Synthesis and Characterization of Soluble Copolyimides Containing Chalcone and Phosphine Oxide Moieties in the Main Chain

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ABSTRACT: The functional diamines 3,3′-diaminochalcone and bis(3-aminophenyl)-3,5-bis(trifluoromethyl)phenyl phosphine oxide were successfully prepared by simple and convenient procedures with short reaction times, and the overall yields were 78 and 70%, respectively. Copolyimides prepared from 3,3′-diaminochalcone, bis(3-aminophenyl)-3,5-bis(trifluoromethyl)phenyl phosphine oxide, and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride exhibited excellent solubility in several organic solvents, such as dimethyl sulfoxide, *N*,*N*-dimethylformamide, *N*-methyl pyrrolidone, tetrahydrofuran, and acetone. They also showed very good thermal stability even up to 450°C for 5% weight loss (by thermogravimetric analysis) in nitrogen and a high glass-transition temperature up to 274°C (by differential scanning calorimetry) in nitrogen. The copolymers' adhesive and photoreactive properties were also investigated, and it was confirmed that the copolyimide containing chalcone and phosphine oxide moieties in the main chain had good adhesiveness and photoreactivity. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 593–598, 2008

Key words: adhesion; copolymerization; polyimides

INTRODUCTION

Polyimides are a class of functional polymers with many desirable characteristics that have been used in many high-technology areas, such as aviation, spaceflight, electronics, composite materials, and separation membranes. Photosensitive polyimides, compared with nonphotosensitive polyimides, simplify greatly the complex, multistep processing required in photolithography processes.[1] Polymers containing chalcone moieties have been widely studied and applied[2–6] because they have high sensitivity to ultraviolet (UV) radiation and good chemical stability with lower shrinkage. However, because of these photosensitive groups, the polymers have low adhesion to metal substrates when they are used in the microelectronics industry. On the other hand, phosphine oxide moieties can improve adhesion properties. Polymers containing phosphine oxide show excellent adhesion characteristics and thermal stability.[7–11] Hence, we have combined phosphine oxide and chalcone moieties to impart good adhesion and photosensitivity properties to polyimides.

In this work, the diamine monomers 3,3′-diaminochalcone (mDAC) and bis(3-aminophenyl)-3,5-bis(trifluoromethyl)phenyl phosphine oxide (mDA6FPPO) were prepared by simple and convenient procedures with short reaction times and high yields. Soluble copolyimides containing chalcone and phosphine oxide moieties in the main chain were synthesized through the copolymerization of mDAC, mDA6FPPO, and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). The structures and properties of the resulting copolymers were also examined.

EXPERIMENTAL

Materials and instruments

3-Nitroacetophenone and 3-nitrobenzaldehyde were used as received from Fluka (Buchs, Switzerland); 6FDA, diphenylphosphinic chloride, and 3,5-bis(trifluoromethyl)bromobenzene were obtained from Aldrich (Lyon, France) without further purification. Potassium carbonate, magnesium powder (98.5%), and hydrazine hydration (85%) were obtained from China Medicine (Group) Shanghai Chemical Reagent Corp. (Shanghai, China). Pyridine, tetrahydrofuran, and *N*,*N*-dimethylformamide were purified by distillation under reduced pressure after being dried over

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calcium hydride; methanol was dried over 4-Å molecular sieves before use. All other reagents and solvents were analytical-grade reagents and were used as received.

The ultrasonic irradiation generator that was used, with a power of 450 W, was a type SK8200HP ultrasonic cleaner (Shanghai, China). Infrared (IR) spectra of the samples were recorded on a Nexus 470 Fourier transform infrared (FTIR) spectrometer (Madison, WI). An elemental analysis was carried out with a Vario EL III CHNSO (Hanau, Germany), and ^{1}H-NMR spectra were measured on a Varian Mercury (Palo Alto, CA) VX-300 (300-MHz) spectrometer in $CDCl_3$ or dimethyl sulfoxide-d_6 with tetramethylsilase (TMS) as an internal standard. The number-average molecular weight of the polymers was determined by gel permeation chromatography with an Agilent (Santa Clara, CA) 1100 series liquid chromatograph. Ultraviolet–visible (UV–vis) spectra were measured on a PerkinElmer (Boston, MA) Lambda-Bio35 UV–vis spectrophotometer at room temperature. Thermogravimetric analysis (TGA) was performed with a PerkinElmer TGS-2 thermal analyzer (Norwalk, CT) at a heating rate of 10°C/min in nitrogen within the temperature range of 40–800°C. Differential scanning calorimetry (DSC) data were obtained with a Mettler–Toledo (Zurich, Switzerland) DSC 822e/400 in nitrogen at a heating rate of 10°C/min.

Preparation of mDAC

3-Nitrobenzaldehyde (0.378 g, 2.5 mmol), 3-nitroacetophenone (0.413 g, 2.5 mmol), and 0.10 g of potassium carbonate were added to 3 mL of methanol in a 100-mL conical flask. The mixture was irradiated by an ultrasonic generator in a water bath at 30–35°C for 5 min. After cooling to the ambient temperature, the crude product was separated by filtration and washed with cold water. The dried crude product, dinitrochalcone, was recrystallized from acetone to obtain white crystals with a melting point of 210–211°C (lit.[12] 210–211°C) and a 91% yield.

A mixture of dinitrochalcone (0.298 g, 1 mmol), 6 mL of 2-propanol, 15 mg of active carbon, and 1.5 mg of $FeCl_3{\cdot}6H_2O$ was stirred at 80°C for 10 min. Then, 85% hydrazine hydrate (1 mL) diluted with 2-propanol (2 mL) was added dropwise over 20 min, and stirring was continued for 3.5 h at 80°C. The reaction mixture was filtered off, and the filtrate was concentrated by rotary evaporation. The residue was recrystallized from H_2O to produce the pure product in the form of white crystals with a melting point of 150–151°C (lit.[5] 132°C) and an 86% yield. The product was characterized by elemental analysis and IR and ^{1}H-NMR spectroscopy data.

Anal. calcd for $C_{15}H_{14}N_2O$: C, 75.61%; H, 5.92%; N, 11.76%. Found: C, 75.53%; H, 5.90%; N, 11.82%. IR (KBr, cm^{-1}): 3404, 3316, 3202, 3051, 1642, 1606, 1461, 1343, 1309, 864, 776, 688. ^{1}H-NMR (dimethyl sulfoxide-d_6, δ): 5.06 (4H, s, —NH_2), 6.45 (1H, d, H-4, J = 9.6 Hz), 6.47 (1H, d, —C=CH—CO—, J = 18.3 Hz), 6.51 (1H, d, H-6, J = 9.6 Hz), 6.53 (1H, s, H-2), 6.78 (1H, d, H-4′, J = 8.4 Hz), 6.80 (1H, t, H-5), 6.83 (1H, s, H-2′), 6.95 (1H, t, H-5′), 6.96 (1H, d, Ar—CH=C—, J = 18.3 Hz), 7.03 (1H, d, H-6′, J = 8.4 Hz).

Preparation of mDA6FPPO

The compound was prepared with a procedure similar to one reported in the literature,[10] but $FeCl_3{\cdot}6H_2O/C$ was used to catalyze the reduction of the aromatic nitro compound to the corresponding amine with hydrazine hydration. The white crystals were produced with a melting point of 225.5°C (by DSC in N_2; lit.[10] 225.5–226.5°C) and an overall yield of 70%. The product was characterized with IR and ^{1}H-NMR spectroscopy data.

IR (KBr, cm^{-1}): 3424, 3349, 1636, 1598, 1366, 1284, 1184, 1129, 779. ^{1}H-NMR ($CDCl_3$, δ): 3.84 (4H, s), 6.84 (2H, q, J = 9 Hz and 1.4 Hz), 6.86 (2H, d, J = 12 Hz), 7.00 (2H, d, J = 12 Hz), 7.23 (2H, m), 7.99 (1H, s), 8.11 (2H, d, J = 12 Hz).

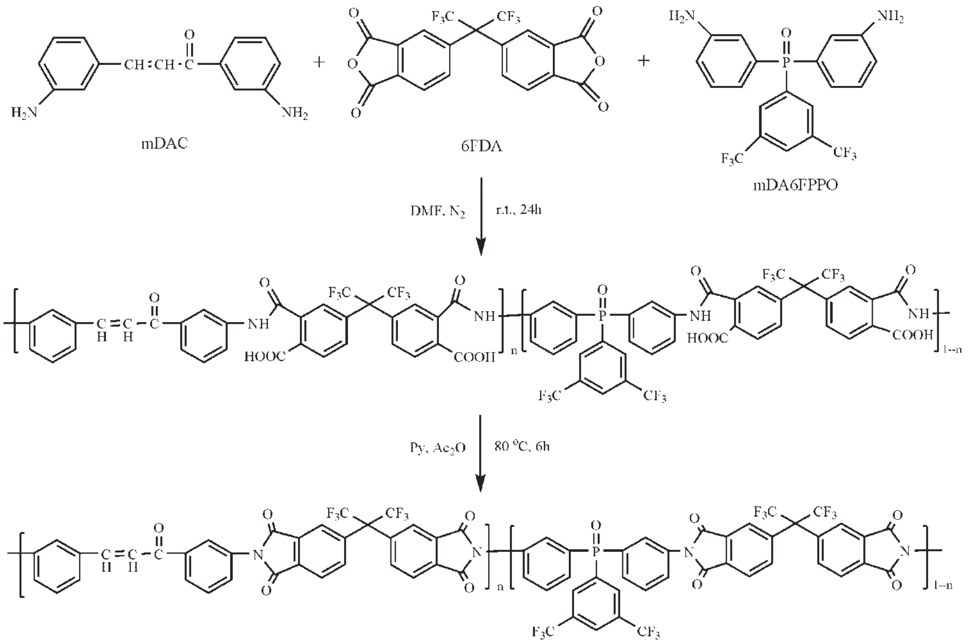
Synthesis of the polyimides

The synthetic route of the polymers is shown in Scheme 1. In a typical procedure, 2 mmol of the diamines (mDAC and/or mDA6FPPO) was dissolved in 15 mL of *N*,*N*-dimethylformamide, and 2 mmol of the dianhydride (6FDA) was added to the solution. The reaction flask was evacuated with a vacuum and then filled with dried nitrogen three times. The reaction mixture was stirred at room temperature for 24 h, and a mixture of 1 mL of acetic anhydride and 1 mL of pyridine was added. The stirring of the mixture was continued at 80°C for 6 h. The resulting solution was poured into methanol, and the white precipitate was collected by filtration. The polyimides were obtained as white powders after being dried in a vacuum oven at 60°C for 24 h.

RESULTS AND DISCUSSION

Synthesis and characterization of the monomers

Two diamines, mDAC and mDA6FPPO, were synthesized according to the synthetic route shown in Scheme 2. The monomer mDAC was synthesized from 3-nitrobenzaldehyde and 3-nitroacetophenone via Claisen–Schmidt condensation, which led to dinitro compound 3,3′-dinitrochalcone, and this was followed by its reduction with hydrazine hydration. Ultrasonic irradiation was used to accelerate the Claisen–Schmidt condensation between 3-nitroben-

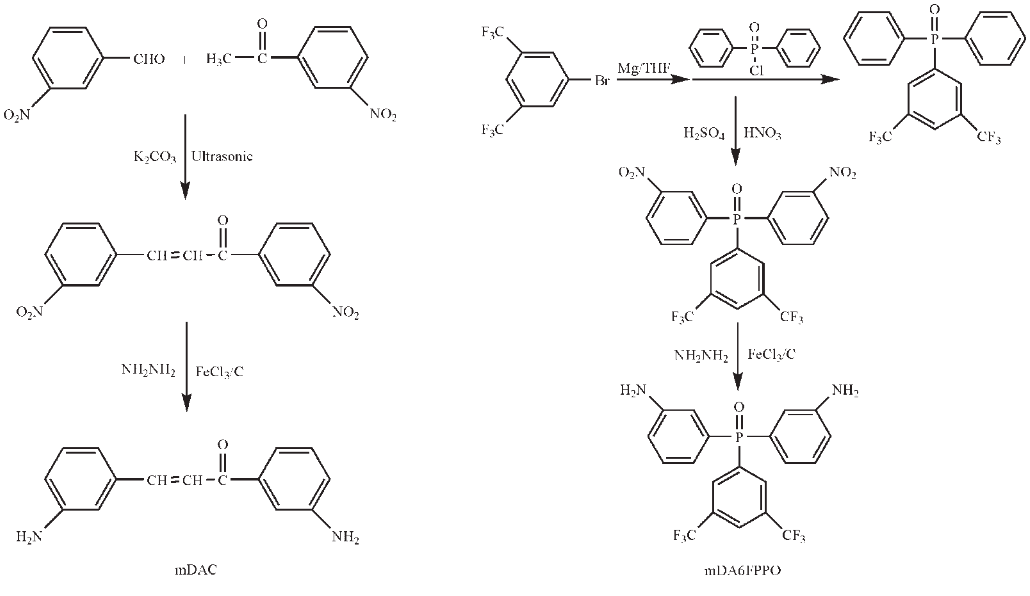


Scheme 1 Synthesis of the copolyimides.

zaldehyde and 3-nitroacetophenone in the presence of potassium carbonate. This method produced a high product yield (>90%) and purity with a shorter reaction period and easier work-up in comparison with previous methods.[5] Then, mDAC was obtained from the reduction of condensation product 3,3′-dinitrochalcone by the $FeCl_3{\cdot}6H_2O/C$ catalyst with 85% hydrazine hydration. The overall yield of mDAC was about 78%, much higher than the overall yield of 22.6% in the literature.[5]

The diamine mDA6FPPO was prepared from 3,5-bis(trifluoromethyl)bromobenzene and diphenylphosphinic chloride through the Grignard reaction, which was followed by nitration and hydrazine hydrate reduction. After purification, the overall yield was about 70%, which was very near the figure of the literature[10] (72.7%). Moreover, hydrazine hydrate reduction has the advantages of milder conditions, lower cost, easier work-up, and environmental friendliness.

FTIR and ^{1}H-NMR spectra were taken to confirm the structures of the monomers. The IR spectrum of mDAC exhibited amine absorption peaks at 3404 and 3316 cm^{-1} from asymmetric and symmetric



Scheme 2 Synthesis of monomers mDAC and mDA6FPPO.

TABLE I
Characteristics of the Polyimides

Polyimide	6FDA : mDAC : mDA6FPPO (molar ratio)	M_n ($\times 10^{-4}$)[a]	λ_{max} (nm)[b]	T_g (°C)[c]	T_d (°C)[d]	Residue (wt %)[e]
PI-a	2 : 2 : 0	1.03	292	292	404	50.7
PI-b	2 : 1 : 1	1.10	304	274	450	50.1
PI-c	2 : 0 : 2	1.02	—	233	493	49.8

[a] Number-average molecular weight measured by gel permeation chromatography at 35°C.
[b] Maximum absorption wavelength in a film.
[c] Glass-transition temperature measured by DSC at 10°C/min in N_2.
[d] Five percent weight loss temperature determined by TGA at 10°C/min in N_2.
[e] Measured by TGA at 800°C in N_2.

stretching of NH_2, respectively. The carbonyl group (C=O) absorption peak appeared at 1642 cm^{-1}, whereas the absorption peak at 1606 cm^{-1} was due to phenyl and C=C group stretching absorption. As expected, mDA6FPPO also showed typical N—H absorption peaks at 3424 and 3349 cm^{-1}. The P=O stretching absorption appeared at 1284 cm^{-1}, and the C—F absorption peaks were observed at 1129 and 1184 cm^{-1} from trifluoromethyl groups.

In the ^{1}H-NMR spectrum of mDAC, the singlet broad peak at 5.06 ppm was due to the amino protons. The two group peaks at 6.47 (doublet, 2H) and 6.96 ppm (doublet, 2H) were due to the olefinic protons, and the coupling constant was 18.3 Hz. The residual signals corresponded to the aromatic protons, the coupling constants of which were 8.4 and 9.6 Hz. As for mDA6FPPO, the resonance signal at 3.84 ppm was due to the amino protons. The signals at 8.11 ppm (doublet, 2H) were from the protons in the ortho position of the 3,5-bis(trifluoromethyl) phenyl group, and the coupling constant was 12 Hz; this was due to the phosphoric moiety. The singlet peak at 7.99 ppm was due to the proton in the para position of the 3,5-bis(trifluoromethyl) phenyl group. The multiplet resonance signals at 7.26–7.20 ppm were due to the protons in the meta position of the 3-aminophenyl units. The signals at 7.00 (doublet, 2H) and 6.86 ppm (doublet, 2H) were from the protons in the ortho position of the 3-aminophenyl units, and the coupling constant was also 12 Hz; this was due to phosphoric moieties. The signals at 6.84 ppm (quartet, 2H) were from the protons in the para position of the 3-aminophenyl units, and the coupling constants were 9 and 1.4 Hz; these were due to the aromatic proton and phosphoric moiety, respectively.

Structures of the polyimides

The polyimides were synthesized through the copolymerization of mDAC, mDA6FPPO, and 6FDA in different molar ratios (Table I). The polymers were prepared according to a two-step procedure, and a mixture of acetic anhydride and pyridine was used for the chemical imidization of poly(amic acid). The polymeric chemical structures were characterized with FTIR and ^{1}H-NMR spectra.

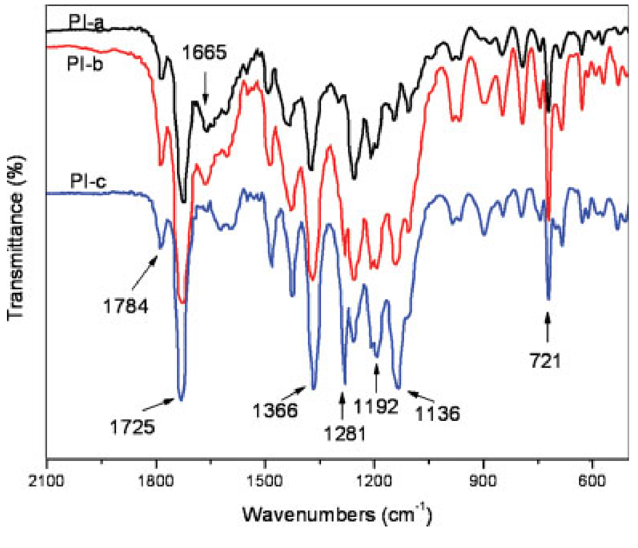


Figure 1 FTIR spectra of the polyimides. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

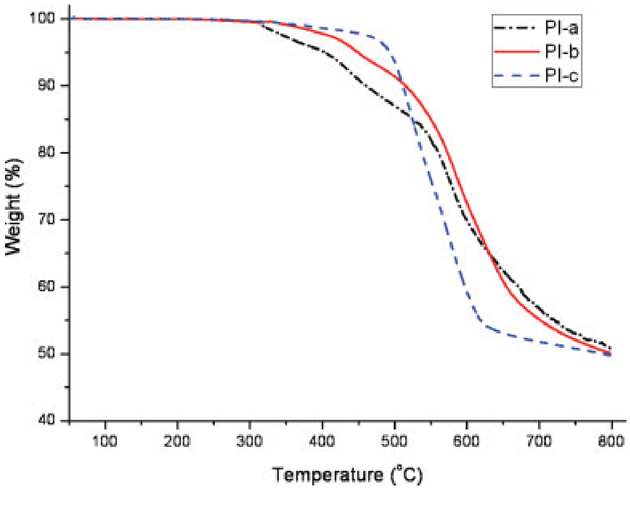


Figure 2 TGA curves of the polyimides. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Solubility of the Polyimides

Sample	DMSO	DMF	NMP	THF	$CHCl_3$	Toluene	CH_3CN	MeOH	Acetone
PI-a	P	S	S	S	P	I	I	I	S
PI-b	S	S	S	S	P	I	P	I	S
PI-c	S	S	S	S	S	I	S	I	S

DMF = *N,N*-dimethylformamide; DMSO = dimethyl sulfoxide; I = insoluble; MeOH = methanol; NMP = *N*-methyl pyrrolidone; P = partially soluble; S = soluble; THF = tetrahydrofuran.

The FTIR spectra of the polyimides are shown in Figure 1. The absorption peaks at 1784 and 1725 cm^{-1} were from asymmetric and symmetric stretching of the imide carbonyl group, respectively. The absorption peak of the carbonyl group in the chalcone unit was observed at 1665 cm^{-1}. The peak at 1366 cm^{-1} was due to the imide C—N vibration. The P═O stretching peak was at 1281 cm^{-1}, and the C—F absorption peaks were at 1192 and 1136 cm^{-1}. The absorption peak at 721 cm^{-1} was from the C—H out-of-plane vibration in the aromatic groups. In addition, the peaks at 1281, 1192, and 1136 cm^{-1} were gradually stronger from PI-a to PI-c, and this was due to an increasing amount of monomer mDA6FPPO. At the same time, the peak at 1665 cm^{-1} gradually disappeared from PI-a to PI-c with a decreasing molar ratio of mDAC. The ^{1}H-NMR spectra of the polymers indicated that the amino proton signals at 4–5 ppm disappeared, and all hydrogen peaks at 7.25–8.57 ppm were due to the aromatic protons and olefinic protons; this was in good agreement with the proposed polymeric structures.

Solubility of the polyimides

The results in Table II show that the copolyimides had excellent solubility in conventional aprotic polar organic solvents such as dimethyl sulfoxide, *N,N*-dimethylformamide, *N*-methyl pyrrolidone, tetrahydrofuran, and acetone. With an increasing ratio of mDA6FPPO from PI-a to PI-c, the solubility was gradually improved. This was indicated by the fact that PI-a was insoluble, PI-b was partially soluble, and PI-c was perfectly soluble in CH_3CN. It is well known that fluorine can enhance polymeric solubility, and the amount of fluorine in the polymeric backbone increased with increasing mDA6FPPO. This could also be attributed to the bulky CF_3 groups and the phosphine oxide moiety of mDA6FPPO.

Thermal properties of the polyimides

The thermal stability of the polymers was studied with TGA in a nitrogen atmosphere. The TGA data and TGA curves of the polyimides are shown in Table I and Figure 2. The 5% weight loss temperature in N_2 of the polymer (PI-b) based on mDA6FPPO and mDAC was 450°C, which was much higher than that of PI-a without the mDA6FPPO moiety (404°C) but lower than that of PI-c without the mDAC moiety (493°C). The char yields of the polymers at 800°C were about 50%. These data indicate that the polymers based on mDA6FPPO possessed very good thermal stability. Furthermore, the thermal stability of the polymers was obviously enhanced by the presence of the mDA6FPPO unit in the polymeric backbone. As expected, the order of the 5% weight loss temperatures was PI-a < PI-b < PI-c. This improvement may have resulted from the fact that the mDA6FPPO unit is more thermally stable than the mDAC unit.

The glass-transition temperatures of the polymers were determined by DSC at a heating rate of 10°C/min under a nitrogen atmosphere. The glass-transition temperatures and DSC curves of the polyimides are shown in Table I and Figure 3. PI-b showed a glass-transition temperature of 274°C, which was higher than that of PI-c based on the mDA6FPPO unit in the backbone (233°C) but lower than that of PI-a based on the mDAC unit in the polymeric backbone (292°C). The results indicated that increasing the molar ratio of mDA6FPPO and decreasing the molar ratio of mDAC reduced the glass-transition

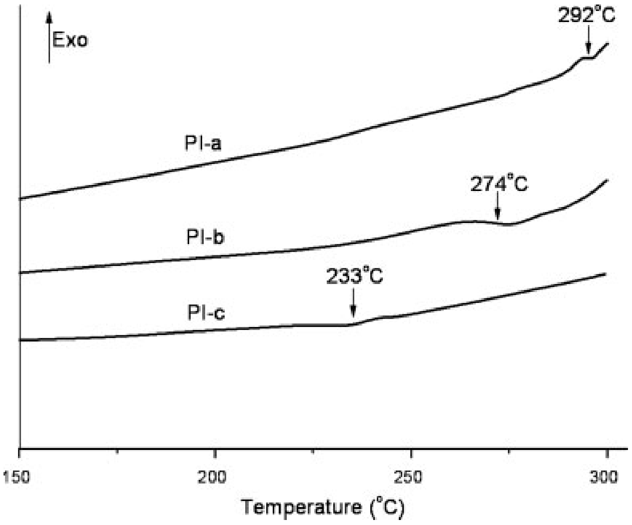


Figure 3 DSC curves of the polyimides.

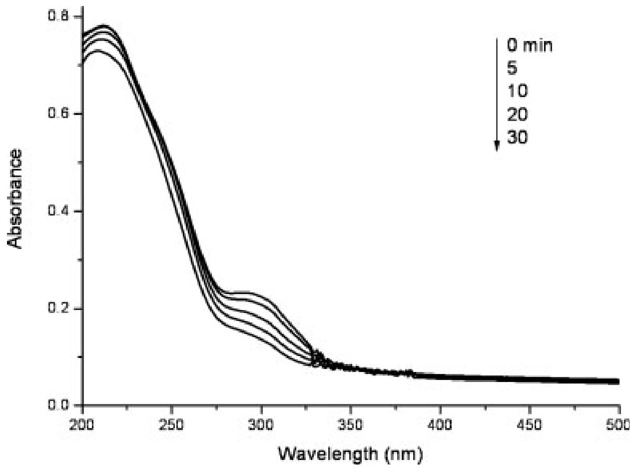


Figure 4 UV–vis spectral changes in PI-b films during UV irradiation.

temperature. This could be attributed to the high free volume present in mDA6FPPO because of the bulky CF_3 moieties and noncoplanarity of mDA6FPPO, whereas mDAC was a rigid unit and had a smaller free volume than mDA6FPPO.

Photoreactivity of the polyimides

The photoreactivity of the resulting polyimides was investigated through observations of UV–vis spectroscopy changes during UV irradiation. PI-b was dissolved in *N,N*-dimethylformamide and spin-coated on a quartz wafer, and a UV–vis absorption spectrum was monitored with the UV irradiation of 254-nm light without filtration for different intervals. In Figure 4, changes in the UV–vis spectra during the irradiation are depicted. The maximum absorption wavelength corresponding to the double bond of the chalcone group was observed at 304 nm. This peak gradually decreased with the irradiation of UV light, and it almost disappeared within 30 min of UV irradiation. The phenomenon indicated photoinduced [2+2] cycloaddition of the double bond of the chalcone group in the polymeric backbone, which resulted in the crosslinking of the polymer and formed analogous cyclobutane structures. Thus, the prepared copolyimides were photosensitive.

Adhesive properties of the polyimides

The polyimides were dissolved in *N,N*-dimethylformamide, coated on Cu foil with a 100-µm coater, and dried at the ambient temperature for 24 h. The adhesive property of the polyimides was estimated by a cross-cut test for films according to GB/T 9286-1998 (equivalent to ISO 2409:1992). As expected, PI-b and PI-c showed much better adhesive strength than PI-a without the phosphine oxide moiety; moreover, the order of the adhesive strength was PI-a $<$ PI-b $<$ PI-c, and PI-c almost did not fractions to be peeled off along the cutting lines. The results demonstrated that the phosphine oxide moiety could evidently promote the adhesive strength of polymers. This improvement could be explained as a function of the polar interaction of the phosphine oxide moiety with the surface of the substrate.[9]

CONCLUSIONS

Two diamine monomers, mDAC and mDA6FPPO, were successfully prepared by simple and convenient procedures with short reaction times, and the overall yields were 78 and 70%, respectively. The copolyimides prepared from mDAC, mDA6FPPO, and 6FDA exhibited excellent solubility, good thermal stability, and a high glass-transition temperature (274°C). The copolymers' adhesive and photoreactive properties were also investigated, and it was confirmed that the copolyimides containing chalcone and phosphine oxide moieties in the main chain had good adhesiveness and photoreactivity.

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