Consecutive solvent evaporation and co-rolling techniques for polymer multilayer hollow fiber preform fabrication

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All-polymer multilayer hollow core photonic fiber preforms were fabricated using consecutive deposition from a solvent phase of two polymers with high and low refractive indices (RI). Processing techniques for two polymer pairs—polystyrene (PS)/poly(methyl methacrylate) (PMMA) and polycarbonate (PC)/poly(vinylene difluoride) (PVDF)—were established. The fabrication process involved consecutive film deposition by solvent evaporation of polymer solutions on the inside of a rotating PMMA or PC tube, used as a cladding material. By injecting right volumes of the polymer solutions into a spinning tube the thickness of each layer could be reliably controlled from 20 to 100 μm. Proper selection of solvents and processing conditions was crucial for ensuring high optical and mechanical quality of a resultant preform, as well as compatibility of different polymer films during co-deposition. Preforms of 10 layers for PMMA/PS material combination and 15 layers for PVDF/PC were demonstrated. Fabrication of preforms with higher number of layers is readily possible and is only a question of preform fabrication time. An alternative method of preform fabrication by co-rolling of polymer bilayers is also presented in this paper, drawing of PMMA/PS, PVDF/PC fibers with up to 32 layers is demonstrated.

I. INTRODUCTION

High laser power delivery and sensing using near- and mid-infrared (IR) radiation (wavelength range 1–12 μm) have been active areas of applied optics in the past decade due to some crucial advantages offered by the IR wavelength range.1–4 Hollow-core multilayer and microstructured fibers for radiation guiding in the IR5–11 have recently received considerable attention as they promise important advantages over their solid-core counterparts in applications related to high power guidance at almost any IR wavelength for military, industry, and medical applications, as well as IR imaging and sensing. Recently, hollow-core fibers were also investigated for guidance of very long wavelengths (λ ∼ 100 μm) in a THz range for chemical sensor and time-resolved measurement applications.12,13 Because of its complexity, fabrication of such waveguides is an active field of research, in which any new manufacturing technology could enable a novel niche application. The main advantage of hollow-core photonic fibers over solid core fibers is in their ability to confine and guide radiation predominantly

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inside a hollow core, thus dramatically reducing radiation propagation loss due to material absorption in the fiber materials, which is especially critical in the mid and far-IR (λ > 3 μm), where most of the materials are highly absorbing.

Four main methods have been identified for hollow-core fiber manufacturing. The first method is the deposition of metallo-dielectric films on the inside of a drawn capillary by liquid-phase coating; technical difficulties in enforcing thickness uniformity in the resultant coatings limits fiber length to 10 m. The second method is a capillary stacking method in which glass capillaries are arranged in a periodic manner and then drawn; so far such fibers have been demonstrated to only guide radiation with wavelengths smaller than 3 μm due to the non-transparency of silica material used in the fabrication. The third and relatively new method is deposition of uniform thin films on a pre-drawn substrate fiber by means of physical or chemical vapor deposition methods; the main challenge of this technology is presumably uniformity of the resultant coatings and a low throughput due to a relatively slow deposition process. Finally, the fourth method uses a bilayer film rolling technique. Film rolling starts with a deposition of a glass (chalcopyride) film on top of a polymer film; the resulting bilayer is then rolled around a mandrel tube, which is later etched away, and the final preform is drawn into a fiber. The main disadvantage of such a fiber is the questionable bio-compatibility of the material combination and challenges in fiber profile optimization due to a strictly periodic reflector geometry imposed by the fabrication method.

In this work, we consider an alternative to method of fabrication (described in Ref. 11) of hollow multilayer preforms. In the hollow multilayered waveguides, radiation confinement in a hollow core is achieved by reflection from a surrounding reflector consisting of a quasi-periodic sequence of thin layers of optically different materials with thicknesses comparable to a wavelength of the transmitted light. The total number of layers is typically 5–30. The critical step in realizing multilayer reflector is a selection of several optically different, but mechanically similar, materials that can be co-processed together to form a high optical quality multilayer preform. The preform, which is an enlarged (by a factor of 10 to 1000) copy of a fiber, is then placed into the furnace where it is heated above the polymer glass transition temperature and finally pulled into a fiber.

Fabrication of the all-polymer hollow multilayer fiber preforms, which we describe in this paper, addresses a need for inexpensive and bio-friendly material combinations for use in biomedical applications. In our group, we have developed processing techniques and established several polymer material combinations to fabricate all-polymer hollow multilayer waveguide preforms by consecutive evaporation of polymer solutions on the inside of a rotating cladding tube. Ten to fifteen layer preforms based on polystyrene (PS)/poly(methyl metacrylate) (PMMA) and polycarbonate (PC)/poly(vinylene difluoride) (PVDF) material combinations have been fabricated. Among advantages of our fabrication method is precise control over the thickness and material composition of the individual layers, which enables fabrication of reflectors with highly optimized geometries. Moreover, functional materials can be incorporated into the layer structure by dissolving active elements such as laser dyes, nanoparticles, etc., in a polymer solution before coating. Potential biocompatibility of an all-polymer material combination opens the possibility of in vivo use of our fibers for laser delivery and sensing. The disadvantage of the proposed method is the necessity for a thorough solvent extraction from the deposited multi-layer, which limits the throughput of a fabrication process. The proposed methodology, combined with the co-rolling method described in Ref. 11 gives a very powerful all-polymer multilayer preform fabrication strategy where co-rolling could be used to create the “bulk” part of a photonic crystal reflector, while a moderate number of “custom-designed” functional layers can be deposited from a solvent phase.

This paper is organized as follows: we first describe materials and solvents used in the process. Then we describe processing conditions for different material combinations and challenges that arise during the co-deposition process. We then present polymer multilayer preforms of two different polymer combinations. Finally, we discuss co-rolling for polymer preform fabrication.

II. MATERIALS

In what follows, we describe fabrication of the fully polymeric multilayer hollow core fiber preforms based on either PS/PMMA or PC/PVDF pairs. Preforms were prepared by consecutive solvent evaporation of polymer solutions inside a rotating cladding polymer tube. Solvent evaporation of polymer solutions provides a versatile fabrication technique for deposition of polymer layers of variable thickness and composition.

Use of polymer pairs for fabrication of photonic waveguides imposes restrictions on materials, which have to be optically, chemically, and thermodynamically compatible. Optical applications require material transparency, thus making crystalline and semi-crystalline polymers less desirable for fiber drawing. Moreover, refractive indices in a polymer pair have to be appreciably different from each other (at least by 10%) to enable a sizable bandwidth for a periodic reflector. Chemically, polymers have to be soluble in nontoxic organic solvents with low boiling points to enable efficient solvent extraction from the cast polymer films. Moreover, solvents

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have to be “orthogonal” to each other so they do not cross-solve the two polymers during a bilayer deposition. Thermodynamically, polymers have to have similar processing temperatures to allow co-drawing.

We have found two polymer/solvent pairs to fulfill all the above requirements. These are the PS/PMMA and PC/PVDF material combinations. For many years, PMMA has been a material of choice for plastic optical fiber fabrication, while PS and PC have been investigated as materials for fiber protective coatings. PS and PMMA blends and co-polymers have been considered in many publications for self-assembly of nanostructures, as well as multilayer thin film formation.

PVDF is a semicrystalline polymer of low refractive index (RI) with partially fluorinated chain structure and is a relatively unexplored polymer for optical applications. Prior work on PVDF and PC blends as well as multilayer thin films is presented in Refs. 27 and 28. Compared with most fluorinated polymers, especially perfluorinated polymers, PVDF is quite inexpensive and shows good solubility in organic solvents. In the present study, a PVDF copolymer containing hexafluoropropylene was chosen because it has lower crystallinity and a lower melting point than a homopolymer; consequently, it also has better solubility than a homopolymer. Glass transition temperatures of the PS/PMMA and PC/PVDF polymer pairs are well matched with differences of only 5 and 14 °C, respectively. Refractive index mismatches between the constituents of each pair are respectively Δn = 0.12 and Δn = 0.18 over the visible and IR spectra. In the Appendix, we present in greater detail some of the optical properties of the studied polymer films in the visible and IR regions. Material parameters of each polymer pair are summarized in Table I, showing good matching of polymer physical and thermodynamic properties.

PS, PMMA, and PC in granules were purchased from Aldrich. PVDF (Solef21216) in powder form was provided by Solvay Solexis. PC and PMMA tubes were purchased from McMaster Carr Canada and cut into 12-in.-long pieces.

Prior to usage, both PMMA and PC tubes were cleaned with a water solution of a generic commercial surfactant. PMMA tubes were further washed in an ultrasonic bath. After further cleaning with 95% ethanol, PMMA and PC tubes were annealed and degassed in vacuum oven overnight at 70 and 120 °C, respectively.

### III. SOLVENTS

For a given polymer pair, the first step is to choose low boiling point, non-toxic solvents. The orthogonal characteristics of selected solvents must be ensured with respect to cross-solving of the polymers in a pair. Thus, to make sure that during the next layer coating the previously coated layer is not destroyed, a solvent to the second component of a polymer pair must be a non-solvent to the first one and vice versa. In addition, other properties of solvents such as vaporization velocity, boiling point, relative toxicity, and price must be considered. Normally, more volatile organic solvents with low boiling points are preferred because it is easier to extract them after the deposition process. Using solubility parameters of polymers and solvents for guidance, for each polymer pair several solvent pairs were tested and compared. Solvents used in this study are listed in Table II, where (+) signifies solubility and (−) signifies non-solubility of a polymer in a given solvent; (%) reflects optimal polymer concentrations in a given solvent.

Although PVDF copolymer-containing hexafluoropropylene shows good solubility compared to most fluorinated polymers, the choice of organic solvents remains quite limited. Commonly used solvents for casting PVDF films such as N,N-dimethylacetamide, N,N-dimethylformamide, 1-methylpyrrolidone, and dimethyl sulfoxide are not suitable as they all dissolve PC to some extent. We found that such solvents as acetone, 1-butanol, acetonitrile, and methyl acetate dissolve PVDF copolymer but not the PC. Because 1-butanol and acetonitrile formed only metastable PVDF solutions, we concentrated our attention on acetone and methyl acetate as PVDF solvents.

In our work, we have also used solvent blends to increase adhesion between the immiscible polymer pairs. Thus, a small percentage of a common solvent could be added to the otherwise orthogonal solvent pair to promote stronger adhesion through interface fusion between the two polymers.

All solvents (obtained from Aldrich) were reagent grade and were used as received. Polymers were dissolved in selected solvents in a covered flask with a magnetic stirrer at room temperature or elevated temperatures to prepare solutions of 5–10% concentration. PMMA and PS solutions were then ultrasonically degassed for about 1 h in a water bath.

### IV. MULTILAYER FILM DEPOSITION PROCESS

Depending upon desired thickness of a polymer layer (in a range of 20–100 μm) a corresponding amount of polymer solution is injected into the polymer tube. The

<table>
<thead>
<tr>
<th>Polymer</th>
<th>RI at 1050 nm</th>
<th>RI difference at 1050 nm</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
<th>Difference in T_m (°C)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>1.60</td>
<td>0.12</td>
<td>100</td>
<td>5</td>
<td>5</td>
<td>1.05</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.48</td>
<td>0.15</td>
<td>105</td>
<td>1.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>1.58</td>
<td>0.18</td>
<td>149</td>
<td>12</td>
<td>14</td>
<td>1.20</td>
</tr>
<tr>
<td>PVDF</td>
<td>1.40</td>
<td>–30</td>
<td>135</td>
<td>–135</td>
<td>135</td>
<td>1.78</td>
</tr>
</tbody>
</table>
tube is then placed horizontally into a rotational stage with one end connected to a nitrogen inlet and another end connected to a fume exhaust. The tube is then rotated with a speed of 1000-2000 rpm. When solvent is evaporated (by visual inspection), the tube is put into an oven to completely remove the residual solvent. A temperature schedule is used with several hours of evaporation at 30–50 °C followed by several hours at 50–70 °C and slow cooling. For a selected solvent pair, coating conditions such as nitrogen flow velocity, rotating velocity of tube, and solution concentration, must be optimized to increase quality of the deposited films. Spin coating is performed under a constant nitrogen flow to prevent moisture and dust in the air from being embedded in a coated film. However, large nitrogen flow rates would cause ripples or bubbles that can be incorporated in the film. We found optimal flow rates to be 0.1–0.5 ml/min at the beginning of the process and 1–3 ml/min at the end of the deposition process when most of the solvent has already evaporated. Polymer solution concentrations of 5–10% were tested with optimal concentrations listed in Table II. Rotation speeds of a spin coater between 1000 and 2000 rpm were found to produce the smoothest preforms.

V. PS/PMMA POLYMER COMBINATION

A. CCl₄/acetonitrile(CH₃CN) solvent pair

For the PS/PMMA pair, CCl₄/acetonitrile (CH₃CN) was initially used for coating. PS solution in CCl₄ gave a perfectly smooth first layer on a PMMA tube. PMMA solution in acetonitrile also gave a good second layer, which was optically transparent and well attached to the first layer. However, a second coated PS layer would exhibit wrinkles at the end of a tube connected to the nitrogen purge no matter how small the nitrogen flow was. When coating the third PS layer from CCl₄ solution, the previously coated layers would crack. In general, backbones of the PS chains tend to stretch in a good solvent such as CCl₄, causing accumulation of residual stress during the relatively fast evaporation process. Cracking could also be caused by CCl₄ diffusion into the previously coated PS layers where it attacks the points of high residual stress. Preforms with up to 2 PS layers were fabricated with CCl₄/acetonitrile solvents.

B. [Cyclohexane (C₆H₁₂) + 5% toluene (C₇H₈)]/acetonitrile (CH₃CN) solvent pair

Cyclohexane has a solubility parameter similar to that of CCl₄. However, when PS was dissolved in cyclohexane at elevated temperatures, the polymer solution became inhomogeneous when cooled during storage. Toluene is a good solvent for both PS and PMMA. When 5% toluene was added into cyclohexane, it dissolved PS very well, even at room temperature. Thus, the (cyclohexane + 5% toluene)/acetonitrile combination was tested for the PS/PMMA pair coating. Unlike CCl₄, a mixture of cyclohexane and toluene is not as strong a solvent as CCl₄. PS film cast from a (cyclohexane + 5% toluene) solution gave a mainly transparent and smooth first PS layer. Casting PMMA layer from acetonitrile solution resulted in a clear and well-attached second layer. The third layer from a PS solution in (cyclohexane + 5% toluene) also gave a mainly transparent and smooth PS film well attached to the second PMMA layer. However, starting from the third layer, micro-bubble formation was observed. Using this layer-by-layer process, a PMMA tube was coated with up to 6 alternative PS and PMMA films. The resulting preform consisted of a 3.5-mm-thick PMMA tube with an inner diameter of 25 mm and 6 alternative PS and PMMA layers with thicknesses of 80 and 50 μm, respectively.

C. [Cyclohexane (C₆H₁₂) + 5%CCl₄]/[acetonitrile(CH₃CN) or acetone(C₃H₆O)] solvent pairs

Using CCl₄ instead of toluene in a solvent blend leads to a considerable improvement in the layer-by-layer deposition process. Coating quality was improved further when acetonitrile was substituted by acetone to dissolve PMMA. When coating was made at elevated temperatures (30–60 °C), considerable improvements in layer morphology and transparency were achieved; preforms of up to 12 alternative layers were readily obtained with both (cyclohexane + 5% CCl₄)/acetone and a (cyclohexane + 5% CCl₄)/acetonitrile solvent pairs for PMMA and
PS, respectively. In Fig. 1, a ten-layer preform and its cross section are shown. Here and in the following figures, optical micrographs were obtained on thin samples under reflected light and the non-polarizing mode of a Leitz microscope; the samples were cut from the tube with a diamond saw. In Fig. 1(b), layers corresponding to different polymers are clearly distinguishable due to different reflective properties of polymer films featuring non-identical refractive indices. The preform in Fig. 1(a) is transparent with a smooth inner surface and without ripples; only a few bubbles at the end of the tube were observable. When the same coating was repeated at room temperature, bubbles and ripples appeared in the multilayer structure. Elevated temperature coating is superior to room temperature coating in two ways. First, at elevated temperatures, cyclohexane dissolves PS better than at room temperatures, increasing chain mobility and preventing polymer chain segments from crystallization. Second, elevated temperatures accelerate solvent evaporation and solvent removal from the polymer matrix. Furthermore, we observed that a multilayer created with (cyclohexane + 5% CCl₄)/acetone solvent pair exhibits sharper interfaces than a multilayer created with (cyclohexane + 5% CCl₄)/acetonitrile solvent pair. Difference in the interfacial structures could be attributed to different degrees of swelling of a PS layer by acetone and acetonitrile solvents causing various penetration depths of PMMA molecular chains into PS polymer layers. Multilayer preforms fabricated under these conditions, with the last layer exposed to the air being PMMA, stay transparent for many months with only a faint onset of opaqueness. After several months of storage, a number of microcracks appeared inside the multilayer, suggesting relaxation dynamics of a stressed multilayer.

D. Degradation of optical properties of solvent-cast PS films during storage

An important question related to the quality of solvent cast films is about degradation of film optical properties during storage due to trapped solvents (solvent-induced crystallization) and interaction with the environment. While in all our experiments PMMA films were always transparent, we observed that opaqueness of PS films depended strongly on a solvent extraction method used in film casting, as well as on PS film exposure to the elements during storage. Thus, PS films exposed to air would typically become opaque in a matter of several days. However, when PS film was stored in vacuum it would stay transparent for several months. When PS film was protected on both sides by the PMMA polymer layers, it would remain transparent even after a year of storage when prepared from (cyclohexane + 5% CCl₄)/acetone at elevated temperatures (due to efficient solvent extraction). However, a PS film protected by the two PPMA layers would become opaque in a matter of days if multilayer was prepared with (cyclohexane + 5% toluene)/acetonitrile at room temperature (due to non-efficient solvent extraction).

Scanning electron microscopy (SEM) was performed on the surfaces of various PS films to understand the above phenomenon. Because the PS layer was well attached to the PMMA tube after coating (due to partial penetration of PS into a swelled PMMA matrix), it was difficult to separate it for SEM observations without destroying the film surface. Instead, we cast PS film on the inside of a quartz tube using solvents and processing conditions identical to the ones described in the previous subsections. After the deposition, it was easy to detach an initially transparent PS film from the quartz substrate. In a typical experiment, the PS films were either left exposed to air or stored in vacuum. PS film stored in the air, after several days, became somewhat opaque with many white dots peppered in the film. After one week of storage, individual white dots coalesced into an opaque film with SEM revealing a fully developed crystalline phase [Fig. 2(a)]. For comparison, SEM performed on the surface of a PS film stored in vacuum, showed the absence of crystallization even after several months of storage [Fig. 2(b)]. Although it seems that the amount of trapped solvent and exposure to the elements are the main factors

FIG. 1. (a) Ten-layer PMMA/PS preform using (cyclohexane + 5% CCl₄)/acetone solvents. (b) Optical micrograph of a preform cross-section.
influencing the long-term optical stability of PS films, more quantitative study is still needed.

E. PC/PVDF combination

For a PC/PVDF pair with a PC tube as a cladding material, several new problems appeared during coating: cracking of the PC tube, appearance of milky color in both the PC tube and deposited PC layers, and detachment of the coated layers. Thus, a non-annealed PC tube would fracture immediately when exposed to acetone, which was originally used as a solvent for PVDF. In general, it was observed that PC exhibits relatively low resistance to organic solvents. This is in part due to the relatively high free volume of loosely packed rigid PC chains, which allows efficient solvent penetration into the polymer matrix. In non-annealed tubes, the penetrated solvent attacks points of high stress and leads to the appearance of a maze of micro-cracks, each several millimeters in length. PC tubes annealed at 120 °C for several days in a vacuum oven demonstrated considerably improved resistance to solvents. Although micro-cracks were no longer observed in annealed PC tubes when exposed to PVDF solution in acetone, occasionally, a single macro-crack of several centimeters of length would appear. Finally, we have found that when PVDF solution in methyl acetate was used instead of acetone, the probability of crack appearance in PC tubes was greatly reduced. No matter what solvent was used to dissolve PVDF, the milky color of the PC tube always appeared when PVDF layers were deposited.

F. (Acetone or methyl acetate)/(CH₂Cl₂ or CHCl₃) solvent pair

The first deposited PVDF layer from either acetone or methyl acetate was always shiny, smooth, and well attached to the PC tube. The second PC layer cast from either CH₂Cl₂ or CHCl₃ coated on the top of the first PVDF layer was also shiny, smooth, and well attached to the previous layer. When a third layer of PVDF was coated, although it was still smooth, the three combined layers would frequently detach from the PC tube, and each layer could be readily separated by peeling. The low adhesion strength between PC and PVDF is a result of their semi-compatibility due to high interfacial tension between C–H-based PC and C–F-based PVDF.

G. (Acetone or methyl acetate + cyclohexanone)/(CH₂Cl₂ or CHCl₃) solvent pair

To improve adhesion strength between the adjacent layers, cyclohexanone was added to a PVDF solution in acetone or methyl acetate. Cyclohexanone dissolves PC very well; however, only a metastable PVDF (Solef21216) solution formed in a pure cyclohexanone. Improved interlayer adhesion was achieved due to solvent wetting of both the PC and PVDF layers, thus causing interpenetration of the polymer chains in the adjacent layers. Two PVDF/PC based preforms were initially fabricated. The first preform contained 7 layers; a mixture of acetone and cyclohexanone (volume ratio of 75 to 25) was used to dissolve PVDF while CH₂Cl₂ was used to dissolve PC. The second preform contained 5 layers; a mixture of methyl acetate and cyclohexanone (volume ratio of 95 to 5) was used to dissolve PVDF, and CH₂Cl₂ was used to dissolve PC. The addition of cyclohexanone into PVDF solution in acetone or methyl acetate considerably improved adhesion between the PVDF and PC layers. Unlike in the case of a PVDF film cast from pure acetone or methyl acetate solvent (for which a complete layer detachment was observed), only a small detachment at the ends of a tube was observed when solvent blends were used, starting with the fifth layer for...
acetate + cyclohexanone and the seventh layer for methyl acetate + cyclohexanone. Moreover, addition of cyclohexanone considerably suppressed the occurrence of large cracks in the PC tube. It was further established that high cyclohexanone content in a PVDF solution caused degradation in the smoothness of the coated polymer films, such as appearance of wrinkles. Thus, for example, $5\text{–}10\%$ cyclohexanone content in a methyl acetate solution produced smoother layers and sharper interfaces than $25\%$ cyclohexanone content.

H. (Acetone or methyl acetate + CHCl$_3$)/(CH$_2$Cl$_2$ or CHCl$_3$) solvent pair

Addition of cyclohexanone into acetone or methyl acetate improved adhesion between PC and PVDF layers; however, because cyclohexanone has a high boiling point ($156\,^\circ\text{C}$), removing residual solvent at elevated temperatures ($>50\,^\circ\text{C}$) and in vacuum after each PVDF layer coating proved to be time consuming, thus making the use of cyclohexanone unfavorable. Low boiling point CHCl$_3$ was then used instead of cyclohexanone to wet the interfaces, but CHCl$_3$ and CH$_2$Cl$_2$ solvents were still used to dissolve PC. For PVDF solutions, 10–20\% CHCl$_3$ was added into a PVDF solution in methyl acetate under strong stirring to avoid precipitation of PVDF until the solution became homogeneous. A multilayer of 15 layers with 40 $\mu$m (PVDF) and 20 $\mu$m (PC) layer thickness was then coated on the inside of the PC tube (Fig. 3), showing good adhesion between layers. Small detachment of the multilayer from the tube was observed near the tube edge after coating five layers; however no detachment was observed in the rest of the tube.

I. Preform fabrication by co-rolling of polymer films

We briefly mention an alternative method of all-polymer multilayer preform fabrication by co-rolling of several different polymer films around the same mandrel. The main advantage of this method is in the absence of the multiple solvent evaporation steps, while the main disadvantage is in the fact that it is difficult to vary the thicknesses and compositions of individual layers. Using this method, we demonstrated 32 layer preforms of PS/PMMA, PC/PVDF, and PS/PVDF material combinations. We used both commercial and home-cast films. Commercial films were provided by the following companies: PVDF, Kynar Flex 2800 by CS Hyde Company; PC, Europlex 99506; PMMA, Europlex 99710 by Degussa, Advanced Polymer Shapes Rohm Gmbh & Co.; and PS, The Dow Chemical Company. Home-cast bilayer films were prepared by polymer solution evaporation on a $12\times8$ in. glass or metal surface, followed by consecutive casting of another polymer on the top of a first one using the orthogonal solvent technique introduced in this paper. The choice of solvents and processing conditions for bilayer formation was similar to the ones described previously in this paper. The resulting bilayer films with thickness of 50–100 $\mu$m were then rolled onto a Teflon mandrel with a consecutive consolidation of a rolled preform at temperatures above the typical thermal transition temperature of a polymer pair. Resulting preforms were then successfully drawn into fibers. In Fig. 4, we show drawn fibers with a 1:20 drawdown ratio of their outside diameter to that of a preform for PVDF/PC and PMMA/PS material combinations.

VI. CONCLUSIONS

In this paper, we have described a novel methodology for fabrication of hollow all-polymer photonic crystal fiber preforms. In particular, we have developed a methodology for the deposition of PS/PMMA and PC/PVDF
polymer multilayers (more than 10 layers with individual layer thicknesses of 25–100 μm) by consecutive evaporation from a solvent phase onto the inside of a rotating polymer cladding tube. The advantage of this layer-by-layer method is in the freedom that it offers in adjusting thicknesses of the individual layers, as well in the possibility of incorporation of functional elements such as laser dyes, quantum dots, etc., into a chosen layer to ultimately implement enhanced optical functionalities of the resultant fiber. The disadvantage of this method is in the requirement of a thorough solvent extraction from a resulting multilayer, which limits the throughput of a process.

We believe that the industrial strength process for fabrication of low-cost, yet functional, multilayer all-polymer photonic crystal fibers will involve both the co-rolling technique to create the “bulk” of the photonic crystal reflector and subsequent deposition (from a solvent phase) of a moderate number of specialty “functional” layers.

REFERENCES

APPENDIX: OPTICAL PROPERTIES OF THE POLYMER FILMS

Optical properties of the polymer films in the visible and IR regions were studied experimentally using spectroscopic ellipsometry and Fourier transform infrared (FTIR) measurements. Four planar polymer films were cast from solvents in a glass Petri dish using the processing conditions described in this paper. Round samples of 5 cm in diameter were prepared with the following thicknesses measured using a Mitutoyo digital micrometer: PMMA, 34 ± 4 μm; PS, 21 ± 3 μm; PVDF, 18 ± 4 μm; PC, 83 ± 4 μm.

The refractive index $n$ of the polymers was determined by variable angle spectroscopic ellipsometry (VASE) in the visible and near-infrared regions between 300 and 1700 nm using angles of incidence from 45° to 65° with a step of 5°. The data were fitted with the Cauchy dispersion model and Urbach absorption tale using the WVASE32 software (J.A. Woollam Co.; curves in Fig. 5). For two values of the wavelength, namely 550 and 1050 nm, additional VASE measurements were performed using angles of incidence from 35° to 75° with a step of 1°. These data were fitted using the same model independently from the spectroscopic data (special symbols in Fig. A1).

Optical transmittance of the above-mentioned films was then measured with a spectrophotometer (Lambda 19, Perkin Elmer) and with FTIR spectrometer (IR-VASE, J.A. Woollam Co.) in the range of 200–3200 nm and 2.50–25.0 μm, respectively. To simplify comparison of transmission properties of films of various thicknesses, the transmission spectra in Fig. A2 are normalized to a thickness of 20 μm. As our film samples were not smooth enough, uncertainty due to additional scattering losses did not allow us to reliably extract bulk absorption losses of the materials. However, transmission spectra still provide a good indication of the material transparency regions in the infrared. For more details on bulk absorption losses of PMMA, PS, and PC polymer materials in the visible, refer to Ref. 31. From Fig. 6, it follows that all four materials are relatively transparent in the visible and near infrared. Another transparency window for all four materials is around 10.6 μm, corresponding to a CO$_2$ laser emission line.