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Synthesis and characterization of novel negative-working aqueous base developable photosensitive polyimide precursors

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Abstract

Through molecular designing, three poly(amic esters) (PAEs) have been synthesized from pyromellitic dianhydride (PMDA), 2,2′-bis-(3-amino-4-hydroxyphenyl) hexafluoropropane (BisAPAF), 4,4′-diaminodiphenyl ether (4,4′-ODA) and 2-hydroxyethyl methacrylate (HEMA). Due to the introduction of photosensitive acrylate groups and aqueous base soluble phenolic hydroxyl groups in the backbone, these poly(amic esters) can be used as the precursors of negative-working, aqueous base developable photosensitive polyimides (PSPIs). These poly(amic esters) were prepared by direct polymerization by using phenyl phosphonic dichloride (PPD) as an activator. The inherent viscosities of these polymers were 0.20 (dL/g). Their structures were characterized by Fourier transform infrared spectroscopy (FTIR) and ^{1}H NMR. In order to improve the photolithographic performance of these PSPIs, different photosensitizers, photoinitiators and a crosslinker have been added in the PSPI formulations. Among them, the Michler's ketone (MK)/tribromomethyl phenyl sulfone (TBPS) system gave the best results. Using a 2.38 wt% aqueous TMAH solution as a developer, patterns with a resolution of 10 μm were obtained from these PSPI formulations. In addition, the effects of the molecular structure of the precursors and the concentration of developer on the photosensitivity of the PSPI formulations were also discussed.

Keywords: Polyimide precursor; Aqueous base; Photosensitive

1. Introduction

Due to their excellent thermal, electrical, and mechanical properties, polyimides (PIs) have been widely used in microelectronic devices such as buffer coating, passivation layers, alpha particle barrier, interlayer insulation and wafer scale packages, etc. [1]. Recently, photosensitive polyimides (PSPIs) have attracted a great interest because they simplify processing steps by avoiding the use of photoresists to obtain the desired patterns [2]. Most PSPIs used in today's microelectronic industry are negative-working, organic solvent developable type. The demands for aqueous base developable PSPIs in IC fabs are increasing due to the environmental and safety concerns and the match of the manufacturing processes of the currently used photoresists.

There are many reports on the preparation of aqueous base developable, positive-working PSPIs [3–11]. Most of them are made from poly(amic acids) or polyimides containing hydroxyl groups with *o*-diazonaphthoquinone (DNQ). However, only a few aqueous base developable, negative-working PSPIs have been reported [12–15]. Although positive-working PSPIs are known to have less swelling during development, they usually suffer from high dark film loss and the difficulty to obtain a thick film. Due to the difference in the photoreaction mechanism, it is easier to obtain a thick film photoresist from negative-working PSPIs than positive-working PSPIs.

In our previous papers [16], we reported the preparation of new aqueous base developable, positive-working PSPIs based on poly(hydroxyamide) and DNQ. In continuation of our work on the development of aqueous base developable PSPIs, we report the preparation and properties of novel negative-working aqueous base developable PSPI compositions that consist of polyimide precursors bearing phenolic hydroxyl groups and acrylate groups, a photoinitiator, a photosensitizer, a photocrosslinker and a solvent. The polyimide precursors are poly(amic esters), which can be totally dissolved in an aqueous base without residue after

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development. The phenolic hydroxyl groups in the polymer render the aqueous base solubility before exposure, and the acrylate groups provide the photo-crosslinking ability after exposure.

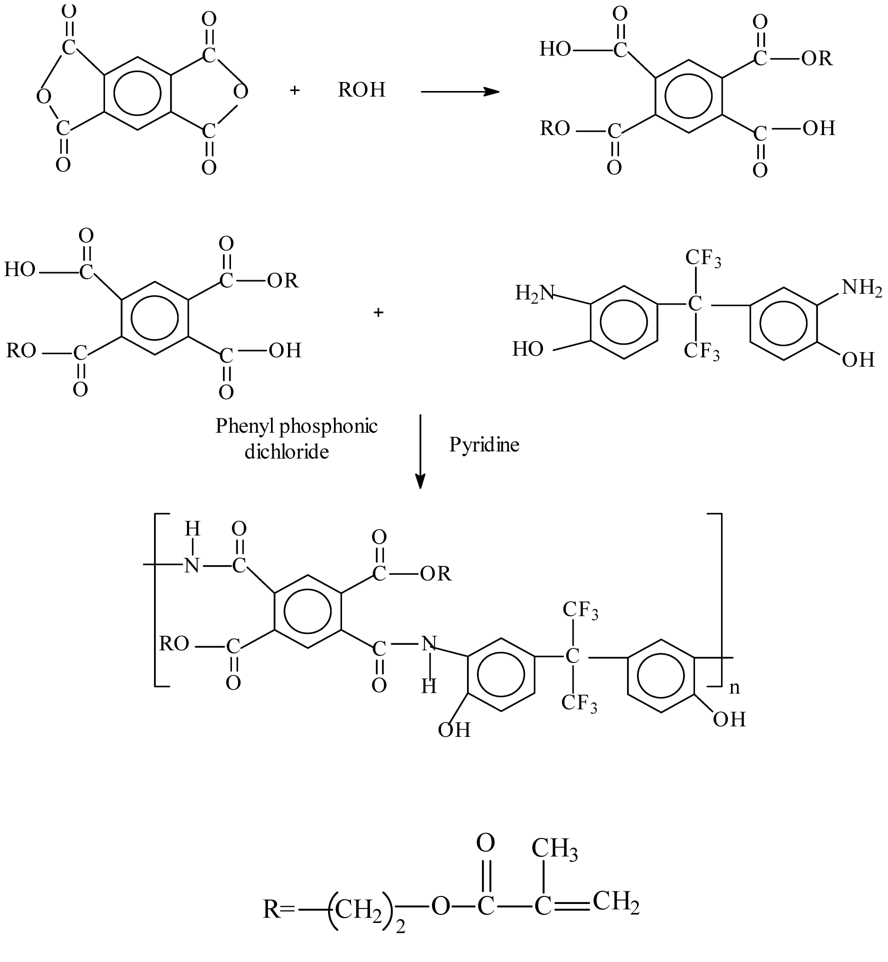
2. Experimental section

2.1. Materials

Pyromellitic dianhydride (PMDA), 2,2′-bis(3-amino-4-hydroxyphenol)hexafluoropropane (BisAPAF) and 4,4′-diaminodiphenyl ether (4,4′-ODA) were purchased from Chriskev. Anhydrous *N*-methyl-2-pyrrolidone (NMP), pyridine and tetra(ethylene glycol) diacrylate (TEGDA) were obtained from Aldrich and used without further purification. 2-Hydroxyethyl methacylate (HEMA), hydroquinone, benzophenone (BP) and phenylphosphonic dichloride (PPD) were obtained from Acros Organics Co. Michler's ketone (MK) and tetramethylammonium hydroxide (TMAH) in 25 wt% aqueous solution were purchased from Lancaster. Tribromomethyl phenyl sulfone (TBPS) and triethanolamine (TENA) were obtained from TCI Co. (Japan). Other chemicals and solvents were obtained commercially and used as received.

2.2. Synthesis of PMDA-BisAPAF-HEMA polyamic ester

To a 250 mL three-necked round bottom flask equipped with a mechanical stirrer and a condenser, 10.91 g (50 mmol) of PMDA, 13.27 g (102 mmol) of 2-hydroxyethyl methacylate (HEMA), 17.60 g (222.5 mmol) of pyridine, 0.2 g of hydroquinone and 50 g of anhydrous *N*-methyl-2-pyrrolidone (NMP) were added. The mixture was heated to 70 °C and stirred at this temperature for 10 h. The solution was cooled to ambient temperature and 65 g of NMP were added. The reaction mixture was cooled to 0–4 °C by using an ice-bath, and 19.50 g (100 mmol) of phenylphosphonic dichloride was added slowly by using an addition funnel. The solution was then stirred at ambient temperature for 2 h, and then cooled to 0–4 °C again. After that, 18.30 g (50 mmol) of 2,2′-bis(3-amino-4-hydroxyphenol)hexafluoropropane (BisAPAF) was added. The reaction mixture was stirred at 0–4 °C for 1 h, and at ambient temperature for 8 h. The resulting viscous solution was precipitated in 1000 mL of a 1:1 (v/v) mixture of methanol/H_2O. The

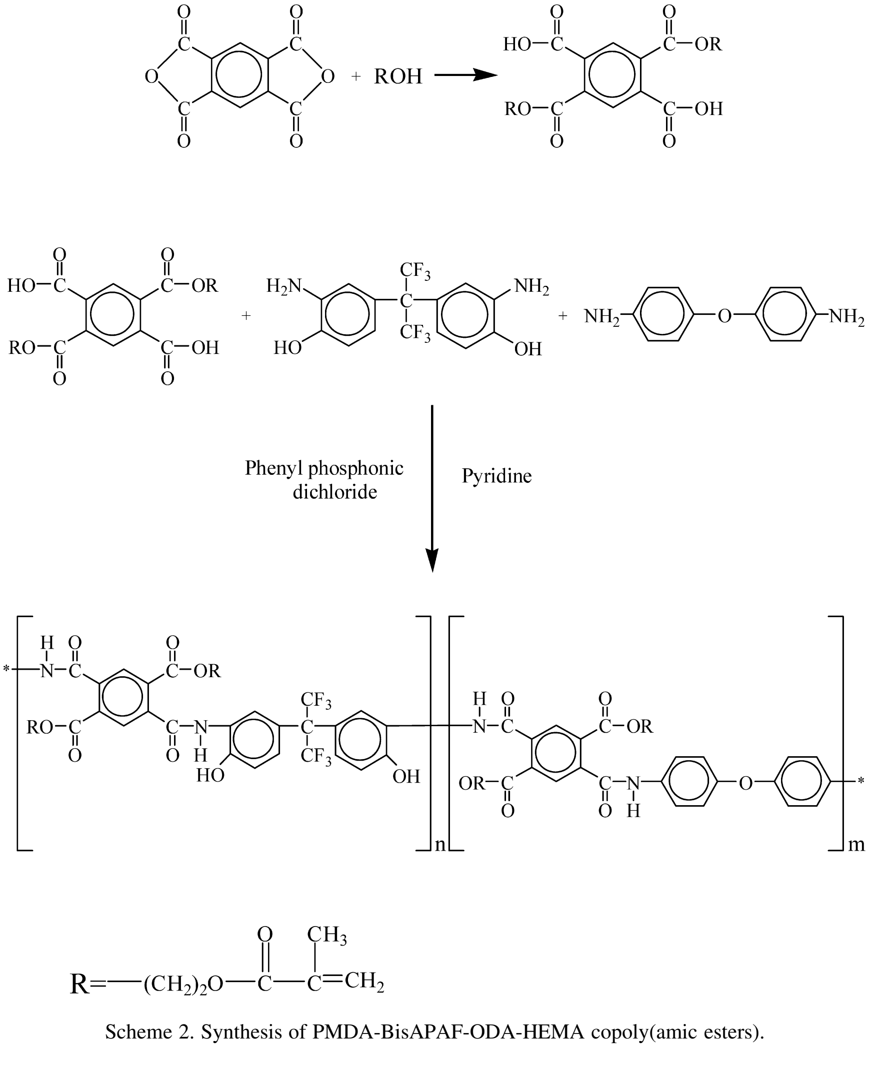


Scheme 1. Synthesis of PMDA-BisAPAF-HEMA poly(amic ester).

polymer was collected by filtration, and washed with de-ionized water three times. The polymer was dried under vacuum at 60 °C for 24 h. The yield was almost quantitative, and the inherent viscosity of the polymer was 0.20 dL/g measured in NMP at the concentration of 0.5 g/dL at 30 °C. ^{1}H NMR (DMSO-d_6): δ 10.2 (s, 2H, OH), δ 9.9 (s, 2H, NH), δ 7.6–8.5 (m, 8H, ArH), δ 5.5–6.0 (m, 4H, =CH$_2$), δ 4.2–4.4 (m, 6H, –CH$_3$), δ 1.8 (s, 8H, –CH$_2$CH$_2$–). IR (KBr): 3400–3100 cm^{-1} (OH and NH), 1728 cm^{-1} (C=O, ester), 1660 cm^{-1} (C=O, amide). Anal. calcd for ($C_{37}H_{22}N_2O_{12}F_6$): C, 54.96; H, 3.74; N, 3.46. Found: C, 54.71; H, 4.09; N, 3.37. The synthesis steps are illustrated in Scheme 1.

2.3. Synthesis of PMDA-BisAPAF-ODA-HEMA copoly(amic esters)

The synthesis of PMDA-BisAPAF-ODA-HEMA copoly(amic esters) is similar to that of PMDA-BisAPAF-HEMA poly(amic ester) except that different molar ratio of ODA (relative to BisAPAF) was added after the addition of BisAPAF. Two PMDA-BisAPAF-ODA-HEMA copoly (amic esters) were synthesized. One was PMDA-75% BisAPAF-25%ODA-HEMA copoly(amic ester). ^{1}H NMR (DMSO-d_6): δ 10.6(s, 0.5H, NH), δ 10.2 (s, 2H, OH), δ 9.9 (s, 1.5H, NH), δ 7.6–8.5 (m, 8.5H, ArH), δ 5.5–6.0 (m, 4H, =CH$_2$), δ 4.2–4.4 (m, 6H, –CH$_3$), δ 1.8 (s, 8H,–CH$_2$CH$_2$–). IR (KBr): 3400–3100 cm^{-1} (OH and NH), 1728 cm^{-1} (C=O, ester), 1660 cm^{-1} (C=O, amide). Anal. calcd for ($C_{36.25}H_{30}N_2O_{11.75}F_{4.5}$): C, 56.76; H, 3.94; N, 3.65. Found: C, 56.06; H, 4.15; N, 3.88. The other was PMDA-50%BisAPAF-50%ODA-HEMA copoly(amic ester). ^{1}H NMR (DMSO-d$_6$): δ 10.6(s, 1H, NH), δ 10.2 (s, 2H, OH), δ 9.9 (s, 1H, NH), δ 7.6–8.5 (m, 9H, ArH), δ 5.5–6.0 (m, 4H, =CH$_2$), δ 4.2–4.4 (m, 6H, –CH$_3$), δ 1.8 (s, 8H, –CH$_2$CH$_2$–). IR (KBr): 3400–3100 cm^{-1} (OH and NH), 1728 cm^{-1} (C=O, ester), 1660 cm^{-1} (C=O, amide). Anal. calcd for ($C_{35.5}H_{30}N_2O_{11.5}F_3$): C, 58.76; H, 4.17; N, 3.86. Found: C, 57.55; H, 4.39; N, 3.62. The inherent viscosities of both polymers were 0.20 dL/g measured in NMP at the concentration of 0.5 g/dL at 30 °C. The synthesis steps are illustrated in Scheme 2.



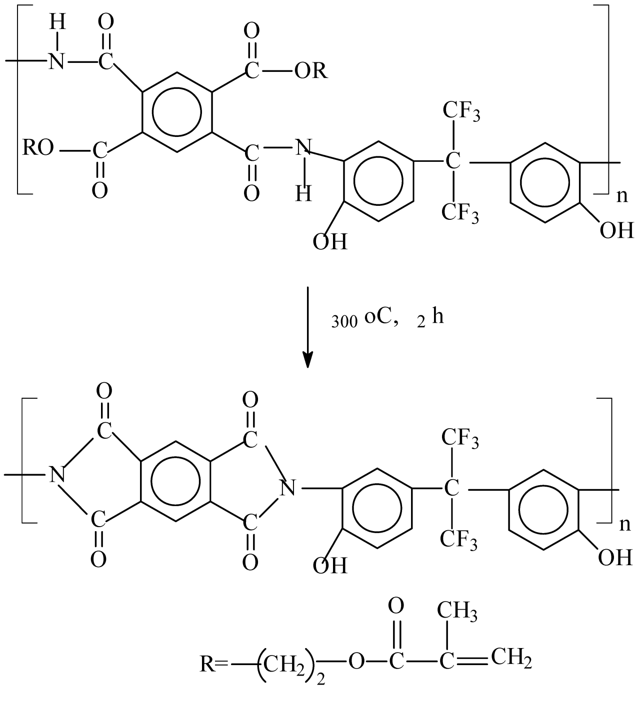
Scheme 2. Synthesis of PMDA-BisAPAF-ODA-HEMA copoly(amic esters).

2.4. Preparation of poly(amic ester) film and thermal conversion to polyimide

5 g of poly(amic ester) powder was dissolved in 15 g of dimethylacetamide (DMAC) to make a 25% (w/w) solution. A film was cast from the viscous solution on a glass plate by a doctor's knife. The film was dried at 100 °C for 1 h, 200 °C for 1 h, and 350 °C for 1 h in a heating oven to convert the poly(amic ester) to a polyimide as shown in Scheme 3. The film was yellow and transparent.

2.5. Characterization

The IR spectra were recorded on a Jasco 460 FTIR Spectrometer. ^1H NMR spectra were recorded on a Brucker Advance 600 Spectrometer. Inherent viscosity was measured using a Cannon-Ubbelohde No. 100 viscometer at a concentration of 0.5 g/dL in NMP at 30 °C. Thermal stability was analyzed using a TA Instrument Thermogravimetric Analyzer (TGA) Q500 at a heating rate of 10 °C/min under nitrogen. The glass transition temperature (T_g) and the in-plane coefficient of thermal expansion (CTE) of cured BisAPAF-PMDA polyimide film were determined using a TA Instruments Thermal Mechanical Analyzer (TMA) 2940 with an extension probe under 0.05 N tension force on the film, at a heating rate of 5 °C /min under nitrogen. The UV–visible spectra were obtained on a Varian Cary 100 UV–VIS spectrophotometer.



Scheme 3. Thermal imidization of poly(amic ester) to polyimide.

2.6. Preparation of photoresist formulation and lithographic evaluation

A representative photoresist formulation is as follows: 1 g of PMDA-75% BisAPAF-25% ODA-HEMA copoly(amic ester) was dissolved in 3 g of NMP. To this solution, 0.03 g (3 phr) of Michler's ketone (MK), 0.08 g (8 phr) of tribromomethyl phenyl sulfone (TBPS) and 0.15 g of tetra(ethylene glycol) diacrylate (TEGDA) were added. The solution was filtered through a 5 μm Teflon filter. It was then spin-coated onto a silicon wafer, and softbaked on a hot plate at 100 °C for 5 min to obtain a film of about 3 μm thick. The film was exposed to a broad band (250–500 nm) Single-Side Mask Aligner (OAI, J500). The wafer was developed in a 2.38 wt% TMAH developer. The film thickness was measured with a Tenco α-step instrument. The characteristic curve was obtained by plotting the normalized film thickness against the exposure energy. After hardbaking at 350 °C for 1 h, the resulting pattern was observed with an optical microscope (OM) (Leica, model DMLM) and a scanning electron microscope (SEM) (Hitachi, model S4100).

3. Results and discussion

3.1. Synthesis of poly(amic esters)

The first practical organic solvent developable, negative-working PSPI was developed by Rubner et al. [17]. The resin they used was a poly(amic ester), in which a photosensitive acrylate group was introduced to the polymer through an ester bond. Based on the same principle, we designed the molecular structure of the aqueous base developable, negative-working PSPIs. As seen in Scheme 1, the acrylate group was attached to polymers by the reaction of hydroxyethyl acrylate (HEMA) and PMDA dianhydride. In addition to the photo-crosslinkable acrylate group, a phenolic hydroxyl group was also incorporated to the polymer backbone to render the aqueous base solubility, which came from the BisAPAF diamine. In our preliminary photolithography test, we found that the PMDA-BisAPAF-HEMA poly(amic ester) had a high dissolution rate in 2.38 wt% TMAH developer. So, we used ODA diamine to partially substitute the BisAPAF diamine and prepared PMDA-BisAPAF-ODA-HEMA copoly(amic esters). In this way, we were able to control the dissolution rate of poly(amic ester) in the TMAH developer. Both PMDA-75%BisAPAF-25%ODA-HEMA copoly(amic ester) and PMDA-50%BisAPAF-50%ODA-HEMA copoly(amic ester) were still soluble in TMAH solution.

As described in previous paper [16], the poly(amic esters) can be prepared from diester diacid chloride and diamine or from direct polymerization of diacid diester with diamine using an activator such as diphenyl

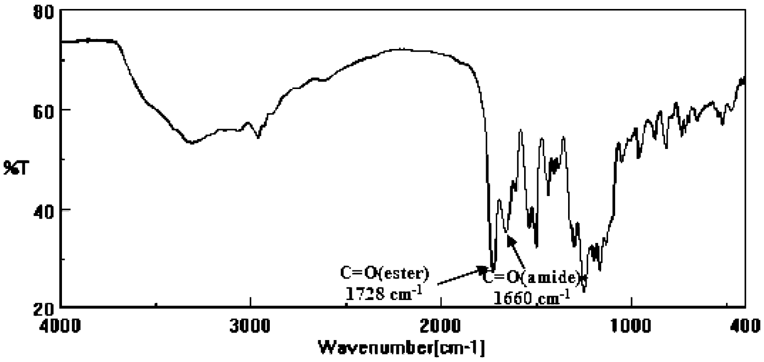


Fig. 1. IR spectrum of PMDA-75%BisAPAF-25%ODA-HEMA copoly(amic ester).

(2,3-dihydro-2-thixo-3-benzoxazoyl) phosphonate (DDTBP), 3,3′-(phenyl phosphinylidene) bis[2(3H)-benzothiazolone], dicyclohexylcarbodimide, phenyl phosphonic dichloride, etc. Due to the simplicity in practice, we chose direct polymerization to prepare the poly(amic esters). First, the PMDA dianhydride was reacted with HEMA to form diester of pyromellitic acid. The diester diacid was directly polymerized with BisAPAF (or/and ODA) by using phenyl phosphonic dichloride as an activator to give the poly(amic esters). The inherent viscosities of these poly(amic esters) were 0.20 dL/g. Cured at 350 °C for 1 h, the films prepared from the poly(amic esters) were transparent and tough, which indicated that the polymer had enough molecular weight. The IR spectrum of the PMDA-75%BisAPAF-25%ODA copoly(amic ester) (Fig. 1) showed a broad absorption band at 3400–3100 cm^{-1} due to the amino (N–H) and hydroxyl (OH) groups, and a amide carbonyl absorption at 1660 cm^{-1}. The ^{1}H NMR spectrum of the

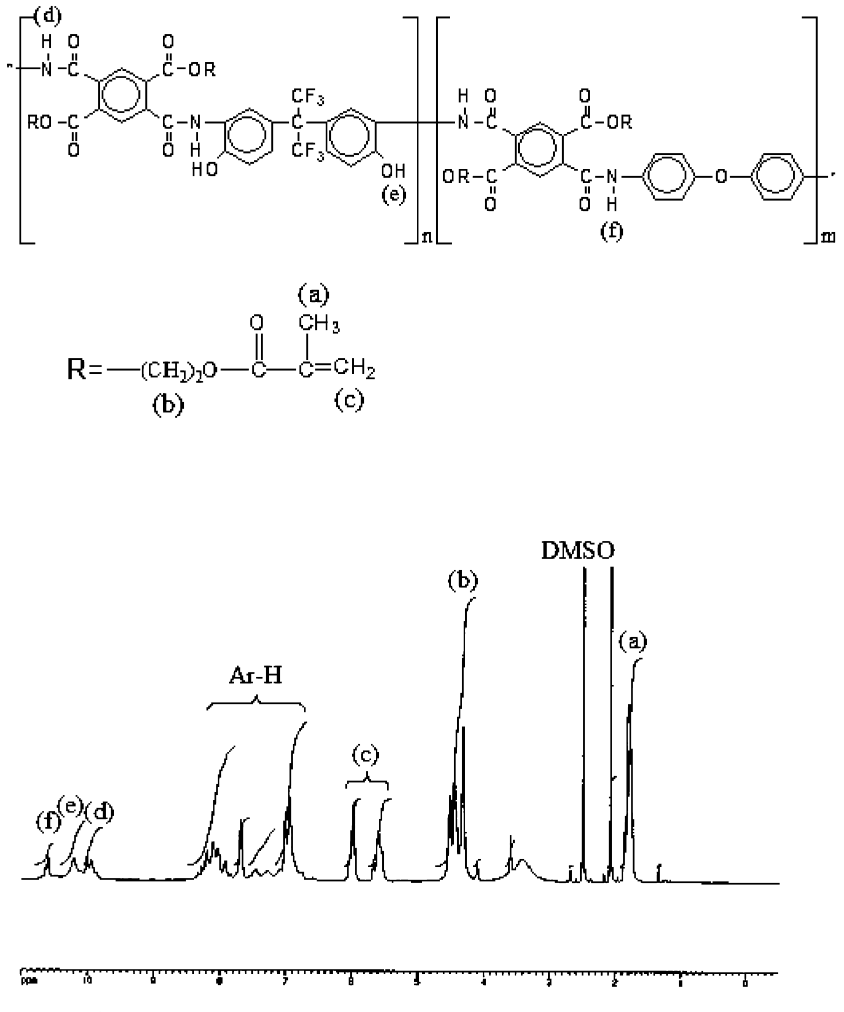


Fig. 2. ^{1}H NMR spectrum of PMDA-75%BisAPAF-25%ODA-HEMA copoly(amic ester).

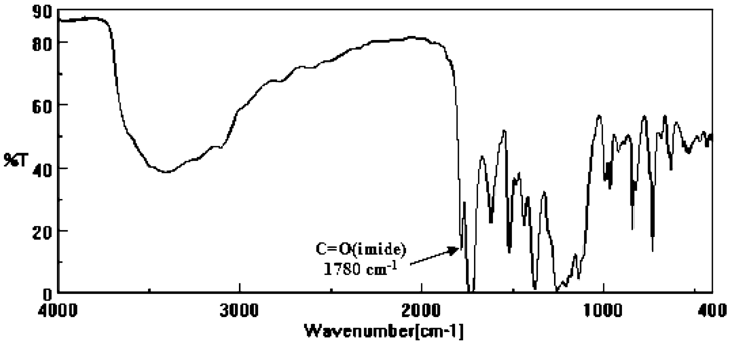


Fig. 3. IR spectrum of PMDA-75%BisAPAF-25%ODA-HEMA copolyimide.

poly(amic ester) (Fig. 2) exhibited the peaks of the hydroxyl proton (10.2 ppm), amino proton (9.9 and 10.6 ppm) and HEMA protons (1.8, 4.4, 5.5 and 6.0 ppm). The appearance of a strong imide absorption at 1780 cm^{-1} and the disappearance of the amide carbonyl absorption at 1660 cm^{-1} in IR spectrum (Fig. 3) of the film prepared from the poly(amic ester) and cured at 350 °C indicated the conversion from copoly(amic ester) to polyimide.

3.2. Polymer characterization

Table 1 summarizes the qualitative solubility of the poly(amic esters) and the corresponding polyimdes. The poly(amic esters) were soluble in a wide range of solvents, but the polyimides did not dissolve in any organic solvents. The incorporation of ODA in the poly(amic esters) decreased their solubility in acetone. Table 2 shows the thermal properties of polyimides derived from these poly(amic esters). The Tgs and in-plane CTEs of these polyimides were measured by TMA. Due to the flexibility of the ether linkage in ODA monomer, the Tg decreased while the CTE increased as the amount of ODA increased. The 5% weight loss temperatures of the cured polyimides, which were obtained with a heating rate of 10 °C/min in both nitrogen and air by TGA, are shown in Table 2. The incorporation of ODA significantly increased the polymer's thermal and thermo-oxidative stabilities. The isothermal stability analysis at 500 °C for 150 min in air (Fig. 4) by TGA further supported the finding.

3.3. Lithographic evaluation

The UV–visible spectra of THF solution of three poly(amic esters) with a concentration of 1 g/L in the 200–600 nm wavelength are shown in Fig. 5. Both the hexafluoroisopropylidene (6F) group in BisAPAF monomer and the ether linkage in ODA monomer could separate chromophoric groups to improve the polymers' transmittance. However, the 6F group seemed to have a better effect. The UV–visible transmittance curves shifted to higher wavelength as the ODA content increased.

In order to find out the effect of the polymer molecular structure and the concentration of TMAH developer on the dissolution time of polymers, a 3 μm

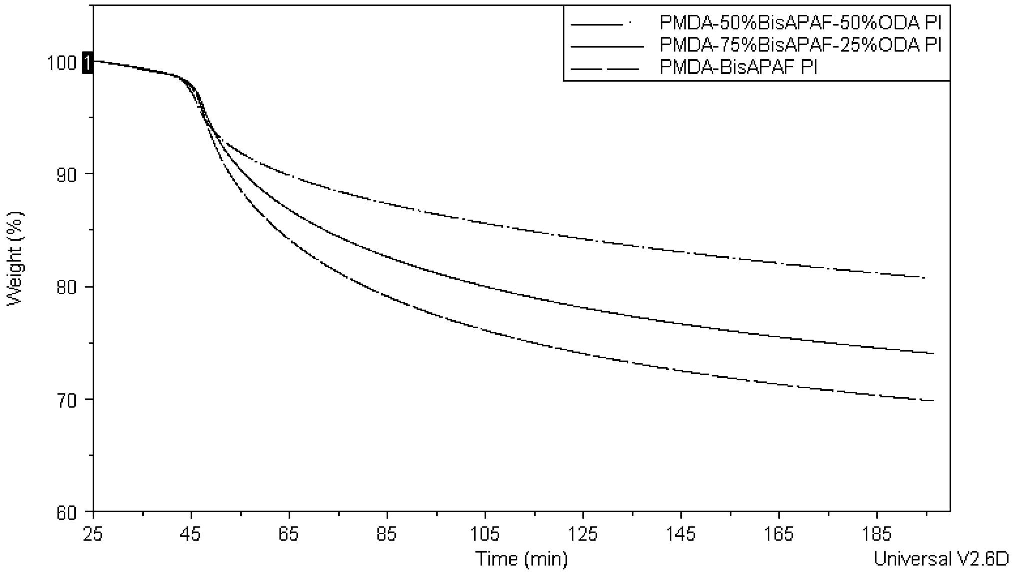


Fig. 4. Isothermal TGA thermograms of cured polyimdes film at 500 °C for 150 min.

Table 1
Solubility of polyamic esters (PAEs) and correlated polyimides (PI)

Solvent	PMDA-BisAPAF-HEMA		PMDA-75%BisAPAF -25%ODA-HEMA		PMDA-50%BisAPAF -50%ODA-HEMA	
	PAE	PI	PAE	PI	PAE	PI
NMP[a]	S[b]	IS[c]	S	IS	S	IS
DMAC[d]	S	IS	S	IS	S	IS
THF[e]	S	IS	S	IS	S	IS
Toluene	S	IS	S	IS	S	IS
Acetone	S	IS	PS	IS	PS[f]	IS
$CHCl_3$	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS

[a] NMP: *N*-methylpyrrolidone.
[b] S: soluble.
[c] IS: insoluble.
[d] DMAC: dimethylacetamide.
[e] THF: tetrahydrofuran.
[f] PS: partially soluble.

Table 2
Thermal properties of polyimdes

Polymer	CTE (μm/m °C)	T_g (°C)	Decomposition temperature (°C), T_5[a]	
			N_2	Air
PMDA-BisAPAF PI	44.9	372.46	485	466
PMDA-75%BisAPAF-25%ODA PI	46.3	362.68	501	475
PMDA-50%BisAPAF-50%ODA PI	49.8	355.49	519	483

[a] T_5 : 5% weight loss temperature.

thick film (after softbaking) of each polymer was dissolved in four different concentrations of TMAH solution. The results are shown in Table 3. As expected, the dissolution time was decreased as the concentration of TMAH increased. We also discovered that the dissolution time increased with the increasing content of ODA in the copolymers, because the phenolic hydroxyl groups decreased as the content of ODA increased. Thus, we could control the developing time by altering either the TMAH concentration or the structure of the polymer. In this study, we chose the commonly used 2.38% TMAH developer and PMDA-75%BisAPAF-25%ODA-HEMA copoly(amic ester) for the lithographic evaluation.

The negative-tone polyimide precursor became insoluble in TMAH after exposure to UV light due to the crosslinking reaction of photosensitive acrylate groups in the polymer. Therefore, no dark film loss was observed in the developed film. Besides the polyimide precursor, the negative-tone photosensitive PSPI formulation usually consists of a photoinitiator, a photosensitizer, a crosslinker and a solvent. The tetra(ethylene glycol) diacrylate was used as the crosslinker to improve the photosensitivity of the formulation, and NMP was the solvent in this study. Three photoinitiator/photosensitizer systems, MK/TBPS, MK/BP, and MK/TENA, have been used. In order to screen these photo-initiation systems, the dissolution rate differences before and after exposure of PMDA-75% BisAPAF-25% ODA-HEMA copoly(amic ester) based PSPI formulations

Table 3
Dissolution times (second) of poly(amic ester) films (3 μm) in different concentrations of TMAH solution

Polymer	0.60% TMAH	1.19% TMAH	2.38% TMAH	4.76% TMAH
PMDA-BisAPAF-HEMA poly(amic ester)	31	9	3	1
PMDA-75%BisAPAF-25%ODA -HEMA poly(amic ester)	200	45	21	5
PMDA-50%BisAPAF-50%ODA -HEMA poly(amic ester)	4800	547	245	65

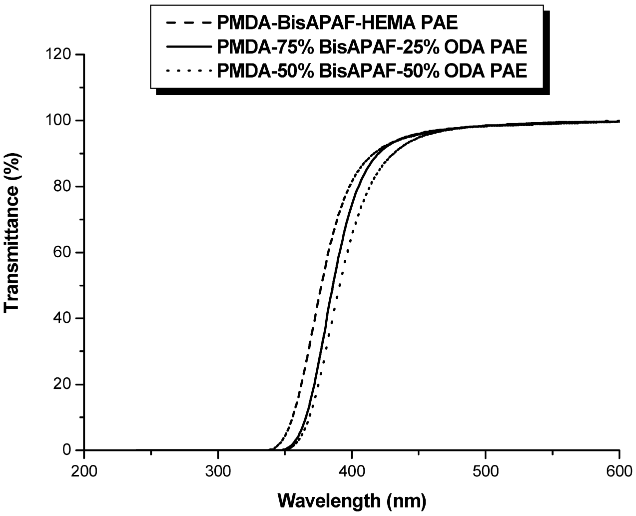


Fig. 5. UV–visible spectra of poly(amic esters) in THF solution.

were measured. The results are shown in Fig. 6, with the MK/TBPS system giving the biggest dissolution rate difference. Using the same polymer as the base polymer and 2.38% TMAH as the developer, we obtained the characteristic curves of these three photo-initiation systems as shown in Fig. 7. Obviously, the MK/TBPS system induced the highest degree of crosslinking under the same amount of exposure dose. In fact, under the dose of 1200 mJ/cm^2, only MK/TBPS system's normalized film thickness could reach 1. Based on these observations, the MK/TBPS system was the best photo-initiation system among these three systems. For this system, the contrast at 0.5 gel fraction ($\gamma^{0.5}$) was 1.11, and the sensitivity to obtain 0.5 gel fraction ($D^{0.5}$) was 452 mJ/cm^2. A resolution of 10 μm pattern with an exposure dose of 450 mJ/cm^2 can be obtained in a 3 μm thick film (cured at 350 °C for 1 h) as shown in Fig. 8. A scanning electron micrograph of this pattern is given in Fig. 9. We further studied the effects of the molecular structure of the precursors and the concentration of TMAH developer on the photosensitivity of the

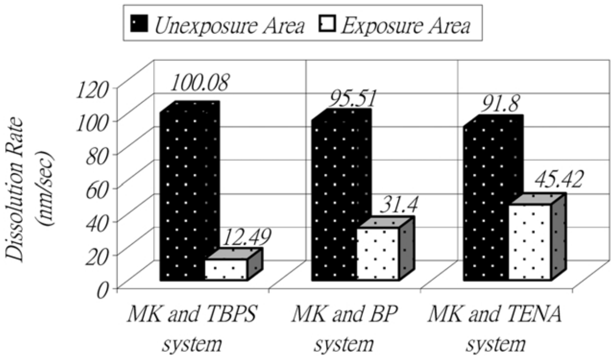


Fig. 6. The dissolution rate differences before and after exposure of PMDA-75% BisAPAF-25% ODA-HEMA copoly(amic ester) based PSPI formulations.

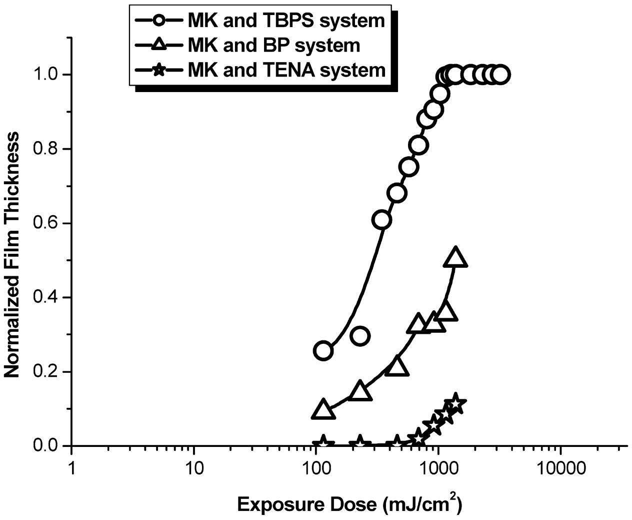


Fig. 7. Characteristic exposure curves of PSPI formulations.

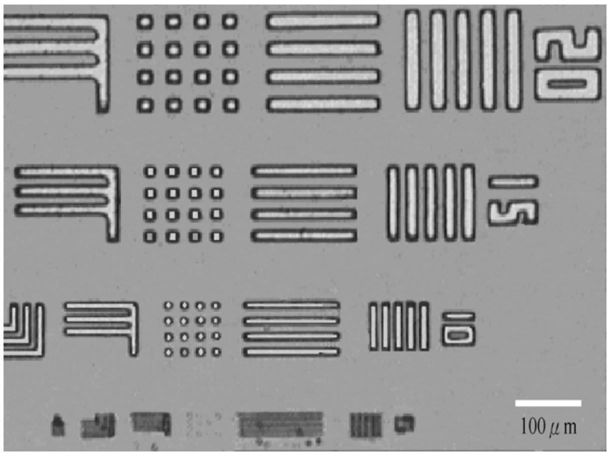


Fig. 8. Optical micrograph of a pattern from PMDA-75% BisAPAF-25% ODA-HEMA copoly(amic ester) based PSPI formulation.

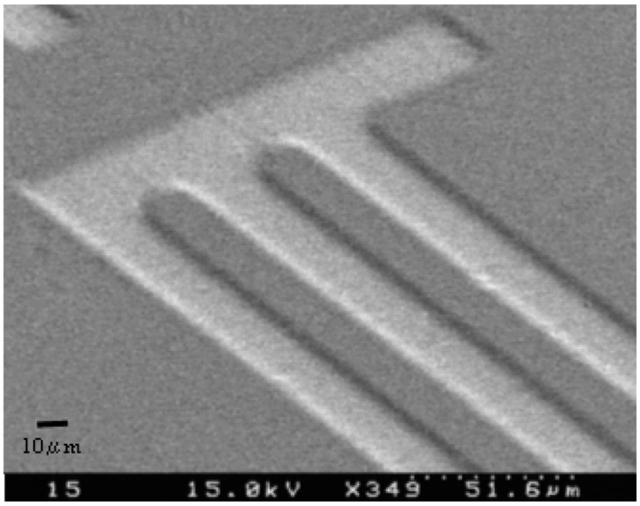


Fig. 9. Scanning electron micrograph of a pattern from PMDA-75% BisAPAF-25% ODA-HEMA copoly(amic ester) based PSPI formulation.

Table 4
Photosensitivity ($D^{0.5}$, mJ/cm^2) of each poly(amic ester) in different concentrations of TMAH solution

Developer	PMDA-BisAPAF-HEMA poly(amic ester) ($D^{0.5}$)	PMDA-75%BisAPAF-25%ODA-HEMA poly(amic ester) ($D^{0.5}$)	PMDA-50%BisAPAF -50%ODA-HEMA poly(amic ester), ($D^{0.5}$)
0.595% TMAH	582	–	–
1.19% TMAH	687	428	–
2.38% TMAH	839	452	323
4.76% TMAH	1064	794	360

PSPI formulations based on MK/TBPS system. The photosensitivity ($D^{0.5}$) of each poly(amic ester) in different concentrations of TMAH solution is shown in Table 4. For the same poly(amic ester), the photosensitivity of PSPI formulation decreased as the concentration of TMAH increased. The more concentrated the TMAH solution, the higher the solubility to the polymer. In order to obtain the same normalized film thickness (0.5 gel fraction), the system needed more exposure energy to induce higher degree of crosslinking. For the same concentration of TMAH solution, the photosensitivity of PSPI formulation increased as the ODA content increased, because the increasing of ODA content reduced the solubility of the polymer. Therefore, it took a smaller amount of exposure dose (lower degree of crosslinking) to obtain the same normalized film thickness (0.5 gel fraction).

4. Conclusions

Novel poly(amic esters) have been synthesized from pyromellitic dianhydride (PMDA), 2,2′-bis-(3-amino-4-hydroxyphenyl) hexafluoropropane (BisAPAF), 4,4′-diaminodiphenyl ether (4,4′-ODA) and 2-hydroxyethyl methacrylate (HEMA) by direct polymerization in the presence of phenylphosphonic dichloride as an activator. Negative-working, aqueous base developable photosensitive resin compositions were prepared from these polymers with photosensitizers/photoinitiators, a crosslinker and NMP. The photosensitive polyimide precursor containing PMDA-75% BisAPAF-25% ODA-HEMA copoly(amic ester), MK/TBPS and tetra(ethylene glycol) diacrylate showed a sensitivity ($D^{0.5}$) of 452 mJ/cm^2, and a contrast of 1.11 in a 3 μm film. A pattern with a resolution of 10 μm was obtained from this composition.

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