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Development of Poly(Phenylene)-Based Materials for Thin Film Applications: Optical Waveguides and Low Dielectric Materials

Hwan Kyu Kim[a]; Christopher K. Ober[a]
[a] Department of Materials Science, and Engineering Cornell University Ithaca, New York

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DEVELOPMENT OF POLY(PHENYLENE)-BASED MATERIALS FOR THIN FILM APPLICATIONS: OPTICAL WAVEGUIDES AND LOW DIELECTRIC MATERIALS

HWAN KYU KIM and CHRISTOPHER K. OBER*

Department of Materials Science and Engineering
Cornell University
Ithaca, New York 14853-1501

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ABSTRACT

We have synthesized and evaluated poly(phenylene)-based materials made via spin-coatable polymeric precursors for such thin film applications as optical waveguides and low dielectric materials. Poly(phenylene) precursors were prepared by radical polymerization of cyclohexadiene-1,2-diol derivatives containing various leaving groups. The precursors were converted into poly(phenylene) either by curing at 300°C or by deep-UV exposure in the presence of a photoacid generator. Poly(phenylene) has a number of desirable properties including good near-IR transmission, low dielectric constant, thermal and environmental stability, low water absorption, and ease of pattern fabrication using microlithographic techniques. Copolymer precursors based on 1,2-diaceto-3,5-cyclohexadiene and styrene derivatives as well as copolymers with *N*-substituted maleimide derivatives were prepared by radical copolymerization. The copolymer precursors were converted into poly(phenylene) copolymers either by annealing at 300°C or by deep-UV exposure in the presence of a photoacid generator. The results of this study indicate that copolymerization allows the incorporation of comonomers that can control dielectric and optical properties as well as glass transition temperature.

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INTRODUCTION

Recently, polymeric waveguides have been playing an increasingly important role in optical interconnect technology, since optical interconnections have many advantages (such as high propagation speed, high space density, and excellent bandwidth) over electrical interconnects. This trend demands new, readily processable polymeric materials which possess good optical transmission in an appropriate wavelength region, thermal and environmental stability, low coefficient of thermal expansion, and good adhesion to a substrate. In addition, it would be an advantage if these materials could be patterned by photolithographic techniques. Several polymers (e.g., PMMA [1], polyimide [2], and polysilyne [3]) have been studied extensively as polymeric waveguides. Their major disadvantages are thermal and environmental instability, and high moisture absorption.

Previously, we reported that poly(phenylene), which was produced by thermal treatment of a soluble precursor, is thermally stable up to 400°C in inert atmosphere and has relatively low dielectric permittivity at room temperature [4]. For this paper we have investigated the synthesis and characterization of poly(phenylene) via novel spin-coatable polymeric precursors. Poly(phenylene) precursors were prepared by radical polymerization of cyclohexadiene-1,2-diol derivatives alone and with selected comonomers (see Scheme 1).

In this study the precursors were spin-coated onto various types of substrates and then converted into poly(phenylene) by curing at 300°C for various times or by UV exposure in the presence of a photoacid generator. The conversion of the precursors into poly(phenylene) was monitored by IR or UV spectroscopy. Such photoaromatization capabilities suggested that poly(phenylene) precursors can be imaged by deep-UV microlithography [5]. This development means that two patterning processes can be used. Poly(phenylene) precursors were processed either by deep-UV microlithography with fewer processing steps, or they were also developed by conventional microlithographic techniques.

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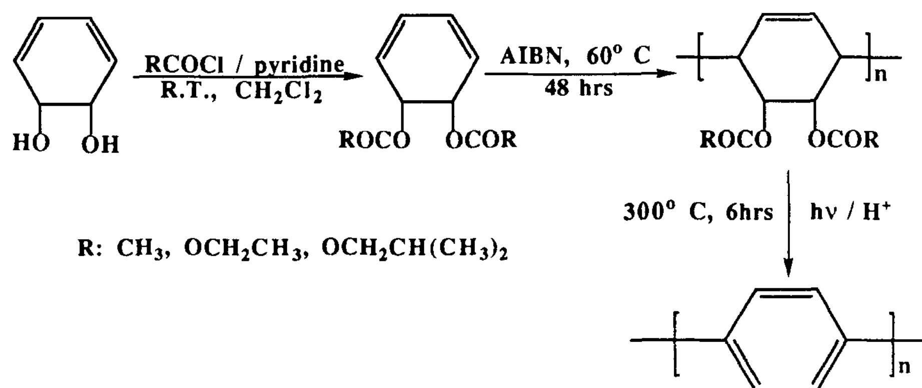

SCHEME 1. Synthesis of poly(phenylene) precursors by radical polymerization, and aromatization to poly(phenylene) by either heat treatment or UV exposure in the presence of a photoacid generator.

To provide control over physical properties, copolymers of 1,2-diaceto-3,5-cyclohexadiene with either styrene derivatives or *N*-substituted maleimides were prepared by radical copolymerization using AIBN. The resulting precursor copolymers could be converted into stable phenylene-based copolymers either by heat treatment at 300°C or by deep-UV exposure in the presence of a photoacid generator. The results of this work indicate that copolymerization permits control of such electronic and physical properties as refractive index and glass transition temperature while still retaining many of the desirable properties of poly(phenylene).

Finally, we have demonstrated and evaluated the application of poly(phenylene) as both optical waveguide and low dielectric material. We have observed that the poly(phenylene) prepared for these applications has a number of desirable properties, including especially good near-IR transmission, thermal and environmental stability, and ease of pattern fabrication using photolithographic techniques.

EXPERIMENTAL

Materials

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3-Aminobenzotrifluoride, 4-aminobenzotrifluoride, 1,2,5,6-tetrafluoro-aniline, acetyl chloride, methyl chloroformate, ethyl chloroformate, isobutyl chloroformate (all from Aldrich), and 3,5-*cis*-cyclohexadiene-1,2-diol (Sigma) were used as received. Styrene derivatives (Aldrich) were purified by chromatographing with neutral alumina. Azobis(isobutyronitile) (AIBN, Kodak) was recrystallized from ethanol. Pyridine (Aldrich) was distilled over NaOH. Other chemicals were used as received.

Synthesis of *N*-(Fluorinated Phenyl) Maleimides

N-(Fluorinated phenyl) maleimides were prepared by a modified method used earlier for *N*-phenyl maleimide [6]. Maleic anhydride (5–20 g) and 60–200 mL ethyl ether were placed in a 250-mL three-necked flask provided with a stirrer, a reflux condenser, and an addition funnel. An equivalent amount of 3-aminobenzotrifluoride, 4-aminobenzotrifluoride, or 1,2,5,6-tetrafluoroaniline in 60 mL ethyl ether was added dropwise to the flask over a period of 30 minutes. The reaction medium was stirred for 4 hours at room temperature and poured into a large amount of water. The solid precipitate was collected by suction filtration, washed with water twice and with petroleum ether, and dried in vacuum to yield the white powder as maleamic acid. To the mixture of 80 mL acetic acid and 8 g sodium acetate was added 4.3 g maleamic acid. The reaction mixture was stirred at 80°C for 1 hour and then cooled down to room temperature. $CHCl_3$ (100 mL) was added to the reaction mixture. The reaction mixture was poured into a large amount of water to precipitate the product which was filtered and then washed with water and petroleum ether. The final product was recrystallized from boiling ethanol (yield: 94%; mp: 133–134°C). ^{1}H NMR ($CDCl_3$) δ: 7.5–7.8 ppm (dd, 4H), 6.88 ppm (s, 2H); ^{19}F NMR ($CDCl_3$) δ: −55.67 ppm; IR (KBr; cm^{-1}): 1724 ($\nu_{C=O}$ in imide), 1616 ($\nu_{C=C}$), 1340 $(\nu_{C-F})_s$, 1106 and 1070 $(\nu_{C-F})_{as}$, 843 ($\delta_{C-H\ (out\text{-}of\text{-}plane\ of\ phenyl)}$). 92% Yield of *N*-(2,3,5,6-tetrafluorophenyl) maleimide; mp: 136–137°C; ^{1}H NMR ($CDCl_3$) δ: 7.5–

7.8 ppm (m, 1H), 6.88 ppm (s, 2H); IR (KBr; cm^{-1}): 1726 ($\nu_{C=O}$ in imide), 1616 ($\nu_{C=C}$), 1265.4 ($\nu_{C-F})_s$, 825 ($\delta_{C-H\ (out\text{-}of\text{-}plane\text{-}phenyl)}$).

In the case of the *N*-(3-trifluoromethylphenyl)maleimide synthesis, the final product was distilled under reduced pressure (yield: 85%; bp: 118–121°C (1.1 mmHg)). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.7–7.5 ppm (multiplet, 4H), 6.85 ppm (singlet, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −55.78 ppm; IR (KBr), (cm^{-1}): 1711 ($\nu_{C=O}$ in imide), 1616 ($\nu_{C=C}$), 1329 ($\nu_{C-F})_s$, 1128 and 1071 ($\nu_{C-F})_{as}$, 895, 835, and 808 ($\delta_{C-H\ (out\text{-}of\text{-}plane\ of\ phenyl)}$).

Synthesis and Polymerization of Cyclohexadiene-1,2-diol Derivatives [4, 7]

A 250-mL three-necked, round-bottomed flask was fitted with a reflux condenser and a pressure-equalizing addition funnel. All systems were thoroughly flamed-dried under dry nitrogen gas. Known amounts of 3,5-*cis*-cyclohexadiene-1,2-diol (0.0454 g-mol) were added to a flask, dissolved in CH_2Cl_2 (70 mL), and purged with dry nitrogen gas. An excess of pyridine (24 g, 0.3 g-mol) was added to the flask and the mixture was stirred at 0°C. An excess of acetyl chloride or alkyl chloroformate in CH_2Cl_2 (20 mL) was added dropwise to the mixture over a period of 30 minutes. The resulting mixture was stirred at 0°C for 1 hour and at room temperature for 16 hours. Water (5 mL) was added, then the mixture was stirred rapidly for 10 minutes. The mixture was then diluted with CH_2Cl_2 (150 mL) and washed with 10% HCl solution (2 × 50 mL), water (50 mL), 5% NaOH solution (50 mL), water (2 × 50 mL), and saturated NaCl solution (50 mL). The organic phase was dried with magnesium sulfate and filtered. Organic solvents were removed by rotary evaporator, and the product was chromatographed with neutral alumina using 40% ethyl ether/hexane as an eluting solvent. The yield of product was gravimetrically measured.

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Polymerization was carried out with AIBN to yield poly(phenylene) precursors, as described in Ref. 7. Precursors were characterized by GPC, IR, UV, NMR, DSC, TGA, and ellipsometry.

In a similar way, copolymerization of diacetate monomer with styrene derivatives such as styrene and 3,5-bis(trifluoromethyl)styrene was carried out with AIBN at 60°C for 48 hours. Radical copolymerization of *N*-(fluorinated phenyl) maleimides and cyclohexadiene-1,2-diacetate was carried out with 2,2′-azobis(isobutyronitrile) (AIBN) in 1,4-dioxane in a sealed tube under vacuum at 60°C for 2 days, as described in Ref. 6. After polymerization, the polymer solution was poured into a large amount of heptane to precipitate the polymer, which was filtered and dried. The resulting copolymers were characterized by ^{1}H NMR and ^{19}F NMR, TGA, IR, and GPC.

Thermal Conversion of Precursors into Poly(Phenylene)

A solution was prepared by dissolving poly(phenylene) precursor (0.15 g) into diglyme or toluene (1.0 g). The solution was filtered through a 0.5-μm Teflon filter and then spin coated at 1000 rpm for 30 seconds on various types of substrates such as a NaCl disk for IR analysis, a silicon wafer (100) for refractive index measurement, or a quartz wafer for UV analysis. The films were annealed at 300°C for

various times. The final films were analyzed by IR, UV, and ellipsometry (refractive index measurement).

In the same way, thermal conversion of the copolymer precursors into poly(phenylene)-based copolymers was attempted. A solution was prepared by dissolving the copolymer precursor (0.15 g) into diglyme or toluene (1.0 g). The solution was filtered through a 0.5-mm Teflon filter and then spin coated on various types of substrates as above. The films were annealed at 300°C at various times. The final films were analyzed by IR or UV spectroscopy.

Acid-Catalyzed Photoaromatization of Precursors Into Poly(Phenylene)

A solution was prepared by dissolving poly(phenylene) precursor (0.15 g) and triphenylsulfonium antimony hexafluoride (photoacid generator: 10 wt%) into diglyme or toluene (1.0 g). The solution was filtered through a 0.5-μm Teflon filter and then spin coated on various substrates. The thickness was measured by a surface profilometer (Tencor Instruments, Alpha Step 200). The films were exposed to a deep-UV source (235–260 nm from high pressure Hg arc lamps) for various times. The final films were analyzed by IR and UV spectroscopy. As above, photoaromatization of the poly(styrene) copolymers into poly(phenylene-*co*-styrene) was attempted.

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Direct Deep-UV and Conventional Microlithography

A solution was prepared of either the poly(phenylene) precursor or the poly(styrene) copolymers (0.15 g) with triphenylsulfonium antimony hexafluoride (photoacid generator: 10 wt%) in diglyme or toluene (1.0 g). The solution was filtered through a 0.5-μm Teflon filter and then spin coated onto appropriate substrates at 1000 rpm for 30 seconds. Thickness was measured by a surface profilometer (Tencor Instruments, Alpha Step 200). The films were exposed to a deep-UV source (235–260 nm from high pressure Hg arc lamps) for various times, baked at a given temperature ($T_g = -20$°C) and then developed with toluene. A picture of the resulting pattern was taken by scanning electron microscopy (SEM).

Poly(phenylene) obtained by thermal treatment of the diacetate precursor on silicon wafers was patterned by conventional microlithography [8], in the manner of polyimides, as discussed in Ref. 9. Photoresist material was based on the use of a novolac resin with a quinonediazide dissolution inhibitor acting as sensitizer.

Spectroscopic Measurements

NMR spectra were recorded at room temperature in $CDCl_3$ solutions with an IBM 300 MHz NR-300 instrument or a Varian XL-400 NMR Spectrometer. Optical spectra were measured over the range of 190–820 nm on either a Hewlett-Packard 8452 UV-diode array spectrometer or an IBM 9430 UV-Visible spectrophotometer in either films or in CH_2Cl_2 solutions. Infrared spectra were recorded on a Galaxy Series 2020 FTIR Mattson instrument. Thermal stability of the polymers was analyzed by TGA using a 951 Du Pont Instrument TGA. GPC analysis was carried out in THF solution using a Waters GPC with three Ultrastyragel columns (linear, 500

Å, and 1000 Å) in series, a model 510 pump, a model 410 refractive index detector, and a model 450 UV detector. The molecular weights and polydispersities reported are based on poly(styrene) standards. The indices of refraction for polymers were measured by ellipsometry using an AutoEL-II Serial No. 7977 or by Perkin-Elmer Lambda 9 UV/VIS/NIR Spectrophotometer. Dielectric constants of the polymer films were measured using a Hewlett-Packard 8409 Automated Network Analyzer over the frequency range of 0.1 to 10 MHz.

RESULTS AND DISCUSSION

A large number of physical and chemical characteristics must be present in polymeric materials to be able to use them in optical interconnect systems. Among them, a very important factor is patternability of the polymer for waveguide fabrication. A photosensitive material may be processed by direct deep-UV imaging and thereby greatly reduce the number of processing steps when compared with conventional microlithography of nonphotosensitive materials. To produce photosensitive linear waveguide materials, we have attempted to introduce photolabile groups into poly(phenylene) precursors. Both diacetate and alkylcarbonate precursors were synthesized because their basic structures resemble the photoimageable components of *t*-BOC poly(styrene) [10] and poly(α-acetoxystyrene) [11].

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Synthesis of Poly(Phenylene) Precursors

Results for the synthesis of poly(phenylene) precursors are summarized in Table 1. Diacetate monomer (M_1) and diethylcarbonate monomer (M_2) polymerized very easily to produce homopolymer precursors. The overall reaction steps are outlined in Scheme 1. The yield of homopolymers was gravimetrically calculated and was in the range of 55 to 60%. Molecular weights (M_n) based on poly(styrene) standards were 20,000 to 40,000 g/mol with polydispersities (M_w/M_n) of less than 2.

TABLE 1. Radical Polymerization of Diacetate Monomer (M_1), Diethylcarbonate Monomer (M_2), and Isobutylcarbonate Monomer (M_3) Using AIBN at 60°C

Monomer	Diacetate monomer (M_1)	Et-carbonate monomer (M_2)	*i*-Bu-carbonate monomer (M_3)	$M_1 + M_3$[a]
Yield, %	60.0	55.0	>95.0	30.0
m_1/m_3[b]	–	–	–	1/4
$M_n \times 10^{-3}$[c]	35	20.2	<0.3	7.3
M_w/M_n	1.84	1.94	–	1.64

[a]Copolymerization of an equimolar amount of comonomer $M_1 + M_3$ using AIBN at 60°C for 2 days.

[b]Copolymer composition as determined by ^{1}H NMR.

[c]Molecular weight based on poly(styrene) standards.

Attempted homopolymerization of di-*i*-butylcarbonate monomer (M_3) using AIBN at 60°C yielded no polymer according to GPC measurements.

The final product was identified by ^{1}H-NMR analysis as phenyl isobutylcarbonate. This result indicated that monomer M_3 was both thermally unstable and slow to polymerize presumably due to steric hindrance between isobutyl carbonate groups. Phenyl isobutylcarbonate can be readily formed by thermal decarboxylation via a six-membered ring intermediate. However, monomer M_3 was found to copolymerize very easily with the diacetate monomer M_1. The yield of copolymer I was 30% with a number-average molecular weight (M_n) = 7300 g/mol and polydispersity (M_w/M_n) = 1.64.

Radical Copolymerization of the Diacetate Monomer with Styrene Derivatives

Copolymerization is a very useful technique for the preparation of new materials, since copolymer composition can be varied not only with different monomers but also with different comonomer ratios. The physical and electronic properties of copolymers can be readily altered and adjusted by the properties of its monomeric components. Thus, copolymerization may allow the incorporation of monomers that impart useful physical properties, although the respective homopolymers themselves may not be appropriate. For many reasons, we attempted to copolymerize the diacetate monomer with styrene derivatives to yield copolymers of the poly(phenylene-*co*-styrene) precursor. Results are summarized in Table 2.

The molecular weight of the copolymer precursors increased with increasing styrene comonomer concentration in the copolymerization of the diacetate mono-

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TABLE 2. Results of Radical Copolymerization of Diacetate Monomer (M_1) with Styrene (M_4) and 3,5-Bis(trifluoromethyl)styrene (M_5) using AIBN at 60°C[a]

Monomer	Diacetate monomer (M_1)	M_1:M_4 (20:1)	M_1:M_4 (10:1)	M_1:M_5 (30:1)
Yield, %	60.0	40.0	30.0	18.0
m_1/m_i[b]	1:0	17:1	2.3:1	6:1
$M_n \times 10^{-3}$[c]	20	28.3	37.1	–
M_w/M_n	1.61	1.61	1.58	–
T_g (°C)[d]	180	170[e]	142	140

[a]Copolymerization of comonomers M_1 + M_i with AIBN at 60°C for 2 days.

[b]Copolymer composition was determined by ^{1}H NMR.

[c]Molecular weight based on poly(styrene) standards.

[d]Homopolymer T_g: poly(3,5-bis(trifluoromethyl)styrene) = 59°C; poly(-styrene) = 100°C.

[e]T_g of copolymer was estimated from the equation of $(1/T_g) = (m_1/T_{g1}) + (m_2/T_{g2})$.

mer with styrene derivatives (see Table 2). The glass transition temperature was reduced from 180°C down to 140°C by incorporation of styrene derivatives. In addition, the optical properties of the polymers were controlled by copolymerization. For example, the refractive index of the heat-cured copolymer of poly(phenylene) with 17 mol% 3,5-bis(trifluoromethyl)styrene was 1.54, while the refractive index of poly(phenylene) itself is 1.70.

Radical Copolymerization of Diacetate Monomer with *N*-(Fluorinated Phenyl) Maleimides

The radical copolymerization of *N*-phenyl maleimides with 3,5-cyclohexadiene-1,2-diacetate (M_1) using AIBN at 60°C was performed to produce a thermally stable poly(phenylene)-based copolymer, because such poly(maleimide)s have been shown to be thermally stable and optically transparent [6]. The results of the radical copolymerizations are shown in Table 3. Radical copolymerization of *N*-phenyl maleimides with 3,5-cyclohexadiene-1,2-diacetate successfully produced copolymers of the diacetate precursor and fluorinated maleimides, with a polymer yield of 16–17%. No homopolymers of *N*-phenyl maleimides were obtained by AIBN initiator at 60°C reacting for 2 days. GPC traces showed that the number-average molecular weight of the copolymers was in the range of 3×10^3 to 4×10^4 g/mol, and the relatively narrow molecular weight distribution of the copolymers ($M_w/M_n \approx 1.50$) was retained. The observation of the relatively narrow molecular weight distribution of the copolymers ($M_w/M_n \approx 1.50$) may be explained by the low yields of the copolymers. When compared with those values obtained for the diacetate precursor polymer in Table 2, the molecular weights and the yields were lower in the copolymers than in the diacetate precursor.

The copolymer composition was analyzed by ^{1}H NMR. The resulting copolymer was more enriched (1/5) in *N*-phenyl maleimide derivatives than the starting comonomer mixture (1/6). ^{19}F-NMR data (see Fig. 1) showed one very sharp peak around −55.8 ppm for the CF_3 group in the *N*-(3-trifluorophenyl) maleimide repeat unit. This chemical shift was similar to that of the monomer, but is much different from that of the homopolymer [12]. This observation may indicate that the *N*-(3-

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TABLE 3. Radical Copolymerization of *N*-Substituted Maleimides (M_i) with 1,2-Diaceto-3,5-cyclohexadiene (M_1) using AIBN at 60°C in THF

Maleimide/M_1	3-CF_3-NPI/M_1	4-CF_3-NPI/M_1	NPI/M_1	M_1
M_i/M_1[a]	1/6	1/6	1/10	0/1[b]
Yield, %	16.4	17.5	32.3	60.0
m_i/m_1	1/5	1/5	–	–
$M_n \times 10^{-3}$[c]	3.38	4.09	3.03	20
(M_w/M_n)	(1.42)	(1.56)	(1.57)	(1.61)

[a]The mole ratio of comonomer in radical copolymerization.

[b]Radical polymerization of 1,2-diaceto-3,5-cyclohexadiene (M_1) under similar conditions.

[c]Molecular weights based on poly(styrene) standards.

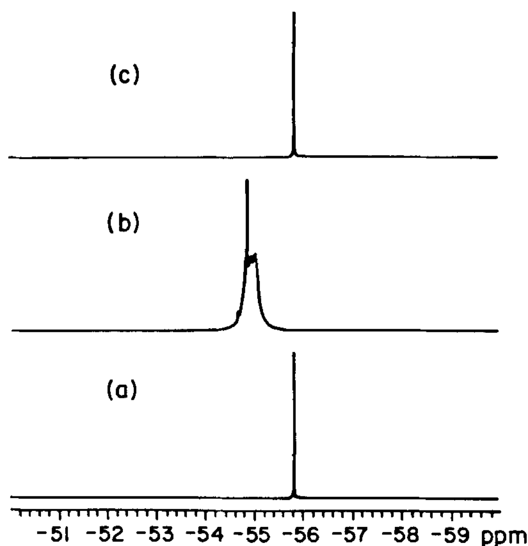

FIG. 1. ^{19}F-NMR spectra of *N*-(3-trifluoromethylphenyl) maleimide monomer (a), poly(*N*-(3-trifluoromethylphenyl)maleimide) (b), and the copolymer of the diacetate monomer (M_1) with *N*-(3-trifluoromethylphenyl) maleimide (c).

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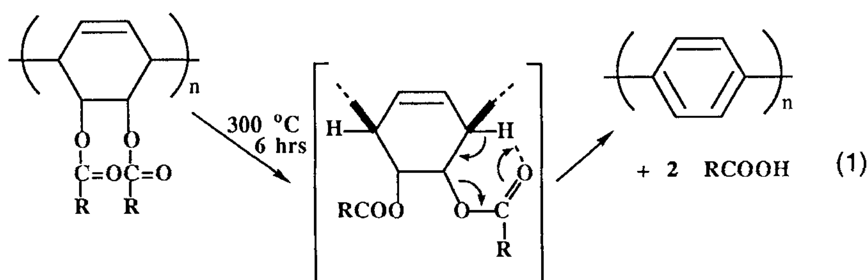
trifluorophenyl) maleimide monomer was incorporated into the copolymer in segments with fewer than three repeating units.

Thermal Conversion of Poly(Phenylene) Precursor into Poly(Phenylene)

The poly(phenylene) precursors could be aromatized to poly(phenylene) by heating in thin films. The thermal processes were monitored by thermogravimetric analysis (TGA), IR spectroscopy, and UV spectroscopy. A typical TGA diagram of the diacetate precursors is shown in Fig. 2. TGA analysis of the diacetate precursor was roughly consistent with the value expected for the loss of two acetic acid molecules followed by aromatization (eq. 1):



The aromatized polymer was stable for several hours at elevated temperatures. The reaction probably proceeds via a cyclic transition state, since the carboxylic acid is a good leaving group. Similar TGA results were obtained for other precursors such as the diethylcarbonate precursor and the copolymer precursors. In the case of the

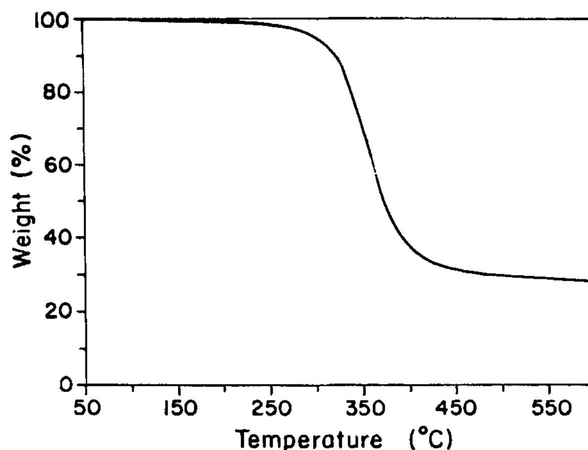


FIG. 2. Thermogravimetric analysis (TGA) of the diacetate precursor.

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diethylcarbonate precursor, an ethylcarbonic acid can be produced and probably decomposes into ethanol and carbon dioxide.

IR data of poly(phenylene) prepared from the diacetate precursor was observed at 812 cm^{-1} for the C—H out-of-plane bending band of the phenyl groups. The spectra of the poly(phenylene) oligomers had an absorption between 840 and 800 cm^{-1} for the C—H out-of-plane bending band for the phenylene groups. As the number of consecutive phenylene units increased, this peak shifted to lower wavenumbers and attained a limiting value of 802 cm^{-1} for a highly conjugated polymer [13]. From IR data, the poly(phenylene) consisted of approximately six consecutive phenylene units, separated by unaromatized sections, probably due to the 1,2-repeat unit structure. The precise structure of the unaromatized unit is unknown. Similar IR data were obtained from the pyrolysis of the diacetate precursors and copolymer I.

Typical UV spectra of the poly(phenylene) prepared from diacetate precursors are shown in Fig. 3. UV spectra showed a maximum absorption around 320 nm tailing into the visible region. Aromatization at higher temperatures (>300°C) results in a red shift. The UV absorption of the polymer increases with an increasing number of consecutive phenylene rings and shifts toward 380–390 nm for a highly conjugated polymer. When compared with the UV spectra of poly(phenylene) oligomers, this poly(phenylene) had on average six consecutive phenylene units, which is consistent with the value obtained from IR data. The lack of change of the UV spectra at higher temperatures suggests that poly(phenylene) is thermally stable up to 400°C.

Thermal conversion of copolymers of diacetate monomer (M_1) with styrene derivatives was also studied by thermogravimetric analysis, IR spectroscopy, and UV spectroscopy. Similar results were obtained from heat-treatment of these copolymers. UV spectra of the poly(phenylene-*co*-styrene) prepared from its copolymer precursor heated at various temperatures are shown in Fig. 4. Elevated temperature (>350°C) results in a blue-shift. These results indicate that curing at higher temperature (>350°C) leads to sustained decomposition of the copolymers.

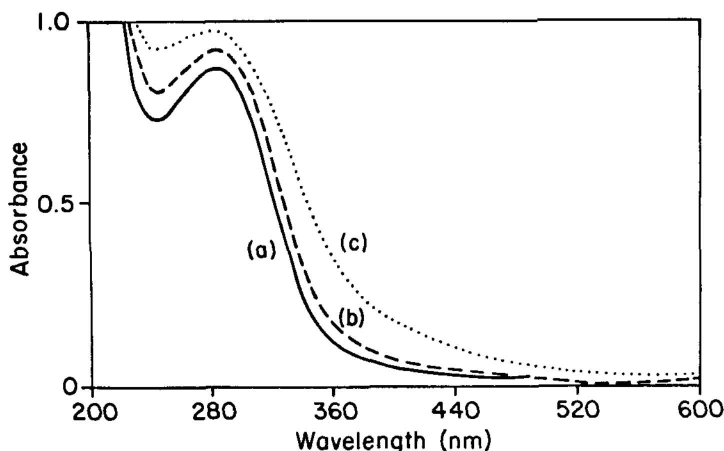

FIG. 3. UV absorption spectra change of poly(phenylene) obtained from heat-treatment of diacetate precursor at various temperatures on a quartz substrate: (a) 300°C for 6 hours, (b) 350°C for 1 hour, (c) 400°C for 1 hour.

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In the case of the copolymer of the diacetate precursor with maleimide derivatives, UV spectra of the cured poly(*N*-(3-trifluoromethyl phenyl) malemide)-*co*-phenylene) (see Fig. 5) did not change upon heating to temperatures up to 350°C when compared with a UV spectrum of poly(*N*-(3-trifluoromethyl phenyl) maleimide-*co*-phenylene) which had been cured at 300°C for 6 hours. Elevated temperature (400°C) results in a small blue-shift. These results suggest that this copolymer is thermally stable up to 350°C. At higher temperatures (>400°C), this copolymer decomposed continuously.

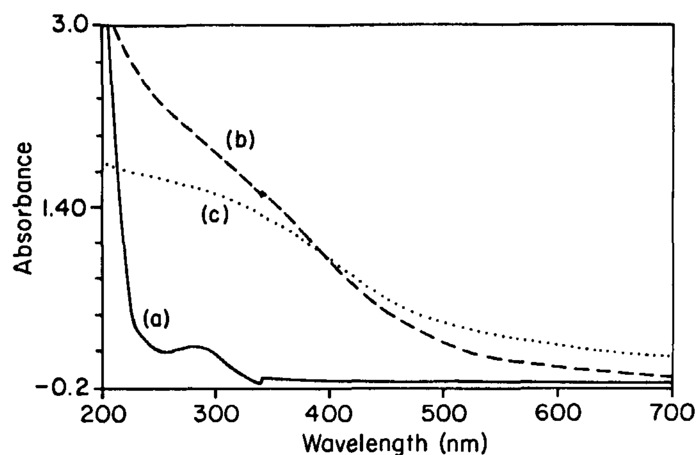

FIG. 4. UV spectral change caused by heat-treatment of poly(1,2-diaceto-3,5-cyclohexadiene-*co*-styrene) as a function of temperature on a quartz substrate: (a) uncured poly(1,2-diaceto-3,5-cyclohexadiene-*co*-styrene); (b) 300°C for 6 hours; (c) 350°C for 1 hour.

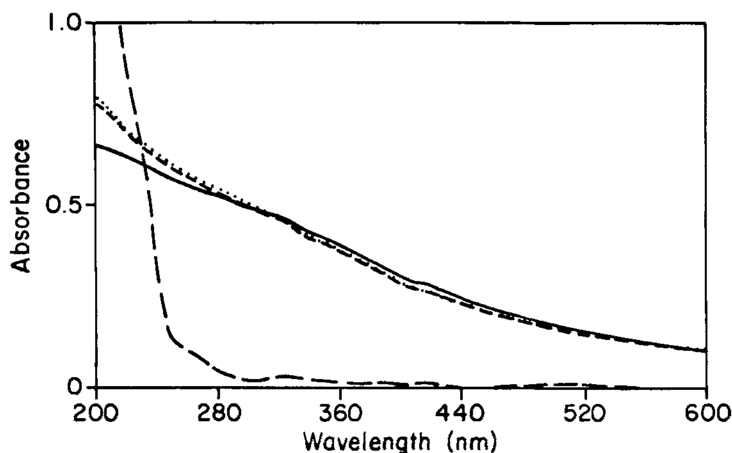

FIG. 5. UV spectral change obtained from heat-treatment of poly(1,2-diaceto-3,5-cyclohexadiene-*co*-*N*-(3-trifluoromethylphenyl) maleimide) as a function of temperature on a quartz substrate: (a) uncured poly(1,2-diaceto-3,5-cyclohexadiene-*co*-*N*-(3-trifluoromethylphenyl) maleimide) (- -); (b) 300°C for 6 hours (· · ·); (c) 350°C for 1 hour (- - -); (d) 400°C for 1 hour (— —).

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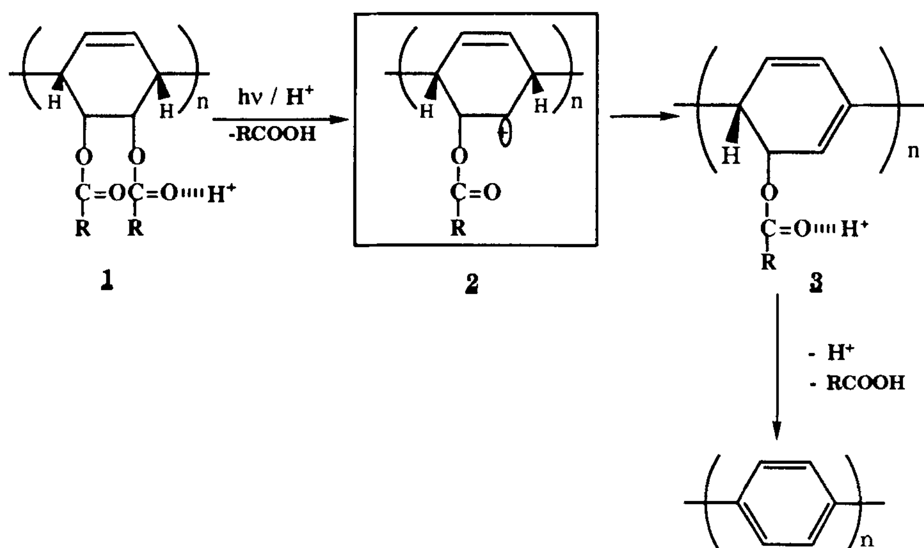
Acid-Catalyzed Photoaromatization of Precursors into Poly(Phenylene)

As mentioned above, the structures of diacetate and alkylcarbonate precursors have molecular features resembling *t*-BOC poly(styrene) and poly(α-acetoxystyrene). We would expect that they would therefore be susceptible to acid-catalyzed thermolytic conversion. Films of the diacetate precursor and the diethylcarbonate precursor were prepared by spin-casting. Acid was introduced either by dipping in methanesulfonic acid or by adding a photoacid generator of triphenylsulfonium antimony hexafluoride [8b, 10, 11], which yields an acid upon deep-UV exposure. The diacetate precursor and the diethylcarbonate precursors were irradiated with deep-UV light [wavelength (λ): 235–260 nm] at room temperature in the presence of an equimolar amount of the photoacid generator to yield poly(phenylene) [14]. The absorption bands shifted to longer wavelength with increasing exposure time. This result indicates that the number of conjugated phenylene rings increased with increasing acid concentration or exposure time.

This photoaromatization process probably proceeds through carbocationic moieties, as shown in Scheme 2. This scheme shows an E1-like elimination which may be prevalent in the case of the acid-catalyzed photoaromatization, similar to the acid-catalyzed thermolytic cleavage of polycarbonates or polyesters [15]. The reaction starts with protonation of a carbonyl group in either the carbonate group or acetate group to afford intermediate **1**. This intermediate is converted into the carbocationic moiety **2** and RCOOH. Elimination of a proton from the carbocationic moiety results in regeneration of an acid catalyst and the formation of a diene-



SCHEME 2. Mechanism for the photoaromatization of poly(phenylene) precursor into poly(phenylene).

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containing polymer 3. This process repeats itself at another leaving group with the eventual conversion of the polymer chain into poly(phenylene). The protons initially formed by UV irradiation are regenerated during the process which explains the chemical amplification of these materials.

When 10 wt% photoacid generator was added to the diacetate polymer, a postbaking process after deep-UV exposure was needed to photoaromatize the diacetate precursor to yield insoluble poly(phenylene). The postbaking process was usually carried out around the glass transition temperature to mobilize the generated acid. The effect of the postbaking temperature on photoaromatization was examined. The resulting UV spectra are shown in Fig. 6. Aromatization was effectively catalyzed when the diacetate polymer was postbaked around its glass transition temperature ($T_g \approx 180°C$), following deep-UV exposure. Unfortunately, the photoacid generator was thermally decomposed near the glass transition temperature of 180°C. The postbaking temperature was, therefore, reduced to 160°C. Photoaromatization was still accelerated at this postbaking temperature, while it did not effectively occur at 140°C (see Fig. 6). These results indicate that the photoaromatization required a postbaking process for mobilizing the generated acid over the polymer backbone. The resulting products obtained from photoaromatization were analyzed by IR, as shown in Fig. 7. At the decomposition temperature of the photoacid generator (180°C), side reactions occurred to produce a by-product, resulting in a new carbonyl peak which appeared at 1810 cm^{-1}. This carbonyl peak was also detected during thermal conversion of the diacetate polymer [7b]. The side product was interpreted as the formation of cyclic carbonate groups. The formation of cyclic carbonate groups has been proven from the model reaction [16] of 1,2-

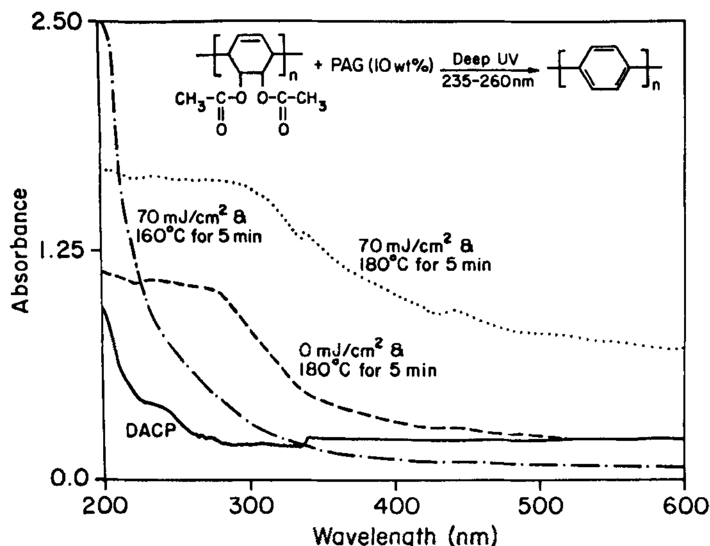

FIG. 6. UV absorption spectra of poly(1,2-diaceto-3,5-cyclohexadiene) and 10 wt% photoacid generator (film thickness: 2.0 μm) after UV exposure (235–260 nm) as a function of postbaking temperature.

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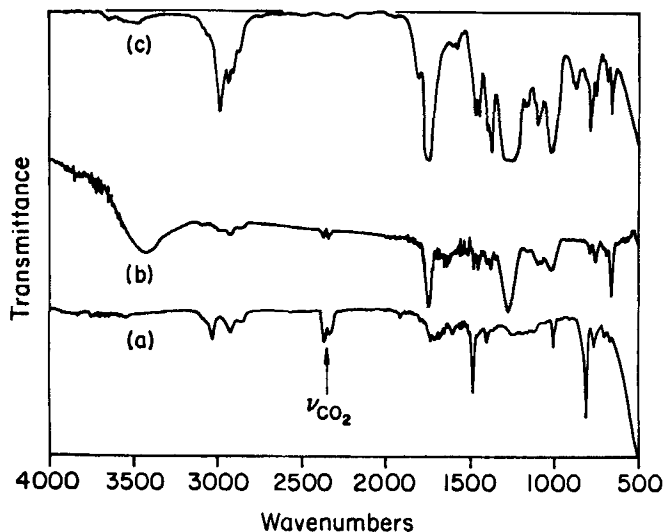

FIG. 7. IR spectra of poly(1,2-diaceto-3,5-cyclohexadiene) and 10 wt% PAG (film thickness: 2.0 μm) after deep UV exposure (235–260 nm) as a function of postbaking temperature: (a) poly(phenylene); (b) diethylcarbonate polymer and 10 wt% photoacid generator after deep UV exposure (32 mJ/cm^2) and then postbaked at 115°C for 3 minutes; (c) diethylcarbonate polymer and 10 wt% photoacid generator after deep UV exposure (100 mJ/cm^2) and then postbaked at 200°C for 3 minutes.

dimethyl carbonate cyclohex-3-ene with methanesulfonic acid to produce a cyclic carbonate cyclohex-3-ene, in which a carbonyl peak appeared at 1810 cm^{-1}.

To reduce the required postbaking temperature, copolymerization with styrene derivatives was investigated. The glass transition temperature (T_g) of the copolymer of the diacetate monomer with 6% styrene was, at 170°C, 10°C lower than that of the homopolymer. This copolymer was irradiated at deep-UV wavelengths in the presence of 10 wt% photoacid generator. The resulting changes are shown in the UV spectra of Fig. 8 which demonstrates that photoaromatization is effectively accelerated by mobilizing the generated acids along the polymer backbone at a postbaking temperature of 140°C. In the case of the copolymer of the diacetate monomer with 17% 3,5-bis(trifluoromethyl)styrene, photoaromatization was carried out at a lower temperature ($<$ 140°C) since the glass transition temperature of copolymer was expected to be around 140°C.

Fabrication by Conventional Microlithography and by Deep-UV Lithography

Microfabrication was achieved by conventional microlithography for films of poly(phenylene) and by deep-UV lithography for photosensitive precursors, as shown in Scheme 3. In the case of conventional microlithography, diacetate precursor films were prepared by spin-coating from 10–20% diglyme or toluene solution on a Si(100) wafer and cured at 300°C for 6 hours. Photoresist material [8, 9] based on a novolac resin with a quinonediazide dissolution inhibitor (thickness: ~2μm) was coated on the poly(phenylene) film and then prebaked at 90°C for 30 minutes. The resulting polymer film was exposed at a mid-UV wavelength (405 nm), developed with MF-312 in water (Shipley), postbaked at 90°C for 2 minutes, and etched

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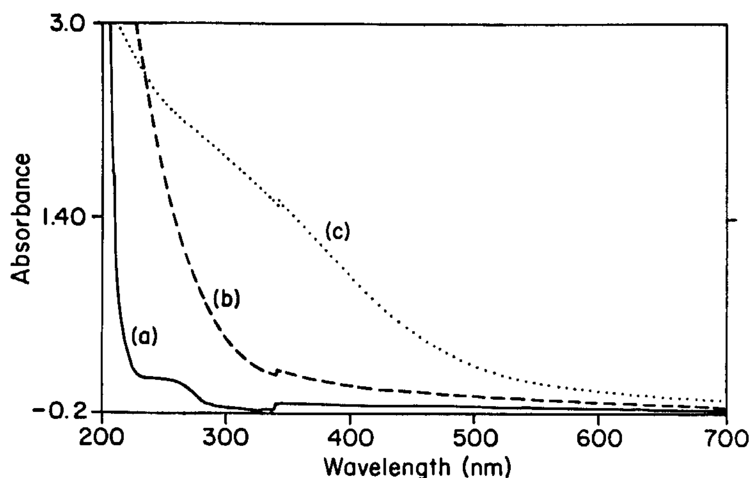
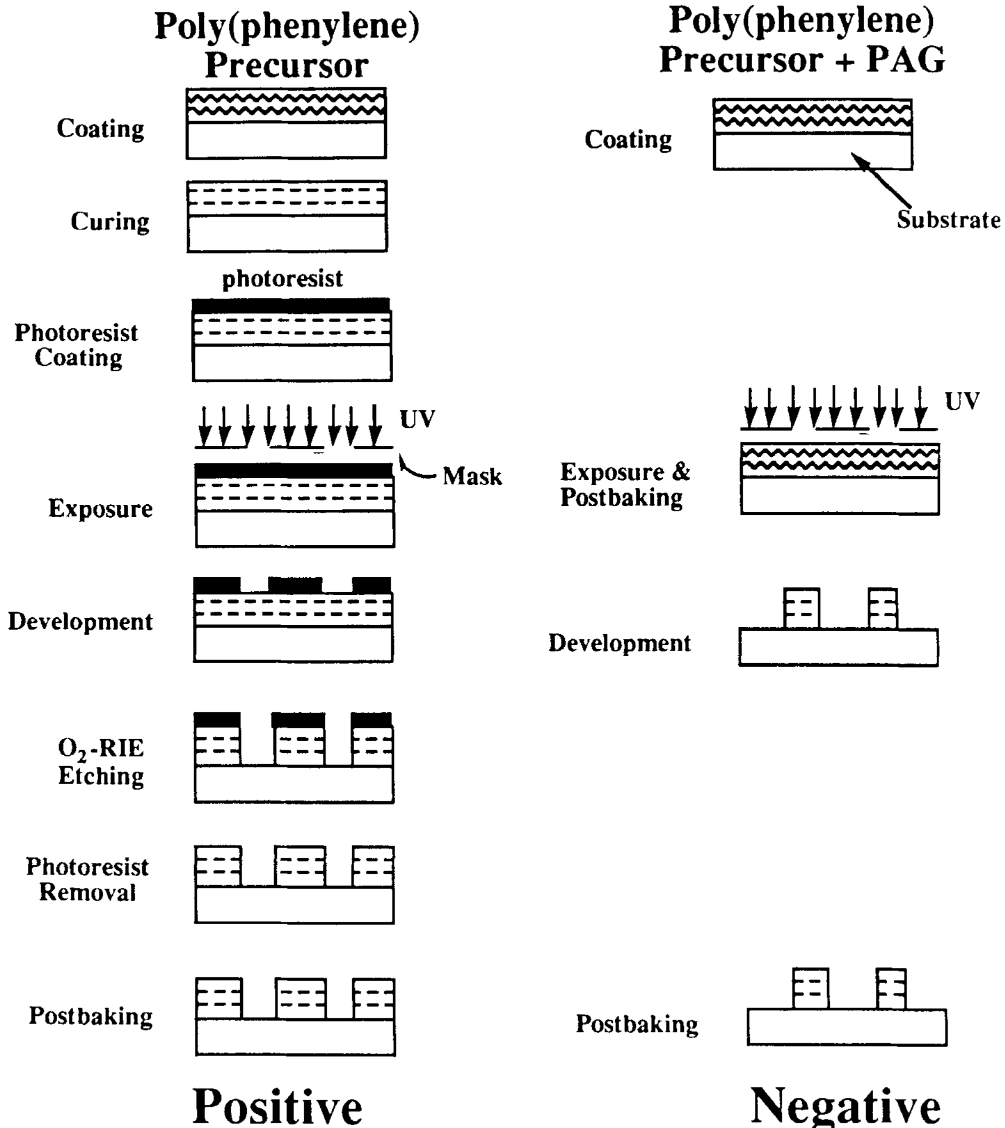


FIG. 8. UV absorption spectra of poly(1,2-diaceto-3,5-cyclohexadiene-*co*-styrene) after deep UV exposure (235–260 nm): (a) poly(1,2-diaceto-3,5-cyclohexadiene-*co*-styrene); (b) poly(1,2-diaceto-3,5-cyclohexadiene-*co*-styrene) with 10 wt% photoacid generator after UV exposure (70 mJ/cm^2) followed by postbaking at 140°C for 3 minutes; (c) poly(1,2-diaceto-3,5-cyclohexadiene-*co*-styrene) cured at 300°C for 6 hours.



SCHEME 3. Optical waveguide fabrication using conventional lithography of poly-(phenylene) and deep UV lithography of the diacetate precursor (PAG = photoacid generator).

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by O_2-reactive ion etching (O_2-RIE). Scanning electron micrographs show the resulting 2 μm-thick test pattern with relatively good resolution (Fig. 9).

Microfabrication was also achieved by deep-UV lithography with the photosensitive diacetate precursor as follows: the diacetate precursor and a photoacid generator of triphenylsulfonium antimony hexafluoride (1-5 wt% of precursor) were dissolved in diglyme or toluene, filtered through a 0.5-μm Teflon filter, and then coated onto a Si wafer. The resulting film was exposed to 105 mJ/cm^2 of

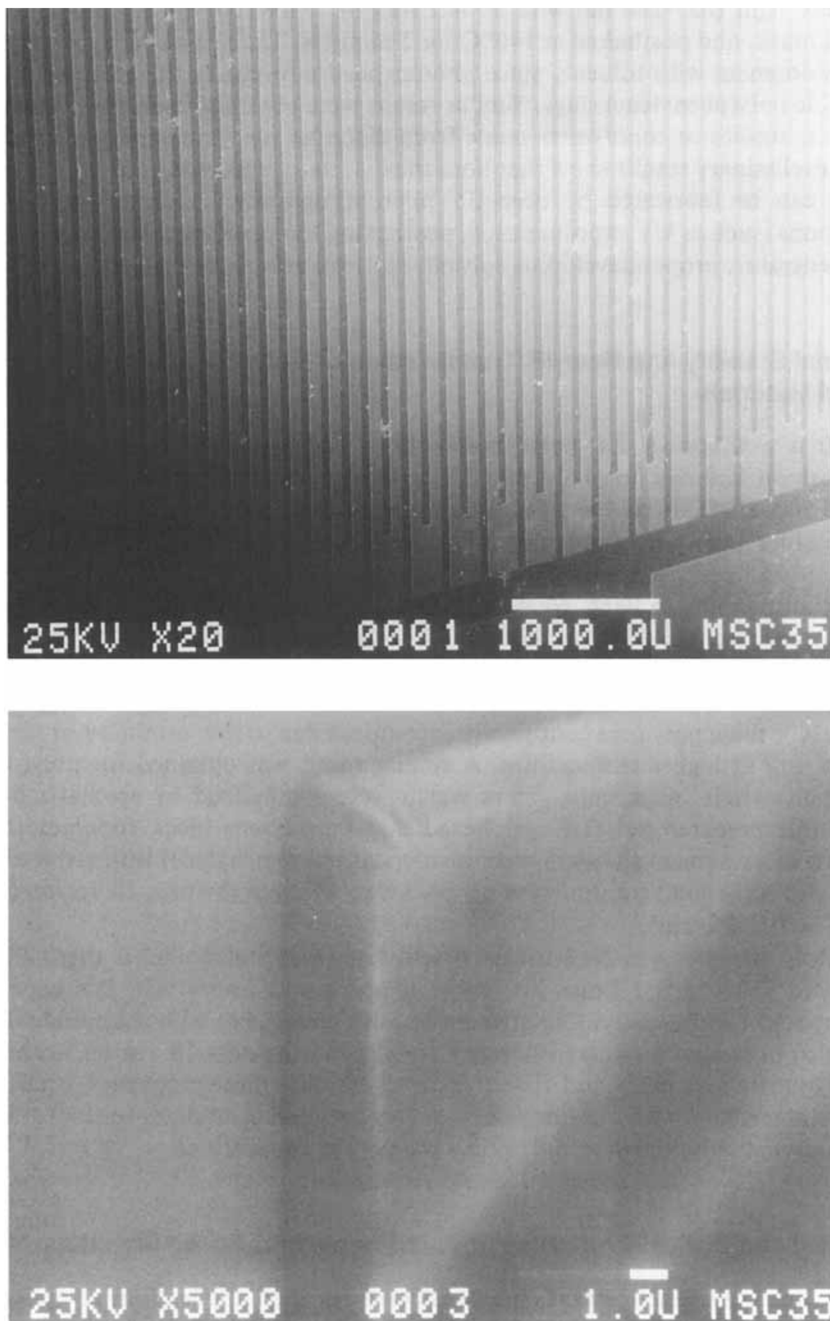

FIG. 9. Scanning electron micrograph of optical waveguide pattern fabricated by conventional microlithography (upper: magnification = 20×; lower: magnification = 5000×).

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deep-UV light (235–260 nm with an intensity of 7 mW/cm^2 at 254 nm) through a quartz mask, and postbaked at 140°C for 5 minutes. The test pattern was produced by development with toluene, since photoexposure results in the formation of the insoluble poly(phenylene) rings. Similar results were obtained in deep-UV-microlithographic studies of copolymers made from diacetate precursor and styrene derivatives. Preliminary results show that both the diacetate precursor or its styrene copolymers can be fabricated by deep-UV microlithography. Optimum performance conditions (such as UV exposure time, postbaking temperature, amount of a photoacid generator, proper developing solvent, etc.) are being investigated.

Thermal Stability and Near-IR Transmission of Poly(Phenylene)-Based Materials

It is well known that poly(phenylene) is remarkably resistant to thermal decomposition and oxidation. In practice, poly(phenylene) is stable to 450°C in air and to 500–550°C in an inert gas. A poly(phenylene) film, which was prepared by spin-coating poly(phenylene) precursors onto a quartz substrate and curing at 300°C for 6 hours, was stable to 450°C in nitrogen for at least 2 hours. It showed good transparency to light. Near-IR measurement showed that poly(phenylene) is highly transparent ($\gg$95%) in the near-IR region (wavelength = 0.8–2.2 μm).

In the case of copolymers of poly(phenylene) with styrene derivatives, these copolymers were thermally stable up to 300°C for 10 hours. At higher temperatures (>350°C), these polymers continually decompose due to the instability of the polystyrene unit at higher temperature. A similar result was obtained for poly(phenylene)–polystyrene block copolymers which were synthesized by aromatization of anionically prepared poly(1,3-cyclohexadiene)–polystyrene block copolymers [17]. Near-IR measurement shows that copolymers of poly(phenylene) with styrene derivatives also have good transmission properties (>95%) in the near-IR region (wavelength = 0.8–2.2 μm).

Poly(phenylene-*co*-*N*-(3-trifluoromethyl phenyl) maleimide) is thermally stable up to 350°C for 1 hour. At higher temperatures (>400°C), this copolymer decomposed continuously. Copolymers of poly(phenylene) with maleimide derivatives also possessed good transparency (>90%) in the near-IR region, with lower values of refractive index and dielectric constant. With these properties, copolymers of poly(phenylene) with maleimide derivatives are good candidates for low dielectric materials in microelectronic and optical waveguide applications.

Physical and Optical Properties of Poly(Phenylene)-Based Materials

When polymeric materials are considered for such applications as optical waveguides, a number of desirable properties must be present. Table 4 summarizes the physical and optical properties of several organic polymers as well as poly(phenylene). Optical properties are an important factor in waveguide applications while a low dielectric constant material is needed to reduce the electronic signal-delay time (T_D). The parameters are related by the following equation [18].

$$T_D = L\sqrt{\epsilon_r}/c \quad (2)$$

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TABLE 4. Physical and Optical Properties for Organic Polymers

Polymer	T_g, °C	CTE,[a] ppm/°C	Refractive index, n	Dielectric constant, ϵ_r
PTFE	130	20.0	1.35	2.0
Poly(methyl methacrylate)	106	–	1.49	2.6
Poly(phenylene) precursors	160-185	–	1.48-1.50	–
Epoxy resin	150	40-50	1.55-1.60	3.5
Poly(imide)	>285	8-45	1.63	3.0
Poly(phenylene-*co*-maleimide) (20/1)	~220[b]	–	1.66	3.23-2.92
Poly(phenylene)	230	–	1.68-1.72	3.67-3.53[c]
Poly(thiophene)	–	–	1.72	–

[a]CTE is defined as the coefficient of thermal expansion.

[b]T_g of poly(phenylene-*co*-maleimide) (20/1) was estimated from the equation of $(1/T_g) = (m_1/T_{g1}) + (m_2/T_{g2})$.

[c]Dielectric constant was measured in the frequency range of 0.01 to 10 MHz.

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where ϵr is the dielectric constant, L is the propagation length, and c is the speed of light. This relationship demonstrates that a low refractive index material will be required for the lowest dielectric constant possible.

The dielectric constant of the poly(phenylene) homopolymer is 3.53–3.67 over a frequency range of 0.1 to 10 MHz, as shown in Fig. 10. This indicates that poly(phenylene) has a dielectric constant comparable to polyimide. Copolymers of phenylene with maleimide derivatives have lower values of dielectric constant and

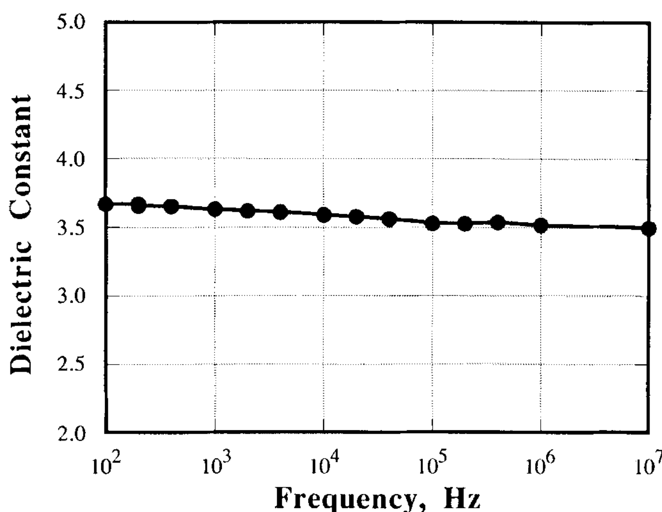

FIG. 10. Plot of dielectric constant for poly(phenylene) as a function of frequency (0.1–10 MHz).

refractive index than poly(phenylene) itself (see Table 4). For use in microelectronics, such polymeric materials should have a high glass transition temperature (T_g) (above 200°C) because the coefficient of thermal expansion (CTE) increases above T_g, a fact which might reduce dimensional stability during high temperature operations. The T_g of poly(phenylene) is approximately 230°C, which places this material in the range required for good dimensional stability.

In addition, a moisture-up take measurement of poly(phenylene) was undertaken using forward recoil spectroscopy (FRES) [4]. Moisture uptake was estimated by comparing the ratio of the hydrogen atoms (H) present in poly(phenylene) exposed to D_2O for 24 hours with the deuterium atom (D) concentration. A value of 0.8 wt% moisture uptake of poly(phenylene) was obtained. This value is much lower than the typical value of 3.5 wt% moisture uptake for polyimide. In progress are measurements of the mechanical and adhesive properties of poly(phenylene) and its copolymers as well as studies of their optical propagation loss.

SUMMARY

Poly(phenylene) and its copolymers are a new family of low dielectric materials with high thermal stability and good near-IR transmission. Their electronic and physical properties were modified in a controlled fashion by copolymerization of the diacetate monomer with both styrene derivatives and *N*-substituted maleimides. The resulting precursor copolymers are a new class of photoimageable polymers. The poly(phenylene) homo- and copolymer precursors could be imaged using deep-UV radiation in the presence of a photoacid generator. With a number of excellent properties, poly(phenylene)-based materials are promising candidates for linear waveguides with high thermal stability and low dielectric properties for use in optical interconnection systems.

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REFERENCES

[1] S. L. Lalama, J. E. Sohn, and K. D. Singer, *SPIE J.*, *578*, 168 (1985).
[2] R. Reuter, H. Franke, and C. Feger, *Appl. Opt. 27*, 4565 (1988).
[3] L. A. Hornak, T. W. Weidman, and E. W. Kwock, *J. Appl. Phys.*, *67*, 2235 (1990).
[4] T. Mates, C. K. Ober, B. Angelopolous, and H. Martin, *Mater. Res. Soc. Symp. Proc.*, *167*, 123 (1990).
[5] H. K. Kim, T. Mates, G. G. Barclay, and C. K. Ober, U.S. Patent Application.

[6] (a) J. M. Barrales-Rienda, J. I. Gonzalez De La Campa, and J. G. Ramos, *J. Macromol. Sci.—Chem., A11*(2), 267 (1977); (b) T. Hagiwara, T. Shimizu, T. Uda, H. Hamana, and T. Narita, *J. Polym. Sci., Polym. Chem. Ed., 28*, 185 (1990).
[7] (a) D. R. McKean and J. K. Stille, *Macromolecules, 20*, 1787 (1987); (b) D. G. H. Ballard, A. Courtis, I. M. Shirley, and S. C. Taylor, *Ibid., 21*, 294 (1988).
[8] J. Pacansky and J. R. Lyerla, *IBM J. Res. Dev. 23*(1), 42 (1979); (b) E. Reichmanis, F. M. Houlihan, O. Nalamasu, and T. X. Neenan, *Chem. Mater., 3*, 394 (1991).
[9] H. Hiramoto, *Mater. Res. Soc. Symp. Proc., 167*, 87 (1990).
[10] J. M. J. Fréchet, E. Eichler, H. Ito, and C. G. Willson, *Polymer, 24*, 995 (1983).
[11] H. Ito and M. Ueda, *Macromolecules, 23*, 2885 (1990).
[12] H. K. Kim and C. K. Ober, Unpublished Results.
[13] (a) P. Kovacic and J. Oziomek, *J. Org. Chem., 29*, 100 (1964); (b) Kovacic and L. C. Hsu, *J. Polym. Sci. Part A-1, 4*, 5 (1966).
[14] H. K. Kim and C. K. Ober, *Polym. Bull., 28*, 33 (1992).
[15] J. M. J. Fréchet, C. G. Willson, T. Iizawa, T. Nishikubo, K. Igarashi, and J. Fahey, *ACS Symp. Ser., 412*, 100 (1989).
[16] Private communication: Dr. D. R. McKean, IBM, San Jose, California.
[17] X. F. Zhong and B. Francois, *Synth. Met., 29*, 35 (1989).
[18] A. Takahashi, A. Nagai, A. Mukoh, M. Wayima, and K. Tsukanishi, *IEEE Trans. Components, Hybrids, Manuf. Technol., 13*, 1115 (1990).

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