

New Photoimageable Dielectric Insulating Copolyester Thin Films: Synthesis and Characterization

FRANK F. SHI, LIZABETH A. SCHNEGGENBURGER, JAMES ECONOMY

Department of Materials Science and Engineering, 1304 West Green St., University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Received 9 August 1996; accepted 5 September 1996

ABSTRACT: In this article, we describe the synthesis and characterization of a new family of photoimageable dielectric insulating polymer films. Four different photoimageable thin films have been prepared from all-aromatic and aromatic/aliphatic copolyesters, which exhibit good photospeed (10–180 s, 15.5 mW/cm² intensity), resolution and line width (10 μ m), thermal stability (330–400°C), adhesion on different substrates, mechanical strength, and reasonable glass transition temperature (120–150°C). One feature of the new photoimageable copolyester is the formation of a low dielectric constant film (2.5 at 1 kHz, 25°C) upon curing at temperatures up to 280°C. The low dielectric constant is a result of foaming arising from evolution of by-products during curing. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1199–1211, 1997

Key words: polyester; photoimageable dielectric; photoresist; microelectronics; multichip module

INTRODUCTION

The drive toward an ever increasing number of functions per chip is expected to continue over the next decade. Progress in very large scale integrated (VLSI) circuit technology has produced significant changes in system design, interconnection, and assembly of electronic equipment. Chips with I/O counts approaching 500 are creating problems at chip periphery and for individual chip packages.¹ The problems with high I/O packages are cascading from the chip to the package and onto the next level of interconnection, the printed circuit board (PCB). One solution to these problems is to focus on an intermediate substrate, such as the Multichip Module Laminate (MCM-L), for bare chip mounting, which reduces the wiring density on the PCB level.²

Correspondence to: J. Economy.

Contract grant sponsors: Morton International, Inc.; Federation of Advanced Materials for Industry (FAMI) at the University of Illinois at Urbana-Champaign. U.S. Department of Energy grant number: DEFG02-ER45439.

Design of an MCM-L holds considerable challenge due to the need for greatly improved materials and simplified fabrication. Polymers used in MCM-L packaging should exhibit a low dielectric constant at high frequency (<3.0 at 1 MHz), low moisture adsorption (<0.5%), good thermal stability (>300°C), a high glass transition temperature (>120°C), a coefficient of thermal expansion (CTE) match with the silicon chip, good chemical resistance, good adhesion to the metal circuitry and to itself, and potential for parallel processing.^{1,3} Polyimides display the necessary high temperature stability and good mechanical properties; however, their drawbacks include high water adsorption (2.0%), relatively high dielectric constant (3.1–5.0 at 1 MHz), poor adhesion to most substrates, and high cost.³ Epoxy-based materials are more economical; but due to their high moisture adsorption (~2%), high dielectric constant (4.5–5.5 at 1 MHz), and limited thermal stability, they may not have the extendibility for use in future packages.¹

Recently, we have been actively developing a

new family of aromatic and aromatic/aliphatic copolyester thermosets.^{4–7} We have already shown that the cured all-aromatic resins provide low moisture adsorption (0.3 wt %), high thermal stability, and good adhesion to various substrates.^{6–9} Moreover, the resin can be recycled (depolymerized) back to the oligomer, which can then be cured again.⁶ Another important feature of this new resin is the ability to prepare foams that are stable at very high temperatures (300–400°C). This represents a significant advance in the field of MCM-L technology since we can control the dielectric constant over a wide range of values by controlling the foaming.^{10,11} For example, a dense film of the all-aromatic copolyester has a dielectric constant of 4.7 (1 MHz, 25°C), while the same film when foamed to 70% of the original density has a dielectric constant of 2.5 (1 MHz, 25°C).¹⁰ The ability to adhere multiple layers of these copolyesters in the solid state under heat and pressure (280°C, 10 GPa) is also very important for parallel processing of the MCM-L. This unique feature arises from rapid interchain transesterification reactions (ITR), which occur across the interface forming strong adhesive bonds.^{4–11}

In light of the above indicated advantages, we recently undertook to modify the all-aromatic copolyester to make it photoimageable to reduce the number of processing steps by one-half (see Fig. 1). Our approach used the method reported by Siemens in Rubner et al.¹² for photosensitizing polyamic acid, namely, to functionalize the carboxylic acid with glycol methacrylate.

In this paper, the synthesis and the characterization of the new aromatic and aromatic/aliphatic photoimageable copolyesters are described. Results on use as a photoimageable dielectric insulator in MCM-L are presented.

EXPERIMENTAL

Materials

Novolac oligomer (GP-2037) with a number-average molecular weight of 844 g/mol was provided by Georgia Pacific Resins, Inc. All other commercially available chemicals were obtained from Aldrich Chemical Co. and used as-received, including acetic anhydride, trimesic acid (TMA, mp > 300°C), 4-acetoxy benzoic acid (ABA, mp 192°C), hydroquinone diacetate (HQDA, mp 122°C), terephthaloyl chloride (mp 80°C), 1,4-bu-

tanediol (mp 16°C), glycerol (mp 20°C), pentaerythritol (mp 255°C), thionyl chloride (SOCl₂), 2-hydroxyethyl methacrylate, hexamethyldisilazane (HMDS), Michler's ketone, and all solvents, such as tetrahydrofuran (THF), pyridine, dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and acetone. The liquid crystalline polymers (LCPs) were provided by Amoco Chemical Corp. (Xydar) and Hoechst-Celanese Co. (Vectra). The Xydar and Vectra films were prepared by Superex Polymer, Inc.

Synthesis

The syntheses of the four photosensitive oligomers detailed below are shown in Figure 2.

Synthesis of All-aromatic Photoimageable Oligomer 1

The precursor used is an all-aromatic copolyester oligomer with carboxylic acid end groups. The synthesis of this all-aromatic copolyester oligomer has been reported previously.^{4,5} The molecular weight of the aromatic oligomer was adjusted to ~800–850 g/mol to make it soluble in certain solvents. All glassware was oven dried overnight at 110°C. About 6 g of the oligomer was dissolved in 100 mL THF and reacted with 15 mL SOCl₂ by refluxing the reaction mixture at 90°C over 8 h. The residual SOCl₂ and THF were then vacuum-evaporated with a rotavapor to produce a polyester oligomer having acyl chloride end groups, which was then dissolved in 100 mL THF with 12 mL (0.09 mol) 2-hydroxyethyl methacrylate. The solution was magnetically stirred at 60°C for 6 h. At each step, moisture was excluded from the reaction vessel. Once the reaction was completed, the solution was poured into 20 volumes of rapidly stirred distilled water. The solid polymer product was collected by vacuum filtration and dried overnight under vacuum at 50°C. The all-aromatic photoimageable oligomer 1 was light yellow, and the yield was around 55%.

Synthesis of Linear Aliphatic/Aromatic Photoimageable Oligomer 2

In a reaction flask equipped with a reflux condenser, 12.2 g (0.06 mol) terephthaloyl chloride and 3.6 g (3.54 mL, 0.04 mol) 1,4-butanediol were dissolved in 100 mL THF. The mixture was allowed to reflux at 90°C for about 6 h and was cooled thereafter to ~60°C. To this intermediate

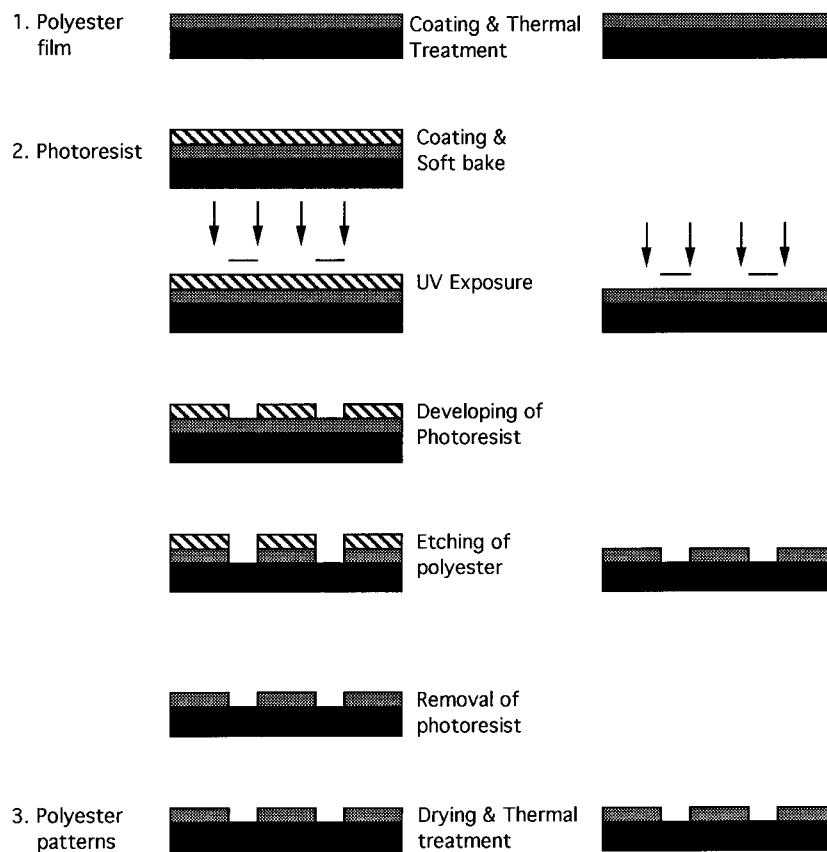


Figure 1 Comparison of the processing steps of the nonphotoimageable and photoimageable dielectric insulating polymer films.

product, 5.2 mL (0.04 mol) of 2-hydroxyethyl methacrylate was added and allowed to react for approximately 6 h. The product was precipitated with distilled water, then vacuum-filtered and rinsed with distilled water, and dried overnight in vacuum at 50°C, giving about 10 g white photoimageable oligomer 2.

Synthesis of Branched Aliphatic/Aromatic Photoimageable Oligomer 3

In a reaction flask equipped with a reflux condenser, 12.2 g (0.06 mol) terephthaloyl chloride and 1.84 g (1.5 mL, 0.02 mol) glycerol were added with 100 mL THF. The mixture was allowed to reflux at 90°C. After 6 hours, the vessel was cooled to ~60°C. To this mediate product, 12 mL (0.09 mol) of 2-hydroxyethyl methacrylate was added and allowed to react for approximately 6 h. The product was precipitated with distilled water, then vacuum-filtered and rinsed with distilled wa-

ter, and dried overnight in vacuum at 50°C, giving about 11 g white photoimageable oligomer 3.

Synthesis of Branched Aliphatic/Aromatic Photoimageable Oligomer 4

12.2 g (0.06 mol) terephthaloyl chloride and 2.04 g (0.015 mol) pentaerythritol were added with 100 mL THF into the apparatus described above, refluxing at 90°C for approximately 6 h and cooled thereafter to ~60°C. To this reaction product, 12 mL (0.09 mol) of 2-hydroxyethyl methacrylate was added and allowed to react for approximately 6 h. The product was precipitated with distilled water, then vacuum-filtered and rinsed with distilled water, and dried overnight in vacuum at 50°C, giving about 10 g white photoimageable oligomer 4.

The chemical structure of the novolac acetate and an all-aromatic oligomer with acetoxy end groups are shown in Figure 3. The synthesis of novolac acetate and all-aromatic acetate, used as

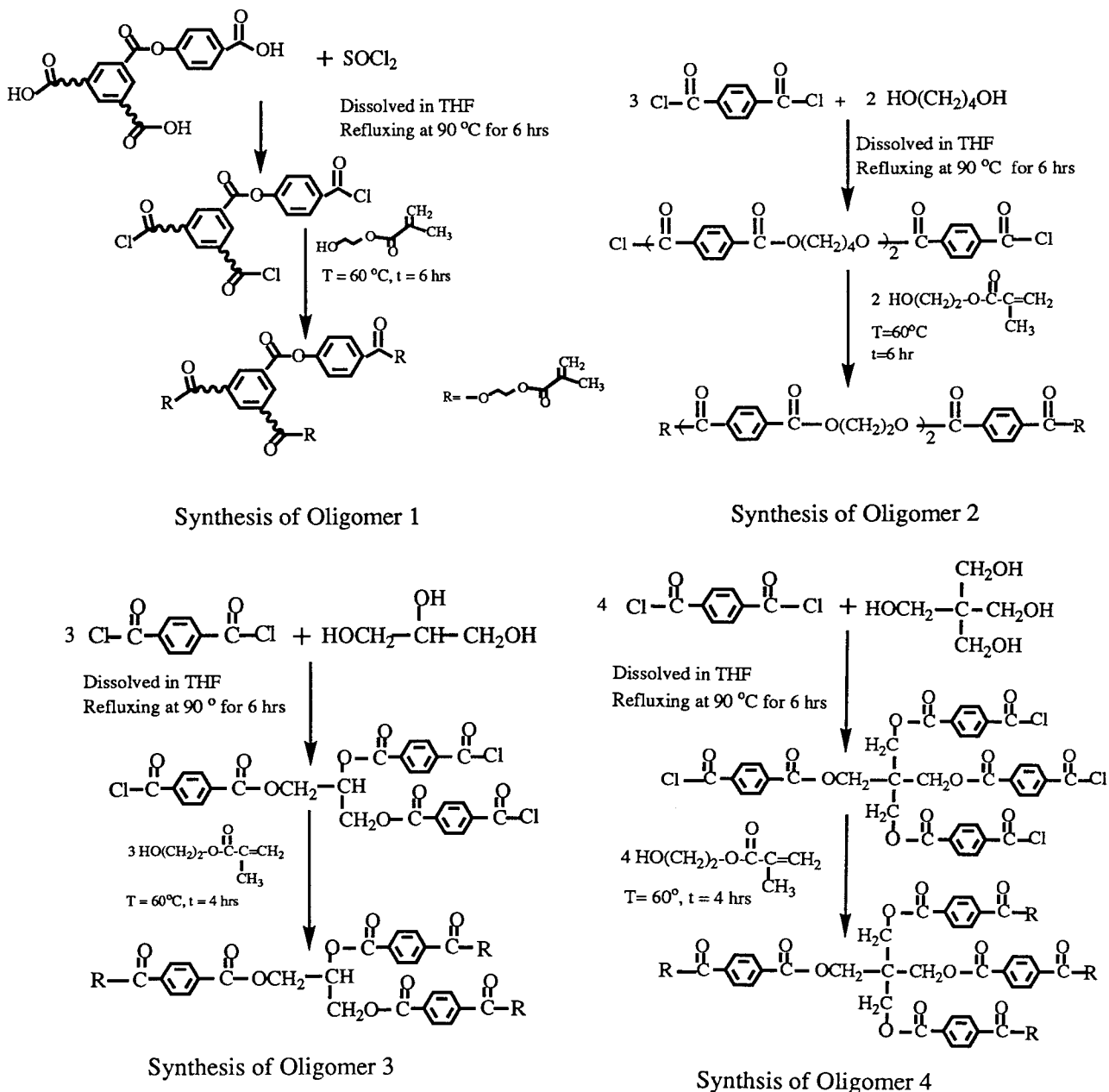


Figure 2 Synthesis of photoimageable copolyester oligomers 1, 2, 3, and 4.

the curing agent in this study, has been reported elsewhere.^{6,7}

Sample Characterization

The sample purity, i.e., the concentrations of metal ions and halides in the oligomers, was determined by an inductively coupled plasma-optical emission spectrometer made by Perkin-Elmer. The ultraviolet (UV) sensitivities of the oligomers were studied using a Cary 2200 UV-Visible Spec-

trophotometer. Thermal analysis was done using TA Instruments DSC 2910 and TGA 2950 ramped at 1°C/min in nitrogen unless otherwise specified. Scanning electron microscopy (SEM) studies were carried out on a Zeiss DSM 960 and a Hitachi S-800 Scanning Microscope. Prior to viewing the photoimaged patterns, the specimens were covered with a thin gold-palladium layer in a Polaron sputtering chamber. Dielectric relaxation experiments were performed on a Hewlett Packard 4284A multifrequency LCR meter. A delta design

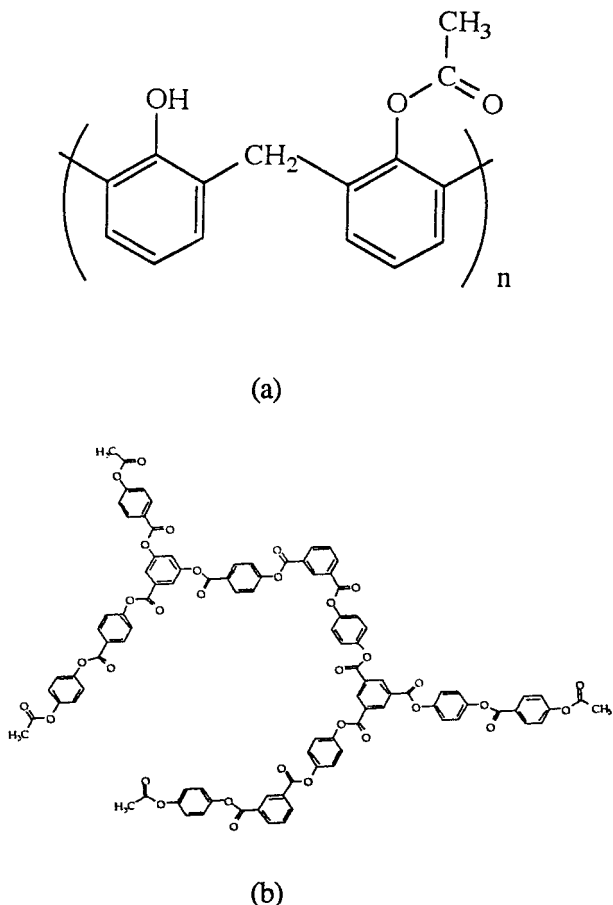


Figure 3 Chemical structure of (a) novolac acetate and (b) all-aromatic acetate.

9023 Hewlett Packard 362 computer system was used to control the heating rate and frequencies at which the data were taken. The films were sputter-coated with 2 mm diameter gold electrodes and placed between polished rigid electrodes.

Film Preparation

The spinner used for spin coating was a Headway Model EC101 photoresist spinner. The solutions containing photoimageable oligomers were spin-coated in air or in a solvent vapor-saturated atmosphere. The films were softbaked at 90°C for 5–10 min before exposure. The film thicknesses were measured by a DEKTAK 3030 Auto Surface Profilometer.

Photolithography and Curing Processing

Photoimaging was carried out using contact exposure on a Karl Suss MJB3 Mask Aligner with

a 270 Watt ultrahigh-pressure mercury vapor lamp in a clean room at $25 \pm 1^\circ\text{C}$, a relative air humidity of $48\% \pm 5\%$, and yellow light to exclude light with a wavelength of $<500\text{ nm}$. Intensity on the exposed surface was 15.5 mW/cm^2 at a wavelength of 365 nm. Developing the photo patterns was achieved by both a dip and spray developing system with acetone as a developer.

The photolithographic processing of these systems is given in Figure 4. The sample compositions and coating conditions are shown in Table I. The photoimaging and developing conditions for different samples are given in Table II.

RESULTS AND DISCUSSION

The synthetic strategy that was used depended on converting the carboxylic acid terminated oligomer to the ethylene glycol methacrylate unit. The acetoxy-terminated oligomer was blended with the ethylene glycol–methacrylate terminated oligomer and acted as an inert diluent. The expectation was that the differential solubility of the regions exposed to UV light versus the regions unexposed would be sufficient to permit develop-

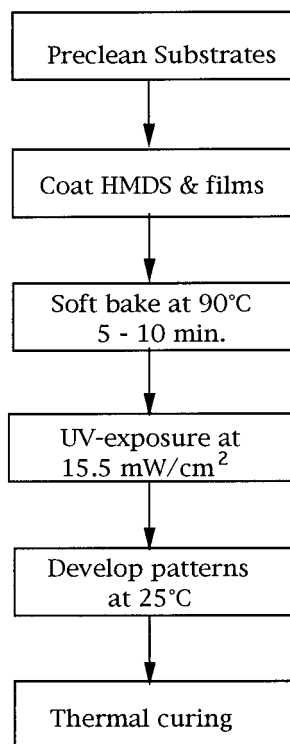


Figure 4 Photolithographic processing flow chart.

Table I Sample Compositions and Spin Coating Conditions

| Sample A + B | Concentration (wt % in THF) | PI ^a (wt %) | Spin Rate (RPM × 10 ³) | Spin Time (s) |
|---|--------------------------------|---------------------------|---------------------------------------|------------------|
| 1. Oligomer 1 + aromatic acetate ⁶ | 25 | 1 | 0.5 ~ 4 | 20 |
| 2. Oligomer 2 + novolac acetate ⁷ | 20 | 1 | 0.5 ~ 4 | 20 |
| 3. Oligomer 3 + novolac acetate ⁷ | 30 | 1 | 0.5 ~ 4 | 20 |
| 4. Oligomer 4 + novolac acetate ⁷ | 35 or 5 | 1 | 0.5 ~ 5 | 20 |

^a P.I., photoinitiator (i.e. Michler's ketone).

ment of good line definition. Another aspect of this strategy required that upon heating of the developed dielectric film, the photocrosslinked bonds would break down at temperatures below 220°C to form the carboxylic acid end groups. Presumably then, the carboxylic acid would then react with the acetate-terminated oligomer at temperatures of 240–280°C to crosslink the structure and generate the desired foam through evolution of reaction by-products. This process of photocrosslinking, followed by thermal degradation of the photocrosslinked bonds to carboxylic acid end groups, and then final curing, is described schematically in Figure 5 using the all-aromatic structure.

The four different photoimageable polyester precursors, which are light yellow or white powders, are stable for months if stored in the dark at room temperature. They can be dissolved in many commonly used solvents for photoresist, such as DMF, THF, pyridine, and NMP, and can be handled using the usual methods of photoresist technology. Their sensitivities can be improved by adding common photoinitiators, such as Michler's ketone. The ready-to-use solutions retain viscosity stability for at least three weeks at room tem-

perature, and the stability time can be increased with increasing dilution or at lower temperature (e.g., a month when refrigerated).

The concentrations of alkali metal ions and other ionic impurities in the photoimageable precursor solutions were measured. Table III gives the concentrations of some typical ionic impurities, and these are within desired values.¹³

Photolithography and Thermal Curing

UV Sensitivity

The UV absorption spectra of the photoimageable oligomers are shown in Figure 6. Note that the oligomers have a strong adsorption centered at approximately 330–340 nm and are almost transparent above 410 nm. Across the absorption band, the quantum efficiency of decomposition of the photoinitiator is approximately constant.¹⁴ The number of molecules converted per unit time at constant flux varies with absorbance; therefore, the materials based on the mixture of photoimageable polyester oligomers and Michler's ketone will be lithographically sensitive to the 365 nm mercury emission line but insensitive to the 410 to 436 nm emission lines.

Table II Photopatterning and Developing Conditions

| Sample | Thickness Before Development (μm) | Exposure Time (s) | | Development Time (s) |
|--------|---|-------------------------|---------|----------------------|
| | | Without PI ^a | With PI | |
| 1 | 2–8 | 200–240 | 150–180 | 30–90 |
| | 8–10 | 240–300 | 180–200 | 90–150 |
| 2 | 2–8 | 120–150 | 45–60 | 30–90 |
| | 8–12 | 150–180 | 60–90 | 90–120 |
| 3 | 3–8 | 90–120 | 25–15 | 30–90 |
| | 8–15 | 120–150 | 25–35 | 90–120 |
| 4 | 3–8 | 90–120 | ~ 10 | 30–90 |
| | 8–15 | 120–150 | 15–25 | 90–120 |

^a PI, photoinitiator (i.e. Michler's ketone).

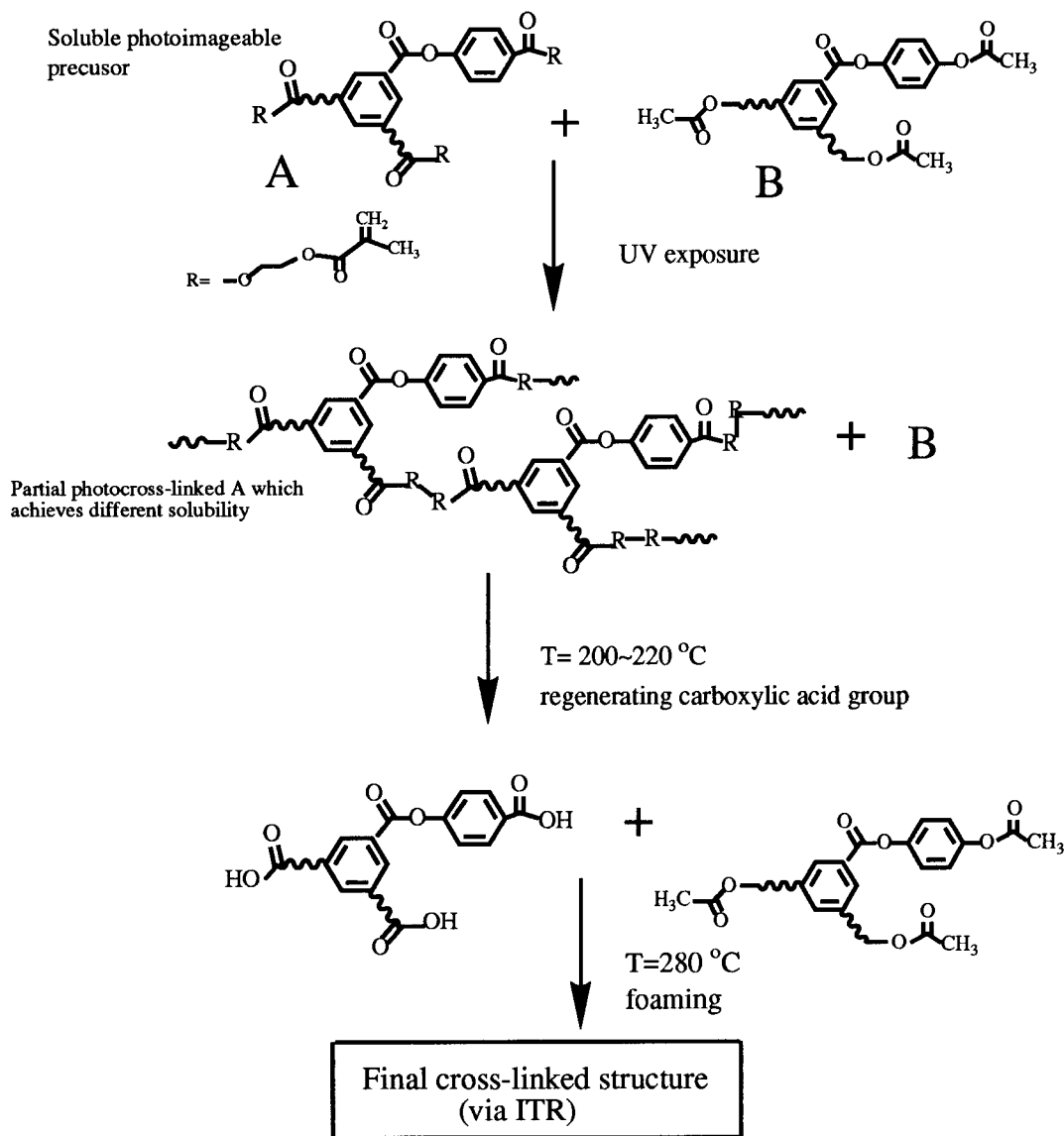


Figure 5 Photochemical and thermal curing reactions of all-aromatic chemistry 1.

Film Preparation

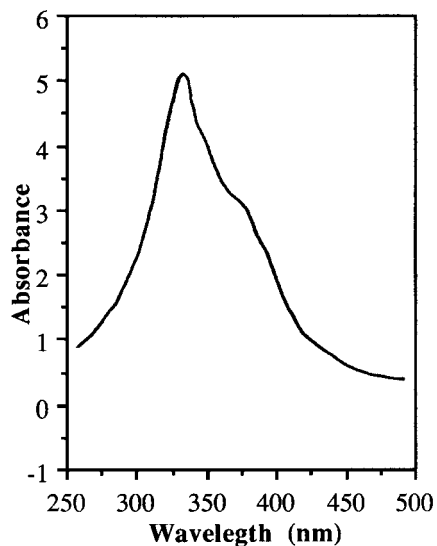
The photosensitive oligomers can be deposited on substrates, such as Si, SiO₂, and LCP films, by both spin and dip coating. The most common problem in the spin coating process has been the ap-

Table III The Concentrations of Ionic Impurities in Photosensitive Polyester Precursors

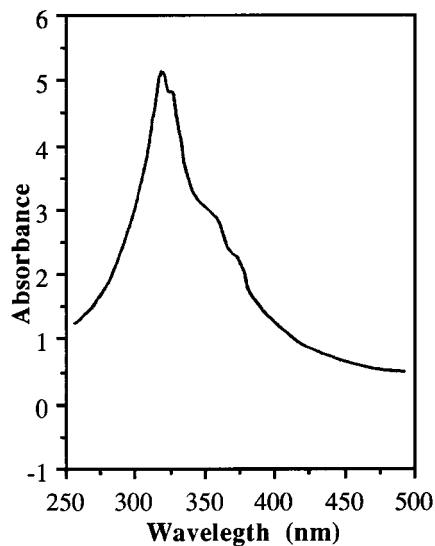
| | |
|----------------------------|----------------------------|
| Na ⁺ < 0.7 ppm | K ⁺ < 0.5 ppm |
| Ca ²⁺ < 0.5 PPM | Mg ²⁺ < 0.5 PPM |
| Fe ²⁺ < 3.0 PPM | Zn ²⁺ < 1.0 ppm |
| Cl ⁻ < 8.0 ppm | |

pearance of orange peel due to rapid drying of the low boiling point solvents during spin coating.¹⁵ This problem was solved by spin coating under a solvent vapor-saturated atmosphere or reducing the spin time. When the evaporation rate was retarded by drying the film under solvent vapor atmosphere, orange peel formation could be successfully prevented. An even easier way to prevent orange peel was to reduce the spin time to 20 s, which is the approximate time required to spin off the bulk of the polymer solution.¹⁵

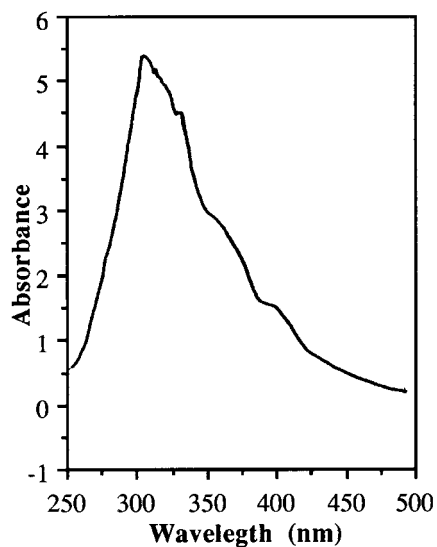
Homogeneous films of the order of 20 μm can be made using spin coating. Figure 7 shows the correlation between the spin rate and the resulting layer thickness for samples 1 and 4. It was found



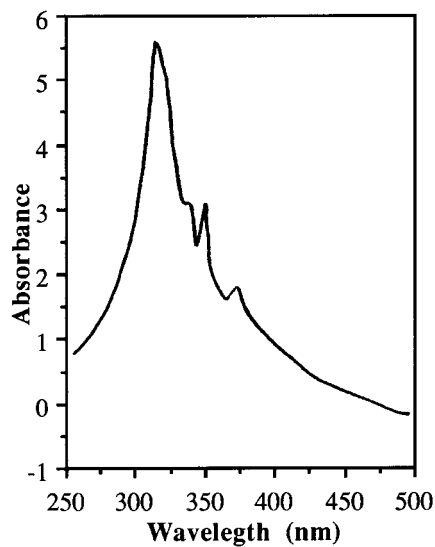
UV-absorption of Oligomer 1



UV-absorption of Oligomer 2



UV-absorption of Oligomer 3



UV-absorption of Oligomer 4

Figure 6 UV absorption spectra of the photoimageable copolyester oligomers 1, 2, 3, and 4.

that the film thickness can be approximated by the relationship $L = KC^{2.1}/W^{0.5}$, where L is film thickness, K is a constant, C is volume fraction of photo oligomers, and W is rotation speed. This is in agreement with the results reported by Lai¹⁵ and comparable to the theoretical models given by Washo¹⁶ and Meyerhofer.¹⁷ It was also observed that thicker films ($>50 \mu\text{m}$) can be prepared by multiple-step

spin coating processing, i.e. spin coating a layer of film and soft baking, and then spin coating a second layer on the previous coated film. Thinner film thickness can be achieved with increasing speed or time or decreasing solution concentration. Extremely thin films ($<1 \mu\text{m}$) were produced from solutions with a concentration of 5 wt % and a spin rate of $> 5 \times 10^3$ RPM.

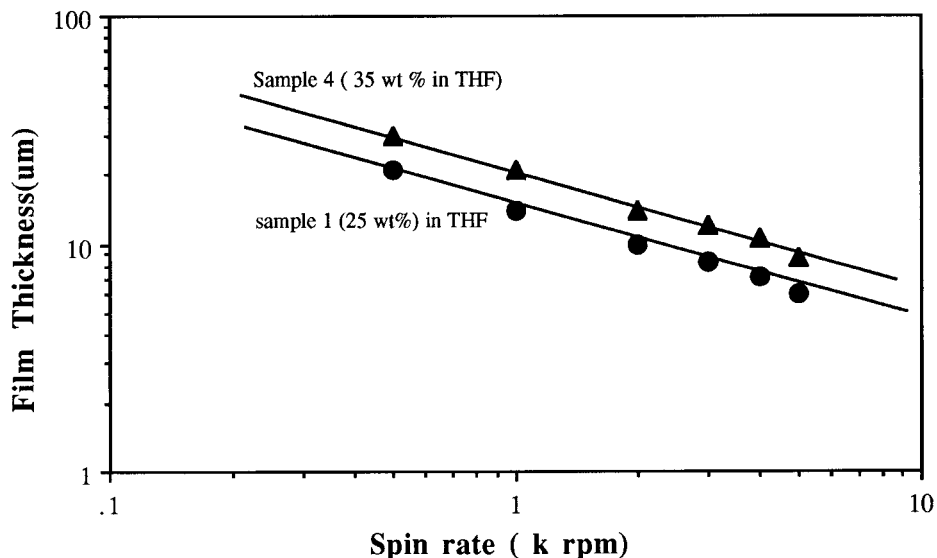


Figure 7 The correlation between the spin rate and the resulting film thickness of the aromatic chemistry 1 and aromatic/aliphatic chemistry 4.

Photoimaging

After film coating and soft baking, the dry films were ready for UV exposure. The UV exposure times depend on the film thickness and the required imaging accuracy. From Table II, it can be seen that the exposure time increases with increasing film thickness and can be dramatically reduced if standard photoinitiators, such as Michler's ketone, are employed. One interesting aspect here is that the four different oligomers display different photosensitivities. For an 8 μm thick film, the exposure time for each sample is 3 min, 1 min, 15 s, and 10 s, respectively. Samples 3 and 4 exhibit very good photospeeds due to the fact that both of these systems have multiple photo-sensitive functional groups. The photospeeds given by these two systems are comparable to the current commercial negative and positive photoresists¹⁴ and even higher than the epoxy based photoimageable materials reported by Knudsen et al.¹ and the photosensitive polyimides reported by Rubner et al.¹²

Developing the exposed films may be achieved with either spray developing or immersion developing using acetone. The development times required are between 30 to 150 s, depending on the film thickness (see Table II). Sharply contoured patterns can be obtained. These materials offer an advantage over the high molecular weight acrylonitrile/butadiene photosensitive polymers and classic epoxidized-butadiene photosensitive

polymers since these two require more aggressive developers and give poor development properties.¹

The resolution of a patterned film is based on the thickness of the film. Figure 8 displays a photoimage of an 8 μm thick all-aromatic copolyester film (sample 1). In Figure 9, our test photomask can be compared with the resulting photopatterns of 5 μm thick aliphatic/aromatic photoimageable films from sample 4. Figure 9 shows a resolution of 20 μm . From the SEM micrographs, one can find that through normal exposure conditions, good images can be obtained. Sample 4 offers the best resolution because it has the highest concentration of photosensitive groups.

Thermal Curing to Crosslinked Copolyester

The patterned films of the photocrosslinked oligomers can be heated up to 180–220°C, which de-

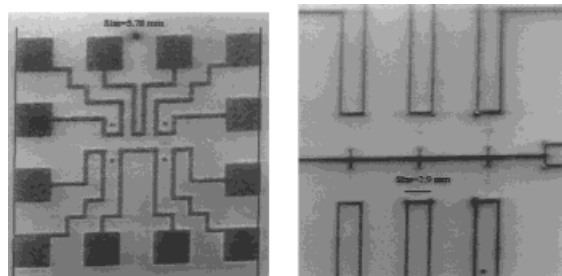


Figure 8 Photoimage of 8 μm thick copolyester film of all-aromatic chemistry 4.

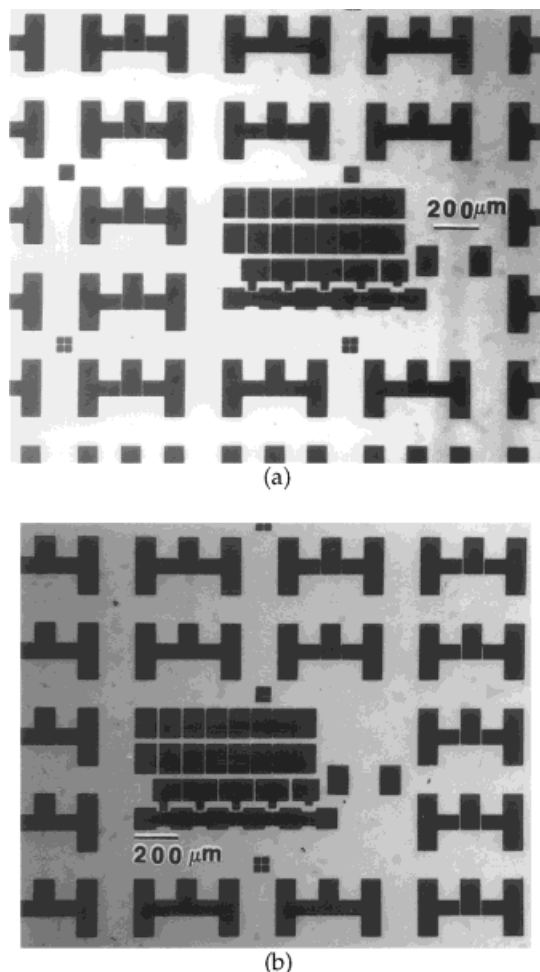


Figure 9 Photoimage of 5 μm thick copolyester film of aliphatic/aromatic chemistry 4.

grades the photocrosslinked bonds¹² and regenerates the carboxylic acid end groups (see Fig. 4).^{4–7} Figure 10 shows the thermogravimetric analysis of photosensitive oligomers 1, 3, and 4. Below 220°C, there is 20, 13, and 14% weight loss for photosensitive oligomers 1, 3, and 4, respectively, due to the degradation of the photocrosslinked bonds. At higher temperatures, these carboxylic acid end groups then react with the acetoxy functional groups of the novolac acetate or all-aromatic acetate to form a stable crosslinked polyester structure. The curing conditions are given in Table IV. Evolution of acetic acid during curing results in controlled foaming of the films to yield sharply lowered dielectric constants. The loss of the acetic acid by-product can be seen in Figure 10. Between 220 and 300°C, there is 9, 22, and 14% weight loss for oligomers 1, 3, and 4, respectively. The by-product weight loss for the all-aromatic photosensitive oligomer 1 is the

least because it continues to cure at temperatures higher than 300°C. The degradation products from the photocrosslinked bonds will also generate volatiles, which could possibly contribute to the foaming at lower temperature; however, in the absence of a stable crosslinked structure, such a foam would have a tendency to collapse. Although the all-aromatic copolyester has a higher T_g and better mechanical properties, the limitations include higher curing temperature (260–300°C) and longer curing cycle (>12 h).⁶ The presence of aliphatic units in the polyester structure has been found to reduce the curing temperatures by 50°C and to reduce curing cycles to as low as 10–15 min.⁷

Figure 11 shows SEM patterns of a cured copolyester film from oligomer 4, while Figure 12 shows the edge profile of a cured film from sample 1. It is worth noting that the polyester patterns retain their initial dimensions, namely, those of the photoimaged patterns, satisfactorily. The shrinkage in pattern dimension is relatively small (less than 0.1 μm for 8 μm thick patterns). This rather small shrinkage in pattern dimension might be due to the adhesion to the substrate and the foaming of the structures. It can be observed that the curing process does not affect contour image profiles. The weight loss results in a modest thickness loss in the vertical direction (offset by foaming), while shrinkage of the lateral pattern dimension is negligible.

Material Characterization

As a dielectric insulating thin film, the material's ability to be photoimaged as well as its physical and dielectric properties are of concern because it is a permanent coating acting both as a photoimaged layer and a dielectric layer in the final construction. Table V summarizes the thermal, dimensional, and dielectric properties of the four photoimaged copolyesters.

Thermal Stability

It was found that the cured polyester patterns were stable for several hours at 250°C in air. Even brief thermal exposures up to 300–350°C did not lead to any adverse effects on the quality of the relief patterns. The T_g of the cured photoimaged copolyesters was studied by DSC scanning and was calculated based on the changes in deflection of the curves.⁷ The T_g values given by different adhesives can vary from 125–150°C (see Table V). The observed differences in T_g are consistent with the difference in chemical structures; i.e., the

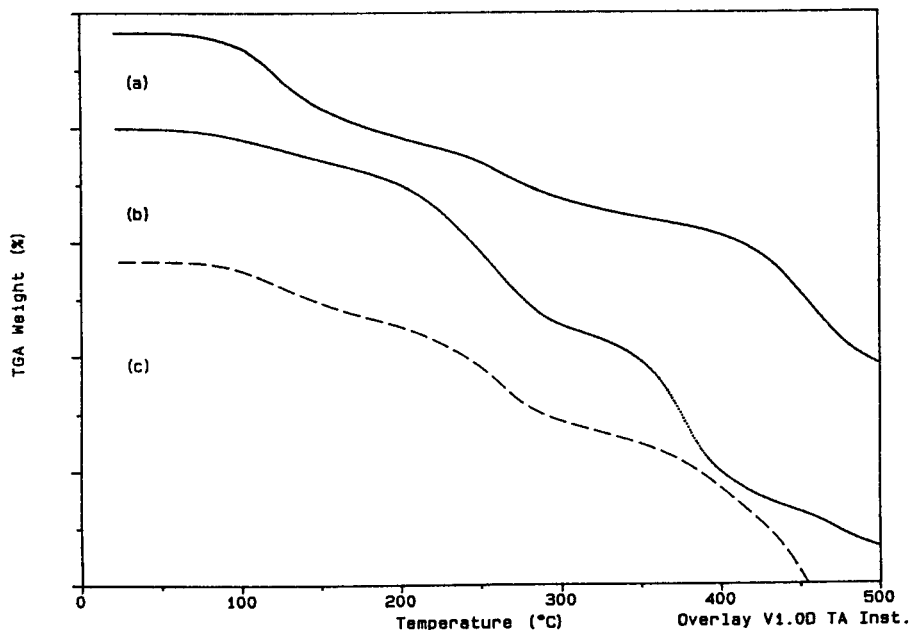


Figure 10 Thermogravimetric analysis of (a) all-aromatic photosensitive oligomer 1, (b) aromatic/aliphatic trifunctional photosensitive oligomer 3, (c) aromatic/aliphatic quadrafunctional photosensitive oligomer 4 heated at 1°C/min. to 500°C. Weight loss at 220°C is as follows: (a) 20%, (b) 13%, (c) 14%. Weight loss between 220°C and 300°C is as follows: (a) 9%, (b) 22%, (c) 14%.

samples with higher density of aromatic units in structure will give higher T_g . From the TGA studies,^{6,7} it was observed that the materials were thermally stable up to 330–400°C in nitrogen (as measured by the point of 5% weight loss).

Dielectric Properties

The dielectric constant of insulating films is another critical property. The dielectric constant has a major effect on circuit design rules. It determines overall thickness and critical density. By measuring the dielectric constants of the different copolyesters at different frequencies, it was found that after curing, the dielectric constant was 4.7 (1 MHz, 25°C) and 2.3 (1 MHz, 25°C) for all-aromatic dense and foamed films,

respectively. The linear aliphatic/aromatic dense and foamed films had dielectric constants of 4.5 and 2.5 (1 kHz, 25°C), respectively.^{10,11} Since the dielectric constant of polymer will decrease with increasing frequency,¹⁸ it is expected that the dielectric constant of the aliphatic/aromatic polymer will be lower than 2.5 at 1 MHz. More important than the base value for the dielectric constant is its stability with respect to changing environmental conditions (e.g., humidity). It has been already shown that the all-aromatic copolyester based thermosets have fairly low moisture absorption, generally less than 0.3 wt %.⁶

Adhesion and Mechanical Properties

The adhesion of the patterned polymer films on the silicon substrates and LCP substrates is very

Table IV Curing Processing Conditions Under Vacuum

| Sample | Precuring Time (h) | Precuring Temperature (°C) | Curing Time (h) | Curing Temperature (°C) |
|--------|--------------------|----------------------------|-----------------|-------------------------|
| 1 | 2 | 220 | 3 | 280 |
| 2 | 2 | 220 | 3 | 240 |
| 3 | 2 | 220 | 3 | 240 |
| 4 | 2 | 220 | 3 | 240 |

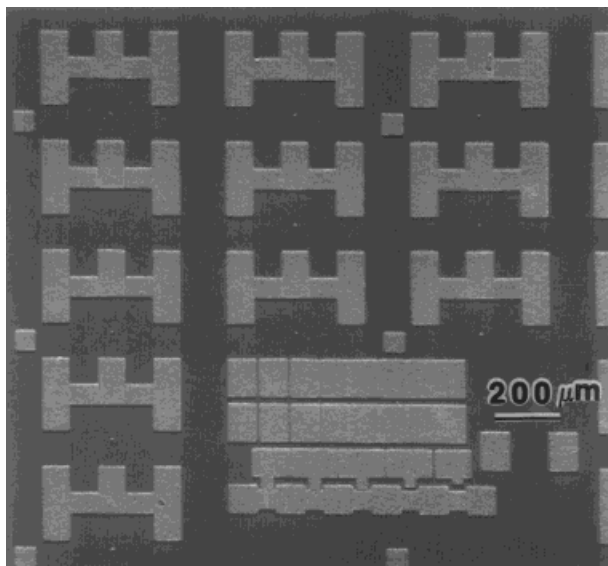


Figure 11 Patterns of a 5 μm thick cured copolyester film of aliphatic/aromatic chemistry 4.

good. For example, it passes the so-called adhesive tape test¹² and water boil test,¹ i.e., sticking on and pulling off a strip of adhesive tape and immersing the films in boiling water for several hours. We have already shown that these materials have good adhesion on some metal substrates such as steel, aluminum, or titanium.^{4–9} The films can be cut by razor blades without causing cracking. Attempts to scratch the layers with a hard pencil did not succeed. The photo-patterned films coated on various LCP film substrates can presumably be stacked upon each other as a multiple

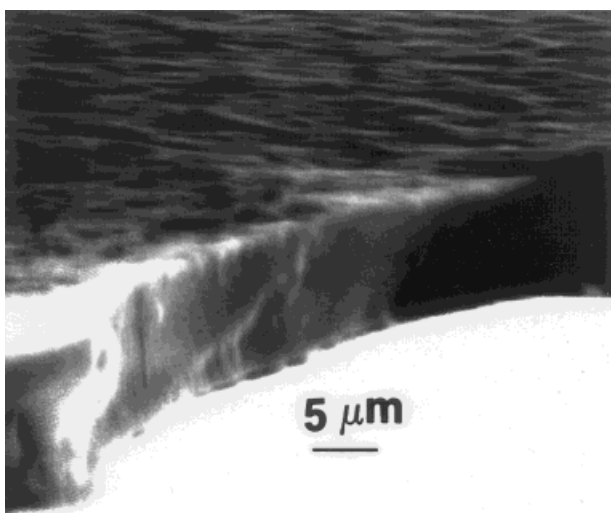


Figure 12 Edge profile of a cured film from all-aromatic chemistry 1.

Table V Thermal, Dimensional, and Dielectric Properties of Photoimaged Films

| Sample | Thermal Stability (°C) | T_g (°C) | Dielectric Constant ^a (25°C) |
|--------|------------------------|------------|---|
| 1 | 400 | 150 | 2.3 (1 MHz) |
| 2 | 350 | 125 | 2.5 (1 kHz) |
| 3 | 330 | 125 | 2.7 ^a (1 kHz) |
| 4 | 330 | 130 | 2.2 ^a (1 kHz) |

^a Lowest dielectric constants reported here for inhomogeneously foamed films.

layered package and bonded under heat and pressure to develop good adhesive bonds at the interface of the cured copolyester films with LCP substrates. Good bonds are obtained while retaining dimensional and thermal stability of the patterned films. LCP films are particularly advantageous as substrates since we can control the CTE and obtain exceptional inherent stiffness.

CONCLUSIONS

The chemistry and characterization of a new family of aromatic and aromatic/aliphatic photoimageable copolyester films were discussed. The present study shows that one can achieve good photospeed (10–15 seconds exposure on 15.5 mW/cm²) and good resolution and line width (10 μm) control. The most striking property of this photosensitive polyester film is that after foaming, its dielectric constant can be reduced from 4.7 to 2.5 at 1 MHz for the all-aromatic system and from 4.5 to 2.5 at 1 kHz for the aromatic/aliphatic system. This new family of photoimageable polymers offers a relatively low cost alternative to photoimageable thin films.

This research is supported by Morton International, Inc., and a graduate research fellowship from the Federation of Advanced Materials for Industry (FAMI) at the University of Illinois at Urbana–Champaign. Scanning electron microscopy was carried out in the Center for Microanalysis of Materials, University of Illinois, which is supported by the U.S. Department of Energy.

REFERENCES

1. P. D. Knudsen, R. L. Brainard, and K. T. Schell, in *The Proceedings of Surface Mount International*, Aug. 28, 1993.

2. J. A. Biancini, *Electr. Packaging Prod.*, **5**, 34 (1992).
3. C. W. Potter, MS Thesis, University of Illinois at Urbana-Champaign, 1994.
4. D. Frich and J. Economy, *ACS Polym. Prepr.*, **69**, 438 (1993).
5. J. Economy, D. Frich, K. Goranov, and J. C. Lim, *Polym. Prepr., Am. Chem. Soc.*, **70**, 398 (1994).
6. D. Frich, K. Goranov, L. Schneggenburger, and J. Economy, *Macromolecules*, to appear.
7. F. Shi and J. Economy, *Polym. Eng. Sci.*, to appear.
8. J. Economy, T. Gogeva, and V. Habbu, *J. Adhesion*, **37**, 215 (1992).
9. J. Economy and A. Andreopoulos, *J. Adhesion*, **40**, 115 (1993).
10. L. A. Schneggenburger and J. Economy, *ICEMCM*, 65 (1995).
11. L. A. Schneggenburger and J. Economy, *Polymer Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **37**, 160 (1996).
12. R. Rubner, H. Ahne, E. Kuhn, and G. Kolodziej, *Photo. Sci. Eng.*, **23**(5), 303 (1979).
13. O. Rohde, M. Riediker, A. Schaffner, and J. Bateman, *Solid State Technol.* **29**(9), 109 (1986).
14. C. G. Willson in *Electronic and Photonic Application of Polymers*, M. J. Bowden and S. R. Turner, Ed., American Chemical Society, Washington, D.C. 1988.
15. J. H. Lai, *Polym. Eng. & Sci.*, **19**, 1117 (1979).
16. B. D. Washo, *IBM J. Res. Dev.*, **21**, 190 (1977).
17. D. Meyerhofer, *J. Appl. Phys.*, **49**, 3993 (1978).
18. P. Hedvig, *Dielectric Spectroscopy of Polymers*, John Wiley & Sons, New York, 1977.