SYNTHESIS AND FABRICATION OF POLYMERIC COMPOSITES, NANOFILAMENTS AND NANOFIBERS

A Thesis in
Chemistry
by
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ABSTRACT

Aluminum oxide particles were modified with 2-bromopropionic acid to afford particles with atom transfer radical polymerization (ATRP) initiators on the surface. Poly(methyl methacrylate)-co-poly(butyl acrylate) (PMMA-co-PBA) copolymer was then grafted onto the alumina particles by ATRP using CuBr/PMDETA ($N,N',N',N'\prime$-pentamethyldiethylenetriamine) as the catalyst. Kinetic and mechanistic studies revealed that the copolymerization process is living and follows the same trends as in liquid-phase ATRP, resulting in the formation of controlled gradient copolymer chains. The aluminum oxide/copolymer composites form stable suspensions in organic solvents.

Nitroxide initiator: 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane was synthesized and used in controlled radical polymerization of methyl acrylate with 1-alkenes. Kinetic studies reveal the polymerization displays living characteristics. Copolymers of methyl acrylate with simple 1-alkenes with controlled molecular weight, polydispersity and composition can be prepared by nitroxide mediated polymerization (NMP). Methyl acrylate-norbornene derivative copolymers can also be polymerized by NMP. The polymers are free of metal catalysts and opens up new applications of nitroxide mediated polymerization systems.

Channels with nanodimensional cross-sections were fabricated by e-beam lithography and top-down silicon processing and used as templates for controlled polymerization. The dimensions of these nanotemplates are 20 nm high, 20 nm to 200 nm wide, and 100 µm long. It was established that these channels are open all the way
without any collapsed regions. Nanostructured polymer filaments with controlled size, location and orientation were grown inside the channels by either radical, coordination and photopolymerization. The presence of the polymers in the channels was verified by oxygen plasma etching, fluorescence mapping, and solubility test. The polymer filaments produced are continuous and, when released from the template, can twist without breaking.

Nanochannels with “built-in” electrode contacts were fabricated and used as growth templates for conductive polymers. Conductive polymers can be either introduced or chemically grown in nanochannels. Conductivity measurements of polypyrrole indicate that channels electrode contacts are ohmic to polymer.

A new “jet-blowing” technique was developed to process polymer into micro and nanofibers. A variety of polymers, including “non-melt processible” polytetrafluoroethylene can be processed in this technique. Polytetrafluoroethylene can form micro and nanofibers below its melting temperature from this process. The fibers have porous, expanded structure and can be coated on surfaces of choice. Surfaces coated with these nanofibers are highly hydrophobic.
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This thesis covers subjects ranging from synthetic polymer chemistry to nanofabrication. Briefly, Chapters 2 and 3 deal with using controlled radical polymerization to synthesize composites and copolymers of polar and nonpolar olefins. Chapters 4 and 5 deal with a joint project with Penn State Nanofabrication Facility. The goal of the project is to synthesize polymer nanofilaments with controlled size, orientation and location. The last chapter is about a new process for fabrication of polymer micro and nanofibers. The discovery was accidental but technologically important.

Chapter 2 describes synthesis of aluminum oxide/gradient copolymer composites by atom transfer radical polymerization (ATRP). ATRP has been applied in synthesis of polymer brushes on particle surfaces to afford novel composite materials. The synthetic methodology involves modification of particles surfaces with ATRP initiators and grafting onto the particles. However, the modification agent has to be synthesized and the particles used were limited to silica and gold. In addition, only homopolymers was grafted before this work. This chapter discusses using commercially available chemicals to functionalize aluminum oxide particles to afford initiation sites for ATRP. Poly(methyl methacrylate)-\textit{co}-poly(butyl acrylate) copolymer was grafted onto particles and kinetic studies reveal that copolymerization on particle surfaces follows the same trend as solution polymerization. Polymers are rich in methyl methacrylate at particle surface and composition of butyl acrylate increases further out on the chain. The composites can form stable suspensions in organic solvents and can be solvent cast into films.
Chapter 3 discusses controlled radical polymerization of polar and nonpolar olefins. The Sen group discovered that methyl acrylate can be copolymerized with 1-alkenes by ATRP. The disadvantage of ATRP system is that the products are colored due to metal catalysts. Products have to undergo multiple washing and purification steps for application. To solve this problem, we explored another controlled radical polymerization system: nitroxide mediated polymerization (NMP), which is a clean process free of metal catalysts. We synthesized nitroxide initiator with high reactivity and studied copolymerization of methyl acrylate with 1-alkenes by NMP. It was found that copolymer of methyl acrylate and 1-alkenes can be synthesized using NMP. The polymerization system displays “living” characteristics. Copolymer with controlled composition and molecular weight can be prepared by NMP. This result opens up new possibilities for synthesis of polymers with desired functionalities.

Chapter 4 and 5 is an interdisciplinary project with the goal of fabrication of polymer nanowires with designed orientation, dimension and location. Although much development has been seen in fabrication of polymer nanowires, one critical technological requirement in application of these nanomaterials is to position the synthesized polymer nanowires into designed patterns to form nanoscale devices. It is difficult to manipulate nanowires synthesized randomly into desired locations. Chapter 4 deals with development of nanochannels with designed dimensions and patterns in which polymer nanofilaments were synthesized in a single integrated step, thus avoiding the difficulties associated with “synthesize-then-position”. A variety of polymer nanomaterials can be made by established polymer chemistry, including radical, metal-
catalyzed and photochemical polymerization. Chapter 5 demonstrated fabrication of nanochannels with built-in electrodes and its use in measurement of conductivity of polypyrrole nanofilaments. We successfully synthesized conductive polymers in nanochannels and we were the first to make direct measurements of conductivity of polypyrrole nanowires other than by scanning probe microscope technique. These discoveries open up possibilities for application of conductive polymers in nanoscale electronic transistors, sensors and other devices.

Chapter 6 discusses processing of polymers into micro and nanofibers by a new “jet-blowing” technique. Before this process, polymers such as poly(tetrafluoroethylene) were considered to be “non-melt processible” because of their high melt viscosity. In this jet-blowing process, PTFE was found to be able to be processed into micro and nanofibers with porous and expanded structure similar to “Goretex®” under high pressure gas through small orifices below its melting temperature. PTFE fibers can be coated on surfaces of different nature and form highly hydrophobic, tacky coatings. The process is simple and environmentally friendly and proves to be a facile technique to process polymers into micro and nanofibers.

In summary, this thesis covers significant advances in polymer chemistry, nanotechnology and material science. These progresses could lead to better process and new advanced materials.
CHAPTER 2

SYNTHESIS OF ALUMINUM OXIDE/GRADIENT COPOLYMER COMPOSITES BY ATOM TRANSFER RADICAL POLYMERIZATION
2.1 Introduction

The development of strategies for the synthesis of novel ceramic/polymer composites is of great current interest because of the unique properties that are likely to emerge from such materials.\textsuperscript{1-11} For example, a quantum dot/polymer composite material has the optical properties of the particles with improved processibility due to the incorporation of the polymer. One of the most important challenges in the area is the synthesis of composites where the polymer chains are covalently bonded to the ceramic particles and where the composition and the length of the chains can be varied in a systematic way. One solution to this problem is a living polymerization system that initiates from the surface of the ceramic particles, such as by atom transfer radical polymerization (ATRP).\textsuperscript{12} To date, ATRP has been employed to anchor homopolymers on to silica, cadmium sulfide/silica, and gold particle surfaces.\textsuperscript{13-16} Before our publication, there was no reports of the use of metal oxides in such procedures and there is no precedent for the ATRP synthesis of copolymers from ceramic surfaces. Thus, there were two unanswered questions: (a) Do copolymerizations follow the living characteristics of liquid-phase ATRP? (b) Can copolymer compositions be predicted from monomer reactivity ratios determined from liquid-phase radical polymerizations?

This chapter describes the synthesis of gradient poly(methyl methacrylate)-co-poly(butyl acrylate) (PMMA-co-PBA) copolymer chains from the surface of aluminum oxide particles by ATRP using the CuBr/PMDETA catalyst system (Figure 2.1). The oxide particles can act as crosslinking sites leading to improved mechanical and thermal
properties for the polymer. In addition, the procedure renders the oxide particles hydrophobic and makes them more compatible with a polymer matrix, resulting in more homogeneous ceramic/polymer blends.\textsuperscript{6} The polymeric coat also prevents agglomeration of the particles and allows higher loading levels in such blends.
Figure 2.1 Synthetic route to Al$_2$O$_3$/PMMA-co-PBA composites.
2.2 Results and Discussion

2.2.1 Modification of aluminum oxide particles.

Previous work on ATRP from silica, cadmium sulfide/silica, and gold particles employed non-commercially available initiators that bind to the surface of these particles.\textsuperscript{13-16} We found that the readily available 2-bromopropionic acid can react with the hydroxyl groups on aluminum oxide surface to afford particles incorporating initiators for ATRP.

2.2.2 Kinetics and mechanism of polymerization initiated from aluminum oxide particles.

We sought to compare the characteristics of ATRP copolymerization initiated from a ceramic surface with that observed in liquid-phase. Based on the initiator concentration obtained by bromine analysis, a monomer/initiator ratio $\sim 10^2$ was chosen for the copolymerization experiments. The conversion of MMA and BA were calculated from the integration of vinylic hydrogens of unreacted monomers relative to DMSO internal standard.
Figure 2.2 Kinetics of copolymerization of MMA and BA from modified Al₂O₃ particles (Conditions: [MMA]₀ = [BA]₀ = 0.01 mol; modified Al₂O₃ particles, 0.47g; [CuBr] = [PMDETA] = 0.03 mmol; 110°C).
As shown in Figure 2.2, the polymerization exhibited first-order kinetics with respect to total monomer conversion. Similar first-order kinetics were also observed for the conversions of the individual monomers.

Matyjaszewski has studied the liquid-phase copolymerization of MMA and BA using the CuBr/PMDETA catalyst system and methyl 2-bromopropionate as the initiator.\textsuperscript{17} Because of its higher reactivity ratio, the uptake of MMA is faster than that of BA. For equal molar monomer feed ratio, 70% of total monomer conversion was reached after 3.6 h. With the NiBr\textsubscript{2}(P\textsuperscript{v}Bu\textsubscript{3})\textsubscript{2}/Al(O\textsuperscript{t}Pr\textsubscript{3})\textsubscript{3}/CCl\textsubscript{3}Br system, MMA was also consumed faster than BA.\textsuperscript{18} As shown in Figure 2.3, the same trend is observed in the present case. For example, after 4 h approximately 90% of MMA was consumed while only about 40% BA had reacted (65% total monomer conversion). A higher reaction temperature was employed due to the heterogeneity of the reaction mixture. There was no polymer found in solution after removal of the alumina particles suggesting that the formed polymer chains were attached to the alumina surface.

The data in Figure 2.3 can also be used to calculate the instantaneous copolymer composition at any given monomer conversion. First, the cumulative copolymer composition is obtained from eq. 1 where subscript 1 denotes the first monomer (MMA) and subscript 2 denotes the second monomer (BA). The instantaneous composition is then obtained from eq. 2.\textsuperscript{17} The values obtained can be compared with theoretical instantaneous compositions obtained using eq. 3\textsuperscript{19} and the reactivity ratios measured from liquid-phase polymerization reactions ($r_1 = 3.0$ for MMA, $r_2 = 0.3$ for BA\textsuperscript{17}).
\[ F_{\text{cum},1} = \frac{(% \text{conv})_1[M_1]_0}{(% \text{conv})_1[M_1]_0 + (% \text{conv})_2[M_2]_0} \quad (1) \]

\[ F_{\text{inst},1} = F_{\text{cum},1} + (% \text{conv}) \frac{\Delta F_{\text{cum},1}}{\Delta (% \text{conv})} \quad (2) \]

\[ F_{\text{inst},1} = \frac{r_1f_1^2 + r_2f_2}{r_1f_1^2 + 2f_1f_2 + r_2f_2^2} \quad (3) \]

where \( f_1, f_2 \) are the instantaneous monomer fractions, \([M_1]_0, [M_2]_0\) are the starting concentration of MMA and BA. \((% \text{conv})_1\) and \((% \text{conv})_2\) are the cumulative conversion of MMA and BA, \(F_{\text{cum},1}\) is the cumulative composition of MMA in the copolymer, \(F_{\text{inst},1}\) is the instantaneous composition of MMA in the copolymer, and \(\Delta(\% \text{conv})\) is the change in monomer conversion.

As shown in Figure 2.4, the two sets of values agree well, suggesting that the reactivity ratios obtained from liquid-phase polymerizations can be used to predict the compositions of copolymers grown on ceramic surfaces. The \(F_{\text{cum},1}\) decreases as calculated from eq. 1, which leads to a decrease in \(F_{\text{inst},1}\) in eq. 2. Figure 2.4 also shows that we have controlled gradient copolymer chains that are MMA rich near the surface and become progressively richer in BA content on going further out. This observation suggests further ways to synthesize novel ceramic/polymer architectures.
Figure 2.3 Conversion of MMA and BA with time (Conditions: \([\text{MMA}]_0 = [\text{BA}]_0 = 0.01 \text{ mol}; \) modified \(\text{Al}_2\text{O}_3\) particles, 0.47g; \([\text{CuBr}] = [\text{PMDETA}] = 0.03 \text{ mmol}; 110^\circ\text{C}\)).
Figure 2.4 Instantaneous copolymer composition versus monomer conversion

(Conditions: [MMA]₀ = [BA]₀ = 0.01 mol; modified Al₂O₃ particles, 0.47g; [CuBr] = [PMDETA] = 0.03 mmol; 110 °C).
In order to measure the molecular weight and polydispersity of the copolymer chains, they were cleaved off the alumina surface using HF and analyzed by GPC. Figure 2.5 show plots of $M_n$ and $M_w/M_n$ as a function of total monomer conversion. For $M_n$, the plot deviates from linearity at higher conversions due to differential uptake of the two monomers. Starting with an equimolar monomer feed ratio, the more reactive MMA is preferentially incorporated at the beginning thus making the monomer composition progressively richer in the less reactive BA. The polydispersity remains fairly low throughout suggesting that the polymerization is “living.” The narrow, unimodal, distribution also confirms that the chains are copolymers rather than mixtures of homopolymers. The polydispersity of copolymers show some increase with increased total monomer conversion, which is different from homopolymerization where polydispersity decreases with increased conversion. This is due to lower reactivity of n-butyl acrylate in ATRP as compared to methyl methacrylate and hence broader polydispersity as MMA is almost consumed at higher total monomer conversions.

The theoretical $M_n$ for the copolymer can be calculated from the $[\text{MMA} + \text{BA}]_0$:[initiator] ratio and the conversion of each monomer. For example, at 90% of MMA and 40% BA conversion (65% total monomer conversion), the theoretical $M_n$ is 43,000. The corresponding $M_n$ value obtained by GPC relative to polystyrene standards is 51,000. The similarity of the numbers suggest that most of the initiation sites on the alumina particles participate in ATRP.
Figure 2.5 Molecular weight and polydispersity of PMMA-co-PBA as function of conversion (Conditions: [MMA]₀ = [BA]₀ = 0.01 mol; modified Al₂O₃ particles, 0.47g; [CuBr] = [PMDETA] = 0.03 mmol; 110 °C).
2.2.3 Characterization of the aluminum oxide/copolymer composites.

IR spectra of the pure Al$_2$O$_3$ particles and Al$_2$O$_3$/PMMA-$co$-PBA composite (M$_n$ ~51,000) are shown in Figure 2.6. The characteristic absorption band of C=O at 1738 cm$^{-1}$ corresponding to the ester groups in the polymer can be observed after PMMA-$co$-PBA is grown from the alumina particles. The presence of an absorption band at 3440 cm$^{-1}$ in the Al$_2$O$_3$/PMMA-$co$-PBA composite indicates that all of the surface hydroxyl groups on the alumina particles did not participate in the reaction with 2-bromopropionic acid.

Scanning electron micrographs (SEM) of starting Al$_2$O$_3$ particles and Al$_2$O$_3$/PMMA-$co$-PBA composite film (M$_n$ ~51,000) are shown in Figure 2.7. According to manufacturer’s specifications, the size of the particles range from 27 to 56 nm. However, SEM (Figure 2.7a) indicates that the particles form agglomerates. Such agglomerates are formed to lower total surface energy. After polymerization, the agglomerates are broken up and the particles (bright dots) distributed homogeneously in the copolymer matrix. The particles are mostly 1 µm in size and are embedded in the polymer matrix. It is very likely that the initial particle agglomeration prevented reaction of all of the surface hydroxyl groups with 2-bromopropionic acid.

While the initial alumina particles settled out rapidly from organic solvents, the alumina/PMMA-$co$-PBA composite (M$_n$ ~51,000) formed a stable colloidal suspension in
Figure 2.6 FT-IR (KBr) spectra of (a) untreated Al$_2$O$_3$ particles and (b) Al$_2$O$_3$/PMMA-co-PBA composite.
Figure 2.7 SEM of (a) untreated Al$_2$O$_3$ particles and (b) Al$_2$O$_3$/PMMA-$co$-PBA composite film prepared by casting from CHCl$_3$. 
chloroform, acetone and toluene. Clearly, this is the result of the increased hydrophobicity of the ceramic surface in the composite.

Finally, the Al₂O₃/PMMA-cot-PBA composite (Mₙ ~51,000) was examined by differential scanning calorimetry (DSC). No glass transition was observed in the temperature range of 0-300°C.

2.3 Conclusions

Aluminum oxide particles can be conveniently modified to afford surface initiation sites for ATRP. Copolymer chains with controlled composition and length can be grown from the particle surface. The copolymerization process is living and follows the same trends as observed in liquid-phase ATRP. This allows the synthesis of controlled gradient copolymer chains that are richer in one monomer near the particle surface and become progressively richer in the other monomer on going further out. The observation suggests additional ways to synthesize novel ceramic/polymer architectures using known ATRP technology. The aluminum oxide/polymer composites show improved compatibility with organic solvents and form stable suspensions.

2.4 Experimental
Materials. CuBr (99.999%), \(N,N,N',N',N''\)-pentamethyldiethylenetriamine (PMDETA, 99%), 2-bromopropionic acid (99%), tetrahydrofuran (THF, 99.9%), and chloroform (99.9%, HPLC grade) were obtained from Aldrich and used as received. Methyl methacrylate (MMA) (99%, Aldrich) and butyl acrylate (BA, 99%, Aldrich) were vacuum distilled from CaH\(_2\) and stored under N\(_2\). Aluminum oxide was purchased from Nanophase, Inc.

Analysis. NMR spectra were recorded on a Bruker DPX-300 spectrometer. The chemical shifts are referenced to CHCl\(_3\). Molecular weights and molecular weight distributions were determined on a Waters size exclusion chromatography (SEC) system using a flow rate of 1 ml/min and a three column-bed (Styrage HR 7.8 x 300 mm columns with 5 µm bead size: 100-10,000 D, 500-30,000 D and 5,000-6,000,000 D), a Waters 410 differential refractometer and a Waters 486 tuneable absorbance detector. SEC samples were run in CHCl\(_3\) at ambient temperature and calibrated to polystyrene standards. Elemental analysis was provided by Galbraith Laboratories. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer using KBr pellets. Scanning electron micrographs (SEM) were obtained on a JSM 5400 instrument. Differential scanning calorimetry was performed on Perkin-Elmer DSC-7 under an argon atmosphere at a scanning rate of 5°C/min.

Modification of aluminum oxide particles with initiator. A mixture of Al\(_2\)O\(_3\) (2.04 g, 0.02 mol), 2-bromopropionic acid (3.04 g, 0.02 mol), and 30 ml of THF was heated to reflux for 15 h. After filtration, excess acid was washed away with acetone and volatile
materials were removed under vacuum. The successful anchoring of the initiator was verified by bromine analysis which gives a bromine content of 0.57%.

**Polymerization of MMA and BA from particle surfaces.** In a typical reaction, 0.47 g of initiator modified particles, CuBr (43 mg, 0.30 mmol), PMDETA (52 mg, 0.30 mmol), MMA (1.00 g, 0.01 mol), BA (1.28 g, 0.01 mol), and 0.10 ml DMSO (internal standard) were degassed by freeze-pump-thaw cycles before being filled with N₂. After polymerizing at 110°C for 4 h, the flask was cooled in ice to stop the reaction and products were suspended in chloroform. DOWEX® MSC-1 ion exchange resin was added to remove the copper catalyst and the suspension became white. After removing the ion exchange resin and evaporating the solvent, a white solid was obtained. Yield: 1.91 g. IR (KBr, cm⁻¹): 3441, 2900, 1738.

For kinetic studies, samples were taken from the reaction at 1 h intervals, filtered and dissolved in CDCl₃. The conversion of MMA and BA were calculated from the integration of vinylic hydrogens of unreacted monomers relative to DMSO internal standard. The specific chemical shifts used were 5.55 ppm (1H, MMA) and 6.37 ppm (1H, BA). For film casting, the composites were suspended in CHCl₃ and added to a glass plate dropwise. Film formed upon evaporation of solvent.

**Cleavage of polymer from alumina particles.** Polymer chains were cleaved from the particles by treatment with HF following the procedure described previously. In a typical procedure, alumina/polymer composite (0.40 g) was suspended in 10 ml
chloroform, and 100 mg Aliquot 336 was added as a phase transfer catalyst. 10 ml of 5% aq. HF was then added and the mixture stirred at ambient temperature for 2 h. The organic layer was removed and polymer isolated by precipitation in methanol. \(^1\)H-NMR (CDCl\(_3\), ppm): 0.8-2.0, 3.6 (OCH\(_3\), MMA), 4.1 (OCH\(_2\), BA). \(M_n = 51,000\). \(M_w/M_n = 1.31\).
2.5 Bibliography


CHAPTER 3

CONTROLLED RADICAL POLYMERIZATION OF POLAR AND NONPOLAR OLEFINS
3.1 Introduction

The copolymerization of polar vinyl monomers with nonpolar alkenes remains an area of great interest because the combination of the two can greatly enhance the range of currently attainable polymer properties.\textsuperscript{1-3} The inherent difficulty in copolymerization of polar vinyl olefins and linear 1-alkenes is that they occur through vastly different mechanisms. Polar vinyl monomers are known to undergo free radical polymerization readily and form high molecular weight homopolymer. On the other hand, 1-alkenes can be polymerized via radical mechanisms only under very harsh conditions. However, 1-alkenes can readily be polymerized by transition metal catalyzed insertion polymerization. Before the discovery by the Sen group that polar and nonpolar olefins can be copolymerized by copper mediated atom transfer radical polymerization (ATRP),\textsuperscript{4} the only successful radical–initiated copolymerization of acrylate with 1-alkenes under mild conditions involves the use of strong Lewis acids that complex to the ester functionality of the acrylate. The resultant highly electron deficient monomer forms a 1:1 alternating copolymer with 1-alkenes in the presence of radical initiators.\textsuperscript{5-7} In the area of metal catalyzed copolymerizations of polar vinyl monomers and nonpolar olefins, Brookhart reported the copolymerization of ethylene and acrylates with cationic palladium diimine compounds.\textsuperscript{8,9} The copolymer is branched and has a maximum incorporation of 12% methyl acrylate. Drent used palladium modified with di(2-methoxyphenyl)phosphinobenzene-2-sulfonic acid and obtained a copolymer of ethylene and acrylates where acrylates were “built-in” the chain.\textsuperscript{10} The acrylate incorporation is 2-
17%. The Exxon group developed a copper bis(benzimidazole) catalyst which can copolymerize ethylene and acrylates.\textsuperscript{11}

The Sen group discovered that copper mediated atom transfer radical polymerization can copolymerize acrylates with norbornene derivatives or simple linear 1-alkenes with a maximum incorporation of 23% 1-alkene in the copolymer.\textsuperscript{4,12} Klumperman et.al. recently studied copolymerization of methyl methacrylate and 1-octene by ATRP.\textsuperscript{13} This result is surprising since it is generally believed that alkyl radicals are unstable and will cause chain termination. It is unlikely to get incorporation as high as 23\% in the copolymer. The first part of this chapter examines mechanistic aspects of addition of 1-alkenes to radicals. It is found that an alkyl radical does not necessarily leads to chain termination. The effect of copper catalyst concentration on the copolymer composition was also studied.

One of the major disadvantages of using ATRP is the color of the polymer obtained as a result of the metal catalyst, typically copper. The metal catalyst needs to undergo multiple washing and exchange process to be almost completely removed. It is natural that we would explore other possible controlled radical polymerization (CRP) system, such as nitroxide mediated polymerization (NMP). Hawker \textit{et.al.} recently synthesized a library of nitroxide initiators and some initiators have as high reactivity as ATRP system.\textsuperscript{14,15} The initiators can be used to polymerize \textit{n}-butyl acrylate and \textit{N},\textit{N}-dimethylacrylamide. The second part of this chapter discusses the work of using these nitroxide initiators for copolymerization of polar and nonpolar olefins. It is found that
acrylates and 1-alkenes can be copolymerized by NMP with controlled molecular weight and polydispersity. In addition, the polymer is free of metal catalysts. NMP proves to be another methodology for synthesis of copolymers of polar and nonpolar olefins.

3.2 Copper mediated copolymerization of polar and nonpolar olefins

3.2.1 Addition of 1-alkenes to ATRP initiator

To investigate the addition of 1-alkenes to radicals, pure ethylene was added to a typical ATRP catalyst system: CuBr and PMDETA. Methyl 2-bromopropionate was initiator and deuterated benzene was solvent. The product was analyzed by $^1$HNMR, $^{13}$CNMR, $^{13}$CDEPT$^{135}$NMR (Figure 3.1(a)) and HMQC (Figure 3.1(b)). From these NMR data it can be concluded that the following reaction takes place:

![Scheme 3.1 Reaction of ethylene to methyl 2-bromopropionate in ATRP](image)

Chemical shifts of 1 in $^1$HNMR(ppm): 1.24(CH$_3$), 1.90(CH$_2$), 2.64(CH), 3.42(CH$_2$Br), 3.72(OCH$_3$). $^{13}$CNMR(ppm): 17.2(CH$_3$), 31.4(CH$_2$), 36.6(CH$_2$Br), 38.2(CH), 51.9(OCH$_3$). Chemical shifts of 2 in $^1$HNMR(ppm): 1.20(CH$_3$), 1.41(CH$_2$), 1.86(CH$_2$), 2.28(CH$_2$), 2.48(CH), 3.36(CH$_2$Br), 3.67(OCH$_3$). $^{13}$CNMR(ppm): 17.5(CH$_3$), 32.9, 33.2, 33.9(CH$_2$), 36.6(CH$_2$Br), 39.6(CH), 52.2(OCH$_3$). In $^{13}$CDEPT
135 all CH2 peaks are down. The molar ratio of one ethylene unit addition product 1 to two ethylene addition product 2 is 2.5:1. Conversion of methyl 2-bromopropionate initiator was 100%. This result is surprising since primary radicals are considered unstable radicals and thermodynamically not favored. However, this result shows that ethylene does add to the radical initiator and forms a primary radical. In addition, the second ethylene can add to the primary radical. This result indicates that in ATRP copolymerization of polar monomers with 1-alkenes, the addition of 1-alkene to a growing polymer chain end does not necessarily prevent addition of more monomers Therefore, copolymer can have certain incorporation of 1-alkenes (up to 20%).
Figure 3.1 (a) $^{13}$CDEPT135 (b) HMQC of products of addition of ethylene to methyl 2-bromopropionate in ATRP.
3.2.2 Effect of Cu(0) on the composition of copolymer

The polymerization mechanism in ATRP is shown in Scheme 3.2.

\[ P_n-Br + \text{Cu}^{I}BrL \xrightarrow{K_{\text{act}}} P_n^* \xrightarrow{K_{\text{deact}}} \frac{1}{K_p} + \text{Cu}^{II}\text{Br}_2L + \text{P}_m \xrightarrow{K_t} P_n-P_m \]

**Scheme 3.2 ATRP polymerization mechanism**

\( P_n \) and \( P_m \) are polymer. L is ligand and M is monomer. The addition of Cu(0) on the molecular weight and 1-alkene incorporation was studied and results were summarized in Table 3.1. For MA/1-alkene polymerization, from ethylene to 1-octene, all the molecular weight of the copolymer decreases with addition of Cu(0). The addition of Cu(0), as seen from Scheme 3.2, reduces the concentration of Cu(II) species and moves the equilibrium towards more radical formation. The molecular weight therefore decreases. It is not clear why 1-alkene incorporation also decreases.

3.2.3 Conclusions

1-Alkenes can be added to a primary alkyl radical chain end in ATRP polymerization system. The concentration of copper catalyst affects the molecular weight and composition of methyl acrylate/1-alkene copolymer. Higher concentration of Cu(I) species result in lower 1-alkene incorporation as well as decrease in molecular weight.
Table 3.1. The effect of addition of Cu(0) on copolymerization of methyl acrylate with 1-alkenes

<table>
<thead>
<tr>
<th>1-Alkene</th>
<th>Cu(I)(mmol)</th>
<th>Cu(0)(mmol)</th>
<th>1-Alkene(%)</th>
<th>M_n c</th>
<th>M_w/M_n c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Hexene b (3.0g)</td>
<td>0.47</td>
<td>0</td>
<td>11.8</td>
<td>12,000</td>
<td>1.3</td>
</tr>
<tr>
<td>1-Hexene b (3.0g)</td>
<td>0.47</td>
<td>0.12</td>
<td>9.4</td>
<td>8,100</td>
<td>1.5</td>
</tr>
<tr>
<td>1-Hexene b (3.0g)</td>
<td>0.47</td>
<td>0.47</td>
<td>3.6</td>
<td>5,300</td>
<td>1.2</td>
</tr>
<tr>
<td>1-Hexene b (3.0g)</td>
<td>1.4</td>
<td>0</td>
<td>10.1</td>
<td>2,000</td>
<td>1.3</td>
</tr>
<tr>
<td>Ethylene b (900psi)</td>
<td>0.23</td>
<td>0</td>
<td>8.6</td>
<td>10,400</td>
<td>1.5</td>
</tr>
<tr>
<td>Ethylene b (900psi)</td>
<td>0.23</td>
<td>0.06</td>
<td>6.6</td>
<td>8,000</td>
<td>1.3</td>
</tr>
<tr>
<td>Ethylene b (900psi)</td>
<td>1.4</td>
<td>0</td>
<td>14.8</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Ethylene b (900psi)</td>
<td>1.4</td>
<td>1.4</td>
<td>8.0</td>
<td>2,800</td>
<td>1.3</td>
</tr>
<tr>
<td>1-Octene c (7.8g)</td>
<td>0.47</td>
<td>0</td>
<td>23.6</td>
<td>4,000</td>
<td>1.2</td>
</tr>
<tr>
<td>1-Octene c (7.8g)</td>
<td>0.47</td>
<td>0.12</td>
<td>19.5</td>
<td>3,500</td>
<td>1.5</td>
</tr>
</tbody>
</table>

aReaction conditions: 90°C, 16h. bMA 5.0g. cMA 3.0g. dDetermined by GPC relative to polystyrene standards using refractive index detector.
3.2.4 Experimental

**General.** All polymerizations were performed in an inert atmosphere. NMR and GPC experimental step and conditions are same as in Chapter 2.

**Polymerization of methyl acrylates with 1-alkenes by ATRP.** The reactions were set up following similar procedure as in reference 4. In a round bottom flask, CuBr, Cu, PMDETA, methyl acrylate, 1-alkenes were added and form a homogeneous mixture. The reaction was set in an oil bath at 80°C for 16 hrs. Product was precipitated in methanol and copper catalyst was removed by passing through the solution through alumina. For reactions with ethylene and propylene, an autoclave and liner was used.
3.3 Nitroxide mediated copolymerization of polar and nonpolar olefins

3.3.1 Synthesis of nitroxide initiator

The nitroxide initiator: 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane 4 was synthesized following established procedure, as shown in Scheme 3.3. Reductive condensation of 2-methyl-2-nitropropane, with isobutylaldehyde gives N-tert-butyl-α-iso-propyl nitronitrone. Reaction of this nitrone with phenylmagnesium bromide followed by oxidation in air leads to 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide 3. The nitroxide is then coupled with the 1-phenethyl radical generated from PbO₂ oxidation of 1-phenylethyl hydrazine.

![Scheme 3.3 Synthetic route of nitroxide initiator](image-url)
3.3.2 Copolymerization of methyl acrylate with 1-alkenes

Table 3.2 shows results of copolymerization of methyl acrylate with 1-alkenes by nitroxide mediated polymerization (NMP). The 1-alkene content was calculated from the ratio of CH resonance of the methyl acrylate units at 2.24 ppm to CH₃ resonance of the 1-alkene units at 0.87 ppm. For methyl acrylate/ethene copolymer, the CH₂ peak at 1.15 ppm from the ethene units in the copolymer was used. It is clear that the reaction is quite general. The molecular weight and the yield increase with longer reaction time. In addition, the copolymer polydispersities are low, suggesting a controlled polymerization process. Size exclusion chromatography (SEC) of the copolymers all give unimodal distributions and the curves from the refractive index and UV-Vis detectors are superimposable indicating the formation of copolymers, rather than a mixtures of homopolymers.

The ¹H NMR and ¹³C NMR spectra of the copolymers closely match those for analogous random polymers prepared by ATRP. For example, in the ¹³C NMR spectrum of the copolymer of methyl acrylate with propene, in addition to resonances at 175.3 (C(O)O), 52.1 (OCH₃), 41.5 (CH) and 35.3 (CH₃) ppm from the methyl acrylate units, broad resonances at 35.9-35.3 and a peak at 28.4 (CH) ppm from propene units were observed.

Table 3.2 shows that increasing the ratio of 1-alkene in the feed increase its incorporation into the copolymer; however, the molecular weight and the yield are
Table 3.2 Nitroxide-Mediated Copolymerization of Methyl Acrylate with 1-Alkenes$^a$

<table>
<thead>
<tr>
<th>Monomer</th>
<th>1-Alkene incorp. (mol %)</th>
<th>$M_n^b$</th>
<th>$M_w/M_n^b$</th>
<th>Yield (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene (700 psi)</td>
<td>13.6</td>
<td>9,000</td>
<td>1.19</td>
<td>1.5</td>
</tr>
<tr>
<td>Propene (100 psi)</td>
<td>15.5</td>
<td>4,200</td>
<td>1.22</td>
<td>1.2</td>
</tr>
<tr>
<td>1-Hexene (0.02 mol, 1.68g)</td>
<td>6.8</td>
<td>6,000</td>
<td>1.08</td>
<td>1.6</td>
</tr>
<tr>
<td>1-Hexene (0.02 mol, 1.68g)$^c$</td>
<td>5.5</td>
<td>11,200</td>
<td>1.13</td>
<td>2.3</td>
</tr>
<tr>
<td>1-Hexene (0.03 mol, 2.52g)</td>
<td>9.7</td>
<td>5,000</td>
<td>1.10</td>
<td>0.7</td>
</tr>
<tr>
<td>1-Octene (0.005 mol, 0.56g)</td>
<td>4.9</td>
<td>6,800</td>
<td>1.16</td>
<td>1.6</td>
</tr>
<tr>
<td>1-Octene (0.02 mol, 2.24g)</td>
<td>8.0</td>
<td>4,900</td>
<td>1.13</td>
<td>1.2</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: Nitroxide initiator, 0.2 mmol; control agent, 0.01 mmol; MA, 0.04 mol (3.44g); 120°C, 15 h. $^b$Determined by SEC relative to polystyrene standards using refractive index detector. $^c$Reaction time 30 h.
decreased. Similar results have been reported previously.\textsuperscript{4,13} Presumably, this is due to the higher concentration of the less stable secondary alkyl radical in the polymerization system. Such radicals are more prone to undergo termination.

### 3.3.3 Copolymerization kinetics

The first order kinetic plot for the copolymerization of methyl acrylate with 1-octene is shown in Figure 3.2. The conversions of methyl acrylate and 1-octene were calculated from the integration of the vinyl CH peak of methyl acrylate at 6.3 ppm and terminal vinyl CH\textsubscript{2} resonance for 1-octene at 4.9 ppm, with respect to DMSO internal standard. The linearity of the plot of total monomer conversion versus time indicates that the copolymerization follows first order kinetics. Similar linear plots were also obtained when the conversion of the individual monomers were plotted versus time.

The relationship between molecular weight, polydispersity, and total monomer conversion is shown in Figure 3.3. The data is shown in Table 3.3. The molecular weight increases linearly with total monomer conversion while polydispersity remains low. These results confirm the “living” character of the copolymerization system.
Figure 3.2 Polymerization kinetics of methyl acrylate with 1-octene (conditions: initiator 0.2mmol, control agent 0.01mmol, MA 0.04mol, 1-octene 0.01mol, 120°C).
Figure 3.3 Dependence of molecular weight and polydispersity of copolymer on total monomer conversion (conditions: initiator 0.2mmol, control agent 0.01mmol, MA 0.04mol, 1-octene 0.01mol, 120°C).

Table 3.3 Molecular weight and polydispersity vs. conversion in MA/1-octene copolymerization

<table>
<thead>
<tr>
<th>Total monomer conversion(%)</th>
<th>Mn</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.8</td>
<td>1,600</td>
<td>1.36</td>
</tr>
<tr>
<td>21</td>
<td>4,200</td>
<td>1.34</td>
</tr>
<tr>
<td>30</td>
<td>6,800</td>
<td>1.13</td>
</tr>
<tr>
<td>38.4</td>
<td>8,100</td>
<td>1.13</td>
</tr>
</tbody>
</table>
3.3.4 Copolymerization of methyl acrylate with norbornene derivatives

Copolymers of acrylates with norbornene derivatives are of interest as materials for deep UV photolithography. Polyacrylates show good adhesion and have been used extensively as photoresist materials but suffer from poor dry etch resistance. On the other hand, polynorbornenes exhibit superior etch resistance and thermal stability, and copolymers of the two may provide the optimum properties.\textsuperscript{16-18} Although the controlled copolymerization of these monomers by copper-based ATRP has been reported, the presence of metal traces in the copolymer precludes its widespread use in the electronic sector. The nitroxide mediated polymerization provides an alternative methodology for the synthesis of metal-free materials.

Our results are shown in Table 3.4. The copolymer compositions were calculated from the NMR integration of the methoxy group from methyl acrylate units versus the total aliphatic region containing resonances from both acrylate and norbornene units. It is clear that the procedure can be applied to a variety of norbornene derivatives although the yields are somewhat low. The copolymers have relative low polydispersity (although higher than that for methyl acrylate/1-alkene copolymers) suggesting that the polymerization proceeds in a “controlled” manner. Again, unimodal distributions and superimposable chromatograms using RI and UV-Vis detectors were observed by SEC indicating the formation of copolymers. The $^1$HNMR and $^{13}$CNMR spectra of the copolymers closely match those for analogous random methyl acrylate/norbornene copolymers prepared by ATRP.\textsuperscript{12}
Table 3.4 Copolymerization of methyl acrylate with norbornene derivatives by NMP

<table>
<thead>
<tr>
<th>Monomer</th>
<th>1-Alkene incorp. (mol %)</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>Yield (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Monomer 1" /> (0.04mol, 3.77g)</td>
<td>18.0</td>
<td>7,000</td>
<td>1.17</td>
<td>1.9</td>
</tr>
<tr>
<td><img src="image2" alt="Monomer 2" /> (0.04mol, 4.32g)</td>
<td>16.1</td>
<td>7,300</td>
<td>1.51</td>
<td>2.1</td>
</tr>
<tr>
<td><img src="image3" alt="Monomer 3" /> (0.04mol, 6.08g)</td>
<td>25.5</td>
<td>4,800</td>
<td>1.43</td>
<td>2.3</td>
</tr>
<tr>
<td><img src="image4" alt="Monomer 4" /> (0.04mol, 6.10g)</td>
<td>24.9</td>
<td>6,900</td>
<td>1.26</td>
<td>2.2</td>
</tr>
<tr>
<td><img src="image5" alt="Monomer 5" /> (0.04mol, 7.76g)</td>
<td>28.1</td>
<td>7,500</td>
<td>1.33</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*Reaction conditions: Nitroxide initiator, 0.4 mmol; control agent, 0.02 mmol; MA, 0.04 mol (3.44g); 120°C, 15 h. *b* Determined by SEC relative to polystyrene standards using refractive index detector.
The living nature of the polymerization system was verified by the synthesis of the block terpolymer: methyl acrylate/norbornene-b-methyl acrylate/1-hexene terpolymer. Copolymerization of methyl acrylate and 1-hexene was initiated starting with a methyl acrylate/norbornene copolymer (M_n = 7,000, PDI = 1.17, 18 mol% norbornene) as macroinitiator. Following polymerization, M_n increased to 8,800 with a PDI of 1.60. SEC of the final product shows unimodal chromatograms using both RI and UV-Vis detectors and they are superimposable. ^{1}HNMR spectrum of the final product showed a triplet from the methyl group of hexene units at 0.87 ppm. The ^{13}CNMR spectrum resembled a similar block terpolymer made by ATRP. The molar ratio of methyl acrylate, norbornene, and 1-hexene in the block copolymer was 1:0.24:0.13. The relative high polydispersity of the final terpolymer suggests that not all methyl acrylate/norbornene copolymer chains initiate polymerization in the second step.

3.3.5 Conclusions

We have demonstrated nitroxide-mediated controlled copolymerization of methyl acrylate with 1-alkenes and norbornene derivatives. Because of the “living” nature of the copolymerization, synthesis of materials with controlled molecular weight, low polydispersity, and predictable composition becomes possible. The procedure broadens the scope of nitroxide-mediated polymerization in the synthesis of metal-free materials with novel properties. The reactivity of NMP system is lower than ATRP system, as demonstrated from higher reaction temperature, longer reaction time and lower yield than ATRP. However, it does away the tedious purification steps in ATRP.
3.3.6 Experimental

**General.** All polymerizations were performed in an inert atmosphere. $^1$H and $^{13}$C NMR spectra were recorded at room temperature on a Bruker PX-300 (300 MHz), a Bruker CX-300 (300 MHz), or a Bruker RX-400 (400 MHz) spectrometer using chloroform-$d$ as the solvent. Chemical shifts were reported in $\delta$ ppm downfield from TMS. Molecular weights and molecular distributions were measured on a Shimadzu size exclusion chromatography using a flow rate of 1mL/min and a three-column bed (Styrage HR 7.8 x 300 mm columns with 5Å bead size: 100-10,000, 500-30,000, and 5000-6,000,000D), a Shimadzu RID 10A differential refractometer and SPD-10A UV-Vis detector. SEC samples were run in CHCl$_3$ at ambient temperature and calibrated to polystyrene standards.

**Materials.** Methyl acrylate, 1-hexene and 1-octene were vacuum transferred from calcium hydride and stored in a Schlenk flask. Norbornene derivatives were donated by BF Goodrich. All other chemicals were purchased from Aldrich and used as received. Nitroxide initiator: 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane was synthesized and purified following established procedure as in reference 15.

**Polymerization of methyl acrylate with 1-alkenes and norbornene derivatives.** For copolymerization of methyl acrylate with ethene and propene: a glass-lined stainless steel autoclave was used in which the nitroxide initiator (0.2 mmol), the control agent (0.01 mmol), and MA (0.04 mol) were added using a glove box. The autoclave was then
charged with ethene or propene and heated in a 120°C oil bath. After the reaction, the gas was vented and methanol was added to the reaction mixture. Volatiles were then evacuated. For other polymerizations: in a typical reaction, the nitroxide initiator (0.2 mmol), the control agent (0.01 mmol), MA (0.04 mol), and 1-alkene (0.02 mol) were added to a flask using a glove box. The reaction was then heated in a 120°C oil bath and worked up as described above.

**Kinetic studies of methyl acrylate/1-octene copolymerization.** The nitroxide initiator (0.2 mmol), the control agent (0.01 mmol), MA (0.04 mol), and 1-octene (0.01 mol) were added to a flask, together with 0.00394 mol of DMSO as the internal standard. Samples were taken at different time intervals using a syringe and analyzed by $^1$HNMR spectroscopy. The conversions of methyl acrylate and 1-octene were calculated from the integration of the vinyl CH peak of methyl acrylate at 6.3 ppm and terminal vinyl CH$_2$ resonance for 1-octene at 4.9 ppm, with respect to DMSO internal standard. The sample mixtures were quenched in methanol. After volatiles were removed, the molecular weight of the copolymer was measured by size exclusion chromatography.

**Synthesis of methyl acrylate/norbornene-$b$-methyl acrylate/1-hexene copolymer.** Methyl acrylate/norbornene copolymer ($M_n$=7,000, PDI=1.17, 18% norbornene) 0.4g, methyl acrylate (1.5g), 1-hexene (0.5g) were added in a round bottom flask and form a homogeneous solution. The reaction mixture was heated to 120°C for 18hrs. Polymer was precipitated by addition of methanol.
3.4 Bibliography

CHAPTER 4

FORMATION OF NANOSTRUCTURED POLYMER FILAMENTS IN

NANOCHANNELS
4.1 Introduction

The realization of the full potential of nanotechnology demands the ability to accurately position a wide variety of nanomaterials to construct complex structures and devices.\(^1\) Current lithographic techniques, including dip-pen lithography, allow precise positioning; however, the range of materials that can be synthesized is limited.\(^2\) Other approaches to forming nanoscale structures involve a two-step synthesizing-and-then-positioning procedure. While a variety of materials, including nanoparticles, nanotubes, and nanorods, can be synthesized in this manner, it seriously limits the ability to control size, location, and orientation on the nanoscale.\(^3\)-\(^8\) The common approach for nanowire fabrication is to use nano-templates for growth and then dissolve them to release the produced nanowires. These nanowires must then be “caught” and directed to their point of use. In this process, the big challenge that must be overcome for mass production of nanowire-based electronics and sensors is that one must be able to align and assemble these nanowires by design, not by statistics. Once nanowires are released from the template, it is very difficult to obtain spatial and orientational control in nanowire assembly as well as electrical contacts at a specific location. In order to circumvent this problem, we developed a new nanomanufacturing technology that utilizes carefully designed nanochannel reactor systems to align oriented nanomaterials as they are produced. Polymers were synthesized in these nanochannel reactors with controlled size with controlled size, orientation and location. The procedure is general, allowing the synthesis of different polymeric materials through a variety of chain-growth mechanisms (e.g., radical, metal-catalyzed polymerization) inside nanochannels, and opens up the
possibility of directed design of “just-in-place” nanoscale structures. With the attainment of controlled alignment, nanomaterials with novel properties and functions can be assembled into usable materials that will play a critical role in advancing future technologies.

This chapter describes a general procedure for the fabrication of nanodimensional channels and their use as templates for the formation of polymer filament arrays with precise dimensional and orientational control in a single integrated step.

4.2 Results and Discussion

4.2.1 Nanochannel fabrication

This part of work was completed by our collaborators in Penn State Nanofabrication Facility. The nanochannel templates were fabricated by the combined use of electron-beam lithography and a sacrificial metal line etching technique (Figure 4.1). The use of electron-beam lithography allowed nanoscale control of the channel dimension, interchannel separation, and orientation, which eventually transformed into the control of the nanofilament dimension, separation, and orientation. In brief, parallel lines of desired width and length were fabricated in a resist film on silicon oxide layer grown thermally on a silicon substrate and then filled with nickel to a desired height. After resist lift-off, only nickel lines remained on the substrate. A silicon nitride capping layer was next deposited over the substrate and finally the sacrificial nickel lines were
etched away thereby creating empty nanochannels imbedded in the capping layer. In this way, we fabricated empty channels as small as 20 nm wide and 20 nm tall as shown in Figure 4.2, which shows five empty, 20 nm wide by 20 nm high, channels in cross-section using a field emission scanning electron microscope (FESEM). The sample was cut in the middle of a 100 μm wide capping layer to create this cross-section. It can be seen that the sacrificial nickel was etched away completely leaving open channels. Other channels with the same height, 20 nm, but different widths, from 30 to 200 nm, were seen to be open as well by FESEM examination. Figure 4.3 shows AFM imaging of two channel grouping sets(a), spaced 10 microns apart, and one grouping set(b).
Figure 4.1 Schematic representation of the procedure used to fabricate nano molecular templates: (a) Silicon wafer with thermal oxide film. (b) PMMA patterned. (c) Sacrificial nickel lines formed after lift-off. (d) After the capping layer deposition, channels access regions were patterned by optical lithography and RIE. (e) Empty channels created after etching sacrificial nickel lines.
Figure 4.2 FESEM cross-section picture showing five 20 nm wide, 20 nm high nanochannel templates, which are spaced 200 nm apart.
Figure 4.3 Atomic force microscopy of the empty channel grouping sets after removal of silicon nitride: (a) The ends of two empty grouping sets (scale bar: 5 microns). (b) The center of a grouping set (scale bar: 2 microns). Line profiles of these grouping sets are also shown.
4.2.2 Polymerization in nanochannels

4.2.2.1 Radical polymerization

Poly(methyl methacrylate) (PMMA) was polymerized in the nanochannels by introducing a solution containing the initiator AIBN (0.5 mol%) dissolved in monomer liquid. Following initiator and monomer introduction, the sample surface was cleaned to remove the monomer, and polymerization was performed by heating at 80°C.

To measure the dimensions of polymer filaments produced in nanochannels, the capping silicon nitride layer was removed by HF etching and the exposed filaments were imaged with FESEM. Figure 4.4(a) shows FESEM image of five 123 nm wide filaments of PMMA, inside nanochannels. These filaments were all 20 nm thick and equally spaced (200 nm). The continuity of polymer filaments indicates the channels were open all the way. In one instance, a twisted PMMA filament with a 170 nm width and a 20 nm height was observed by FESEM as shown in Figure 4.4(b). These results show that the polymer filaments are formed with the same dimensions as the corresponding nanochannels. Thus, the nanochannel templates precisely define the dimension and location of polymer nanofilaments and, most notably, nanofilaments can be released without breaking.

An oxygen plasma exposure was utilized to verify the exposed filaments seen in Figure 4.4 were organic polymers, since an oxygen plasma can etch only the polymer but not an inorganic dielectric or metal. Figure 4.5 shows FESEM of polymer filaments
before and after oxygen plasma etching. This establishes that the filaments in the channel region were polymers. Clearly the oxygen plasma did not etch the silicon lines beyond the channel region.
Figure 4.4 (a) FESEM picture of a set of PMMA nanofilaments. Each filament is 120 nm wide, 20 nm thick, and separated 200 nm from others. (b) FESEM picture of a twisted polymer nanofilament having 170 nm width and 20 nm height.
Figure 4.5 FESEM pictures of polymer nanofilaments before (top) and after O\textsubscript{2} plasma etching (bottom).
Solid-like behavior of PMMA wires was confirmed by intermittent contact atomic force microscopy. Figure 4.6 is a scan at low force (ca. 100 nm free-oscillation amplitude, 80 nm scanning oscillation amplitude; tip force constant 0.65 Newton/meter; resonant frequency 43.5 kilohertz) showing a PMMA nanofilament. The filament was then scanned at a single spot for several line scans at large force (0 nm scanning oscillation amplitude). The original fiber was then re-scanned showing where it was cut by the AFM tip. The underlying silicon surface remained undamaged. Figure 4.6(b) shows line profiles of the nanofilament before and after cutting.

Fluorescence imaging was also used to verify polymer formation along entire nanochannels without void or collapsed region. Since the silicon nitride capping layer was transparent to UV-Vis light, this layer was not removed. Poly(1-pyrenylmethyl methacrylate) in channels was obtained by introducing a homogeneous solution of 1-pyrenylmethyl methacrylate and AIBN in toluene into the channels and heated at 80°C. Fig 4.7 shows the fluorescence imaging of formed polymers in the nanochannels. The fluorescence from ten different polymer line groups with designed widths ranging from 200 nm to 20 nm was detected by fluorescence microscope where different line width groups were separated by 10 µm as shown in Figure 4.7. Individual polymer nanofilaments can not be resolved in this image. This picture confirms that the polymerization did take place in the channels, and that the channels were open without collapsed regions. As the polymer was exposed for longer times, it bleached as shown in the rectangular area in Figure 4.7. To confirm what we see is fluorescent polymer, not
Figure 4.6 AFM of polymer nanofilament cutting, the left picture shows scan of one PMMA nanofilament at low tapping force, the right shows the same nanofilament scanned again at low force after scanning a single line at high force, scale bar is 100 nm. (b) Line profiles of the nanofilament before and after cutting.
Figure 4.7 Fluorescence imaging of poly(1-pyrenylmethyl methacrylate) in the nanochannels. The capping layer was not removed. The radiation was passed through a 365 nm excitation filter, and the fluorescence light was filtered by a 395 nm long pass emission filter.
monomer, the capping layer was removed and scanned with SEM. Then the sample was treated with toluene. After treatment, the sample was again imaged with SEM, which shows the polymer filaments remains intact. Since toluene is a good solvent for the monomer but not the polymer, the fluorescent lines in Figure 4.7 are polymer, not monomer.

4.2.2.2 Insertion polymerization

Heterogeneous metal-catalyzed polymerization in nanochannels through diffusion of monomer vapor was demonstrated by production of poly(norbornene) filaments at 25°C using [Pd(CH₃CN)₄][BF₄]₂ catalyst loaded via wet impregnation. Polymers with dimensions consistent with that of designed nanochannels were formed (Figure 4.8). It can also be noted that in the wider channels the filaments have some defects. This may be attributed to the diffusion of monomer in the channels. As shown in Scheme 4.1, in insertion polymerization, the monomer vapor needs to diffuse into catalytic site to continue polymer growth. In narrower channels the polymer grown from both side of the

![Scheme 4.1 Palladium catalyzed polymerization in nanochannels](image)
Figure 4.8 SEM of poly(norbornene) nanofilaments with widths of (a) 200 nm (b) 130 nm (c) 100 nm.
channel wall can meet each other and form continuous filaments. But in wider channels, the diffusion of monomer vapor into growing polymers becomes more difficult and polymer grown from both sides of the channel wall may not meet, therefore defects forms in the polymer filaments.

4.3 Conclusions

We have demonstrated the use of hard etching methods to create nanoscale templates with precise dimensional and orientational control, and their use in the production of polymer filaments with cross-sections as small as 20 nm high by 20 nm wide. The procedure is general as illustrated by the radical and coordination polymerizations that were performed in these nanochannels. The polymers grown follow the dimensions of the channels, allowing the precise control of the dimension, location and orientation of polymers. The approach opens up the possibility of “just-in-place” manufacturing and processing of patterns and devices from nanostructured polymers using well-established polymer chemistry.

4.4 Experimental

**Nanochannel fabrication.** Figure 4.1 describes the steps used to fabricate the nanochannel templates in this work. The nanochannel templates were fabricated via combined use of e-beam lithography and sacrificial metal line etching technique. The process begins with the growth of a 40 nm thick SiO$_2$ film on a silicon wafer. Then the e-
beam resist poly(methyl methacrylate), 100 nm thick, was spun on the wafer. Electron beam exposures were performed using beam energy of 100 kV. Ten different line widths were fabricated from 20 ~ 200 nm. For each line width, a set of five lines was placed in a row with equal spacing of 200 nm. Different line width grouping sets were separated by 10 µm. The dose for reliable removal of the resist with a resolution of 20 nm was 4000 µC/cm². Upon wet development, 20 ~ 200 nm width lines (trenches) were produced in the e-beam resist film. Nickel, the sacrificial material used to create the channels, was deposited to a thickness of 20 nm on the developed e-beam resist film, and then the e-beam resist was lifted off. This produced nickel lines of 20-200 nm in width and 20 nm in thickness in the areas not covered by the resist. A silicon nitride layer of 500 nm thickness was next deposited at 100°C in electron cyclotron resonance plasma enhanced chemical vapor deposition from a SiH₄ + N₂ + Ar gas mixture. This silicon nitride was used to form a transparent, non-collapsing capping layer. Subsequent lithography steps and reactive ion etching were used to define regions that gave access to the ends of the channels. In the final step, the sacrificial nickel lines were etched thereby creating empty nanochannels of 20-200 nm in width and 20 nm in thickness.

**PMMA nanofilaments.** A homogeneous solution of AIBN (0.5mol%) and MMA was introduced into the nanochannels by capillary force and sample surface was carefully cleaned with acetone. The nanochannel sample was heated at 80°C for 20 minutes.
**Poly(norbornene) nanofilaments.** A solution of $[\text{Pd(\text{CH}_3\text{CN})}_4][\text{BF}_4]_2$ in acetonitrile was introduced into nanochannels by capillary force. After the sample surface was cleaned it was exposed to norbornene vapor at room temperature for 24 hrs.

**Etching of capping layer.** Silicon nitride capping layer can be etched with 20% HF at room temperature for 5 minutes.

**Characterization.** FESEM was taken on a Leo 400 scanning electron microscope. AFM was obtained on Digital Instruments Dimension 3000.
4.5 Bibliography


CHAPTER 5

CONDUCTIVE POLYMER NANOFILAMENTS IN NANOCHANNELS
5.1 Introduction

Conjugated polymers such as polypyrrole are promising nanowire materials for future applications in nano-electronics and sensors due to their electrical, environmental stability, and processing properties.\textsuperscript{1,2} The application of conductive polymer as nanowires for connecting molecular devices has been proposed.\textsuperscript{3}

Conductive polymer nanowires can be easily synthesized by template-based technique.\textsuperscript{4} However, in developing nanoelectronic devices based on polymers, the electrodes and active semiconductor layers must be patterned at a submicron scale. Micro- or nanopatterning of polymers is necessary for electrical addressing and wiring of circuits. Recently, soft lithography and scanning probe microscopy techniques have shown to be useful techniques in patterning of conductive polymers.\textsuperscript{5} Other efforts include electric field induced orientation,\textsuperscript{6} fluid flow induced orientation,\textsuperscript{7} Langmuir-Blodgett alignment,\textsuperscript{8} and nano-imprinting using semiconductor superlattices.\textsuperscript{9} In general, the nanowire pick and place needed in some of these approaches and the nanowire contacting needed in all of them are very time-consuming and arduous.

On the basis of the results in Chapter 4, we fabricated nanochannels with “built-in” four-point electrodes and conductive polymers were synthesized in these nanochannels. Conductivities of polymers were successfully measured and the channel electrode contacts prove to be ohmic to conductive polymers. This approach results in positioned, oriented, contacted, and individually addressable nanowires.
5.2 Results and Discussion

5.2.1 Fabrication of channels with four-point probe

The devices were fabricated by our collaborators in Penn State Nanofabrication Facility. To measure the conductivity of polymers, nanochannels with four-point probe were designed. The procedure was similar to nanochannel fabrication procedure described in Chapter 4 except that after the nickel line deposition, a thin layer of titanium was deposited, followed by deposition of platinum. The titanium layer serves as adhesion layer between the nickel and platinum. Subsequent etching removes both nickel and titanium. An optical microscope image of the template is shown in Figure 5.1. The conductivity of empty channels was measured to be zero. Before nickel etching, the conductivity was determined to be $1/4$ of conductivity of bulk nickel. The nanochannels were built with two reservoirs on either side of the channel to facilitate movement of the solution into the nanochannels.
Figure 5.1 Nanochannels with four-point electrode probe and reservoir.
Figure 5.2 shows test of deionized water in this channels with four-point probe. Here a 100 nm wide, 20 nm high channel group was used. Deionized water was introduced at 30sec and current sees an immediate increase to 400pA. After water was removed by wipes at 90sec, current sees an immediate drop to zero. This result shows channels are open without collapsed regions. It is not clear why there is a second peak at about 50sec with a current around 680pA. This peak is seen in all pristine channel devices. One possibility is there were residual ions from etching process and the ions contribute to the conductivity when water is present in the channels.
Figure 5.2 Water conductivity in nanochannels.
5.2.2 Poly(aniline sulfonic acid) in nanochannels

Figure 5.3 shows current-voltage (I-V) curve of a pre-made conductive polymer: poly(aniline sulfonic acid) (5wt% in water) in nanochannels. The resistance of the polymer can be calculated from Ohm’s law:

\[ R = \frac{V}{I} \]  \hspace{1cm} (5.1)

where \( R \), \( V \), \( I \) are the resistance, voltage and current, respectively.

The relationship between resistance and conductivity is as follows:

\[ R = \frac{1}{\mu} \cdot \frac{L}{S} \]  \hspace{1cm} (5.2)

where \( \mu \), \( L \), \( S \) are conductivity, length and cross section area of the nanowire, respectively.

By substituting \( R \) in eq. 5.2 with 5.1, the conductivity of nanowire can be calculated as follows:

\[ \mu = \frac{I}{V} \cdot \frac{L}{S} \]  \hspace{1cm} (5.3)

Using eq. 5.3, the conductivity of poly(aniline sulfonic acid) as measured from Figure 5.3 is 0.005S/cm, which is close to the literature value (0.02-0.1S/cm, Aldrich). When the distance between the electrodes increases, the length of polymer wire \( L \) that is measured also increases. According to eq. 5.3, this should result in the decrease in current, which is what we see in Figure 5.3. Solid line is measured from two electrodes with distance of 10 \( \mu \)m, while dashed line is measured from two electrodes with distance of 30 \( \mu \)m. The slope in the solid line is higher than the slope in the dashed line, which indicates the resistance of the solid line is lower than that of the dashed line.
Figure 5.3 I-V curve of poly(aniline sulfonic acid) in nanochannels (100 nm), real time measurement. Solid line is measured from two electrodes with distance of 10 µm, dashed line is measured from two electrodes with distance of 30 µm.
It can also be noted that when the applied voltage is zero, there is still some current. The measured residual current (>150pA) is above the detection limit of the semiconductor analyzer and therefore is not noise. The residual current may be due to the contribution of ions in the polymer since the polymer is ionic. The polymer may clog the channel openings, which makes the evaporation of water in nanochannels a slow process and the presence of water can facilitate the movement of free ions.

5.2.3 Polypyrrole in nanochannels

5.2.3.1 Oxidation of pyrrole

The I-V curve of polypyrrole made from oxidation of pyrrole by iron (III) chloride is shown in Figure 5.4. There are differences in I-V between real time measurements (measure voltage as soon as current is applied) and hold, delay measurements (apply voltage for 3sec, wait 3sec, then measure current). This may be a result of residual ionic conductivity as ion movements are affected by different current applying methods. In the scanned voltage area, however, the I-V curve is generally linear, which indicates the formation of conductive polypyrrole in the channels. Conductivities of polypyrrole calculated from these I-V curves are in the order of $10^{-4}$ S/cm, which is lower than conductivity of bulk polypyrrole. Polypyrrole thus formed may have weak contact with built-in electrodes and hence lower conductivity is measured. Another possibility is that iron chloride may not cover all channel walls and polypyrrole may not be well ordered and continuous.
Figure 5.4 I-V curve of polypyrrole in nanochannels (FeCl$_3$ 1M, pyrrole 0.5M, measured on electrodes C and D).
5.2.3.2 Electropolymerization

I-V curve of polypyrrole from electropolymerization of pyrrole in sulfuric acid is shown in Figure 5.5. The channels used here are 60 nm high, 5 µm wide and 100 µm long. The I-V between any of the two electrodes is linear and conductivity was calculated to be 1 S/cm. The conductivity is in agreement with that of bulk polypyrrole material. It can be concluded that polypyrrole forms all the way in the channels. The conductivity is also in agreement with four-point measurements, which indicates good contact between electrodes and formed conductive polymer. The I-V characteristics were found to be unaffected by voltage sweep rate or direction, which indicates there is no contribution from ionic conductivity.

To date, conductivity of polypyrrole nanotube has only been measured by conductive scanning probe microscope.\textsuperscript{11,12} One disadvantage with using this technique is that conductivity may change with different forces applied.\textsuperscript{11} Our approach provides a direct pathway to measure conductivity of polypyrrole nanowires. The linearity of I-V curve also shows the built-in electrode contacts we developed is ohmic to polypyrrole.
Figure 5.5 I-V curve polypyrrole from electropolymerization (pyrrole 0.1M, H$_2$SO$_4$ 0.1M, pyrrole/H$_2$SO$_4$=1:6 (v/v), measured on electrodes C and D).
5.3 Conclusions

Nanochannels with four-point built-in electrodes were fabricated using lithography technique. Conductive polymers can be formed in the channels by introducing premade polymer or by polymerization in the channels. Polypyrrole formed by electropolymerization has similar conductivity as bulk polymers. The nanochannels with built-in electrode contacts are ohmic to polypyrrole.

5.4 Experimental

Materials. Pyrrole (Aldrich) was distilled and stored in a refrigerator. H$_2$SO$_4$ (99.999%), FeCl$_3$ (99.99%) were purchased from Aldrich and used as received. Water was purified from Barnstead Nanopure II system and its conductance is measured to be negligible.

Oxidation of pyrrole. Iron chloride (aq., 1M) solution was placed on one reservoir as shown in Figure 5.1. A micromanipulator was used to push the solution in contact with the opening of the channels. After observation of the drying of the solution (the solution inside channel is also presumably dried), pyrrole (aq. 0.5M) solution was placed on another reservoir and was pushed into channel area with micromanipulator. Movements of solution were monitored under microscope to avoid contact of pyrrole and iron chloride and formation of polymers on surface. Conductivity measurements began after 20 minutes of introduction of pyrrole.
**Electropolymerization.** In electropolymerization, a mixture of pyrrole (0.1M) and sulfuric acid (0.1M) (v/v=1:6) was applied to the channels. Current was applied between two furthest electrodes (A and D). Sweeping current was in the range of 0-25nA. The movement of solution was closely monitored under microscope to make sure no solution was on top of the four-point electrodes.

**Conductivity measurements.** Conductivity was measured by a Hewlett Packard 4145 semiconductor parameter analyzer. DC measurements were performed where voltage is applied through two micromanipulators in contact with two electrodes in the device. Voltage was increased or decreased at designated steps. In real time measurements, current was measured immediately after a voltage is applied. In hold, delay measurements, a voltage is applied for 3sec, after waiting 3sec, current was measured.
5.5 Bibliography


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R. Science 2003, 300, 112.


CHAPTER 6

A NEW PROCESS FOR FABRICATION OF POLYMERIC MICRO AND
NANOFIBERS
6.1 Introduction

Micro and nanofiber is an area that attracts research and development effort in academia and industry. The development of applications of nanofibers include: conducting and semi-conducting nanofibers for flexible nanoelectronics,\(^1\) nanofibers as scaffolds for bone and soft tissue repair,\(^2\) controlled release of drugs,\(^3\) hydrogen storage in nanofibrous media especially in carbon nanofibers,\(^4\) high performance filter media,\(^5\) catalysis using high surface area nanofibrous supported catalysts,\(^6\) and smart functional fabrics.\(^7\)

Methods currently used for producing micro and nanofibers include: 1). Electrospinning\(^8\): a well-established process for the fabrication of nanofiber mats from polymers that are soluble in a moderately volatile liquid; 2). Melt-blowing\(^9\): in which jets of gas impinge on a polymer extruded through a modular die.

However, polymers with extremely high melt viscosity, such as polytetrafluoroethylene (PTFE), are considered “non-melt processible”.\(^{10}\) Typical polymers have a melt viscosity of \(10^2\text{-}10^5\) poise, while PTFE has a melt viscosity of \(10^{10}\) poise. Therefore, it is impossible to make PTFE nanofibers from a melt-blowing process. PTFE is only soluble in expensive fluorocarbon solvents, which made the electrospinning process impractical.
Recently, people begin to realize fluoropolymers can be processed in supercritical carbon dioxide.11 PTFE can be swollen in supercritical carbon dioxide, then processed by extrusion, molding and sintering. This chapter describes a new process—“jet-blowing” in making polymeric micro and nanofibers. Polymers that can be processed include typical thermoplastics: poly(ethylene) (PE), poly(methyl methacrylate) (PMMA), poly(p-phenylene sulfide) (PPS), as well as non-melt processible PTFE.

6.2 Comparison of melt-blowing and jet-blowing

Formation of fibers by melt-blowing depends upon the extrusion of polymers of rather low viscosity at high temperatures through orifices into a zone where hot air is blown at very high velocity from two opposed sides of each orifice at the emerging polymer stream (Figure 6.1(a)). In this “jet-blowing” process, a two phase mixture of gas and polymer is blown through a single nozzle at pressures ranging from 1,000 psi to 30,000 psi, forming a jet consisting of a mixture of gas and polymer fibers (Figure 6.1(b)). The nozzle configurations of melt-blowing and jet-blowing are also different. Melt-blowing typically uses an Exxon nozzle as shown in Figure 6.2(a). Polymer extruded from the central holes is stretched by air impinging from the two outer slots. The configuration of the nozzle in jet-blowing is shown in Figure 6.2(b). The nozzle has 1/16” inner tubing diameter with capillary of 20-150 microns in diameter, 0.5-2 mm in length drilled from other side by electrical discharge machining (EDM). The detail is give in the experiment part. Polymer is stretched in this capillary and blown out together with high pressure carrying gas.
Figure 6.1 (a) Melt-blowing. Polymer extruded from the central hole is stretched by air impinging from the two outer slots.

Figure 6.1 (b) Jet-blowing. Two-phase mixture of gas and polymer enters tube from the left. The mixture is blown through the small capillary at the right, forming fibers.
Figure 6.2 (a) Exxon melt-blowing die.

Figure 6.2 (b) Jet-blowing nozzle configuration.
6.3 Results and Discussion

6.3.1 Jet-blowing conditions

6.3.1.1 Pressure

Typically, a minimum pressure of 1,000 psi was used and polymer fibers can be collected above this pressure. The maximum pressure that can be reached in jet-blowing process depends on the dimension of the capillary. For capillaries of 20, 50, 150 microns in diameter, the maximum pressure that can be reached are 24,000, 16,000 and 6,000 psi, respectively.

6.3.1.2 Temperature

Temperature is a critical factor that affects the morphology of polymers from in this jet-blowing process. Higher temperature favors formation of fibers while lower temperature favors formation of particles. Figure 6.3 shows SEM of PTFE starting material (Teflon® 7A). Jet-blowing of this PTFE around 220°C yields polymers with similar morphology, as well as small amount of fibers and particles with size of 100 nm or less. Figure 6.4(a),(b) show SEM of such fibers and particles. The diameter of the particles are about 50-100 nm. When a temperature of 290°C was used, the polymer from jet-blowing are predominantly micro and nanofibers, which will be discussed later in this chapter.
One important feature of jet-blowing process of PTFE is that PTFE fibers can be obtained below its melting temperature. The exact mechanism for the formation of fibers is not clear at this point. However, it is known that high pressure gas, especially nitrogen, has considerable solubility in PTFE\textsuperscript{14} and the dissolved large amount of gas may act as small molecule plasticizers, which greatly reduce the viscosity of polymer. The polymer is then carried by passing high pressure gas and stretched in the capillary into fibers.

Temperature is also an important factor that affects morphology of other polymers. For poly(p-phenylene sulfide), at lower temperatures 260\degree C, only particles can be collected. When a temperature of 300\degree C was used, products were predominantly fibers. For HDPE, at a temperature of 120\degree C, no product can be obtained from jet-blowing process. However, when a temperature of 180\degree C was used, products consist mainly of fibers. The reason that PTFE can be processed into fibers below its melting temperature while PE cannot is probably due to higher solubility of gas in fluorinated polymer and hence more effective softening of the polymer.

6.3.1.3 Gas

The absorption of gas on polymers also affects the morphology of products from jet-blowing process due to their different solubility in polymers. Figure 6.5(a),(b),(c) show PTFE materials collected from jet-blowing process in He, Ar and N\textsubscript{2} carrying gas at 310\degree C, respectively. The absorption of He in PTFE is much lower than that of Ar and
Figure 6.3 Scanning electron micrographs of PTFE starting material (Teflon® 7A).
Figure 6.4 Nanoparticles of PTFE from jet-blowing in N\textsubscript{2} carrying gas at 220\degree C.
Figure 6.5 PTFE from 150 micron capillary in (a)He (b)Ar (c)N$_2$ carrying gas at 310$^\circ$C.
N\textsubscript{2}. Jet-blowing product from He are mainly globules. For Ar and N\textsubscript{2}, products were mainly fibers. Further experiments on solubility of these gases in PTFE are needed to quantitatively provide us information about the relationship between solubility and fiber morphology.

6.3.2 PE, PMMA and PPS fibers

This jet-blowing process is applicable to a wide range of polymers, including thermoplastics such as PE, PMMA; high temperature engineering plastics such as PPS and PTFE. Figure 6.6, Figure 6.7 and Figure 6.8 show PE, PMMA, and PPS fibers from jet-blowing process. As can be seen, the fibers diameter ranges from 150 nm to a few microns, and are hundreds of microns in length. A temperature above the glass transition temperature of each polymer is needed to obtain fibers. The melting temperature for PE and glass transition temperature of PMMA and PPS and processing temperature are listed in Table 6.1.
Table 6.1 Melting/glass transition/processing temperature of polymers

<table>
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<tr>
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<th>PE</th>
<th>PMMA</th>
<th>PPS</th>
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<tbody>
<tr>
<td>$T_m/T_g$ ($^\circ$C)</td>
<td>130</td>
<td>108</td>
<td>290</td>
</tr>
<tr>
<td>Processing Temperature ($^\circ$C)</td>
<td>180</td>
<td>140</td>
<td>340</td>
</tr>
</tbody>
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Figure 6.6 SEM of PE fibers from 150 micron capillary in N₂ carrying gas at 180ºC.
Figure 6.7 SEM of PMMA fibers from 50 micron capillary in N\textsubscript{2} carrying gas at 140\textdegree{}C.
Figure 6.8 SEM of PPS fibers from 150 micron capillary in N\textsubscript{2} carrying gas at 340°C.
6.3.3 PTFE fibers

PTFE, with commercial name Teflon®, Dyneon® and others, is one of the most important thermoplastics and has excellent properties in chemical inertness, thermal stability, water repellence and others. As mentioned, the processing of PTFE, however, is difficult due to its high melt viscosity and is considered to be non-melt processible. In jet-blowing, however, PTFE can be readily processed into fibers or particles. The results are discussed below.

6.3.3.1 Fiber morphology

SEM of the fiber structures are shown in Figure 6.9(a),(b),(c). In Figure 6.9(a), it can be seen that PTFE fibers form a dense “mat”.

A closer look at the individual fibers show that fibers consist of nanostructured strands and porosity (Figure 6.9(b),(c)). These structures are similar to Gortex® PTFE fibers which have expanded and porous fiber structure. SEM of Goretex® fibers is shown in Figure 6.10. While Gortex® is made from multiple step extrusion and stretching process,15 this jet-blowing process can produce these PTFE fibers in a single and easy step without the use of solvents.
Figure 6.9 SEM of PTFE fibers from 150 micron capillary in N$_2$ carrying gas at 310°C.
Figure 6.10 SEM of Gortex® fibers
6.3.3.2 Raman spectrum

Raman spectrum of PTFE fibers is shown in Figure 6.11. Peaks of at 1383, 1304 (symmetric CF$_2$ stretching mode, depolarized), 1222 (asymmetric CF$_2$ stretching mode, depolarized), 733 cm$^{-1}$ are characteristic of PTFE. The lack of a tail for the peak at 1383 cm$^{-1}$ indicates the PTFE polymer fibers are highly crystalline and that significant decomposition does not occur at the 310°C temperature used for processing these fibers.$^{16}$ Micro Raman proves to be a good technique in chemical identification of fibers from jet-blowing process.

6.3.3.3 EDAX analysis

Electron dispersive X-ray analysis on fibers was performed on individual fibers to confirm the fibers are PTFE. In EDAX analysis, the sample is bombarded with electrons (from electron gun in SEM). These bombarding electrons collide with the electrons in the sample and knock some of them off. A vacancy generated by loss of an electron in the inner shell is filled by an electron from an outer shell, and X-ray can be generated during this process. The energy of X-ray thus generated was determined by the energy gap between the energy in the shell where the transferring electron is from and the energy in the shell where the transferring electron is moving to. Such energy gap is determined by the nature of elements and vary from one element to another. Therefore, analysis of such
Figure 6.11 Raman spectrum of PTFE fiber.
Figure 6.12 EDAX on PTFE fiber. The inset shows an SEM image of the fiber for which the EDAX spectrum was collected.
X-ray spectrum can give us chemical identification of the sample. Figure 6.12 shows EDAX result and the inset shows the fiber on which EDAX was taken. The peaks were analyzed by the computer. It is evident that the fiber exhibits a strong fluorine peak, which proves the fibers are PTFE, not glass fibers which are often used to reinforce PTFE.

6.3.3.4 Thermal properties

Two brands of PTFE were used in experiments. Du Pont Teflon® 7A with high molecular weight and 3M Dyneon® TF9201 with low molecular weight. The starting material and fibers collected from the jet-blowing process were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results are summarized in Table 6.1.

It can be seen that the melting temperature of the fiber is the same as starting material, again confirming the fibers are PTFE. It is well known that after melting of highly crystalline PTFE at 341°C, the melting temperature of PTFE will decrease to 327°C upon second heating. DSC of pure Teflon® 7A starting material confirms the first and second melting point at 341°C and 327°C, respectively. The fact that the melting temperature of PTFE from jet-blowing is the same as the starting material strongly indicates that the polymer has never reached its melting state in the process. The jet-blowing process, therefore, can be used to process PTFE well below its melting temperature and the product maintains the melting point of unsintered PTFE.
The heat of fusion of Teflon® 7A fiber is less than the starting Teflon® 7A powder. This indicates a decrease in crystallinity of high molecular weight Teflon® 7A. The Dyneon® PTFE low molecular weight fibers maintain the properties of the starting material. The decrease in crystallinity may be the result of the disruption of the crystalline phase in unsintered PTFE by high pressure carrying gas.

6.3.3.5 Surface properties

The rough structure of the polymer fiber “mat” results in highly hydrophobic surfaces. The reason is that the surface is covered with fiber and the air between the fibers. A water droplet is thus “suspended” on top of the fibers with air underneath, therefore it cannot wet the surface. The water contact angles of PE and PTFE fiber and the corresponding polymer are listed in Table 6.2. The contact angle of the fibers is much higher than those of the pure polymer. In PTFE, the fiber mat is nearly superhydrophobic (surface contact angle greater than 150° is defined as superhydrophobic). A picture of water on a silicon wafer and on a wafer coated with PTFE fiber is shown in Figure 6.13. This jet-blowing process, therefore, provides an easy way to form highly hydrophobic surfaces.

It is also noted that although the starting material does not stick to surfaces, the polymer fibers can adhere to surfaces of different nature, including glass, silicon, metal and polymer surfaces. The coating of fibers can withstand mechanical shock and is tacky.
### Table 6.2 Thermal properties of PTFE starting material and PTFE fibers

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting temperature ($^\circ$C)</th>
<th>Heat of fusion (J/g)</th>
<th>Weight loss at 500$^\circ$C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon 7A® powder</td>
<td>341.2</td>
<td>79.29</td>
<td>1.2</td>
</tr>
<tr>
<td>Teflon 7A® fiber</td>
<td>339.7</td>
<td>56.93</td>
<td>1.1</td>
</tr>
<tr>
<td>Dyneon® TF9201 powder</td>
<td>325.7</td>
<td>79.72</td>
<td>0.8</td>
</tr>
<tr>
<td>Dyneon® TF9201 fiber</td>
<td>324.3</td>
<td>79.10</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Table 6.3 Water contact angles of polymer and polymer fiber coated surfaces

<table>
<thead>
<tr>
<th>PE</th>
<th>PE fiber on glass</th>
<th>PTFE</th>
<th>PTFE on silicon wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>96$^\circ$</td>
<td>130$^\circ$</td>
<td>112$^\circ$</td>
<td>140$^\circ$</td>
</tr>
</tbody>
</table>
Figure 6.13 Water droplet on a (a) silicon wafer (b) wafer coated with PTFE fibers.
6.4 Conclusions

A new process- “jet-blowing” was developed to form polymeric micro and nanofibers. High pressure gas shears polymer through small orifices and polymers were blown in a gas “jet” and form fibers. A variety of polymers, including “non-melt processible” PTFE can be processed in this technique. In particular, PTFE material can be processed below its melting temperature and the fibers have Goretex® structure. Polymer fibers can adhere to surfaces of different nature and form nearly highly hydrophobic surfaces.

6.5 Experimental

Materials. PTFE (Teflon® 7A) was obtained from Polysciences, Inc. Dyneon® TF9201 was donated by 3M. PPS (M_n=10,000), PE (high density, M_w ca. 125,000), PMMA (M_w 120,000) were purchased from Aldrich. Polymers are all in powder forms.

Tubing and nozzle configurations. The diameter of the tube that the polymer initially resides in is 3/16" (4.76 mm). After going through an adapter the 1/4" ID tube goes into an HF9 female opening (Figure 6.14(a)) which then becomes the HF4 female opening (Figure 6.14(b)). HF9 opening is for 1/4" ID-9/16" OD tubing. HF4 opening is for 1/16" ID nozzle. Figure 6.14(c) shows the general configuration of the tubing. The adapter is a reducing one from HF9 to HF4. The polymer is then constrained by a 1/16" diameter
nozzle (Figure 6.3(b)). Then finally the nozzle is reduced to the 20-150 micron capillary that is about 0.5-2 mm long made by electrical discharge machining (EDM).

**EDM of 0.5-2mm capillary in nozzle.** The tool wire was made from the following steps. A copper wire (MWS Inc.) with desired diameter was chosen and Strip-X (GC Electronics, Rockford, IL) was applied to remove surface oxidation layers. After that the copper wire was cut into 1-2mm long and mounted into wire holder (Hylozoic Products, Mountlake Terrace, WA) with V-groove. The tip of wire that sticks out of the groove should be no more than twenty time longer than the diameter of the wire. Silver paint is then applied to hold the tool wire in place.

In electric discharge machining (EDM), a metal tool and metal workpiece are immersed in a dielectric fluid (such as oil, kerosene, or deionized water) and brought into close proximity by a servomechanism capable of precisely positioning the tool. An electric discharge is initiated across the gap between the tool and the workpiece, and current is allowed to flow for a short time before the discharge is terminated. This process is repeated many times each second, producing a series of discharges each of which erodes away a small portion of the workpiece. The servomechanism monitors the discharge behavior and advances or retracts the tool as necessary to maintain stable machining.

Material is removed predominantly by melting; under certain conditions vaporization or mechanical shock may also contribute to the process. Discharges tend to
occur where the gap between the tool and workpiece is narrowest; this maintains a fairly uniform gap width over the entire machining area, so that the hole eroded in the workpiece conforms to the shape of the tool.

The tool wire was mounted in a EDM machine (Hylozoic Products Micro EDM System). The nozzle for drilling was mounted in a workpiece holder and brought in close proximity of the tool. Typically, discharge energy of 0.2 microjoules and peak power of 0.1 watts were used. The depth of the hole drilled was preset by the EDM machine and closely monitored by a multimeter.

**General experimental set-up.** Figure 6.15 shows the overall configuration for the jet-blowing apparatus. The compressor pump is Cast Iron Series (Model J133), from U.S. Electrical Motors (St. Louis, MO). The high pressure plunger pump is from Newport Scientific (Model 46-14021-2). The nozzle and tubing containing the polymer are heated with electrical heating tape and controlled by a standard temperature controller. The polymer is loaded either in powder or pellet form into the tubing. High pressure gas, usually at high temperature, blows the two phase polymer/gas mixture from the tubing into the nozzle. The polymer/gas mixture exits the nozzle in the form of a jet. Fibers form during this jet blowing process. These fibers can then be collected and coated on a surface of choice. The tubing and nozzle was placed in a glove bag flushed with argon.

**Temperature measurements inside nozzle.** A thermocouple high pressure adapter was connected to the tubing and nozzle. To measure temperature inside nozzle, thermocouple
was inserted all the way into the 1/16” nozzle through the adapter. The temperature was measured by a Keithley multimeter (Model 2010).

**Characterization.** Scanning electron micrographs were obtained on a JSM 5400 instrument and also a JEOL 6700F. Differential scanning calorimetry and thermal gravimetric analyses were obtained with a TA instruments SDT2960 at heating rate of 10°C/min under argon atmosphere. Raman spectra were collected on individual fibers by means of a Dilor XY micro-Raman spectrometer with 514 nm laser excitation.
Figure 6.14 (a),(b) Jet-blowing adapters (c) tubing configuration.
Figure 6.15 General jet-blowing experiment set-up.
6.6 Bibliography


VITA

Mr. Bin Gu was born in Nanjing, China. He got his bachelor’s degree from Department of Chemistry in Fudan University in 1996. He then studied polymer science in Fudan University under the guidance of Professor Qiangguo Du. After getting his master’s degree, he came to Penn State in 1999 and joined Dr. Ayusman Sen group. While in graduate school he received Dalalian Fellowship for graduate research. He graduated from the Sen group in August, 2004 and began his postdoctoral appointment in Dr. Qiming Zhang’s group in Electrical Engineering department in Penn State University.