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A comparative thermogravimetric study of polymers designed as dry-developing photoresists

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ABSTRACT

We report a thermogravimetric study of the uncatalyzed and photo-acid-catalyzed decomposition of a series of polyformals and polycarbonates. Some of these polymers have previously been proposed as solventless photoresists. Such polymers should decompose at much lower temperatures when heated in the presence of strong acid than when heated in the absence of acid. In addition, decomposition should lead only to volatile break-down products. We found that most of these polymers underwent clean uncatalyzed thermal decomposition. When heated in the presence of acid, the onset of thermal decomposition occurred at much lower temperatures, as expected, but was accompanied by formation of significant amounts of non-volatile product. We also found that the extent of acid-catalyzed cross-linking (i.e., formation of non-volatile product) in the benzylic polyformals was greater than that for benzylic polycarbonates.

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1. Introduction

Polymers that can be chemically modified by post-synthesis processing have many useful applications, including coatings, cross-linking agents, blowing agents, imaging materials, adhesives and as additives for post-reaction within preformed polymers. Polymers used as photoresists for microelectronic device fabrication represent one such class of materials. Over the past several decades, the development of new photo and electron beam resist materials with improved properties has proceeded at a fast pace as various laboratories strive to implement a variety of new conceptual designs. From our perspective, in the context of the experiments described in this paper, the most relevant early work is the radiation induced depolymerization of poly(phthalaldehyde) [1,2], the thermolytic cleavage of poly(4-*t*-butoxycarbonyloxystyrene) [3,4] and simple *t*-BOC derivatives of alcohols, phenols and enols [5] based on the known acid-catalyzed decomposition of *t*-BOC group.

A major transformation of photoresist technology took place following the invention of chemically amplified photoresists by Fréchet, Willson and Ito in the 1980's. In this strategy, chemical amplification [6] is the result of a photoinitiated catalytic reaction. Imaging is accomplished through irradiation of a film of the polymer (resist film) containing a small amount of a photoactive compound (a photoacid generator, PAG) that generates acid upon irradiation. The acid leads to a catalytic decomposition of the polymer upon heating. For positive resists the acid leads to catalytic decomposition of the polymer upon heating. The product of the decomposition has enhanced solubility in base. For many negative resists; the acid catalyzes a cross-linking reaction. In other systems, it leads to a polarity change so that the unexposed region dissolves preferentially. The acid produced by exposure to light acts as a catalyst and is not consumed stoichiometrically in the reaction process. It is this property which leads to chemical amplification, as each photochemically produced molecule

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of acid can cleave a large number of active bonds before being eventually destroyed in an occasional terminating side reaction. The topic of chemical amplification in photoresists has been reviewed by Ito in 2003 [7], and in 2005 [8].

In the late 1980's, these authors extended the idea of chemical amplification to solventless photoresists [9,10]. These types of photoresists are typically polycarbonates or polyformals, which when heated in the presence of acid, decompose to volatile products. If all of the breakdown products are volatile, a negligible amount of residue would remain. For positive photoresists, photo-irradiation of this kind of polymer film, followed by heating, should lead to exposure of a bare substrate. This type of property was also reported for a series of polyphthalaldehydes [11,12]. The performance requirements for a truly solventless photoresist are very stringent. Among the reasons for lack of implementation were concerns about possible contamination of the exposure device by residual non-volatile by products, and image quality. One reason suggested for the lower image quality was the decrease in film thickness, which was greatly reduced due to the loss of volatile by products from the exposed areas [10]. A reviewer commented that many of the problems with thermal processing were overcome by incorporating Si in polyphthalaldehyde, providing an all-dry bilayer resist system. The reason this approach was not adopted was that it was too drastically different from the industry standard technology employing aqueous base as a developer, and that it did not demonstrate competitively high resolution.

More recently, Kohl et al. reported a study of the photoacid catalyzed thermal decomposition of poly(propylenecarbonate) [13]. They found that in the presence of certain photoacid generators, particularly a diaryliodonium derivative, they could obtain acid-catalyzed thermal decomposition with little non-volatile residue. Another recent report described a dry-developing photoresist based upon thin films of a relatively low molar mass dye molecule [14]. This naphthoquinone derivative sublimed at ca. 105 °C, whereas its photorearrangement product required much higher temperature. It was shown to act as a negative photoresist capable of generating sub 100 nm patterns. Another recent report describes photoresists based on photoacid-induced main chain scission of polycarbonates. Here the authors employed liquid development (isopropyl alcohol or aqueous base), rather than dry development, for pattern development [15]. White and Henderson [16] used a dry-developing photoresist for fabrication of 90 μm channels in a microfluidic device. Their polymer was an alternating copolycarbonate of a norbornene derivative and 2,5-dimethylhexane-2,5-diol. They carried out the photoexposure of this polymer in the presence of a sulfonium salt as the photoacid generator.

We are interested in photopatterning of polyformal and polycarbonate thin films, with micrometer resolution, under dry development conditions, following photoexposure at 248 nm (excimer laser) or 266 nm (Nd:YAG laser). As a step toward reaching this goal, we have reinvestigated the photo-induced, heat-activated, acid-catalyzed decomposition of a number of different polyformals and polycarbonates with the idea of obtaining a better understanding of the photothermal decomposition process and its limitations. Relying primarily on thermal gravimetric analysis (TGA) as our analytical tool, we compare the acid-catalyzed and uncatalyzed thermal decomposition of these polymers.

The polyformals were synthesized by phase transfer catalysis through the reaction of diols with excess dibromomethane in the presence of tetrabutylammonium bromide plus aqueous base. The polycarbonates were synthesized by reacting an activated diol with one equivalent of diol in solution in the presence of 18-crown-6 plus anhydrous potassium carbonate. These syntheses follow procedures described by Fréchet and coworkers [9,10,17]. The polyformal synthesis was originally developed by Cameron and Law [18], and later extended by Percec et al. [19,20].

2. Experimental section

2.1. Instrumentation

All 1D (^{1}H and ^{13}C) and 2D NMR spectra were acquired in deuterated chloroform on a Varian 400 or a Varian Mercury 300 spectrometer. Mass spectra were obtained with an AB/Sciex QStar mass spectrometer. Elemental analysis was carried out with a 2400 Series II CHNS Analyzer. Molecular weights, relative to polystyrene standards, were measured by gel permeation chromatography (GPC) using a Viscotek™ VE 2001 GPC Solvent pump, TDA 302 Triple detector array. The measurements were carried out at 35 °C with tetrahydrofuran (THF) as the eluting solvent with two ViscoGEL™ Columns (GMHHR-M and GMHHR-H). The flow rate was 0.6 mL/min and the injected volume was 100 μL. Thermogravimetric analysis (TGA) was performed on a TA-Instruments TGA Q500, with a heating rate of 10 °C/min in a nitrogen atmosphere.

2.2. Materials

All chemicals were of the highest purity available. The tetrabutylammonium bromide (TBAB), and 18-crown-6 were purchased from Fluka whereas 4-(phenylthiophenyl)diphenyl sulfonium triflate (1), potassium carbonate, 4-nitrophenylchloroformate, 1,1′-carbonyldiimidazole (CDI), cyclohexane-1,4-diol (2a) (mixture of *cis* and *trans* isomers), 1,4-phenylenedimethanol (2d), 1,3-phenylenedimethanol (2e), pyridine, 4-dimethylaminopyridine (DMAP), dichloromethane and dibromomethane were purchased from Aldrich, Canada. 1,1′-(1,3-Phenylene)diethanol (2c), 1,1′-(1,3-Phenylene)bis(ethane-1,1-diyl) bis(4-nitrophenyl) dicarbonate (3c), cyclohex-2-ene-1,4-diol (2b) (*trans* isomer), and 1,2,3,4-tetrahydronaphthalene-1,4-diol (2f) (mixture of cis and *trans* isomers) were purchased from SynDesign Inc., USA (http://www.syndesign.net). In addition, a sample of the polycarbonate C_{bd} (by GPC, M_w = 11000; M_w/M_n = 4.7) was also purchased from SynDesign. THF was purchased from ACP Chemicals Inc., Montreal, Canada. The 18-crown-6, tetrabutylammonium bromide (TBAB) and all liquid reagents were used as received, except dichloromethane, which was dried by distillation over CaH_2.

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