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Development of improved photosensitive polycarbonate systems for the fabrication of microfluidic devices

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A technique was recently developed for the fabrication of microfluidic devices that involves using thermally sacrificial polymeric materials in conjunction with other conventional microelectronic processes. This method provides more versatility and choice for construction materials than other current techniques, and it enables the integration of higher levels of functionality into microfluidic systems (i.e., fully integrated multilevel fluidic systems with functional valves, pumping systems, other microelectromechanical system components, and microelectronic devices). This article describes recent results related to the development of photodefinable polycarbonates with improved properties for thermally sacrificial polymer applications. Results of the synthesis and characterization of a polycarbonate that can be directly patterned with the use of photoacid generators via acid-catalyzed thermolysis of polycarbonates are presented. © 2003 American Vacuum Society. [DOI: 10.1116/1.1622934]

I. INTRODUCTION

A. Microfluidic fabrication techniques

The need for innovative fabrication methods that allow for the integration of higher levels of functionality into microfluidic and lab-on-a-chip devices is growing almost as rapidly as the number of applications for these miniature devices. The ability to make fully integrated, multilevel fluidic systems that incorporate microelectromechanical and microelectronic components is essential for this field to reach its full potential. While lab-on-a-chip devices have shown commercial viability in a variety of biological applications, such as electrophoretic separations and deoxyribonucleic acid (DNA) sequencing, there has not been as much progress in other potential impact areas such as clinical diagnostics, portable sensors, and microchemical reactors. These applications can benefit greatly from miniaturization, but advancement in these and other areas has been limited by the inability or extreme difficulty in fabricating devices with complex fluidic networks interfaced with a variety of active and passive electrical and mechanical components. There are a variety of limitations associated with the two most prevalent device fabrication techniques, which involve the bonding of either patterned glass¹ or elastomeric polymer² layers. While these two fabrication methods have been used in microfluidic applications, and processes and devices are being developed to extend the use of these methods, such fabrication techniques possess limited capabilities for many applications. The bonding of glass plates together leads to an obvious source of defects and low device yields² and building onto structures that have large surface topographies is impossible due to the requirement that the layers be extremely flat. Layering of elastomeric polymers, such as poly(dimethylsilox-

ane), has some distinct advantages over the glass bonding methods including the use of simple and inexpensive materials and tools. However, the surface chemistry of these materials must be tightly controlled in order to achieve effective layer bonding, and such materials are often incompatible with organic solvents and low molecular weight organic solutes. Finally, such rubbery materials are generally incompatible with processes requiring elevated temperatures.³

A technique was recently developed that utilizes thermally sacrificial polymer materials for the fabrication of microchannels and which offers several advantages over current methods (Fig. 1).⁴ This process eliminates the need for bonding of various prepatterned layers. Instead, it employs the sequential layer build-up methods developed for integrated circuit (IC) fabrication. This compatibility with IC processes provides all of the mass fabrication advantages of such methods and more flexibility with respect to the integration of different materials. In addition, since it is possible to process and build fluidic devices directly on functional IC devices, this method provides the ability to fabricate devices with high levels of electrical and mechanical functionality. Originally developed using functionalized polynorbornene polymers (PNB), the process begins by coating a thermally sacrificial polymer onto a substrate and patterning this polymer into the shape of the desired channels and devices. These polymeric structures are then overcoated with a permanent structural material, such as an inorganic glass or polymer. These steps can be repeated to produce complex, multilayered, three-dimensional systems. Finally, the completed device structure is heated to the decomposition temperature of the sacrificial polymer (e.g., 425 °C for the original PNB materials), at which point the sacrificial material volatilizes to leave behind the desired open-channeled structures.

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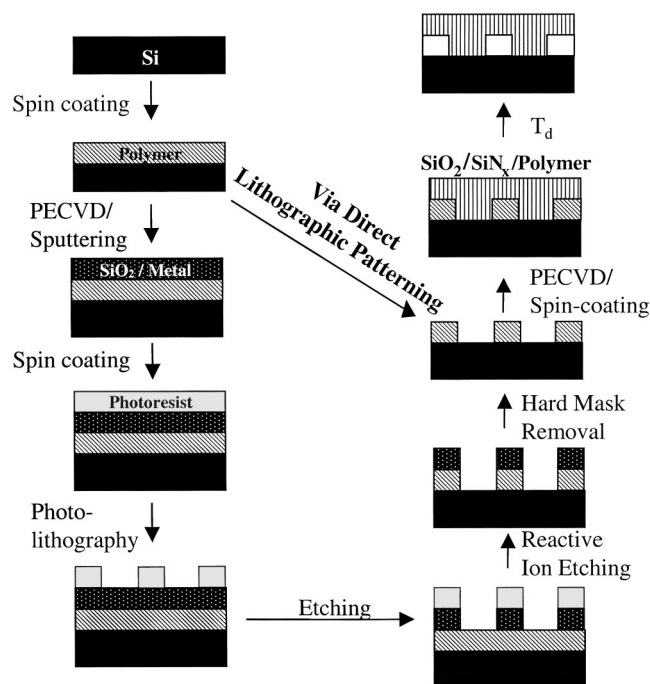


FIG. 1. Process flow of microchannel fabrication utilizing sacrificial polymers. As shown, the fabrication process is greatly simplified when a photosensitive sacrificial material is used.

B. Materials for fabrication utilizing sacrificial polymers

Two disadvantages exist with the original sacrificial polymer fabrication process based upon the use of PNB: (1) complex patterning of the sacrificial polymer and (2) the high temperatures at which the device must be heated in order for the sacrificial polymer to cleanly decompose. While these limitations do not restrict the use of the original PNB materials for the microelectronics industry,^{4,5} they place substantial constraints on their use in microfluidic device fabrication. Ideally, materials and processes used in lab-on-a-chip technologies should be both cost efficient and amenable to high-throughput fabrication so that inexpensive and potentially disposable devices can be made. The multistep patterning process required in the original process flow (see Fig. 1) is particularly time consuming and requires the use of expensive plasma etching equipment. In addition, the high temperature needed for the decomposition of PNB greatly limits the number of substrate and structural materials that can be used. Many cost-effective fabrication materials, such as plastic substrates and polymer encapsulating materials, degrade below or near the 425 °C decomposition temperature of PNB.

As is shown in Fig. 1, the first of these limitations can be overcome by simply using photosensitive sacrificial materials. This has been shown to greatly simplify the fabrication process by developing and examining photosensitive PNB materials.⁶ Photosensitive sacrificial materials also provide the opportunity to utilize gray-scale lithographic methods to produce complex structures that are indeed structured in all three dimensions.⁶ In order to make this approach compatible

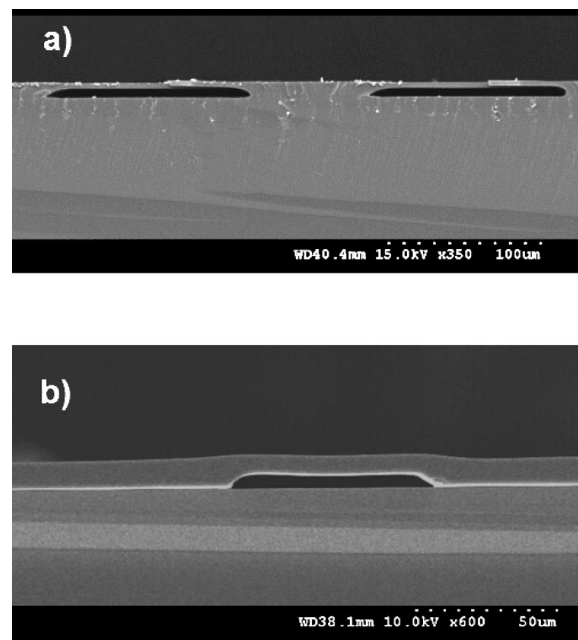


FIG. 2. (a) Microchannels fabricated using PPC (see Ref. 7). Here, the overcoat material is bisbenzocyclobutene and the substrate is a silicon wafer. (b) Microchannels fabricated with a sacrificial PPC/PAG system using an Avatrel 2000P (Promerus Electronic Materials) dielectric polymer overcoat (see Ref. 10).

with a wider range of device materials, polymers with lower decomposition temperatures are needed. Polycarbonates (PCs) were identified as a class of polymers that can decompose cleanly and possess the desired lower decomposition temperatures (200–300 °C). Preliminary studies of poly(propylene carbonate) or (PPC) showed promising results [Fig. 2(a)],⁷ but PPC still requires the complex multistep processing to create the desired structures.

C. Polycarbonate systems as photosensitive sacrificial materials

One approach to create photosensitive PCs involves incorporating cross linkable groups into the PC, thus making a negative-tone system. While negative-tone materials are useful for some applications, it was deemed more attractive to make a positive-tone system by loading the polymer with an additive that promotes the photochemically activated breakdown of the polymer. PCs are known to undergo acid-catalyzed decomposition,⁸ and loading PCs with a photoacid generator (PAG) has been shown to drastically reduce their decomposition temperature.⁹ PPC was loaded with a PAG to examine its usefulness in this type of direct photopatterning process [Fig. 2(b)].¹⁰ While it has been demonstrated that PPC can be used to produce microchannels, the use of the material is still limited by its low glass-transition temperature (T_g) which is less than 40 °C. This low T_g leads to deformation of the patterned structure when elevated temperatures are needed during subsequent processing of the device. Therefore, a variety of sacrificial polycarbonate structures and synthetic routes to produce such materials have been examined.

While aliphatic PCs are traditionally synthesized by copolymerizing CO₂ and an epoxide in the presence of an organometallic catalyst at high temperatures and pressures,¹¹ a different PC synthesis was identified as a more attractive approach for quickly producing and screening a range of different PC structures. Frechet and co-workers⁹ used a solid-liquid phase transfer catalysis to synthesize PCs at low temperature and pressure by reacting an activated diol monomer with a second diol in the presence of 18-crown-6, potassium carbonate (K₂CO₃), and an organic solvent.⁹ In addition to the milder reaction conditions, this route has an added advantage over the traditional synthesis in that it quickly provides for greater degrees of functionality due to the wide variety of diols commercially available and the ability to produce a well defined PC "terpolymer." Such terpolymers are possible using only two monomers, since CO₂ is not used directly (the carbonate linkage is formed in the polymerization), and the polymerization produces an alternating comonomer structure. This inclusion of multiple monomers with strict control over polymer architecture is not possible with the conventional high-pressure polymerization. Therefore, the synthetic route used in this work provides a convenient pathway for producing a variety of polymers that can be used to optimize the thermal and imaging properties of the photosensitive PC system.

II. EXPERIMENTAL PROCEDURES

A. Materials

The following materials were purchased from Sigma-Aldrich (St. Louis, MO) and used as received: PPC [*M_w* = 50 000], ethyl acetate, hexane, carbonyl diimidazole (CDI), potassium metal, anhydrous dichloromethane, 2,5-dimethyl-2,5-hexanediol, and anhydrous potassium carbonate. Tetrahydrofuran (THF) was purchased from Aldrich and dried over alumina. 18-crown-6 and 5-norbornene-2-endo-3-endo-dimethanol were purchased from Sigma-Aldrich and purified by recrystallization from acetonitrile and sublimation, respectively. The PAG used in this work, triphenylsulfonium tris(perfluoromethanesulfonyl) methide (TPS-C1), was obtained from 3M Corporation (St. Paul, MN) and used as received.

B. Synthesis of polycarbonate

1. Synthesis of the bis(imidazole carboxylate) of 2,5-dimethyl-2,5-hexanediol

To a solution of 10.08 g (69.0 mmol) of 2,5-dimethyl-2,5-hexane diol in 100 ml dry THF, 0.28 g (7.16 mmol) of potassium metal was added under an argon atmosphere. After refluxing this solution until all of the potassium had dissolved, the solution was transferred to a solution of 24.53 g (151.28 mmol) CDI in 80 ml dry THF using standard Schlenk line techniques. The stirred reaction was refluxed for 90 min. After cooling to room temperature, the reaction mixture was concentrated to approximately 100 ml using a rotary evaporator. The solids were dissolved with 150 ml of ethyl acetate, and the organic solution was washed twice with 50

ml 5% HCl solution and three times with distilled water (50 ml for each wash). The organic layer was dried over magnesium sulfate, filtered, and the solvent was removed using a rotary evaporator. The white solid product was then recrystallized using ethyl acetate and hexane (1:1 volume mixture). The purified product was obtained in a 79.0% yield (18.22 g) and confirmed as the desired product by elemental and spectroscopic analysis.

a. Elemental analysis Found (C: 57.65, H: 6.74, N: 16.59); Theory (C: 57.47, H: 6.63, N: 16.59).

¹H-NMR (CDCl₃): 1.60 ppm (s, 12H, CH₃), 2.00 (s, 4H, CH₂), 7.04 (s, 2H, CH imidazole), 7.35 (s, 2H, CH Im), 8.06 (s, 2H, CH Im).

¹³C-NMR (CDCl₃): 26.18 ppm (CH₃, HD), 34.62 (CH₂, HD), 87.06 (C, HD), 117.30 (CH, Im), 130.64 (CH, Im), 137.24 (CH, Im), 147.17 (C=O).

1. Synthesis of polymer I

A mixture of 5-norbornene-2-endo-3-endo-dimethanol (3.92 g, 25.4 mmol), the bis(imidazole carboxylate) of 2,5-dimethyl-2,5-hexanediol (8.50 g, 25.4 mmol), a catalytic amount of 18-crown-6 (0.53 g), 42 ml of anhydrous dichloromethane, and an excess of K₂CO₃ (12.7 g) was prepared under an inert atmosphere. The reaction was stirred and refluxed at 40 °C for 41 h. The mixture was diluted with 50 ml CH₂Cl₂. The resulting suspension was centrifuged for 20 min. After decanting the solution, the residue was washed an additional two times with 50 ml of fresh CH₂Cl₂, filtered, and the filtrate was added to the decanted solution. The combined solutions were concentrated to approximately 10 ml on a rotary evaporator. The polymer was then precipitated three times in methanol and dried *in vacuo*. The desired product was obtained and confirmed by elemental and spectroscopic analysis.

a. Elemental analysis Found (C: 64.50, H: 8.11); Theory (C: 64.75, H: 8.01).

¹H-NMR (CDCl₃): 1.33 (d, 1H, CH₂ norbornene bridge), 1.46 (s, 12H, CH₃ HD), 1.51 (d, 1H, CH₂ NB bridge), 1.83 (s, 4H, CH₂ HD), 2.56 (s, 2H, CH—CH₂O NB), 2.95 (s, 2H, CH-bridge NB), 3.70 (m, 2H, CH₂—O NB), 3.87 (m, 2H, CH₂—O NB), 6.19 (s, 2H, HC=CH NB).

¹³C-NMR (CDCl₃): 25.70 (CH₃, HD), 34.30 (CH₂, HD), 40.53 (CH—CH₂O, NB), 45.27 (CH-bridge, NB), 49.00 (CH₂, NB bridge), 67.01 (CH₂—O NB), 83.53 (C, HD), 135.47 (HC=CH NB), 153.23 (C=O).

C. Characterization of polymer

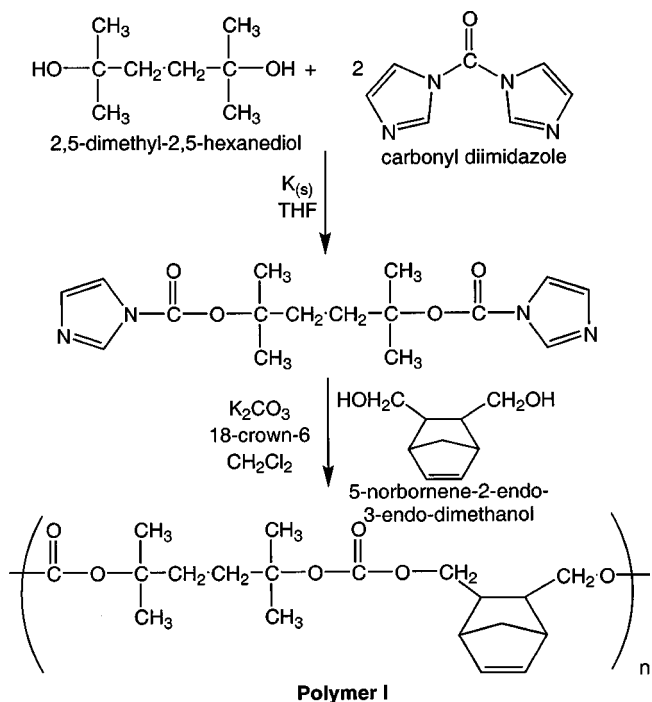
Nuclear magnetic resonance (NMR) spectroscopy was accomplished using a Varian Gemini 300 MHz instrument. Scanning electron microscope (SEM) pictures were obtained using a Hitachi 3500H SEM. Thermal decomposition temperatures were determined using a TA Instruments Q500 thermogravimetric analyzer with a constant heating rate of 10 °C/min and a sample size of approximately 15 mg. The glass transition temperatures were determined with a TA Instruments Q100 differential scanning calorimeter (DSC) in Conventional Modulated differential scanning calorimetry

mode. The heating rate was 3 °C/min and the temperature was modulated using an amplitude of 1 °C and a period of 60 s. Approximately 7 mg of polymer were used and the T_g reported is the inflection T_g (i.e., midpoint at half heat flow).

Imaging experiments were performed by contact printing using an Oriel Instruments 500W Oriel 87000 Series Hg–Xe flood exposure tool in a base-filtered cleanroom environment. This base-free environment is an important condition for properly characterizing the fundamental properties of such materials since trace amounts of basic species in normal room air (i.e., amines, etc.) can quickly neutralize the relatively small amounts of acid in these materials and thus alter the ability to observe the desired acid-catalyzed phenomena. Films were spin cast onto silicon (100) wafers using a Cost Effective Equipment (CEE) 100 CB spin coat and bake system at thicknesses on the order of 6 to 10 μm . After prebaking the spin-coated wafer using the CEE 100 CB hot plate at 90 °C for 5 min to remove residual casting solvent, ultraviolet exposure was performed using a resolution test pattern. After exposure, the wafer was baked at a temperature which induced acid-catalyzed decomposition (115 °C for PPC, 80 °C for polymer I). Any residue remaining on the wafer was removed by washing with isopropanol.

III. RESULTS AND DISCUSSION

The synthetic route used to synthesize Polymer I is depicted in Scheme 1. As mentioned previously, this reaction occurs at low temperature and pressure, 40 °C and 1 atm, respectively. It also does not require an organometallic catalyst which could leave traces of metallic species upon de-



Scheme 1. Synthetic route used for the formation of Polymer I. The reaction occurs at atmospheric pressure, low temperatures, and without complex organometallic catalysts.

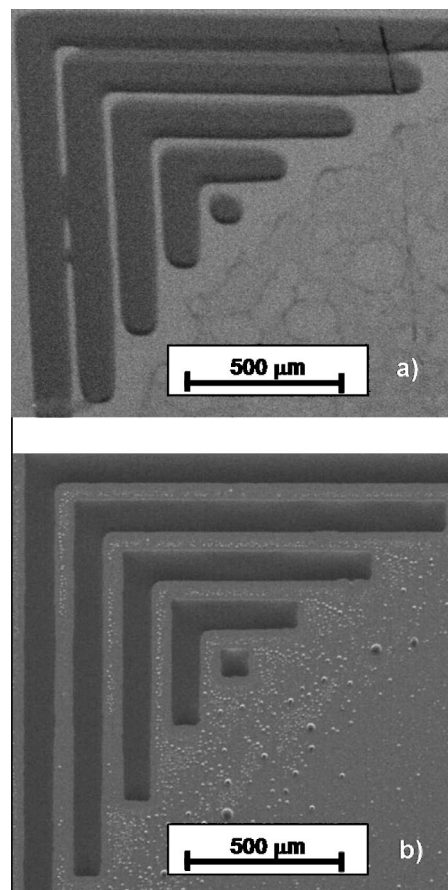


Fig. 3. Scanning electron micrographs of (a) patterned PPC and (b) polymer I with TPS-C1 as the PAG. The combination of the low glass-transition temperature and the relatively high temperature required for acid-catalyzed decomposition (115 °C) of the PPC material has negative effects on the resolution of the photosensitive system as evidenced from the merging of lines and broadening of the expected 90 μm 1:1 line/space pattern. The same size structures patterned in polymer I have much sharper edges and the integrity of the pattern is maintained. Although polymer I has a similar T_g to PPC, it requires a much lower development temperature (<80 °C).

composition. This type of contamination could potentially react with or bind to materials flowing through a microfluidic device. While the synthesis used in this work has many attractive features and the activation of a diol with CDI is a fairly robust reaction, the polymerization itself is extremely sensitive to impurities. Both the activated diol and free diol must be purified by either sublimation or recrystallization for the reaction to proceed.

The thermal and imaging characteristics of Polymer I were compared to commercially available PPC which was shown to be a potential photosensitive sacrificial material.^{7,10} Both PPC and Polymer I undergo one-step decompositions to near 0 wt % remaining residue. 5% weight loss is reached at 230 °C for PPC and 214 °C for Polymer I. Although the decomposition temperature for Polymer I is slightly lower than that of PPC and the glass-transition temperatures are comparable (23 °C for PPC versus 26 °C for Polymer I), the temperature required for the acid-catalyzed decomposition of Polymer I is significantly lower than that of PPC. This is due to the different decomposition mechanisms of these materials

and makes Polymer I significantly better than PPC for the fabrication of microfluidic devices. As can be seen in Fig. 3, the low T_g of PPC combined with the relatively high "development" temperature needed to fully decompose the polymer causes a significant flow of the polymer which results in rounded edges in patterned structures. The flow is evident in the PPC as shown in the widening of lines and shrinking of spaces in Fig. 3 as compared to the same patterns produced in Polymer I. This has a direct effect on the resolution capability of the photosensitive system, with limits of approximately 100 μm for PPC versus less than 30 μm for Polymer I for 1:1 line/space patterns. The profilometry (data not shown) also showed that the height of the patterned PPC was lower than that of the film thickness before patterning, again indicating the flow of the patterned polymer. No such thickness shrinkage was observed in patterns formed in polymer I.

IV. CONCLUSIONS

A PC has been synthesized that can be used as a thermally sacrificial polymer for microchannel fabrication. This PC possesses improved imaging properties as compared to PPC for use as a photodefinable sacrificial polymer. This polymer, and similar PCs made using the same general architecture, promise to improve the fabrication of multilevel integrated microfluidic devices. An advantage of the synthesis used in this work is the ease and flexibility possible in tailoring the monomers and resulting polymer architecture. This architectural control allows for optimization of both the thermal and imaging properties of the PC. While Polymer I has obvious advantages over PPC, it is not yet clear if this polymer possesses the ideal characteristics for a photosensitive sacrificial material. This polymer is soluble in many of the solvents

used in the formulation of possible overcoat materials such as SU-8. While this issue might be resolved by simply optimizing the processing materials and conditions, work is currently underway to study the various desired properties with respect to the variations in the polymer structure, with particular interest in increasing the glass-transition temperature of the sacrificial material.

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