New fluoropolymer materials

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Abstract

We report the synthesis of two classes of fluoropolymers that could impact several key lithographic techniques; one has potential applications in next generation photolithography (193 nm, 157 nm, and immersion lithography) and the other in lithographic techniques which are emerging as viable alternatives to photolithography for future applications (i.e., soft lithography).
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1. Introduction

Carbon dioxide has emerged as a viable environmentally friendly alternative solvent which is non-toxic, non-flammable, inexpensive, and readily available in high-purity from a number of sources. Our group has pioneered the use of liquid and supercritical CO_2 for both the homogeneous solution polymerizations [1] and heterogeneous precipitation polymerizations [2,3] of fluorinated monomers.

Teflon® AF is an amorphous copolymer of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD). It combines the properties of amorphous plastics like good optical transparency and solubility in organic solvents with those of perfluorinated polymers like high thermal stability, excellent chemical stability and low surface energy. Moreover Teflon® AF has some unique properties: it has the lowest dielectric constant (1.90 for Teflon® AF 2400) and the lowest refractive index (1.29 for Teflon® AF 2400) known for a solid organic polymer [4]. The low refractive index and exceptional optical clarity makes it well-suited for use as an optical material. However, handling TFE is not straightforward because it decomposes explosively at temperatures above $-20\,^{\circ}C$ even in the absence of oxygen. We have developed and recently reported the environmentally friendly synthesis of Teflon® AF in carbon dioxide (Scheme 1) [5].

In addition, we have developed a novel solvent resistant photocurable perfluoropolyether (PFPE) for microfluidic device fabrication [6]. Microfluidics has emerged as a ubiquitous technology that has found applications in genome mapping, rapid separations, sensors, nano-scale reactions, ink-jet printing, and drug screening [7–12]. Current microfluidic devices are based on soft materials which allows for the manufacture and actuation of devices containing valves, pumps, and mixers [7–11]. Poly(dimethylsiloxane) (PDMS) has rapidly become the material of choice for many microfluidic device applications [8–12]. Many current PDMS devices are based on Sylgard 184® (Dow Corning) which cures thermally through a platinum-catalyzed hydrosilation reaction. Complete curing can take up to 5 h. PDMS offers numerous attractive properties in relation to microfluidics. It has a low surface energy around 20 erg/cm^2 which usually facilitates easy release from molds after patterning [8,10]. Another important feature of PDMS is its outstanding gas permeability. This allows for gas bubbles within channels to permeate out of the device and is also useful in sustaining cells and microorganisms inside the features. The non-toxic nature of silicones is also beneficial in this respect and allows for opportunities in the realm of medical implants [10]. Despite the advantages of PDMS for microfluidics technology, this material suffers from a serious

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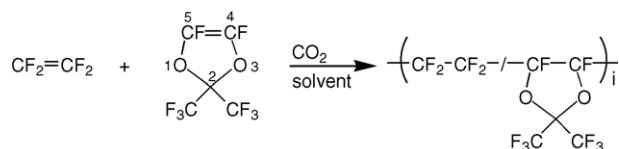
Scheme 1. Reaction scheme for the environmentally friendly synthesis of Teflon® AF in CO_2 [5].

drawback in that it swells in most organic solvents. Whitesides et al. have recently reported in detail on the limited compatibility of PDMS-based microfluidic devices with a range of organic solvents [13]. The swelling of PDMS-based devices makes it impossible for organic solvents to flow inside the channels. Thus, an elastomer which exhibits the attractive properties of PDMS along with a resistance to swelling in common organic solvents would greatly extend the versatility of microfluidic devices to a wide variety of new chemical applications and other domains yet to be explored.

2. Results and discussion

2.1. Copolymerization of tetrafluoroethylene and PDD in CO_2

Copolymers of TFE and PDD were synthesized in CO_2 and characterized using NMR spectroscopy, FTIR spectroscopy, differential scanning calorimetry and solution viscosity (Table 1). Compared to poly(tetrafluoroethylene) which is a highly crystalline polymer and insoluble in organic solvents below 300 °C, TFE/PDD copolymers of certain compositions are soluble in perfluorinated organic solvents like hexafluorobenzene, perfluorooctane or Fluorinert® FC-75 at room temperature which facilitates their characterization.

As can be seen from Table 1 a range of copolymers were successfully synthesized in CO_2. The reaction conditions were systematically varied to investigate the influence of initiator concentration, temperature, and feed composition on the copolymer properties. As expected the molecular weight of the polymers was found to decrease with increasing initiator concentration (Table 1, nos. 4–6). Reducing the reaction temperature to 25 °C resulted in a slightly higher yield and molecular weight (Table 1, no. 7) compared to the reaction run at 35 °C (Table 1, no. 5).

A series of experiments were carried out at different feed compositions to investigate the influence of the copolymer composition on the glass transition temperature (Table 1, nos. 1–4, 8–9, 12–14) while keeping the other conditions constant. Compositions were determined by a simple method using infrared spectroscopy that we have developed [5]. No melting peaks were observed in the DSC traces for any of the copolymers. The lowest T_g of 67 °C was obtained at a feed composition of 20 mol% PDD. With increasing PDD content, the glass transition temperature increases strongly because there is less conformational flexibility due to the fixed and bulky ring structure of the dioxole monomer unit (Fig. 1). The T_g reaches the highest value for the PDD homopolymer with a T_g of 334 °C. As can be seen from Fig. 1 the slope of the curve increases strongly at higher PDD contents. Intermolecular polar interactions between the CF_3-groups of the PDD monomer units probably also contribute to an increase of the glass transition temperature at high PDD contents.

In addition, no difference could be found between a fluorinated commercial sample (Teflon® AF 1601) and a copolymer synthesized in CO_2 having a similar composition using ^{19}F NMR spectroscopy, IR spectroscopy, and differential scanning calorimetry. Teflon® AF is typically synthesized by an emulsion polymerization technique using

Table 1
Reaction conditions and properties of TFE/PDD copolymers ($P = 2000$ psi, 138 bar), $t = 5$ h, $T = 35$ °C)

No.	T (°C)	PDD in feed (mol%)	PDD in polymer		c^a (%)	Amount initiator[b] (mol%)	Yield (%)	Intrinsic viscosity (mL/g)	$T_g{}^c$ (°C)
			NMR (mol%/wt.%)	IR (mol%)					
1	35	20	–[d]	–	18	0.1	66	–	67
2	35	30	29.7/50.8	30.2	20	0.1	51	–	76
3	35	40	40.5/62.4	41.2	19	0.1	59	–	92
4	35	50	48.0/69.3	48.4	24	0.1	34	80	109
5	35	50	51.8/72.4	52.2	21	0.3	67	33	108
6	35	50	53.4/73.7	53.7	23	0.5	72	19	101
7	25	50	51.9/72.5	54.8	20	0.3	74	35	102
8	35	60	61.3/79.4	62.4	20	0.1	50	–	131
9	35	73	74.5/87.7	70.8	19	0.3	54	–	155
10	15	73	76.3/89.1	73.8	18	0.3	54	–	160
11	60	73	75.4/88.2	72.0	19	0.1	39	–	151
12	35	80	81.9/91.7	82.5	18	0.1	46	–	179
13	35	90	92.2/96.6	91.6	20	0.1	47	–	231
14	35	100	100	100	21	0.4	69	–	334

[a] Concentration of monomers (w/v).

[b] Initiator bis(perfluoro-2-N-propoxypropionyl) peroxide. Concentration related to total molar amount of monomers.

[c] Determined during second heating: 25–400 °C, first heating: 25–300 °C, heating rate: 10 °C/min.
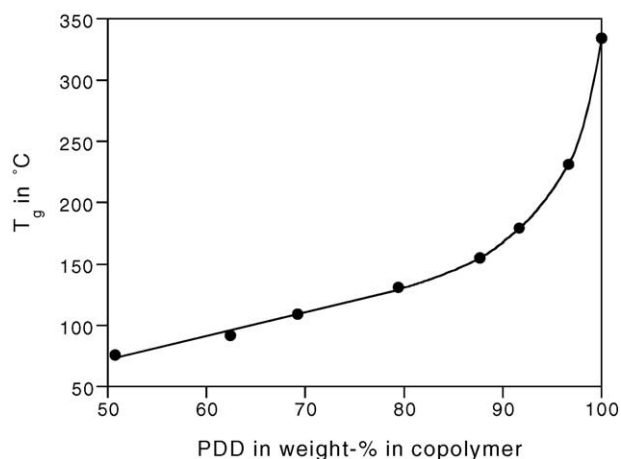
[d] Copolymer insoluble in C_6F_6.

Fig. 1. Dependence of the glass transition temperature on the copolymer composition [5].

ammonium persulfate as the initiator which results in the formation of COOH end-groups and also requires additional steps to remove the water. For some applications these unstable groups are removed commercially by treating the polymer with elemental fluorine. With our approach we can synthesize and isolate the copolymers directly with properties comparable to those of the fluorinated commercial product. Moreover, there is no need for an expensive fluorination step and the TFE can be handled more safely as a mixture with CO_2.

2.2. Solvent resistant photocurable PFPE's for microfluidic device fabrication

As mentioned PDMS-based microfluidic devices cannot be used with organic solvents due to detrimental swelling. Our approach to this problem has been to replace PDMS with perfluoropolyethers (PFPEs) and we have developed the first fabrication of a microfluidic device based on photocurable PFPEs [6]. PFPEs are a unique class of fluoropolymers that are liquids at room temperature, exhibit low surface energy, low modulus, high gas permeability, and low toxicity with the added feature of being extremely chemically resistant [14]. DeSimone et al. have reported extensively on the synthesis and solubility of PFPEs in supercritical carbon dioxide [15]. The reaction involves the methacrylate-functionalization of a commercially available PFPE diol with isocyano-ethyl methacrylate. Subsequent photocuring of the material is accomplished by blending with a photoinitiator and exposing it to UV radiation (Scheme 2).

To measure solvent resistance, tests using classical swelling measurements [16] were performed on both the crosslinked PFPE DMA and PDMS (Sylgard 184®). Sample weights were compared before and after immersion in dichloromethane for several hours. The data shows that after 94 h the PDMS network had swelled to 109% by weight, while the PFPE network showed negligible swelling (<3%).

The PDMS and PFPE precursor materials and the fully cured networks have similar processing and mechanical properties. Rheology experiments showed the viscosity of the uncured PFPE DMA at 25 °C to be less than the uncured Sylgard 184® (0.36 and 3.74 Pa s, respectively). However, because both materials are viscous oils at room temperature standard PDMS device fabrication methods could still be employed.

Dynamic mechanical thermal analysis was performed on the fully cured materials. Both the PFPE and PDMS networks exhibit low temperature transitions (−112 and −128 °C, respectively) as evidenced by maxima in the loss modulus E'' (Fig. 2). This transition accounts for the similar elastic behavior of the two crosslinked materials at room temperature.

Device fabrication was accomplished according to the procedure illustrated in Fig. 3. This method utilizes partial curing techniques to adhere the two layers without
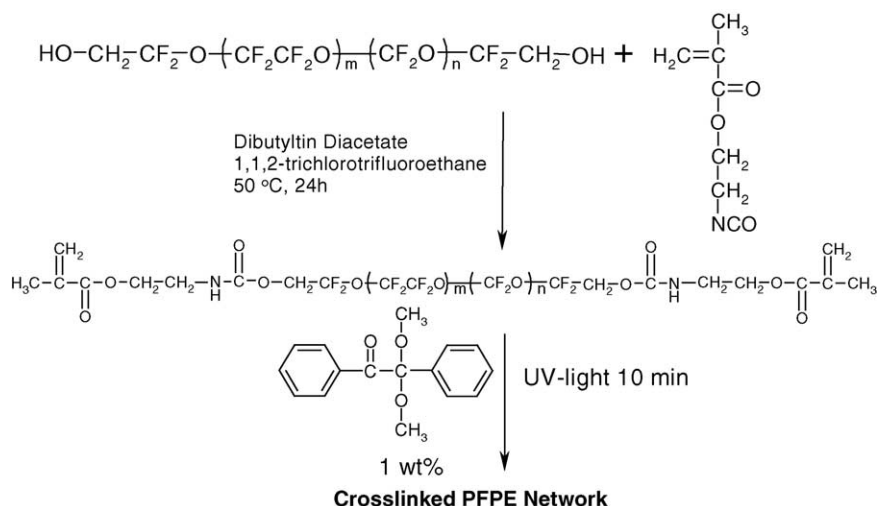
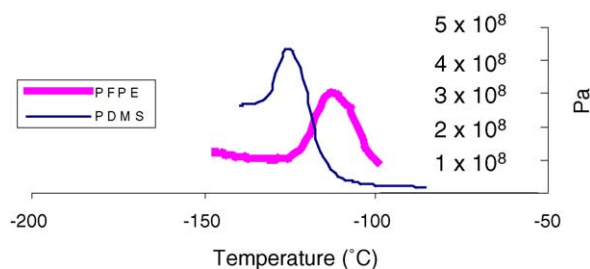Scheme 2. Synthesis and crosslinking of photocurable PFPEs [6].

Fig. 2. DMTA traces of crosslinked PDMS and PFPE materials showing maxima in the storage modulus as a function of temperature [6].
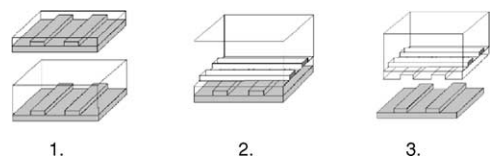

Fig. 3. Procedure for device fabrication. (1) A small amount of the PFPE DMA containing 1 wt.% DMPA is spin-coated onto a patterned silicon wafer to a thickness of 20 μm. Separately, a thicker layer (~5 mm) is formed by pouring PFPE DMA containing 1 wt.% DMPA into a mold surrounding a patterned wafer. Both wafers are then exposed to UV light for 30 s. (2) The thick layer is peeled off the wafer, rotated 90°, and placed on top of the thin layer. The entire device is then exposed to UV light for 10 min to adhere the two layers together. (3) The device is peeled off the wafer [6].

compromising feature sizes [9]. The PFPE DMA material was easily spin-coated and molded using procedures designed for Sylgard 184®.

To compare the solvent compatibility of devices made from the two materials, a dyed solution containing dichloromethane, acetonitrile, and methanol was introduced into both a PFPE and a PDMS channel by capillary action (Fig. 4). The PFPE channels showed no evidence of swelling as the solution traveled easily through the channel. A pronounced reverse meniscus was observed indicating good wetting behavior. In contrast, no solution entered the PDMS device because the channel was plugged shut when it made contact with the droplet due to swelling. As a control, a dyed methanol solution was easily introduced in the PDMS channel in the same manner.

Actuation of the valves was accomplished by introducing pressurized air (~25 psi) to small holes that were punched through the thick layer at the beginning of the channels. When the solution was present in the channel, valve actuation was easily observed (Fig. 5).
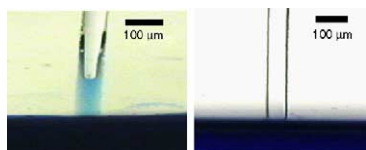

Fig. 4. Dyed solution of methylene chloride, acetonitrile, and methanol entering the channel in the PFPE device (left). No solution entered a PDMS channel of the same size due to swelling (right) [6].
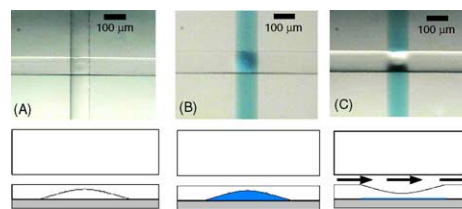

Fig. 5. (A) Top-down view of channels containing no solvent. The channels on the thin layer (fluid) run vertical, while those on the thick layer (air) run horizontal. (B) Thin layer channel filled with dyed solution of acetonitrile, dichloromethane, and methanol. (C) Valve actuation produced by introducing 25 psi of air into the thick layer channel. Beneath each picture, a cartoon representation of the valve cross-section is shown [6].

3. Experimental

3.1. Reagents

TFE was obtained from DuPont as a 50 wt.% mixture in CO_2 and used as received. PDD (DuPont) was purified by filtration through silica gel (230–400 mesh, Sigma). Teflon® AF 1601 (fluorinated and unfluorinated) was obtained from DuPont. SFC purity CO_2 was obtained from Air Products. Bis(perfluoro-2-*N*-propoxypropionyl) peroxide was prepared in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon® 113), according to a published procedure [17], and stored over dry ice. The concentration was determined by iodometry and was typically 11 wt.%.

3.1.1. Synthesis of Teflon® AF in CO_2

The experimental set-up is shown in Fig. 6. Polymerizations were conducted in a 25 mL high pressure reaction view cell equipped with a stirring bar, thermocouple, rupture disc and a sapphire window which permits visual observation of the reaction mixture with an endoscope. In a typical run the high pressure cell was purged with CO_2 to remove oxygen. Then the base of the cell was cooled to about 5 °C with an ice-bath and PDD was charged via syringe while purging with argon. After sealing the cell the ice-bath was removed and the TFE/CO_2 mixture (50 wt.%) was introduced with a manual pump (HIP, Model 62-6-10) under stirring. To weigh in a determined amount of TFE the pump was pressurized to 103 bar (1500 psig). The volume of the TFE/CO_2 mixture was calculated from the density at 103 bar (1500 psi g). By repeated opening of the valve between the pump and the reaction view cell and repressurizing to 103 bar (1500 psi g) the calculated volume was introduced. During this procedure the temperature of the autoclave stayed below 10 °C. Then the reaction view cell was heated to the desired reaction temperature which was typically 35 °C and the initiator solution was transferred via syringe to a small tube connected to the CO_2 line. The reaction view cell was then pressurized with additional CO_2 using a syringe pump (ISCO, Model 260 D) while simultaneously introducing the initiator. After the reaction, the CO_2 was slowly released and the residual copolymer in the high pressure cell was
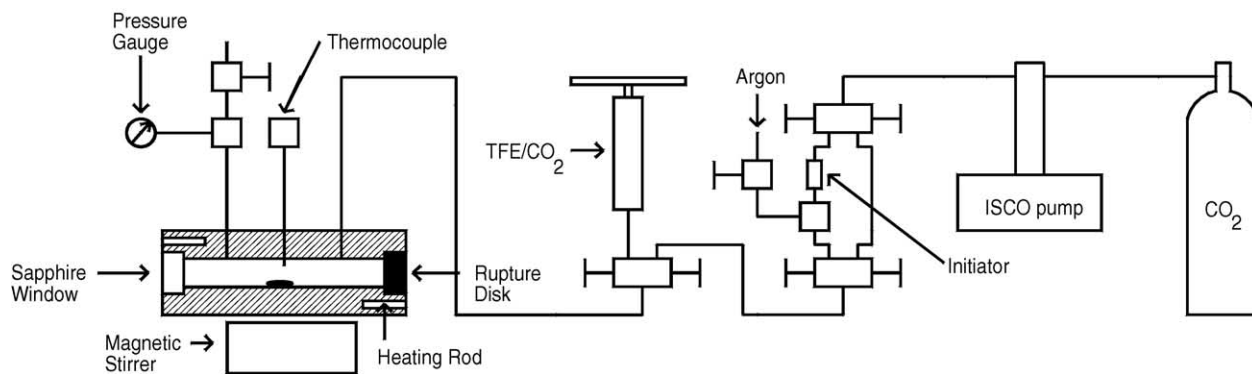
Fig. 6. Schematic of the experimental set-up [5].

extracted three times to 138 bar (2000 psi g) with CO_2 to remove unreacted monomer and initiator residue.

3.1.2. Synthesis of solvent resistant photocurable PFPE's for microfluidic device fabrication

The synthesis and photocuring of the PFPE's materials (Scheme 2) is based on earlier work done by Bongiovanni and co-workers [18]. The reaction involves the methacrylate-functionalization of a commercially available PFPE diol (Mn = 3800 g/mol) with isocyanato-ethyl methacrylate. Subsequent photocuring of the material is accomplished by blending it with 1 wt.% of 2,2-dimethoxy-2-phenylacetophenone (DMPA) and exposing it to UV radiation (λ = 365 nm).

4. Conclusions

A range of TFE/PDD copolymers were synthesized in CO_2 at low temperatures. The molecular weight could be controlled by changing the initiator concentration. Copolymers with different compositions were prepared having a broad range of glass transition temperatures from 67 to 334 °C. No difference could be found between a fluorinated commercial sample (Teflon® AF 1601) and a copolymer synthesized in CO_2 having a similar composition using ^{19}F NMR spectroscopy, IR spectroscopy and differential scanning calorimetry. A simple method to determine the copolymer composition based on infrared spectroscopy has been developed. The synthesis of the copolymers in CO_2 has several advantages compared to conventional polymerization techniques: the low reaction temperature and the use of a perfluorinated initiator potentially results in a copolymer whose properties are comparable to those of the fluorinated commercial product. An additional fluorination step is therefore unnecessary. The product is obtained in dry and pure form without contaminant from solvents or surfactants. Moreover the use of TFE/CO_2 mixtures instead of pure TFE improves the safety of the polymerization process. The presented method therefore offers an interesting alternative to conventional polymerization techniques. We are currently extending this approach for the environmentally friendly synthesis of advanced photoresists for 193 nm, 157 nm, and immersion lithography as well as for imageable dielectrics.

In addition we have also developed a novel solvent resistant microfluidic device fabricated from PFPE-based elastomers. Photocuring decreases fabrication from several hours to a matter of minutes. The device showed a remarkable resistance to organic solvents. This work has the potential to expand the field of microfluidics to many novel applications. Current efforts to use a PFPE-based device in a novel approach to DNA synthesis are underway.

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