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Acid-catalyzed photoaromatization of poly(cyclohexadiene-1,2-diol) derivatives into polyphenylene

Hwan Kyu Kim and Christopher K. Ober*

Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853-1501, USA

SUMMARY

Substituted poly(cyclohexene)s, used as poly(phenylene) precursors, have been 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 elevated temperatures or by deep-UV exposure in the presence of a photoacid generator. These reactions were investigated by both IR and UV analysis. Our results with the conversion of precursors into poly(phenylene) via photoaromatization suggest that polyphenylene precursors can be imaged by deep-UV microlithography (as a new class of photoimageable thermally stable polymers).

INTRODUCTION

Recently, we have explored the synthesis and characterization of poly(phenylene) via spin-coatable polymer precursors for use as optical waveguides. Optical waveguides are becoming increasingly important as communications media in advanced microelectronics. A number of very stringent criteria are placed on materials used in this application including tansparency over the transmission wavelengths of diode lasers, low propagation loss and compatibility with current microfabrication technology. We have observed that the poly(phenylene)s from soluble precursors have a number of desirable properties for optical waveguide applications including good near-IR transmission, low dielectric constant, thermal and environmental stability, and ease of pattern fabrication using lithographic techniques (1).

Previously, we reported that poly(phenylene), which was produced by thermal treatment of a soluble precursor, is thermally stable up to 450 °C and has dielectric permittivity at room temperature similar to polyimides (2). The poly(phenylene) precursors were prepared by radical polymerization of cyclohexadiene-1,2-diol derivatives containing various leaving groups including methyl carbonate and acetate functions. Several new leaving groups were studied and are described here including the successful introduction of isopropyl carbonate. Copolymers incorporating this monomer were synthesized and converted into polyphenylene.

The ability to be directly photoimaged makes polymers with potential as wavegudies even more intrinsically valuable since many waveguide fabrication steps can be eliminated. In this

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*To whom offprint requests should be sent paper, we will also discuss the production of polyphenylene via the acid catalyzed transformation of several spin-coatable polymer precursors. The precursors could be photoconverted into poly(phenylene) using UV exposure in the presence of a photoacid generator or cured via the introduction of methane sulfonic acid into cast films. The resulting changes in going from the unsaturated precursor polymer to the highly conjugated polyphenylene could be readily monitored by either UV or IR spectroscopy.

EXPERIMENTAL

1. **Materials** Acetyl chloride, methyl chloroformate, ethyl chloroformate, isobutyl chloroformate (Aldrich), and 3,5-cis-cyclohexadiene-1,2-diol (Sigma) were used as received. Azobis(isobutyronitile) (AIBN) was recrystallized from ethanol. Pyridine was distilled over NaOH. Other chemicals were used as received.

2. **Synthesis and Polymerization of Cyclohexadiene-1,2-diol Derivatives** (2,3) Monomer synthesis and polymerization were carried out with AIBN to yield polyphenylene precursors, as described in Reference (3). In a similar manner, copolymerization of diacetate monomer with iso-butyl carbonate monomer was carried out with AIBN at 60 °C for 48 hours. Precursors were characterized by standard techniques including gel permeation chromatography, IR and UV spectroscopy, NMR, and thermal analysis.

3. **Thermal Conversion of Precursors into Polyphenylene** A solution was prepared by dissolving polyphenylene precursor (0.2 g) into toluene (1.0 g). The solution was filtered through a 0.5-mm Teflon filter and then spin coated on various types of substrates such as NaCl disc for IR analysis, or quartz wafer for UV analysis at 1000 rpm for 30 seconds. The films were annealed at 300 °C for various times. The final films were analyzed by IR or UV spectroscopy.

4. **Acid-catalyzed Photoaromatization of Precursors into Polyphenylene** A solution was prepared by dissolving polyphenylene precursor (0.2 g) and triphenylsulfonium antimony hexafluoride (photoacid generator: 10 % wt.) into toluene (1.0 g). The solution was filtered through a 0.5-mm Teflon filter and then spin-coated on various types of substrates such as a NaCl disc (for IR measurement) or a quartz wafer (for UV measurement) at 1000 rpm for 30 seconds. The film 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.

RESULTS AND DISCUSSION

Synthesis of Polyphenylene Precursors Many characteristics are required in polymer materials to be able to apply them in for optical interconnect systems. Among these properties, an important factor is patternability. Principally two patterning processes (4,5) for polymeric materials, deep-UV microlithography and conventional microlithography, are used. Photosensitive materials which can be developed by deep-UV microlithography will reduce the number of processing steps, when compared with conventional microlithography of non-photosensitive materials. Such simplified processing would be a big advantage in the application of polymers as optical waveguides. For this reason, we have attempted to introduce photosensitivity into polyphenylene precursors. Diacetate and alkylcarbonate precursors have been synthesized as the photosensitive materials, because their structures have many similarities to *t*-BOC polystyrene (6) or poly(α-acetoxystyrene) (7). The results were summarized in Table 1.

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

monomer	diacetate monomer (M_1)	Et-carbonate monomer (M_2)	i-Bu-carbonate monomer (M_3)	$M_1 + M_3^\dagger$
yield, %	60.0	55.0	> 95.0	30.0
m_1/m_3^*	-	-	-	1 / 4
$M_n^{**} \times 10^{-3}$	35	20.2	< 0.3	7.3
M_w/M_n	1.84	1.94	-	1.64

†: copolymerization of an equimolar amount of comonomer $M_1 + M_2$ with AIBN at 60 °C for 2 days.
*: copolymer composition was determined by ^{1}H NMR.
**: molecular weights based on polystyrene standards.

Diacetate monomer (M_1) and diethylcarbonate monomer (M_2) polymerized very easily to produce homopolymer precursors. The yield of homopolymers was gravimetrically calculated and was in the range of 55 to 60 %. Molecular weights (M_n) based on polystyrene standards ranged from 20,000 to 40,000 g/mol with relatively low polydispersities (M_w/M_n <2.0) . Polymerization of di-i-butylcarbonate monomer (M_3) with AIBN at 60 °C yielded no polymer by GPC. The final product was analyzed by ^{1}H NMR and indicated that the final product was benzene iso-butylcarbonate. This result indicated that this monomer (M_3) was quite unstable and suggested that it had difficulty in polymerizing due to the steric hindrance between iso-butyl carbonate groups. Iso-butylcarbonate benzene can be formed by thermal decarboxylation through a six-membered ring intermediate. The same monomer (M3) however copolymerized with diacetate monomer (M_1) very easily. The yield of copolymer I was 30 % with the number average molecular weight (M_n) = 7,300 g/mol with a polydispersity (M_w/M_n) = 1.6.

Thermal Conversion of Precursors into Polyphenylene The resulting polyphenylene precursors could be aromatized by heating in film form. The thermal processes were monitored by thermogravimetric analysis (TGA), IR spectroscopy, and UV spectroscopy. The TGA analysis of diethylcarbonate precursor was consistent with the value expected for the loss of two carbonate groups followed by aromatization. The residue was quite stable for several hours at elevated temperatures. The reaction probably proceeds via a cyclic transition state, since both the methlycarbonic acid or the carboxylic acid are good leaving groups. The former group probably decomposes into ethanol and carbon dioxide (3). Similar TGA results were obtained for both the diacetate and the copolymer precursors.

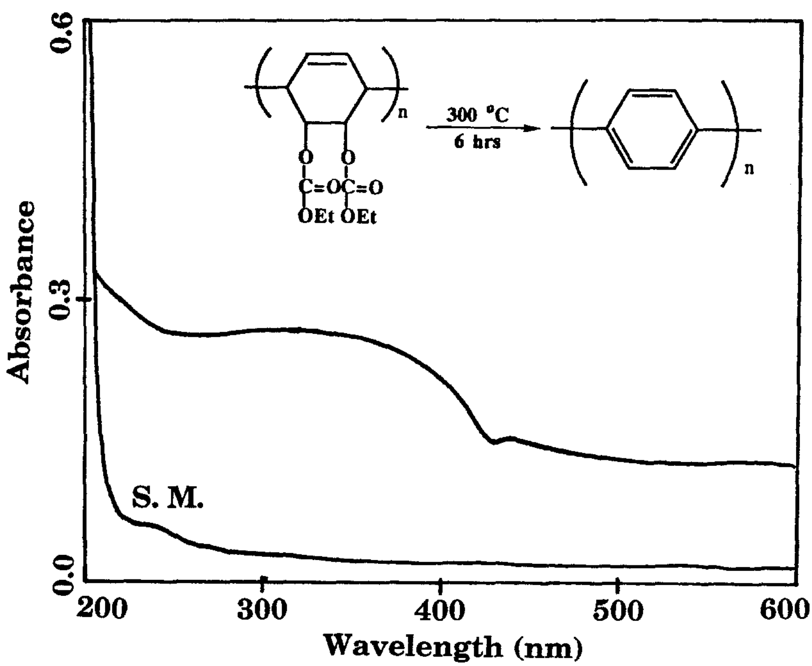


Fig. 1. UV Spectrum of Polyphenylene Obtained from Heat-treatment of Diethylcarbonate Precursor on a Quartz Film.

IR data of the polyphenylene prepared from thermally aromatized diethylcarbonate precursor showed at 812 cm^{-1} the C-H out-of-plane bending band of the phenyl groups. Spectra of polyphenylene oligomers show an absorbance between 840 and 800 cm^{-1} for the C-

H out-of-plane bending band of the phenyl groups. As the number of consecutive phenylene units increases, this peak shifts to lower wavenumbers and attains a limiting value of 802 cm^{-1} for highly conjugated polymer (8). When compared with the IR spectra of poly(phenylene) oligomers, the polyphenylene produced in this study consists of approximately six consecutive phenylene units separated by unaromatized sections. These unaromatized sections, the precise structure of which is unknown, are perhaps due to the 1,2-repeat unit structure found in the precursor. Similar IR data were obtained from pyrolysis of diacetate precursors and copolymer precursor.

The typical UV spectrum of the polyphenylene prepared from diethylcarbonate precursor which had been pyrolyzed at 300 ^{o}C for 6 hours is shown in Fig. 1. The UV spectrum showed a maximum absorption around 320 nm tailing into the visible region. The UV absorption, like the IR spectrum, depends on the number of the consecutive phenylene rings. The UV absorption increases with increasing number of consecutive phenylene rings and shifts toward 380-390 nm for the highly conjugated polymer. When compared with UV spectra of polyphenylene oligomers, this polyphenylene again has approximately six consecutive phenylene units which is consistent with the value obtained from IR data.

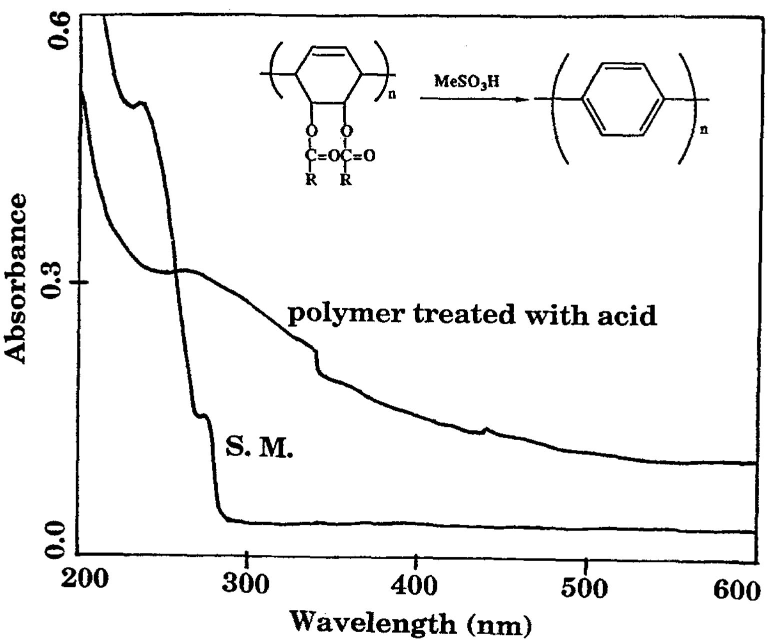


Fig. 2. UV Spectrum of Polyphenylene Obtained from Acid-catalyzed Aromatization of Diethylcarbonate Precursor with Methanesulfonic Acid on a Quartz Film.

Acid-catalyzed Photoaromatization of Precursors into Polyphenylene Since the structures of diacetate precursor and alkylcarbonate precursors resemble *t*-BOC polystyrene or poly(α-acetoxystyrene), we would expect that they should be susceptible to acid-catalyzed thermolytic conversion. The films of diacetate precursor and diethylcarbonate precursor prepared by spin-casting were dipped into methanesulfonic acid, washed with water, and then dried at 90 °C for 3 minutes. The final product was analyzed by UV spectroscopy. The resulting UV spectrum (Fig. 2) showed that the final product absorbed in the ultraviolet region tailing into the visible. This absorption behavior indicates that both the diacetate precursor and the diethylcarbonate precursor were catalyzed by the strong acid to produce polyphenylene.

Instead of an acid introduced by diffusion into a thin film of precursor, we can introduce a strong protonic acid from a photoacid generator (4(b),6,7), which yields an acid upon deep-UV exposure. Both the diacetate precursor and diethylcarbonate precursors were subjected to deep-UV radiation (wavelength(λ): 235-260 nm) in the presence of an equimolar amount of a photoacid generator (triphenylsulfonium antimony hexafluoride) to yield polyphenylene. This reaction is not significantly affected by various leaving groups and therefore appears to proceed through acid-catalyzed photoaromatization. A typical UV spectral change as a function of exposure time is shown in Fig. 3. The figure also showed that 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).

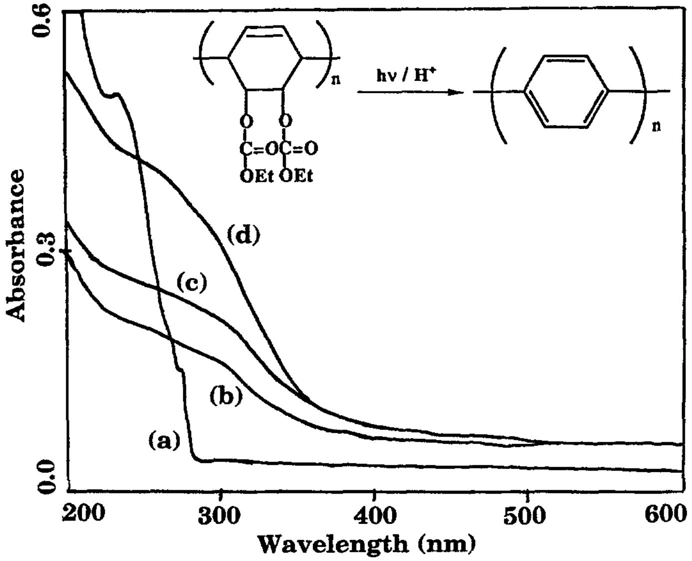
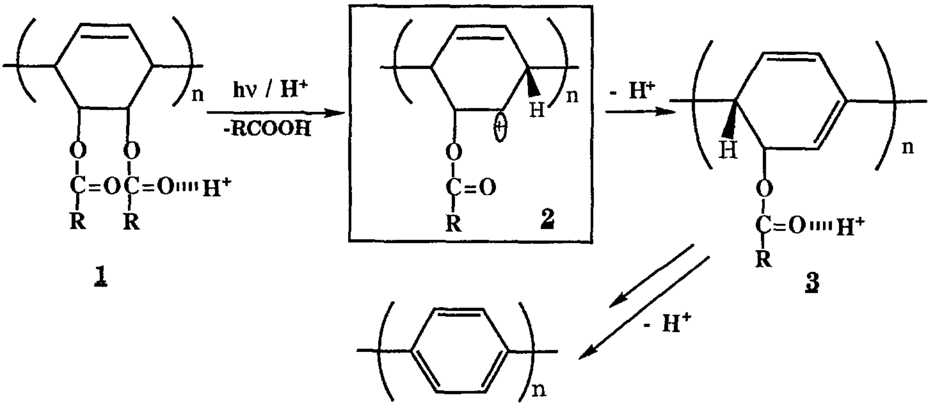


Fig. 3. UV Spectra of Diethylcarbonate Precursor with a Photoacid Generator as a Function of the Deep-UV Exposure Time, (a) 0mJ/cm^2; (b) 18 mJ/cm^2; (c) 36 mJ/cm^2; (d) 54 mJ/cm^2.

This photoaromatization process probably proceeds through carbocationic moieties, as shown in Scheme 1. Scheme 1 shows the E1-like elimination which may prevail in the case of the acid-catalyzed photocuring conversion, similar to the acid-catalyzed thermolytic cleavage of polycarbonates or polyesters (9). The reaction starts with protonation of a carbonyl group in either a carbonate group or an acetate group to afford intermediate **1**. This intermediate is then converted by formation of carbocationic moiety **2** and RCOOH. Elimination of a proton from the carbocationic moiety results in regeneration of the acid catalyst and the formation of a diene-containing polymer **3**. This process continues to occur on the remaining leaving groups with the eventual formation of polyphenylene. The protons initially produced by UV irradiation are regenerated in the process and explain the chemical amplification of this resist material.



Scheme 1. Mechanism of the Acid-catalyzed Photoaromatization of Polyphenylene Precursors into Polyphenylenes.

CONCLUSIONS

The precursor polymers based on substituted poly(cyclohexadiene-1,2-diol) can be readily converted into polyphenylene by deep-UV exposure in the presence of a photoacid generator. This capability renders the precursor polymers imageable by deep-UV microlithography and the polyphenylene precursors are therefore a new class of photoresist materials. Our previous investigations suggest that polyphenylene is a good candidate for both thin film dielectric and optical waveguide applications in microelectronics, and these studies are continuing.

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