Polyimides Derived from a Methylene-Bridged Dianhydride

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SYNOPSIS

A series of linear aromatic polyimide films that are based on a novel methylene-bridged dianhydride, 3,3'-bis(3,4-dicarboxyphenoxy)diphenylmethane dianhydride, have been synthesized and characterized. High molecular weight polyamic acids were prepared by combining this dianhydride with numerous aromatic diamines. The effects of thermal and chemical imidization of the polyamic acids are discussed as they relate to the dielectric constant, optical transparency, and solubility of the resulting polyimide films. The objective of this work was to obtain low dielectric, optically transparent, and soluble polyimides that can be easily processed as coatings or composite matrices for advanced aerospace and electronics applications.

INTRODUCTION

Linear aromatic polyimides have long been known for their usefulness in meeting aerospace requirements as high-performance films, coatings, and structural materials. The label of "high performance" for these polymers has implied toughness, flexibility, low density, high-temperature stability, chemical and radiation resistance, and mechanical strength. Within the past few years, the list has expanded to include low dielectric properties,[1,2] optical transparency,[3,4] and improved solubility.[5,6]

Polyimides have been widely used as insulation for aerospace cables and wires, and they are finding new uses in the microelectronics industry. A polymer must be an excellent insulator (low dielectric constant) in order to service this industry.

The need exists also for high-temperature, highly optically transparent or colorless film and coating materials for applications on large space components such as solar cells, space mirrors, thermal control coating systems, and antennae. In addition, high-performance polymers that are soluble and therefore easily processable are needed for many space applications. State-of-the-art linear aromatic polyimides are by nature insoluble in common organic solvents and therefore difficult to process.

In this study, a series of linear aromatic polyimide films have been prepared based on a novel methylene-bridged dianhydride, 3,3'-bis(3,4-dicarboxyphenoxy) diphenylmethane dianhydride (PDMDA):
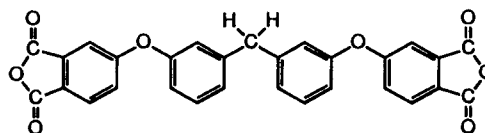
with the goal of achieving a combination of characteristics including low dielectrics, high optical transparency, and solubility. Earlier work on polyimides containing methylene bridging units has dealt with CH_2 groups in the diamine.[6-8]

EXPERIMENTAL

Materials

The chemicals used in the preparation of the PDMDA dianhydride were obtained commercially and used as received except for the 4-nitro-N-phenylphthalimide. It was prepared by reacting 4-nitrophthalic anhydride in a solution of acetic acid with an equimolar amount of aniline and heating to reflux for ~ 2 h. The solution was concentrated by dis-

tilling off some of the acetic acid and was then allowed to cool. The resulting precipitate, 4-nitro-N-phenylphthalimide, was filtered, washed with cyclohexane, and dried *in vacuo*.[9] The aromatic diamines used in the preparation of the PDMDA-containing polyimides as follows: 2,2-bis(4-aminophenyl)-hexafluoropropane (4,4'-6F), 4,4'-oxydianiline (4,4'-ODA), 3,3'-diaminobenzophenone (3,3'-DABP), and 4,4'-methylenedianiline (4,4'-MDA) were obtained from commercial sources with melting points of 79, 187, 152, and 87°C, respectively. The 3,3'-oxydianiline (3,3'-ODA), 2,2-bis[4-(3-aminophenoxy)phenyl]hexafluoropropane (3-BDAF), 4,4'-bis(4-aminophenoxy)benzophenone (4-BAPBP), and 4,4'-bis(3-aminophenoxy)benzophenone (3-BAPBP) are experimental materials that were obtained from Mitsui Toatsu Inc. with melting points of 78, 133, 152, and 137°C, respectively. The 2,2-bis-[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF) (mp 162°C) is an experimental material obtained from the Ethyl Corporation. The 3,5-diaminobenzotrifluoride (3,5-DABTF) (mp 183°C) was synthesized in-house.[10] The N,N-dimethylacetamide (DMAc) used as a solvent for the diamines and resulting polyamic acids was obtained commercially at > 99.5% purity.

Dianhydride Preparation

The PDMDA dianhydride was prepared as follows [see Fig. 1(a) and (b)]: In a 1 L three-neck flask equipped with a mechanical stirrer, 50.0 g (0.252 mol) of 3,3'-diaminodiphenylmethane was dissolved in a solution of 72 mL of concentrated sulfuric acid and 380 g of water. To this solution at 5°C was added 34.5 g (0.500 mol) of sodium nitrite dissolved in 100 mL of water over a period of 0.5 h and the resulting solution was then held below 5°C for an additional 1.3 h. After diazotization was complete, an additional 500 mL of cold water was added.

A hydrolyzing solution was prepared by dissolving 200 mL concentrated sulfuric acid and 112 g sodium sulfate in 200 mL of water. The temperature of this solution was raised to 110°C and the diazonium salt solution from above was added dropwise to the hydrolyzing solution over 1.5 h. After complete addition, the mixture was held at 110°C for 0.8 h. After cooling and dividing into two portions, each portion was extracted six times with 50 mL of ether. The tar remaining in the reaction flask was also extracted thrice with 100 mL each of ether. The combined ether extracts were washed with 20 mL of water and dried with anhydrous magnesium sulfate. The ether
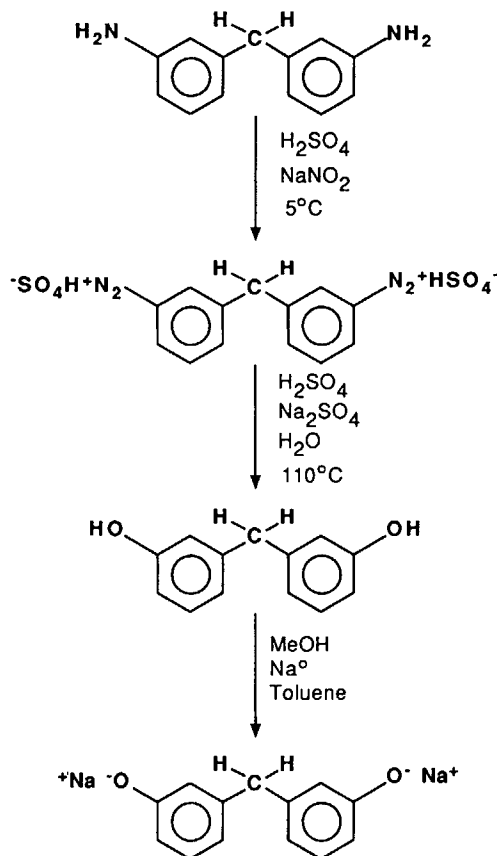
Figure 1 (a) Route for preparing 3,3'-dihydroxydiphenylmethane, disodium salt.

was removed *in vacuo*. The product was distilled through a short column, with bp of 210–275°C (0.5 mm), and then recrystallized from benzene to afford 29.6 g (58.7%) of 3,3'-dihydroxydiphenylmethane, with mp of 94.5–100.5°C.

The 3,3'-dihydroxydiphenylmethane (12.9 g, 0.065 mol) was reacted with a solution of 40 mL anhydrous methanol containing 2.97 g (0.130 mol) of freshly cut sodium metal and 100 mL toluene. The mixture was taken to reflux and cooled before the solvents were removed *in vacuo*. This disodium salt was dissolved in 150 mL anhydrous DMAc before 34.9 g (0.130 mol) of 4-nitro-N-phenylphthalimide was added. The mixture was heated at 60–80°C with stirring for 2 h. The resulting viscous mass, when cooled, was slurried three times with 500 mL water, filtered, and dried. The crude yield was 33.6 g (80.5%) with mp of 200–216°C. Recrystallization from toluene gave N,N'-diphenyl-bis(3,4 dicarboxyphenoxy-3'-phenyl)methane diphthalimide, with mp of 220–224°C.

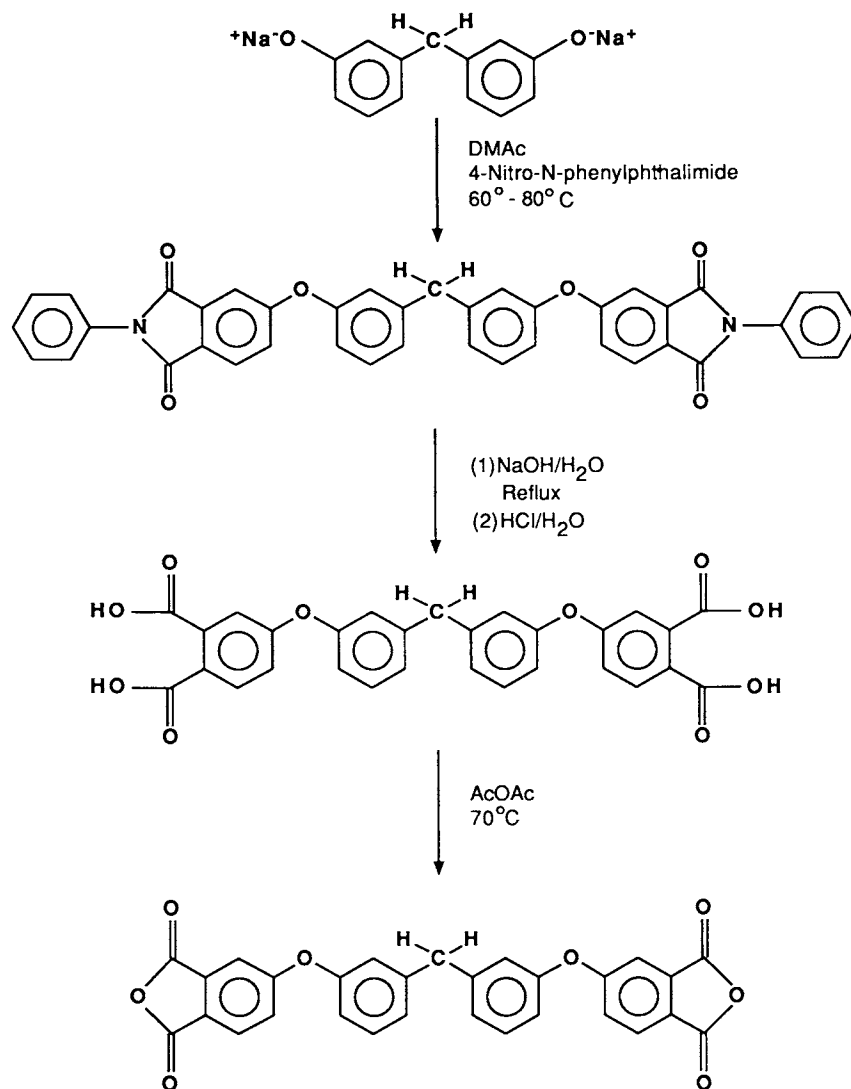The hydrolysis of 25 g of the N,N'-diphenyl-bis(3,4-dicarboxyphenoxy-3'-phenyl)methane di-

Figure 1   (b) Route for preparing PDMDA.

phthalimide was conducted in a solution of 270 g of sodium hydroxide in 2 L of water at reflux for 20 h. Additional water was periodically added to replace that lost as a result of the aniline–water azeotrope. The resulting tetracarboxylic acid salt was acidified by pouring into excess aqueous 6N hydrochloric acid. The resulting tetracarboxylic acid was rinsed with water and vacuum-dried at 110°C. The yield was 17.2 g (84%) and the produce had a mp between 143 and 220°C. This broad melting was, no doubt, due to melting and cyclodehydration occurring simultaneously.

The crude tetracarboxylic acid (17.2 g) from above was slurried in 100 mL acetic anhydride at 70°C for 3.3 h, filtered hot to remove trace insolubles, and cooled at 0°C overnight. The dianhydride precipitated as an off-white fine powder. Vacuum drying

afforded 11.7 g (61%) of PDMDA. DTA analysis gave one sharp endotherm at 147.5°C.

Preparations of Polyamic Acids and Polyimide Films

As shown in Figure 2, polyamic acid resins were prepared at ambient temperature by reacting PDMDA in a stirring solution of DMAc with an equimolar amount of the diamine to total 15% weight solids. The solutions were allowed to stir between 8 and 14 h. Four polyimide films per resin were prepared by casting polyamic acid resins on soda-lime glass plates using a doctor blade with gaps set to ensure final film thicknesses of two $\sim$ 1 mil and two $\sim$ 0.5 mil films (after thermal curing). The amic acid films were air-dried in a low-humidity, dustfree chamber
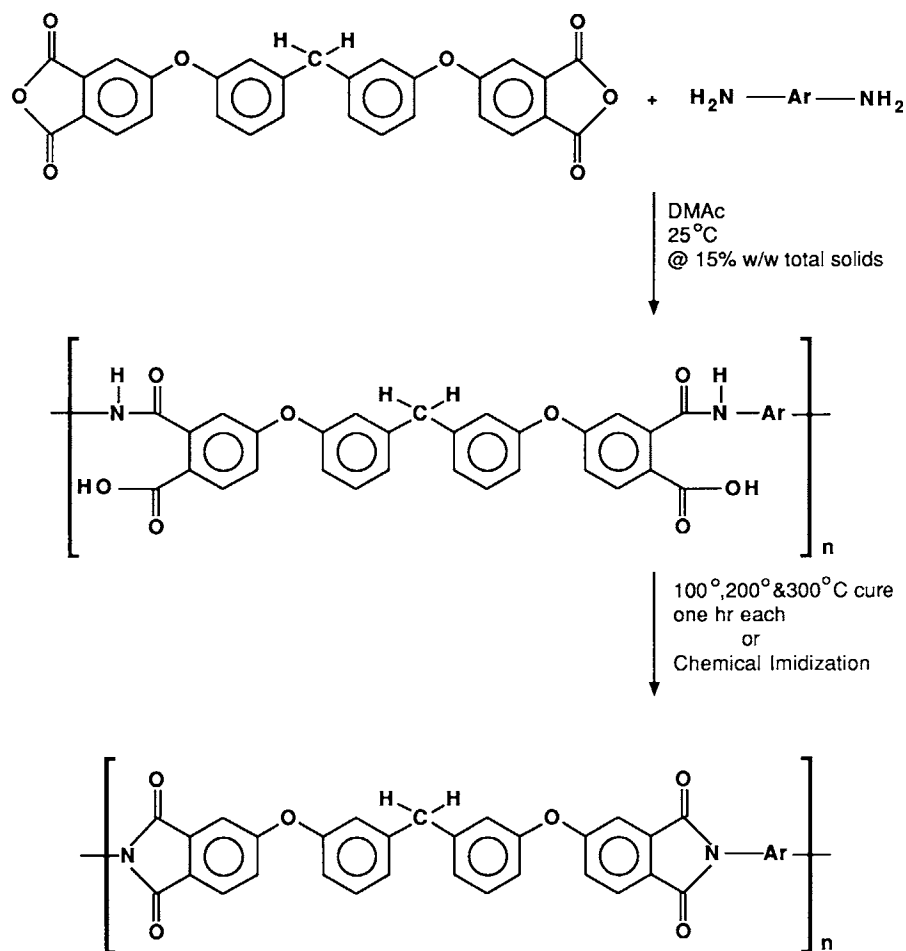
Figure 2   Route for preparing PDMDA-containing polyimides.

for ∼ 7 h. A 1 mil and 0.5 mil pair were thermally imidized in a forced air oven and the other pair thermally imidized in a vacuum oven, 1 h each at 100, 200, and 300°C. Upon cooling to room temperature, films were removed from the glass plates by immersing in water. An alternate means of imidization was carried out chemically by adding the polyamic acid solution to a 50/50 volume solution of stirring pyridine/acetic anhydride, stirring the resulting solution for ∼ 10 min, precipitating the polyimide in water, and vacuum drying at room temperature.

Characterization

The inherent viscosities of the polyamic acid solutions were determined in DMAc at 0.5% (w/v) at 35°C using an Ostwald viscometer. Apparent glass transition temperatures (T_g) of fully cured 1 mil-thick polyimide films were measured by thermo-

mechanical analysis (TMA) on a DuPont 943 analyzer in static air at 5°C/min. Thermal decomposition temperatures were obtained by thermogravimetric analysis (TGA) using a Seiko Instrument SSC 5000 thermal analysis system with an air flow of 50 cc/min and a heating rate of 2.5°C/min after a 15 min hold at 100°C. Dielectric constants of the films were obtained using a Hewlett Packard 8510 Automated Network Analyzer over a frequency range of 8–12 GHz. Transmission UV-visible spectra were obtained on 0.5 mil-thick films using a Perkin-Elmer Lambda 5 UV-VIS spectrophotometer in the reflectance mode with an integrating sphere attachment. Infrared spectra were obtained on the 0.5 mil-thick films using a Perkin-Elmer 1430 ratio recording infrared spectrophotometer. Melting points were determined by differential thermal analysis using a heating rate of 20°C/min on a DuPont Model 910 differential scanning calorimeter with a Thermal Analyst 2000 system.

RESULTS AND DISCUSSION

Synthesis of the PDMDA dianhydride, containing a methylene diphenoxy bridging group, was initiated via a diazonium replacement to first convert methylenedianiline to the corresponding bisphenol. The disodium salt of the bisphenol in DMAc was reacted with 4-nitro-N-phenylphthalimide to produce the bisimide. Refluxing in aqueous sodium hydroxide, aniline was azeotroped (with water) from the bisimide slurry followed by acidification of the resulting solution to form the corresponding tetracarboxylic acid. The cyclic dianhydride was then formed by reacting the tetraacid with acetic anhydride, precipitating and vacuum drying the final product. The formula of the PDMDA dianhydride was confirmed by elemental analysis.[11] The calculated percentages for carbon and hydrogen showed good agreement with the analytical carbon and hydrogen percentages:

   Calcd: ($C_{29}H_{16}O_8$) C, 70.73%; H, 3.28%.
   Found: C, 70.95%; H, 3.28%.

Structures of the diamines used to prepare the polyimides of this study are shown in Table I. The inherent viscosities of the polyamic acids varied between 0.35 and 1.26 dL/g. The polyamic acids containing the *para*-oriented diamines had higher viscosities than did the same polyamic acids that differed only due to the *meta*-oriented diamine. All polymerizations produced imidized films that were tough and flexible, and no cracking occurred when films were creased with the fingernail.

Glass Transitions

Apparent glass transition temperatures (T_g) of the thermally cured films ranged from 155 to 234°C (see Table I). In cases where the polyimide structures differed only by the *meta*-oriented and *para*-oriented amino groups in the diamine, the *meta*-oriented diamine yielded polyimides with a lower T_g value of the two isomers. For each polyimide, the air-cured film had the higher T_g value than did the same vacuum-cured film. The T_g values differed on average ~ 23°C for films cured in air vs. vacuum. Only one polymer contained a methylene bridge in both the dianhydride and diamine. This polyimide system resulted in a difference in T_g values between vacuum and air-cured films that was approximately twice the average T_g difference of the other polyimides. The PDMDA/4,4'-MDA polyimide had a vacuum and air T_g difference of 49°C. Previous work on methylene-containing aromatic polyimides has been

reported wherein the methylene unit was located in the amine portion of the polymer chain.[6] In most cases, T_g's of films cured in air were higher than in an inert (nitrogen) atmosphere due to thermooxidative cross-linking of the methylene bridge.
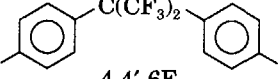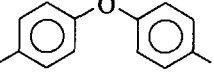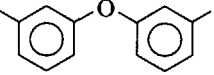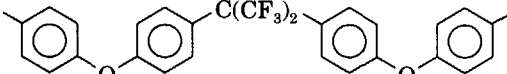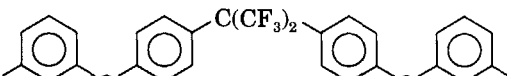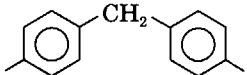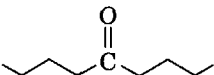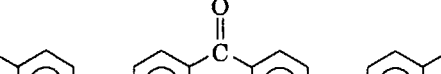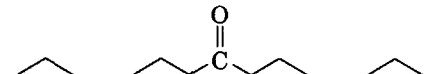
Thermogravimetric Analyses

Also listed in Table I are the thermogravimetric analyses (TGA) of the polyimide films. The 10% weight loss temperatures for TGA ranged between 466 and 504°C. The polymer decomposition temperatures (PDT), which were taken as the intersection of tangents drawn to the zero and maximum weight loss portions of the dynamic TGA curves, ranged from 501 to 525°C. For each *meta*- and *para*-oriented isomer pair, the 10% weight loss temperature was lowest for the polyimide containing the *meta*-oriented diamine. Each vacuum-cured film had the higher 10% weight loss temperature compared with the same air-cured film, except for the 3,3'-DABP-,3,5-DABTF- and 3-BAPBP diamine-containing films. Actual TGA curves of several of the PDMDA polymers are shown in Figure 3 and compared to that of commercial Kapton H film. The representative vacuum-cured films showed varying percentages of weight gain (beginning at ~ 200°C) before any weight loss occurred. This weight gain for vacuum-cured films accounts for their higher 10% weight loss temperature over the air-cured films. Vacuum-cured films showed a weight gain between 0.43 and 1.47%, picking up oxygen and possibly converting to C=O.
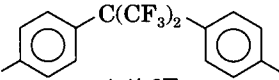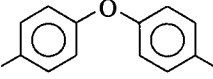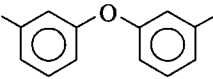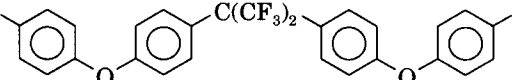
Dielectric Constants
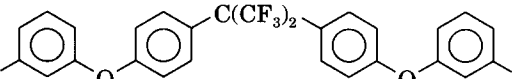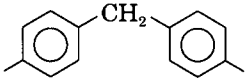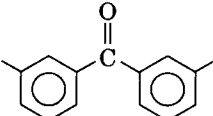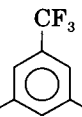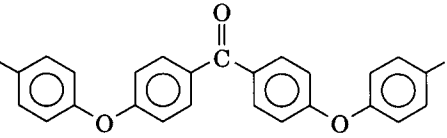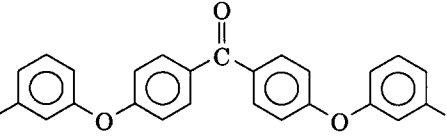
Shown in Table II are the dielectric constants for the PDMDA series, which ranged between 2.66 and 3.11 at 10 GHz. Measurements were made after desiccating films overnight in a drybox. All films possessed lower dielectric constants than did the commercial Kapton H film, measuring 3.2 at 10 GHz. Consistently, the vacuum-cured films had a lower dielectric constant than did the corresponding air-cured films. The four vacuum-cured polyimides that contain the trifluoromethyl groups had the lowest dielectric constants (2.66–2.74) of the PDMDA series. These findings are in agreement with previously reported values for trifluoromethyl-containing polyimides.[1] The PDMDA/4,4'-MDA vacuum-cured film, which contains methylene-bridging groups in both the dianhydride and diamine, had the next to the lowest constant with 2.82. The carbonyl-bridged

Table I Properties of Polyimides Prepared from PDMDA

Polymer Ar	η_{inh} (dL/g)	T_g (°C)	TGA 10% wt loss	PDT
4,4'-6F	0.49	195[a] (219)[b]	501 (486)	522 (512)
4,4'-ODA	0.89	177 (200)	504 (488)	515 (514)
3,3'-ODA	0.58	161 (182)	497 (474)	513 (511)
4-BDAF	1.26	180 (202)	497 (497)	514 (520)
3-BDAF	0.83	155 (180)	494 (485)	513 (514)
4,4'-MDA	0.84	174 (234)	482 (469)	507 (513)
3,3'-DABP	0.72	170 (205)	466 (486)	501 (525)
3,5-DABTF	0.35	182 (212)	476 (485)	512 (509)
4-BAPBP	0.90	179 (199)	483 (468)	508 (504)
3-BAPBP	0.60	160 (184)	477 (479)	504 (506)

[a] Films cured to 300°C in vacuum.
[b] Films cured to 300°C in air.

Table II Properties of Polyimides Prepared from PDMDA

Polymer Ar	Dielectric Constant[a]	Film Appearance[b]	UV cut-off[b] nm
4,4'-6F [C(CF$_3$)$_2$]	2.66[c] (2.76)[d]	Colorless (pale yellow)	362 (362)
4,4'-ODA [O]	2.89 (2.98)	Colorless (pale yellow)	368 (370)
3,3'-ODA [O]	2.85 (2.90)	Colorless (pale yellow)	362 (365)
4-BDAF [C(CF$_3$)$_2$]	2.66 (2.75)	Colorless (pale yellow)	360 (368)
3-BDAF [C(CF$_3$)$_2$]	2.68 (2.77)	Colorless (pale amber)	360 (360)
4,4'-MDA [CH$_2$]	2.82 (3.11)	Pale to colorless (amber)	366 (433)
3,3'-DABP [C=O]	2.96 (3.11)	Pale to colorless (pale amber)	370 (374)
3,5-DABTF [CF$_3$]	2.74 (2.92)	Colorless (pale amber)	365 (370)
4-BAPBP [C=O]	2.97 (3.06)	Pale to colorless (pale amber)	372 (376)
3-BAPBP [C=O]	2.92 (3.03)	Pale to colorless (pale amber)	368 (372)
Commercial Kapton H Film	3.2	Bright yellow	475

[a] At 10 GHz, 1 mil film.
[b] 0.5 mil film.
[c] Films cured to 300°C in vacuum.
[d] Films cured to 300°C in air.
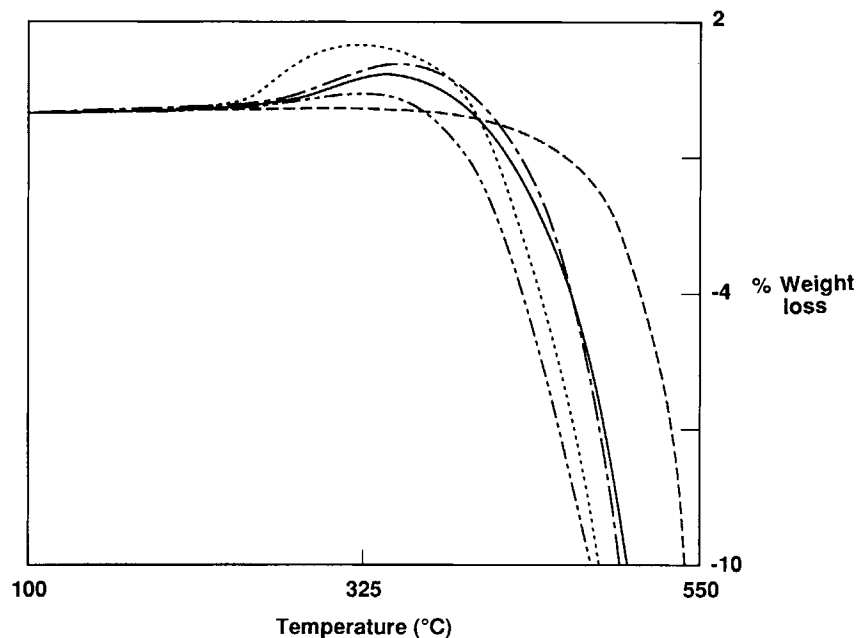
Figure 3 Thermogravimetric analyses of PDMDA vacuum-cured films: (- - -) Kapton
H; (———) PDMDA/4,4'-6F; (— - —) PDMDA/4-BDAF; (----) PDMDA/4,4'-MDA;
(-- — --) PDMDA/3-BAPBP.

films had the highest dielectric values of the vacuum-cured films. There were no major deviations from these data and those obtained on the air-cured films: The PDMDA/4,4'-MDA and PDMDA/3,3'-DABP air-cured films possessed the highest (3.11) dielectric constants. The fact that the dielectric constants of these two air-cured films are so similar supports the theory that CH_2 groups are converting to $C = O$.

Film Appearance

Film color of the PDMDA polymers varied from colorless to transparent amber (see Table II), vacuum-cured films generally being pale to colorless and air-cured films having pale yellow to amber color. Infrared analysis, as shown in Figure 4, shows the formation of a peak at $\sim 1670\ cm^{-1}$ in the spectra
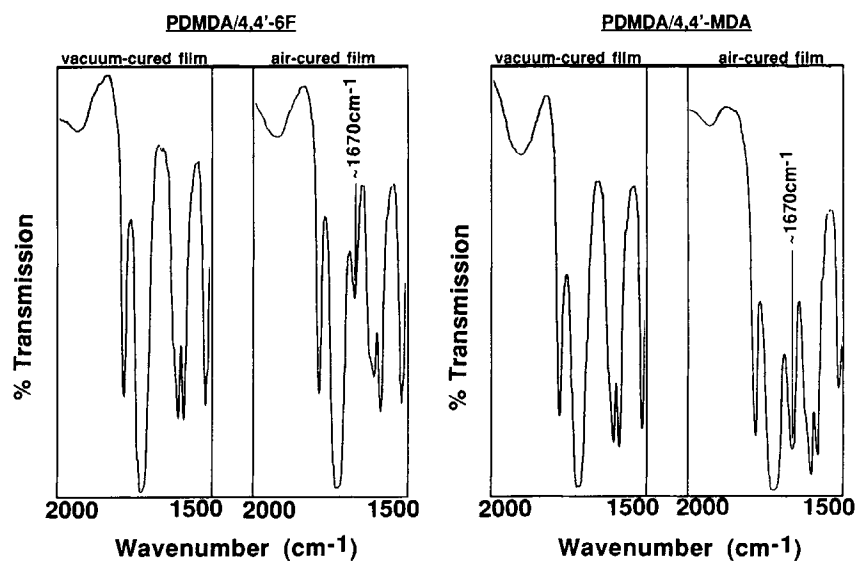
Figure 4 Infrared spectra of methylene-bridge oxidation.

for the PDMDA/4,4'-6F and more prominently for PDMDA/4,4'-MDA air-cured films. The same vacuum-cured films are absent of this spectral peak. The two polyimides shown in Figure 4 are representative of the entire PDMDA series. The thermooxidation of the methylene-bridging groups of the polyimides resulted in some conversion to carbonyl-bridging groups. The PDMDA/4,4'-MDA polyimide contains methylene-bridging groups in both the dianhydride and diamine; therefore, its infrared spectrum shows a stronger carbonyl absorption peak than does the spectrum for PDMDA/4,4'-6F polyimide containing a methylene-bridging group in only the dianhydride portion. The carbonyl $C = O$ chromophore is known to increase color intensity in polyimide films.[4] By comparing two representatives of the polyimides prepared (shown in Fig. 5), one can visualize the color variances regarding the film appearances that ranged from colorless to amber. For each polyimide, the vacuum-cured film is much lighter in color than is its air-cured counterpart. Of the 10 polyimides, the PDMDA/4,4'-6F system is the overall lightest in color and the PDMDA/4,4'-MDA system is the darkest, the other polyimide systems falling between the two overall extremes. Note that the vacuum-cured MDA-containing film is extremely light in color. After thermally curing in air, the color of the PDMDA/4,4'-MDA film greatly increased in intensity. The intensity of this film was greater than those containing $C = O$ links in the diamine. The increase in intensity was due not only to conversion of CH_2 to $C = O$, but to additional thermal cross-linking.

UV-Visible Transmission of Films

The UV-visible cutoff frequencies for the PDMDA series are shown in Table II. UV-visible cutoffs were obtained by drawing a tangent to the spectral curve at a point where the tangent line is most vertical and reading the point where the tangent line intersects the wavelength axis. The lower the cutoff frequency, the more transparent the film is to the transmission of solar energy. Generally, the PDMDA polyimides had UV-visible cutoff frequencies that were lower than the cutoff frequency for commercial Kapton H film. Displayed in Figures 6 and 7 are the UV-visible spectra for four representative polyimides. The UV-visible spectra of vacuum-cured films are displayed in Figure 6. PDMDA/4,4'-6F film was the most transparent while the PDMDA/4-BAPBP film was the least transparent of the vacuum-cured PDMDA series. Compared to
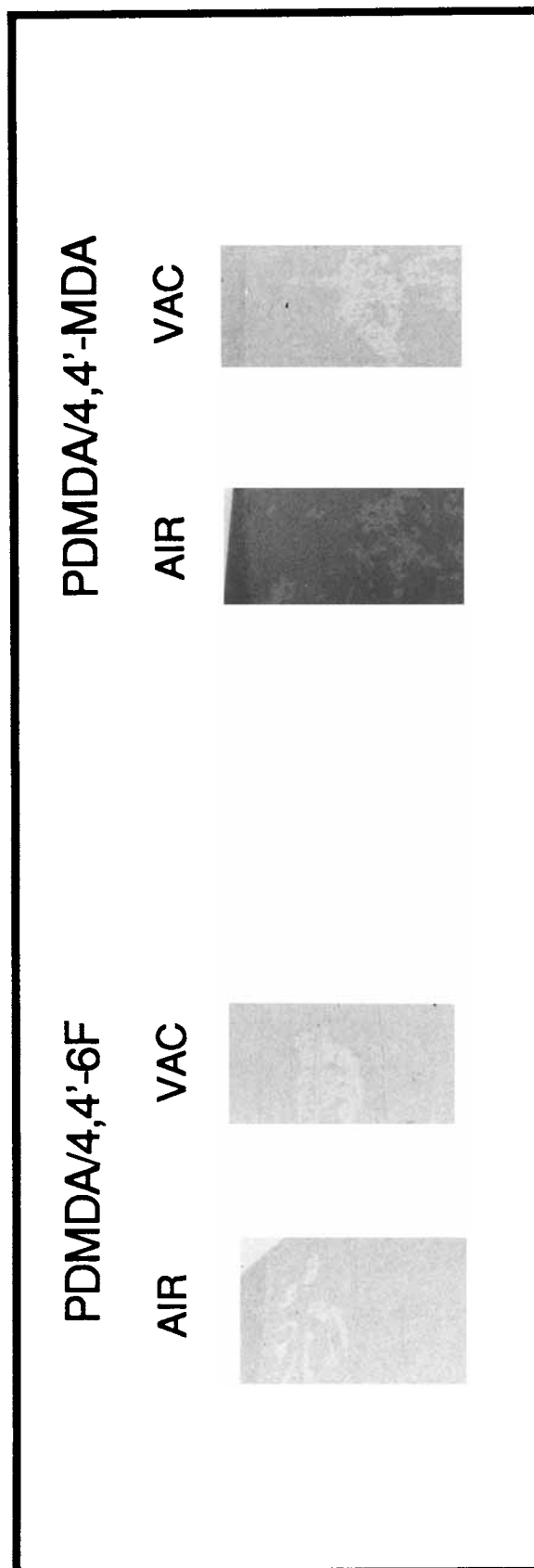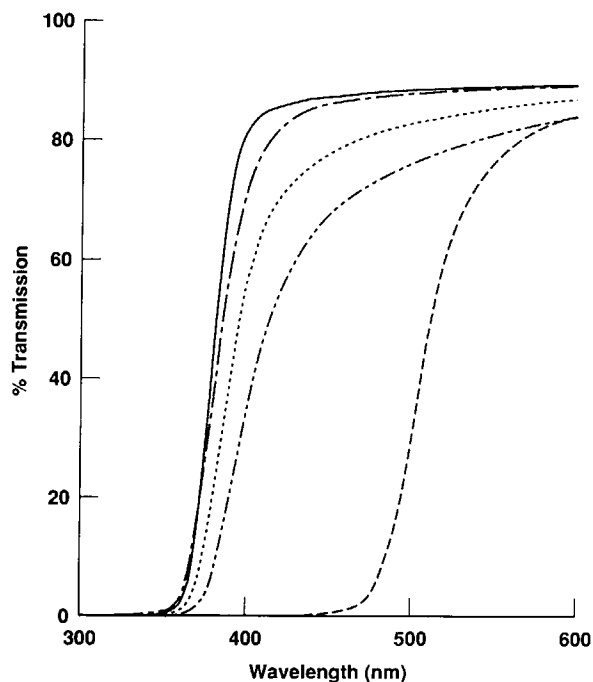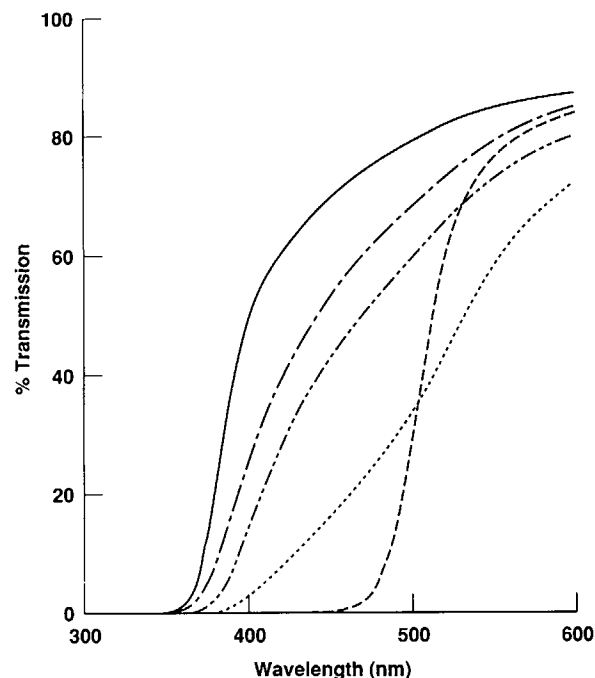

Figure 5   Air vs. vacuum-cured PDMDA films.

Kapton H film, however, they were exceedingly more transparent. The transmission spectrum of each vacuum-cured film of the PDMDA series fell between the spectra for the 6F containing film and the 4-BAPBP containing film. At the 500 nm wavelength, which is the peak intensity for solar radiation, the 4,4'-6F-, 4-BDAF-, 4,4'-MDA-, and 4-BAPBP-containing films were, respectively, 88, 88, 83, and 78% transparent. Kapton was approximately 35% transparent. After thermally curing the PDMDA series in air, the percent transmission at 500 nm dropped considerably for several films. The UV-visible spectra of four representative air-cured films are shown in Figure 7. The PDMDA/4,4'-6F film was again the most transparent but the air-cured PDMDA/4,4'-MDA was now the least transparent, owing its greatly reduced transparency to thermooxidative cross-linking in both dianhydride and diamine portions of the polyimide as referred to earlier in the section on film appearance. The reduced transparency of the air-cured films appears to be only a color effect in the visible region because there was very little effect on the UV cutoffs when compared with the cutoffs for the vacuum-cured films, the major exception being the PDMDA/4,4'-MDA polyimide with an air and vacuum difference

Figure 7 UV-visible spectra of air-cured films: (‒ ‒ ‒) Kapton H; (———) PDMDA/4,4'-6F; (— - —) PDMDA/4-BDAF; (- - - -) PDMDA/4,4'-MDA; (-- — --) PDMDA/4-BAPBP.

of 67 nm compared to an average of ~ 4 nm for the other PDMDA polyimides.

Film Solubility

The vacuum-cured polyimides containing the trifluoromethyl groups were expected to be soluble.[6] However, all thermally cured (air or vacuum) films were insoluble at ambient temperature in DMAc, N,N-dimethylformamide, and chloroform. This phenomenon is possibly attributed to a higher degree of thermal cross-linking introduced by the PDMDA portion of the polyimide. Solubility, however, was obtained for the PDMDA/4-BDAF system that was chemically imidized. The imide powder could be redissolved in DMAc or chloroform and cast as a transparent film.

The ability to render the PDMDA polymer soluble via chemical imidization allows it to be easily processed, spray-coated, etc. Upon thermal treatment, the polymer then becomes insoluble, which is an added benefit for many applications where an insoluble film or coating is desired as a final end product. For example, a soluble polyimide is desirable in the making of high-performance aircraft composites where the polymer can be applied to the

Figure 6 UV-visible spectra of vacuum-cured films: (‒ ‒ ‒) Kapton H; (———) PDMDA/4,4'-6F; (— - —) PDMDA/4-BDAF; (- - - - -) PDMDA/4,4'-MDA; (-- — --) PDMDA/4-BAPBP.

fiber in a low boiling solvent yet yield upon thermal treatment an insoluble composite resistant to harsh chemicals such as hydraulic fluids.

CONCLUSIONS

A novel methylene-bridged dianhydride, 3,3'-bis - (3,4 - dicarboxyphenoxy)diphenylmethane (PDMDA), was synthesized and therefrom were prepared 10 high molecular weight polyimides. For each PDMDA polyimide, the air-cured film had a higher T_g value than did the same vacuum-cured film. The vacuum-cured films showed a weight gain by TGA starting at $\sim 200°C$ before any weight loss occurred. All films had lower dielectric constants than did commercial Kapton H film. Air-cured films had slightly higher dielectric constants and lower optical transparency than did vacuum-cured films due to oxidative cross-linking. Film color ranged from pale to colorless for vacuum-cured films and from pale yellow to amber for air-cured films. Infrared spectra of the PDMDA-containing polyimides showed carbonyl formation in the air-cured films as a result of thermooxidation of the CH_2 groups in the PDMDA dianhydride. The increased color of air-cured films was an effect of the carbonyl formation. All PDMDA polyimides had UV-visible cutoff frequencies that were lower than the cutoff frequency for commercial Kapton H film. At 500 nm, all vacuum-cured films were more transparent than was the commercial film. After thermally curing in air, the transparency at 500 nm of the PDMDA films declined. All thermally imidized films were insoluble at ambient temperature in DMAc, N,N-dimethylformamide, and chloroform. Chemical nimidization of PDMDA/4-BDAF yielded a polyimide powder that was soluble in DMAc or chloroform, therefore making it more processable for composite fabrication. Upon thermal treatment, however, this polymer can be rendered insoluble for enhanced chemical resistance. The overall performance of the PDMDA-containing polyimides is quite interesting and their lowered dielectric con-

stants, optical transparency, and solubility characteristics should render these new polyimides useful in electronic and aerospace applications.

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