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Synthesis and characterization of addition-type polyimides functionalized with diamine chromophore

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Summary

The Bismaleimide-Diamine Chromophore (**2**) prepolymers were prepared in acetone. The structure of the prepolymer was characterized. The prepolymer exhibited excellent film-forming quality and good solubility in low boiling point solvent. Thermal and NLO properties of the cured polyimides were evaluated. The chromophore content strongly influenced the thermal properties and order parameter Φ.

Introduction

A great deal of research has been focused on polyimide-based materials for second-order nonlinear optical (NLO) application due to their low dielectric constants, high glass transition temperatures and compatibility with semiconductor processes. Among all kind of polyimides, condensation-type polyimide for NLO application has been widely investigated.[1] With the normal condensation polymerization technique, the aromatic diamine monomer can be easily incorporated with dianhydride to form ploy(amic acid) (PAA) in strong polar solvent, such as DMF, DMAc, NMP etc. Because of the poor solubility of cured polyimides, in general, PAA solution is cast to produce a film at first, then thermally imidized to polyimide film. In the course of imidization, water is released. Such water evolution results in an increase in conductivity of the film and a reduction of the effective electric field for poling.[2] Moreover, for condensation-type polyimide, the densification effect, which is favorable to high E-O coefficient, could occur only at a rather high temperature (>300°C).[3] That means, remarkable increase of the poled order in polyimide film should be observed above 340°C. In contrast, addition-type polyimide is able to be cured without evolution of the volatile by-product. Furthermore, addition-type polyimide would exhibit the densification effect at lower temperature owing to their crosslink structure of polymer molecule. These features of addition-type polyimide offer a great promise for the fabrication of NLO materials.

It is well known that bismaleimides (BMI) are one of thermoseting resins, known for their high temperature stability, hot-wet strength and fatigue resistance.[4] The unsaturated end groups of BMI can be polymerized thermally without evolution of volatile by-products.

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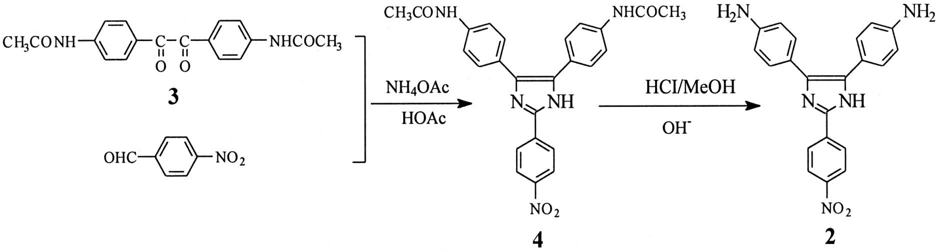
They suffer, however, from brittleness resulting from the high crosslink density. One of the important modification is the use of an other monomer, such as diamine (DA), giving a BMI-DA prepolymer with terminal double bonds.[5] The prepolymer can be further thermally polymerized to crosslink polyimide. Herein, we wish to report the studies on the functionalized addition-type polyimide produced from bismaleimide-diamine chromophor (BMI-DAC) prepolymer, which is the polymer with the NLO chromophore incorporated along the main chain backbone. This would lead to processable NLO material with good thermal properties and optical characteristics.

Experimental

Synthesis of Monomer

N,N'-Bismaleimido-4,4'-diphenylmethane (**1**) was selected as a BMI monomer, which is commercially available and purified by recrystallization from methanol/chloroform, followed by chromatography on silica gel. The solvents used were purified by normal methods.

It was reported[6] that 2-(4-nitrophenyl)-4,5-di(aminophenyl)imidazole (**2**) is a good NLO chromophore with thermal stability, which can be used as a co-monomer incorporated into the main chain of polyimide. The modified synthetic route to **2** was shown in Scheme 1.



Scheme 1

2-(4-nitrophenyl)-4,5-di(acetamidophenyl)imidazole **4**

A mixture of 4,4'-diacetamido benzil **3**[7] (1.622g, 5mmol), ammonium acetate (3.854g, 50mmol) and p-nitrobenzilaldehyde (0.756g, 5mmol) in glacial acetic acid (50ml) was stirred at 110°C for 2h under N_2. After cooling, the resulting homogeneous solution was poured over crushed ice. The dark red precipitate was filtered and washed with cold water, then dried under vacuum. The crude product was recrystalized from ethanol/water, giving a dark red solid **4**, 1.94g (yield 83%). mp: >300°C, IR (KBr)cm^{-1} 3300, 1670, 1600, 1520, 1330, 1250, 900. ^{1}H NMR (DMSO-d_6) δ(ppm): 10.18(s, 1H); 9.7(s, 1H); 8.32(d, 2H, J=8Hz); 8.25(d, 2H, J=8Hz); 7.6(d, 2H, J=8.6Hz); 7.48 (d, 2H, J=8.6Hz); 2.13(s, 6H). ^{13}C NMR (DMSO-d_6): δ(ppm) 116.5, 146.5, 143.1, 138.8, 138.5, 136.3, 128.7, 127.4, 125.7, 124.4, 119.0, 24.2. Anal. Calcd for $C_{25}H_{21}N_5O_4$: C, 65.93%; H, 4.64%; N, 15.37%. Found: C,65.97%; H, 4.45%; N, 15.22%.

2-(4-nitrophenyl)-4,5-di(aminophenyl)imidazole **2**

A solution of **4** (1.5g, 3.3mmol) in methanol (30ml) with concentrated hydrochloric acid (10ml) was refluxed for 30min. After cooling to room temperature, the resulting yellow solution was poured over crushed ice. The pale yellow precipitate was filtered and dissolved in water (5ml). To this aqueous solution 4-5 drops of ammonia liquor was added. The precipitate was filtered and washed with cold water then dried under vacuum. Recrystalization from ethyl acetate gave a deep purple solid **2** 1.12g (yield: 92%). mp: 295~296°C. IR (KBr) cm^{-1}: 3362, 3208, 1622, 1511, 1335, 1236, 1180, 854. ^{1}H NMR (DMSO-d_6) δ(ppm): 12.69(s, 1H); 8.31(d, 2H, J=9Hz); 8.27(d, 2H, J=9Hz); 7.36(d, 2H, J=8Hz); 7.31(d, 2H, J=8Hz); 6.70(d, 2H, J=9Hz); 6.65(d, 2H, J=9Hz); 5.36(br, s, 2H); 5.31(br, s, 2H). ^{13}C NMR (DMSO-d_6) δ(ppm): 148.0, 146.0, 141.8, 136.7, 129.1, 126.9, 126.2, 124.4, 113.7. Anal. Calcd for $C_{21}H_{17}N_5O_2$: C, 67.91%; H, 4.61%; N, 18.86%. Found: C, 67.77%; H, 4.57%; N, 18.89%.

Preparation of prepolymers

The prepolymers were prepared by refluxing the solution of BMI (**1**) and diamine chromphore (**2**) in acetone for 4~8h, until a homogeneous solution was formed. Acetone was removed by rotary evaporator. Prepolymer was obtained as shinning powder after further removal of residual acetone under vacuum. The prepolymers prepared with molar ratios of BMI/DAC (1:1, 1:0.65 and 1:0.35) were denoted by *sample* **1**, **2** and **3**, respectively.

Film casting

Films for the studies of thermal behavior were prepared as follow: The 15% solutions of the prepolymer *sample* **1-3** in THF were cast on a glass slide. The solvent was evaporated in a convection oven at 60°C overnight. Then, thermally treated samples were made by gradually increasing the temperature as following program: 150°C for 2h, 200°C for 2h and 250°C for 2h, finally cured at 280°C for 30min. After the heat treatment, the films, *sample* **1a-3a**, corresponding to sample **1-3** respectively, were removed from the glass slide by soaking it in cold water, then dried in vacuum. The thickness of the cured film was about 1-2μm.

To prepare thin films for *in-situ* electrochromic study and UV-vis spectra measurements, the THF solutions of the prepolymers *sample* **1-3** were filtered through a 0.2-μm syringe filter and then spin cast onto glass slide. The films were dried in an oven at 60°C for two days under vacuum, giving *sample* **1b-3b**. The thickness of the films were about 0.5-1μm.

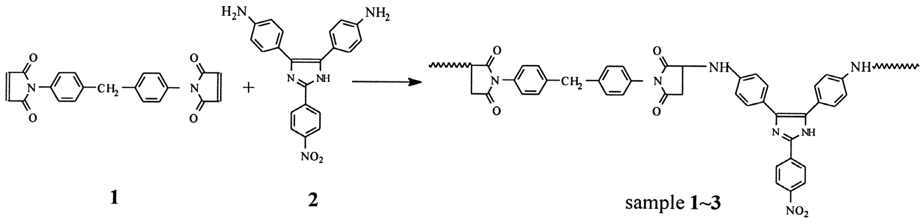
Measurements

The ^{1}H and ^{13}C NMR spectra were collected on Varian XL-200 NMR spectrometer. The FT-IR spectra were recorded on PE FT-IR 1760X spectrometer. DSC was performed by PE DSC-7 series and TGA by PE TGA-7 series under the heating rate of 20°C/min. UV-vis spectra were recorded on Shanghei 756MC UV-vis spectrometer. The UV-vis spectrometer was equipped with heating and corona-poling apparatus to allow the *in-situ* measurements of the spectra at different temperature during the poling process. The poling voltage was 5.5KV at the needle point. The poling and thermally curing of the films *samples* **1b-3b** were simultaneously carried out with a tip-to-plane distance of 1.0 cm in programmed increasing temperatures from 60 to 240°C. The order parameter Φ was determined as an equation: $\Phi=1-A_1/A_0$, where A_0 and A_1 are the UV-vis absorbances of the polyimide films before and after corona poling.[8]

Results and Discussion

Synthesis and Characterization of Prepolymers

According to the method described by Varma,[9] the prepolymers were synthesized through the Michael addition reaction of BMI and DAC in acetone (Scheme 2). The prepolymers exhibited excellent film-forming quality and solubility even in the lower boiling point solvents, such as acetone, THF etc. So, the residual solvent in the film is easily removed, and it's influence on the poling efficiency could be minimized.



Scheme 2

In order to follow the polyaddition reaction process, FT-IR spectra of the reaction mixtures of BMI/DAC(1:1) in acetone were recorded at different reaction time. As reported by Ciulio,[10] a very strong band at 1150cm^{-1} is associated with $\nu_{C\text{-}N\text{-}C}$ of the maleimide ring (MI), that is, the terminal double bond remained in prepolymer molecule. Other identified bands of maleimide ring are at ~830, ~690cm^{-1}. On the other hand, the weak bands at 2900-2850cm^{-1} and strong band at 1180cm^{-1} are due to the formation of succinimide ring (SI) in polyaddition reaction. The ratio of MI/SI could be used for monitoring the polyaddition reaction process. Meanwhile, *sample* **1-3** exhibit different ratio of MI/SI determined by FT-IR spectra. The higher the ratio of BMI to DCA, the larger the MI/SI in prepolymer is. Comparing the spectra of prepolymers formed in reaction time of 4h and 8h, negligible difference is observed. It indicated that the polyaddition reaction proceeds at a rather fast rate and reaches a equilibrium under that reaction condition.

The ^{1}H NMR spectra of prepolymer *sample* **1** show the signal at 8.3 ppm assigned to nitro group-linked phenyl proton and AA'BB' quartet at 6.8 and 7.1 ppm to phenyl protons of **2** moiety, and the multiplet at 7.3 ppm to phenyl protons of BMI. Absorption at 7.2 ppm, observed in all *sample* **1-3**, verifies the presence of the olefin proton of terminated maleimide ring. The signals at 2.2, 3.0 and 5.2 ppm are due to the protons of succinimide ring. From these, it can be deduced that the prepolymers have the polyaspartimide structure along the molecule backbone and terminal double bond structure. The absorptions around 1.75 ppm could be attributed to the formation of acetone imide, stemming from the reaction of acetone with amino groups.

Curing Behavior

The FT-IR spectra of prepolymer *sample* **1** treated at different temperature are shown in Fig. 1. When *sample* **1** was treated at 150øC for 2h, the peak at 1180cm^{-1} associated with succinimide ring became very noticeable, while the bands at 1150cm^{-1} associated with maleimide rings exhibit a small shoulder. That means the Michael addition of NH to double bond of MI still exists in prepolymer sample at 150°C. After *sample* **1** was further treated at 200°C for 2h, the peak at 1150cm^{-1} disappeared, indicating the double bond of maleimide ring was completely reacted. Furthermore, a new band at 1640cm^{-1} started to appear, which is assigned to carbonyl group of amide resulting from crosslink reaction (Scheme 3). It seems to be reasonable that the succinimide ring was opened by the attack

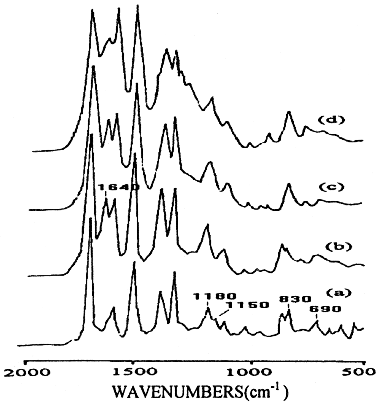
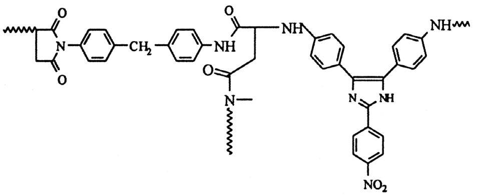


Fig.1 FTIR spectra of sample 1 at different curing stages (a) 150 °C, 2h (b) 200 °C, 2h (c) 250 °C, 2h (d) 280 °C, 0.5h



Scheme 3

of the amine (including secondary amine) hydrogens leading to an amide structure (aminolysis). At the subsequent curing stage (up to 250°C), the increases of the bands at 1640cm^{-1}, accompanying the decreases of the bands at 1180cm^{-1}, further demonstrate that the crosslingking through the formation of amide group would keep on with increasing the treatment temperature.

The glass transition temperature(Tg) of *sample* **1** treated at different temperature were determined by DSC. The curing temperature strongly influences the Tg of cured polymer. As expected, with programmed heating from 150°C to 280°C, the Tgs of *sample* **1** increase from 203 °C to 293 °C correspondingly (Fig. 2). In the temperature region of above 200°C, the Tgs of *sample* **1** increase sharply, indicating that the crosslink reaction occurs mainly in this temperature region.

Table1. Thermal and optical properties of polyimides

polyimides	chromophore content(wt%)	Tg(°C)*	thermal decomposition(N_2) Td$_1$ (°C)	Td$_2$ (°C)	Yc$_1$ (%)	Φ**
sample **1a**	65.2	262	335	452	42.8	0.14
2a	54.9	280	340	463	51.7	0.16
3a	39.6	303	344	485	62.5	0.04

* finally cured at 250 °C ** determined from Fig. 5

The Tgs of the cured polymers sample 1a-3a were listed in Table 1. As indicated in Table 1, the content of diamine chromophore **2** has a noticeable effect on glass transition temperature. The Tg of pure BMI resin cured at 280°C for 10h was 342°C.[11] However, in the case of BMI-DAC adduct, chain propagration through Michael reaction of the amine to the BMI double bond would reduce the crosslink density, and thereby increase the flexibility of the polyimide. With the increase of diamine chromophore content, the Tg of polyimides decrease.

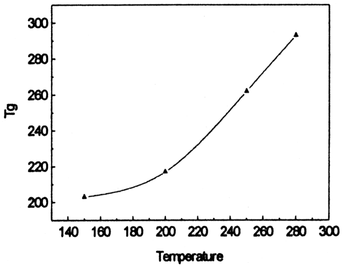


Fig. 2 The relatioship between Tg.s(°C) of cured sample1 and different cuing temperatures (°C)

The thermal properties of cured polyimides *sample* **1a-3a** were evaluated from TGA. Fig. 3 shows the TGA curves and Table 1 summarizes the decomposition temperature (Td_1 and Td_2) and the char yield at 600°C (Yc_1). It could be found that cured polyimides are stable up to 300°C, and then start lossing weight. Not similar to the TGA curves of BMI resin,[11] these BMI-DAC addition-type polyimides degrade by a two-step process, the first step occurs between 350 and 400°C with a 10-20% weight loss. The pathway is likely to be a retro-Michael addition reaction. The second step begins at 500°C and 50% residue is obtained at 600°C. It is worthy to note that with the increase of the diamine chromophore content, the thermal stabilities become worse to some extent.

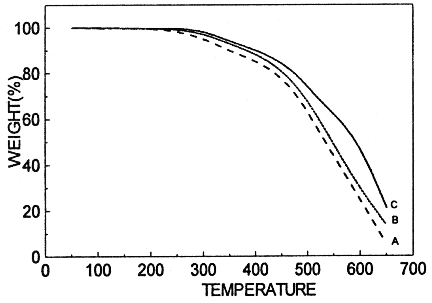


Fig. 3 TGA traces of the cured samples
A. 1a B. 2a C. 3a

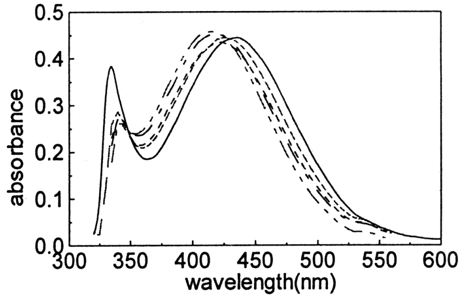


Fig. 4 Optical absorption spectra of sample1 in acetone/methnol solution at different ratios:
from right to left: 10/0; 8/2; 5/5; 2/8; 1/9.

UV-vis spectra and order parameter

Prepolymer *sample* **1** with BMI/DA 1:1 was chosen for solvatochromic study. As shown in Fig. 4, the UV-vis absorption spectra of *sample* **1** in acetone has a maximum absorption at λ_{max}= 440nm. Up on the addition of methanol as a non-solvent, there is a blue shift of about 20nm. The results are different from that obtained from other type of soluble NLO polymers in which a red shift was observed.[12]

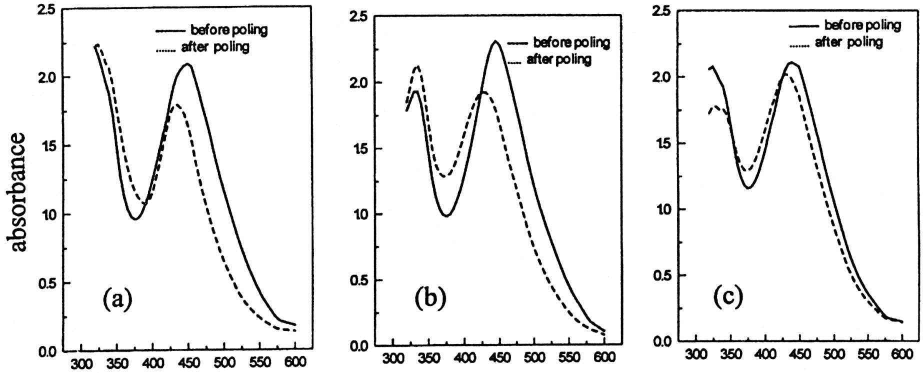


Fig. 5 Uv-vis spectra of samples 1b~3b before and after poling
(a) 1b (b) 2b (c) 3b

To induce the second-order optical nonlinearity, the prepolymer films (*sample* **1b-3b**) were poled and thermally polymerized at the same time. After poling, the maximum absorption were blue-shifted from 450 to 435nm for *sample* **1b**, 445 to 432nm for *sample* **2b** and 444nm to 432nm for *sample* **3b**, respectively (Fig. 5). If there is no any electric field applied, the samples only showed a slightly blue shift before and after heating without the change of absorbance. However, it was found from Fig. 5 that the absorbances of the samples markedly decrease after poling due to the alignment of the chromophore's dipole moment. The order parameter Φ, which is related to the poling efficiency, is markedly influenced by the content of diamine chromophore (Table 1). It is worthy noting that among the three, *sample* **2b** (BMI/DAC=1/0.65) has the highest Φ value (0.16), while *sample* **3b** (BMI/DAC=1/0.35) exhibits the smallest Φ value (0.04). Sample **1b** which has the highest chromophore content (BMI/DAC=1/1) is not favorable to Φ, maybe, due to the aggregation effect of the chromophore molecules. Based on the results above, it can be indicated that the chromophore content in the NLO polyimide should be optimized for a balance of thermal and NLO properties.

Conclusion

The Bismaleimide-Diamine Chromophore (**2**) prepolymer were prepared in acetone. The structure of the prepolymer was characterized by FT-IR and ^{1}HNMR. The prepolymer had excellent film-forming quality and solubility in low boiling point solvent. The prepolymer can be cured thermally without evolution of volatile by-product. The curing temperature strongly influenced the Tg of cured polymer. BMI-DAC addition-type polyimides degraded by a two-step process, in which Td_1 were between 335-344°C and Td_2 452-485°C. The thermal properties and order parameter Φ strongly depended on chromophore content. *Sample* **2b** (BMI/DAC=1/0.65) has the highest Φ value (0.16). The chromophore content in the NLO polyimide should be optimized for a balance of thermal and NLO properties.

Acknowledgment

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