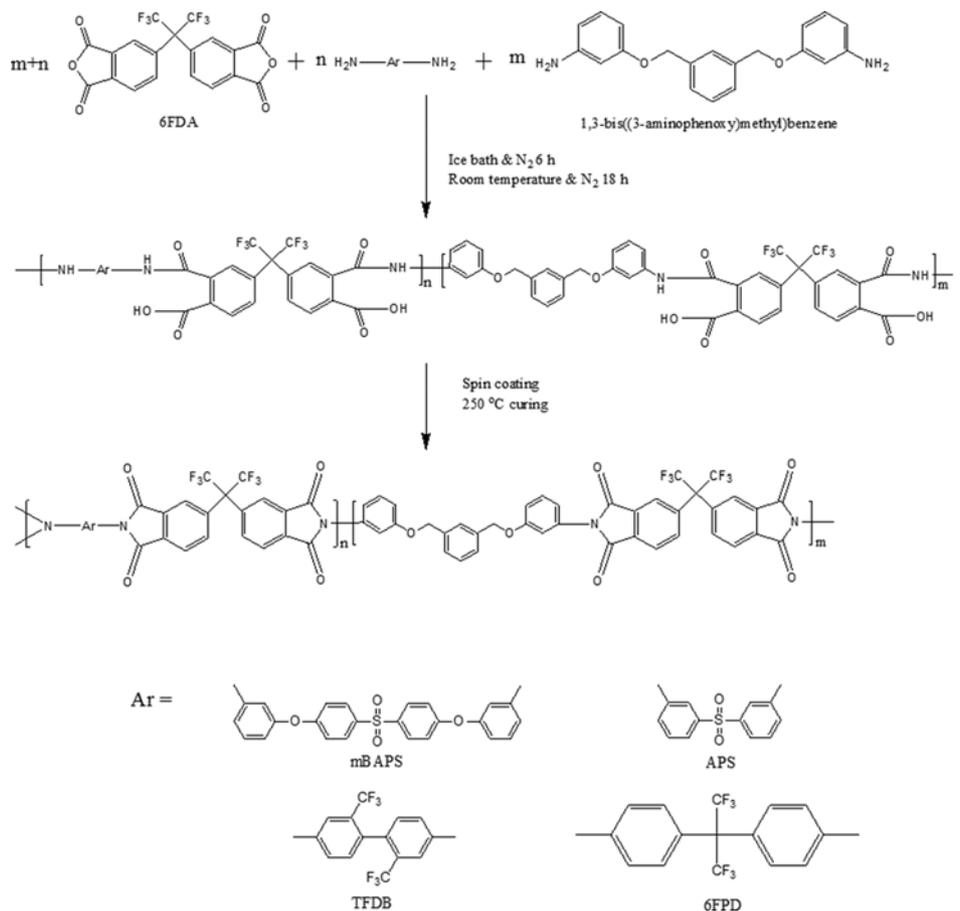
Scheme 1. Scheme for synthesis of 1,3-bis((3-aminophenoxy)methyl)benzene.

tained solution was poured into pure water and solidified. After 24 h, the solidified mixture was filtered using pure water and dried at 80 °C in a dry oven to obtain the intermediate dinitro product. The product, which was obtained as a powder, was dissolved in ethanol with Pd/C and hydrazine monohydrate. The mixture was heated in an oil bath at 75 °C for 7 h and stirred at room temperature for 12 h. The resulting mixture was filtered using Celite 545 and ethanol. The residual solvent was removed by rotary evaporation, and the product was poured into pure water to obtain a solid. The solid was dried at 60 °C in a dry oven to obtain the desired 1,3-bis((3-aminophenoxy)methyl)benzene. The reaction is briefly depicted in Scheme 1.

3. Synthesis of Polyimides (PIs)

Colorless PIs containing the new diamine were prepared via three steps. First, mBAPS and the new diamine were dissolved in DMAc at various ratios. Second, the same molar amount of 6FDA was dissolved and stirred in the solution for 30 min. Finally, the solution was stirred in an ice bath for 6 h and then at 25 °C for 18 h. The resultant solution contained 20 wt% solute in DMAc.

The solution was spin-coated onto a glass plate with a diameter of 10 cm. The film thickness (20–30 μm) was controlled by adjusting the coating time and rotation speed. The spin-coated film was cured according to the following steps: 100 °C for 1 h, 150 °C for 0.5 h, 200 °C for 0.5 h, 250 °C for 2 h in vacuum, with a 2 °C min⁻¹ temperature increase. The cured PI film was separated from the glass



Scheme 2. Scheme for synthesis of PIs.

Table 1. Synthesis ratios and note of PI

	The new diamine (NDA)	Diamines (mBAPS, APS, TFDB, 6FPD)	Dianhydride (6FDA)	Name
Ratio	0	10	10	Diamine
of PI	0.5	9.5	10	Diamine-NDA 5
	1	9	10	Diamine-NDA 10

plate after soaking in pure water for a sufficient length of time. The chemical reaction for the PIs with the new diamine is shown in Scheme 2. The other PIs based on different monomers were prepared by according to the same procedure.

3. Characterization

^1H NMR spectra of the new diamine were measured with an AVANCE III HD 400 (Bruker Biospin) instrument. Fourier transform infrared (FT-IR) spectra of the PIs were measured with an Excalibur Series FT-IR (DIGILAB Co., USA) spectrometer. The thermal stability of the PIs was obtained using a Q50 thermogravimetric analyzer (TGA, TA Instrument Co., USA) over the range 35–800 °C, at the rate of 20 °C min⁻¹, in a nitrogen atmosphere. The glass transition temperatures (T_g) were measured with a Q10 differential scanning calorimeter (DSC, TA Instrument Co., USA) in a nitrogen atmosphere. The PIs were heated from 30 °C to 350 °C at the rate of 10 °C min⁻¹. The residual stresses of the PIs were measured using a thin film stress analyzer. The samples were heated from 25 °C to 300 °C at the rate of 10 °C min⁻¹. A Si (100) wafer (diameter=76.2 mm) was used as the substrate. Ultraviolet-visible (UV-vis) spectra of the PIs from 200 nm to 1,000 nm were measured with a UV-vis spectrophotometer (V530, JASCO Co., Japan). The yellow indices (YIs) of the PIs were measured with a Minolta spectrophotometer (CM-3500D, Konica Minolta). The ASTM D1925 method was used to calculate the YI according to:

$$\text{YI} = 100 \times (1.274641506 X - 1.057434092 Z) / Y \quad (1)$$

where X, Y and Z are the tristimulus values [13].

RESULTS AND DISCUSSION

1. NMR Spectra

To confirm the synthesis of the new diamine, we observed the ^1H NMR spectra of the intermediate nitro compound and the new diamine. As seen in Fig. 1(a) and (b), a peak due to the aromatic protons of a benzene ring structure appeared between 6.2 and 7.6 ppm [11]. An aliphatic proton peak was seen at 1.25 ppm [12]. Meanwhile, a peak corresponding to the amine group proton was observed only at 3.65 ppm, as seen in Fig. 1(b). These NMR data confirm that the new diamine was synthesized as shown in Scheme 1.

2. FT-IR Spectra

FT-IR spectra of the PI (250–4,000 cm⁻¹) shown in Fig. 2 confirm the synthesis of PIs with the new diamine. Imide peaks (C=O bond at 1,710 cm⁻¹ and C-N bond at 1,377 cm⁻¹) were observed in the spectrum of each sample [13]. The stretching of the -CF₃ bond of 6FDA was observed at 1,300 cm⁻¹ in each spectrum. The band at 1,240 cm⁻¹ was assigned to the C-O-C modes. Figs. 2(a) and 2(b) each show a peak associated with the sulfone modes at 1,150 cm⁻¹. These results indicate that a colorless PI based on the four kinds of

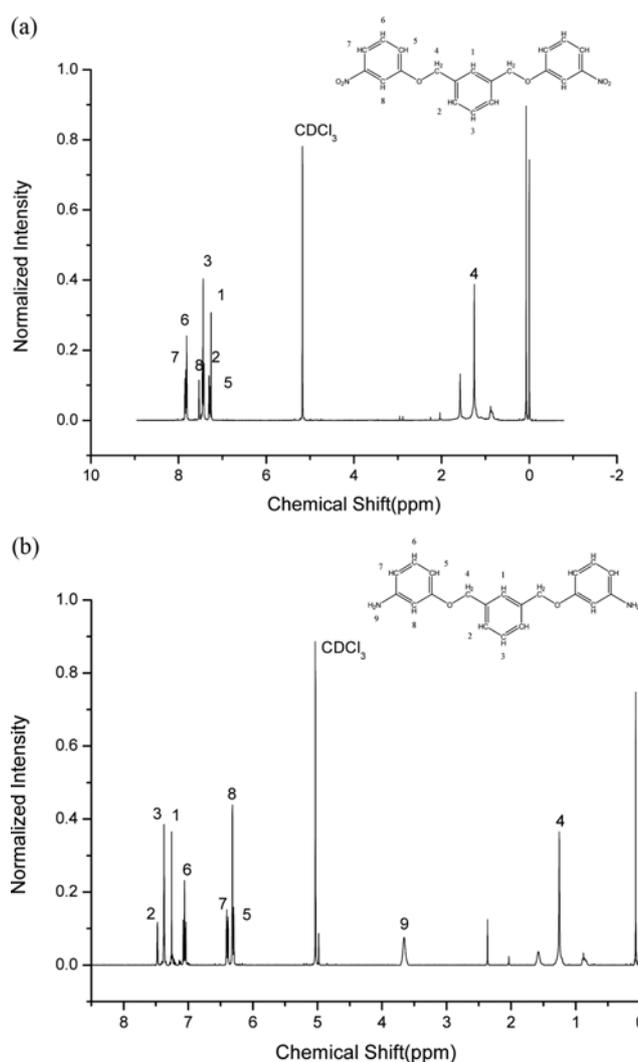


Fig. 1. ^1H NMR spectra of (a) nitro compound and (b) new diamine.

diamines and the new diamine was successfully synthesized.

3. Thermal Properties

To observe the effect of the new diamine on the thermal properties of the colorless PIs, we measured the thermal degradation temperature at 5% weight loss ($T_{5\%}$) by TGA and the glass transition temperature by DSC. The results are shown in Fig. 3, Fig. 4 and Table 2.

The TGA profiles indicated a small difference in $T_{5\%}$ between the four kinds of PIs containing the new diamine and the corresponding reference PI. The small amount of new diamine in the PI simply acts as an interlinkage in the bulk polymer chain and hence does not have any marked effect on the thermal stability. In addition, the new diamine contains three benzene rings that show

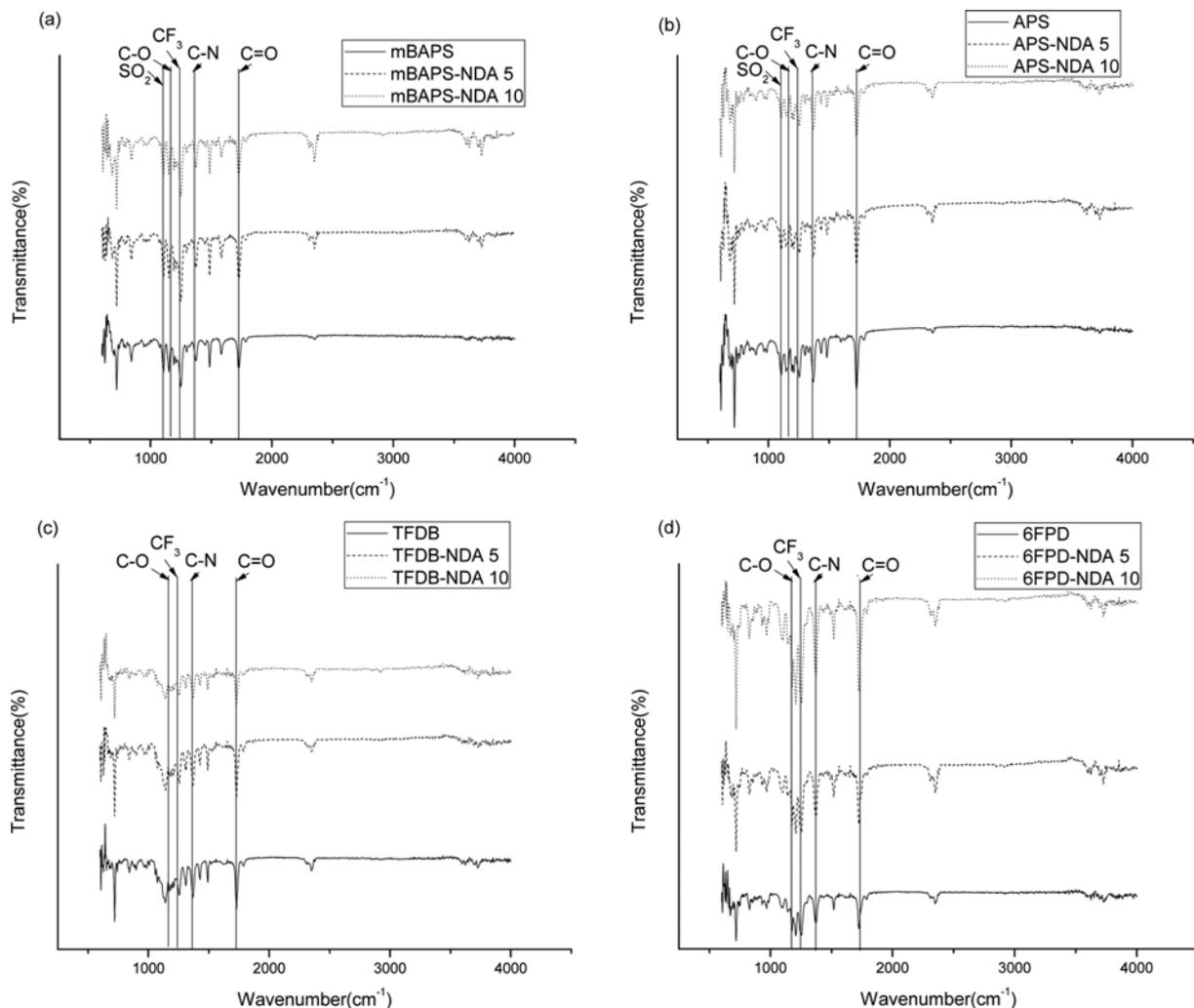


Fig. 2. FT-IR spectra of polyimide.

high thermal stabilities. Therefore, the PIs with the new diamine exhibit high thermal stabilities, even above 500 °C.

DSC analysis revealed the T_g for the colorless PIs containing the new diamine. The T_g is largely affected by the morphology of the bulk polymer [14]. We synthesized the new flexible diamine to affect the bulk structure of the PI. The results of DSC analysis revealed the effect of the new diamine on the flexibility of PI. The new diamine acts as a linkage, as shown in Fig. 5. The T_g values of the four PIs decreased from 10 °C to 60 °C. The rate of this decrease was different for each PI and was found to depend on the structure of the diamine, (although the same dianhydride was used in all cases.

mBAPS and APS had the same sulfone group in their structures; however, the T_g value decreased by as much as 25 °C for APS-NDA 10, while its effect was halved for mBAPS-NDA 10. It is possibly due to flexible ether groups already existing in mBAPS, leading to new diamine with two ether groups having less effect. TFDB and 6FPD, which contained the bulky $-\text{CF}_3$ group, also showed the same trend in T_g . The T_g value of 6FPD-NDA 10, which has a bent structure with a $-\text{CF}_3$ bridge decreased by 25 °C, and that of TFDB-NDA 10, which has a rigid structure, decreased

by 60 °C.

4. Residual Stress Analysis

The residual stress profiles of the PI films on a Si (100) substrate are depicted in Table 3. The residual stress behaviors of the PI films differed with respect to the monomer structure [15] and the amount of the new diamine. Interlayer residual stress between the PI and the substrate must be controlled to prevent cracks, loss of stability, and detachment from the substrate [15]. Furthermore, the residual stress must be sufficiently low for the colorless PIs to be applied to flexible displays. When the colorless PI is used in a multilayered device, more substantial tension forces act at the folding point than at the other points. Therefore, to maintain interlayer adhesion and prevent cracks, we must reduce the stress between colorless PI and the substrate.

We designed the new diamine such that residual stress in the colorless PIs was reduced and their flexibility improved. Residual stress measurements confirmed the remarkable effect of the new diamine. First, mBAPS and APS colorless PIs, which contained sulfone functional groups, showed relatively low residual stress. The corresponding diamines (mBAPS, APS) had a relatively linear structure despite the bulky CF_3 group in the dianhydride (6FDA). The

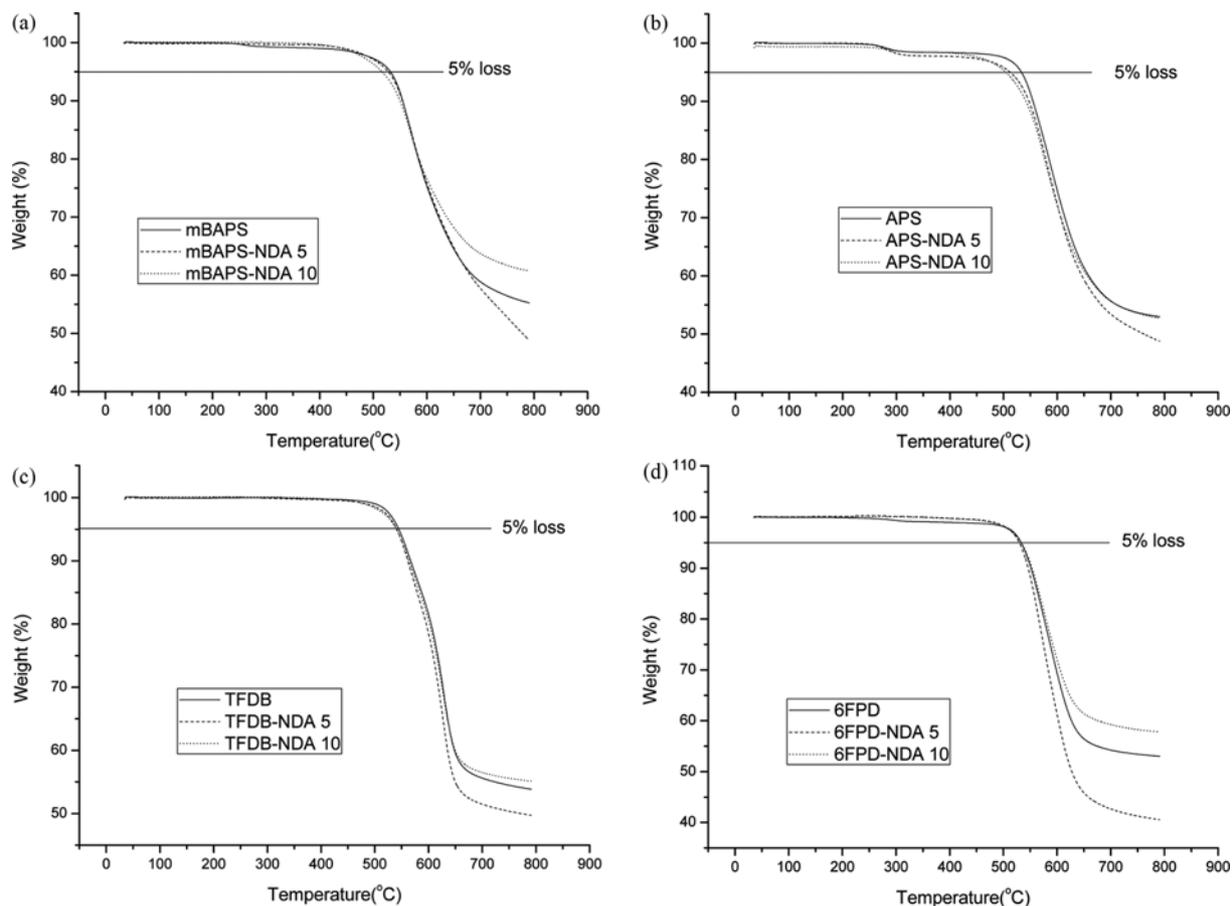


Fig. 3. TGA analysis of polyimide.

Table 2. Thermal properties of polyimide

	mBAPS	mBAPS-NDA 5	mBAPS-NDA 10	APS	APS-NDA 5	APS-NDA 10
$T_{5\%}$ (°C)	532.0	528.0	516.0	533.0	512.0	504.0
T_g (°C)	244.0	239.0	233.0	274.0	263.0	247.0
	TFDB	TFDB-NDA 5	TFDB-NDA 10	6FPD	6FPD-NDA 5	6FPD-NDA 10
$T_{5\%}$ (°C)	545.0	541.0	540.0	533.0	530	533.0
T_g (°C)	330	298.0	270	309.0	293.0	282.0

residual stress barely decreased for mBAPS-NDA 5 because the two ether bonds in mBAPS contributed to the flexibility of the backbone between the benzene rings. However, when we added twice the amount of the new diamine, the residual stress decreased from 25.44 MPa to 16.04 MPa. When the new diamine was added with the same ratio in APS PI, which has no ether bond, the residual stress decreased from 25.64 MPa to 17.45 MPa and 8.59 MPa.

Second, the TFDB and 6FPD colorless PIs contain bulky $-CF_3$ groups and have relatively high residual stress. The modulus of the PI film is high because of the rigid structure. In these bulky and rigid structures, the new diamine is critical for reducing the residual stress. Macroscopically, the new diamine acts as a linkage in the bulk polymer chain; the rigid polymer chain becomes flexible and the residual stress decreases. Due to their bulky main backbone, the initial residual stress was higher and the effect of new

diamine was more drastic. The residual stress decreased from 56.51 MPa to 15.76 MPa in the TFDB series and from 53.64 MPa to 15.63 MPa in the 6FPD series.

5. Optical Properties

Commercially available PI films such as Kapton are transparent and brown. However, the four kinds of PIs used in this experiment were transparent and colorless. Transparency is related to the physical characteristics of a polymer matrix. The bulky CF_3 groups in the colorless PIs create voids between the polymer chains. Therefore, light can penetrate the film through these voids. The brown color of the PI is a result of the CTC that is formed between an EWG and EDG [16]. In general, brown PIs contain strong CTCs between the EWG ($-C=O$) and EDG ($-N-$) [17]. However, the colorless PIs used in this experiment have strong EWGs ($-CF_3$) that hinder CTC production. The PIs become colorless with a decrease-

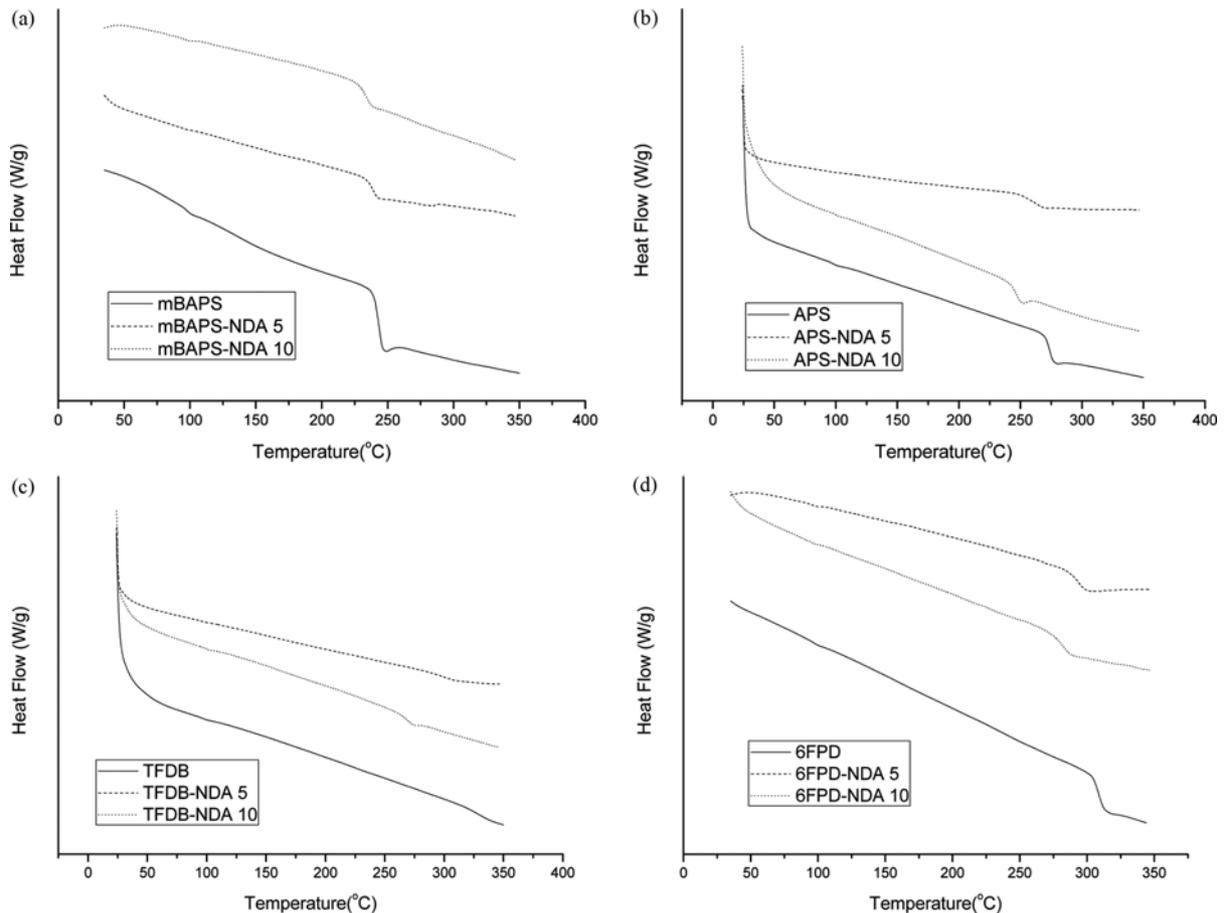


Fig. 4. DSC analysis of polyimide.

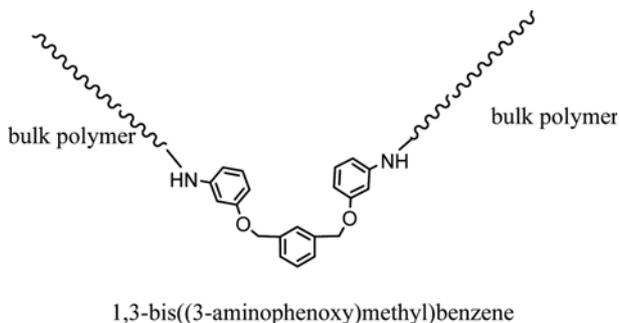


Fig. 5. The effect of the new diamine on the flexibility of the polymer chain.

ing number of CTCs.

To analyze the effect of the new diamine on the optical properties of the films, we measured the transmittance using UV-visible

spectroscopy and the YI; the results are shown in Table 4. The transmittance was similar or showed very slight difference with an increase in the amount of the new diamine. Although the new diamine increased the flexibility of the polymer matrix, the voids in the polymer matrix were barely affected. We concluded that the small thickness difference was an influencing factor. However, as the amount of the new diamine increased, the YI slightly increased, as shown in Table 4. The CTC balance of the reference colorless PI was disrupted because the new diamine has an EDG (-O-), and the yellow color reappeared.

CONCLUSIONS

We synthesized a new diamine to improve the flexibility of PI films by reducing the residual stress. Because designed diamine has carbon and ether bonds between the benzene rings, we predicted that it will act as interlinkage in the polymer chain, even in

Table 3. Residual stress of polyimide at room temperature

	mBAPS	mBAPS-NDA 5	mBAPS-NDA 10	APS	APS-NDA 5	APS-NDA 10
Residual stress (MPa)	25.40	25.40	16.0	25.60	17.50	8.60
	TFDB	TFDB-NDA 5	TFDB-NDA 10	6FPD	6FPD-NDA 5	6FPD-NDA 10
Residual stress (MPa)	56.50	23.40	15.80	53.60	21.20	15.60

Table 4. Optical properties of polyimide

	mBAPS	mBAPS-NDA 5	mBAPS-NDA 10	APS	APS-NDA 5	APS-NDA 10
Transmittance (500 nm)	87.70%	87.10	84.80%	86.60%	86.80%	86.40%
Cut off wavelength (Tr 50%)	398 nm	388 nm	388 nm	376 nm	376 nm	374 nm
Yellow Index	2.82	3.90	4.24	1.20	3.78	6.99
	TFDB	TFDB-NDA 5	TFDB-NDA 10	6FPD	6FPD-NDA 5	6FPD-NDA 10
Transmittance (500 nm)	86.90%	88.40%	84.0%	85.60%	85.30%	86.50%
Cut off wavelength (Tr 50%)	386 nm	386 nm	394 nm	390 nm	392 nm	392 nm
Yellow Index	2.26	5.77	8.02	2.27	5.59	8.68

small quantities. But we also expected that these flexible bonds should have a trade-off relationship with thermal and optical property. When the new diamine was added to four kinds of colorless PIs, notable changes in the properties of the films were seen. As the amount of the new diamine increased, the T_g values of the colorless PIs decreased, the YI increased, and the residual stress dramatically decreased. Thus, a controlled amount of new diamine was used to optimize its effect on the resulting colorless PI.

The new diamine did not have any notable effect on the thermal degradation temperature of the colorless PIs because only a small amount of the diamine was used and the benzene ring in the new diamine had high thermal stability (the modified PIs showed a high thermal stability above 500 °C). DSC analysis confirmed the effect of the new diamine on the flexibility. The T_g value, which is related to the flexibility of the backbone, decreased when the new diamine was added. Similarly, the residual stress of the colorless PIs decreased because of the flexible structure of the new diamine. The new diamine acted as a linkage between the bulky polymer chains, and the modulus between the PI and the substrate decreased. The transmittances of the colorless PIs with and without the new diamine remained similar. However, the YI slightly increased due to the EDG in the new diamine disrupting CTC balance thus causing yellow color of the films.

In conclusion, we improved the flexibility of colorless PIs. Although the yellow color reappeared, the properties related to the flexibility of the PIs were improved. The YI results varied with respect to the new diamine content; thus, controlling the diamine content would allow for application of the resultant product to flexible devices.

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REFERENCES

1. D.-H. Kim, J.-H. Ahn, W. Choi, H.-S. Kim, T.-H. Kim, J. Song, Y. Huang, Z. Liu, C. Lu and A. Rogers, *Science*, **320**, 507 (2008).
2. Y. Yang, J. Park, Y. Jung, S. Lee, S. Park and S. Kwon, *J. Appl. Polym. Sci.*, **134**, 44375 (2017).
3. S. Ando, *J. Photopolym. Sci. Technol.*, **17**, 219 (2004).
4. M. K. Ghosh and K. L. Mittal, *Polyimides: Fundamentals and applications*, Marcel Dekker, New York (1996).
5. W. Qu, T.-M. Ko, R. H. Vora and T.-S. Chung, *Polymer*, **42**, 6393 (2001).
6. Y. Jung, Y. Yang, S. Kim, H. Kim, T. Park and B. Yoo, *Eur. Polym. J.*, **49**, 3642 (2013).
7. H. Yeo, M. Goh, B.-C. Ku and N.-H. You, *Polymer*, **76**, 280 (2015).
8. J. Kato, A. Seo and S. Shiraishi, *Macromolecules*, **32**, 6400 (1999).
9. K.-H. Nam, J. Seo, K. Seo, W. Jang and H. Han, *Macromol. Res.*, **22**, 669 (2014).
10. H. Chung, J. Lee, W. Jang, Y. Shul and H. Han, *J. Polym. Sci. Part B Polym. Phys.*, **38**, 2879 (2000).
11. R. Iqbal, M. K. Khosa, M. A. Jamal, S. Ilyas, M. T. Hussain and M. Hamid, *Polym. Adv. Technol.*, **27**, 221 (2016).
12. S. Mallakpour, H. Ayatollahi and M. R. Sabzalian, *Polym. Sci. Ser. B*, **56**, 464 (2014).
13. K. Kim, T. Yoo, H. Ha, J. Kim, P. Han and H. Han, *Macromol. Chem. Phys.*, **217**, 1174 (2016).
14. K. Kim, T. Yoo, J. Kim, H. Ha and H. Han, *J. Appl. Polym. Sci.*, **132**, 41412 (2015).
15. W. Jang, J. Seo, C. Lee, S. Paek and H. Han, *J. Appl. Polym. Sci.*, **113**, 976 (2009).
16. M. Hasegawa and K. Horie, *Prog. Polym. Sci.*, **26**, 259 (2001).
17. R. A. Dine-Hart and W. W. Wright, *Macromol. Chem. Phys.*, **143**, 189 (1971).