MACROMOLECULAR ARCHITECTURES BASED ON WELL-DEFINED POLY(PENTAFLUOROSTYRENE): DESIGN, SYNTHESIS, CHARACTERIZATION AND APPLICATIONS

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Summary

Fluoropolymers are potential candidates for dielectric interlayer because of their good chemical and thermal stability, and the lowest dielectric constants (κ’s) among the bulk polymers. However, their applications in sub-micron and nano-level electronics are hindered by difficulties in processing. Amphiphilic fluoropolymers with well-defined molecular weight, controllable chemical component, and various molecular structures are of great interest because of their unique solution and associative properties. The aims of this thesis were to prepare well-defined fluoropolymers and copolymers with favorable solution properties, as well as to prepare ultra-low-κ (<2.0) nano-structured fluoropolymer films via introducing nanopores into the polymer matrix.

First of all, comb-shaped copolymers consisting of rigid fluorinated polyimide (FPI) backbone and flexible polystyrene (PS) brushes (FPI-cb-PS), or poly(pentafluorostyrene) (PFS) brushes (FPI-cb-PFS), were synthesized by atom transfer radical polymerization (ATRP) from the bromide-containing FPI macrorinitiators (FPI-Br). In addition to having a dielectric constant as low as 2.1, the resulting comb-shaped FPI-cb-PFS copolymer also exhibited good processability, good thermal stability (470°C) and good mechanical properties. The FPI-cb-PFS copolymer is thus a potential ultra-low-κ material for sub-micron and nano-level electronics.

Nanoporous fluoropolymer films were also prepared via selective UV decomposition of the PMMA blocks in the well-defined PFS-b-PMMA copolymers prepared via ATRP. The nanoporous fluoropolymer films with pore size in range of 30-50 nm and
porosity in range of 15-40% were obtained from the PFS-\textit{b}-PMMA copolymers of different PMMA contents. Dielectric constants approaching 1.8 were achieved in the nanoporous fluoropolymer films having almost completely decomposed PMMA blocks.

Consecutive surface-initiated ATRPs of pentafluorostyrene and divinyl benzene from silane-functionalized SiO$_2$ nanoparticles gave rise to core-shell structured silica-\textit{graft}-poly(pentafluorostyrene)-\textit{block}-poly(divinyl benzene) (SiO$_2$-\textit{g}-PFS-\textit{b}-PDVB) nanospheres. SiO$_2$-\textit{g}-PFS-\textit{b}-PDVB (SiO$_2$ core and polymer shell) nanospheres of about 80-150 nm in diameter were allowed to agglomerate on a silicon substrate to form a film of about 3 µm in thickness. Under UV irradiation, the PDVB outer layer with residual double bonds on the core-shell nanospheres underwent inter- and further intra-sphere crosslinking to strengthen the film. Removal of the silica cores of the crosslinked nanospheres by HF etching gave rise to the nanoporous fluoropolymer film. The high porosity contributed by both the interstitial spaces among the nanospheres and the hollow cores of the nanospheres led to a dielectric constant as low as 1.7 for the resulting film.

Block copolymers of PFS and poly(\textit{tert}-butyl acrylate) (PtBA), or PFS-\textit{b}-PtBA copolymers, were synthesized via consecutive ATRP’s. Amphiphilic block copolymers of PFS and poly(acrylic acid) (PFS-\textit{b}-PAAC copolymers) were prepared via hydrolysis of the corresponding PFS-\textit{b}-PtBA copolymers. The amphiphilic PFS-\textit{b}-PAAC copolymers were cast into porous membranes by phase inversion in aqueous media. Membranes with well-defined pores of sizes in the micrometer range
were obtained as a result of inverse micelle formation. The pH of the aqueous media for phase inversion and the PAAC content in the PFS-\textit{b}-PAAC copolymers could be used to adjust the pore size of the membranes.

Finally, tadpole-shaped (or rod-coil) block-graft copolymers, consisting of a PFS block and a glycidyl methacrylate polymer (PGMA) block with grafted PtBA side chains, or PFS-\textit{b}-(PGMA-\textit{g}-PtBA) copolymers, were synthesized by consecutive ATRP’s. Hydrolysis of the PtBA side chains in the block-graft copolymer into the PAAC side chains gave rise to an amphiphilic PFS-\textit{b}-(PGMA-\textit{g}-PAAC) macromolecule with a brush-shaped hydrophilic head (rod) and a hydrophobic tail (coil). The formation of well-defined and uniform micelles from the present well-defined block-graft copolymers was also demonstrated.
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<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
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<td>AFM</td>
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CHAPTER 1

INTRODUCTION
Fluoropolymers possess many desirable chemical and physical properties such as high thermal stability, enhanced chemical resistance to aging and weather resistance, oil and water repellency, chemical inertness and low flammability and refractive index. Arising from these special physicochemical properties, fluoropolymers, as a family of high-performance material, are widely used in aerospace, aeronautics, optics, microelectronics, paints and coatings, and engineering structures and as biomaterials.

Polymeric architectures based on fluoromonomers, and complex molecular structures, such as diblock copolymer, triblock copolymers, comb-shaped copolymers, tadpole-shaped copolymers, dumbbell-shaped and hyperbranched copolymers, possess the unique physicochemical properties of the fluoropolymer segment such as high temperature resistance, excellent chemical inertness and low surface energy, and those of the other functional polymers segment such as good biocomparability and environment sensitivities. They are expected to exhibit unique properties in solution and solid state. Thus, fluorinated copolymers are potentially useful as biomedical and dielectric materials. Fluorinated copolymers, for example, can be used to prepare dielectric interlayers because of their low dielectric constants, chemical inertness and good thermal stability.

Ultra-low dielectric constant interlayers are required to reduce the resistance-capacitance time delay, cross-talk, and power dissipation in the new
generation of high density integrated circuits. According to the SIA (Semiconductor Industry Association) roadmap, interlayers with a dielectric constant of less than 2.5 are required for use in the new generation of integrated circuits, and of less than 2.0 for the future’s [Maier, 2001]. Among all the bulk polymeric materials, fluoropolymers, such as polytetrafluoroethylene, have the lowest dielectric constant of about 2.0-2.2. However, the difficulties in processing these fluoropolymers hindered their application in sub-micrometer- and nanometer-scale electronics. Thus, the synthesis of fluorinated block copolymers with good thermal property, low-κ value, high molecular weight, as well as good processability (good solubility in common organic solvent) is of great interest.

Attempts have been made to reduce the dielectric constant of materials to less than 2.0 [Maier et al., 2001]. Among the efforts, introduction of air gaps and nanopores into polymer films has received much attention. The incorporation of air, which has a dielectric constant of about 1, can greatly reduce the dielectric constant of the resulting porous structure. Since the bulk fluoropolymers have the lowest dielectric constant in the organic polymeric materials, introduction of nanopores into fluoropolymers would reduce their dielectric constants down to 2.0 or below. [see Chapter 2]

Amphiphilic polymer architectures is expected to exhibit special solution properties and micelle formation arising from the immiscibility between highly hydrophobic
block and hydrophilic block, as well as competing thermodynamic effects. Micelles fabricated from self-assembly of amphiphilic block copolymers could be used as nanoreservoirs in controlled drug delivery, gene therapy and phase transfer catalysis [Riess, 2003], and as templates for the fabrication of nanostructured hybrids [Neiser et al., 2004]. Micelle formation involving the amphiphilic copolymer was governed not only by the components of copolymers, but also by the molecular structure of the copolymers. Thus, the synthesis of amphiphilic block copolymers with well-defined molecular weights and the study of the micelle formation in these materials will be of great interest.

The fluoropolymers and copolymers with well-controlled molecular weight and structures can be synthesized by anionic and cationic process [Imae, 2003]. However, the stringent reaction conditions have limited the wide-spread application of these methods in industry. Recent development in control living radical polymerization, especially in atom transfer radical polymerization (ATRP), has provided a powerful tool for synthesizing well-defined polymers [Patten et al., 1998; Matyjaszewski et al., 2001]. Most importantly, the tolerance for functional groups and impurity makes ATRP a versatile tool for synthesizing complex polymeric architectures. Complex polymeric architectures with varying compositions, functionalities and topologies could be prepared by ATRP [see Chapter 2]. Some fluoropolymer architectures, such as di-block, tri-block and star block copolymer have been prepared by ATRP [Chapter 2].
Even though some fluorinated block copolymers have been prepared via ATRP and the physical and chemical properties of these copolymers have been studied, little research has been done on the synthesis and physicochemical properties of the amphiphilic fluorinated block copolymers with well-defined structure and architectures. Furthermore, little work has been carried out to prepare fluorinated block copolymers with low dielectric constant, high molecular weight, good thermal property and good processability, as well as nanoporous ultra-low-κ fluoropolymer films with well-defined and controllable pore sizes.

The overall purpose of this thesis is to synthesize of fluoropolymer with various macromolecular structures, including diblock, comb-shaped and tadpole shape copolymers via ATRP’s. In addition, the objectives of this thesis include:

(i) to prepare fluorinated copolymers with low-κ value, good processability, improved mechanical property and good thermal stability.

(ii) to prepare nanoporous ultra-low-κ fluoropolymer film with well-defined pore size

(iii) to prepare three-dimensionally-ordered porous fluoropolymer membrane from self-assembly and reverse micelle formation of diblock amphiphilic fluoropolymer.

(iv) to study molecular structure and micelle formation of amphiphilic tadpole-shaped fluoropolymer
The Chapter 2 presents an overview of the related literatures. In Chapter 3, comb-shaped copolymers, consisting of fluorinated polyimide (FPI) backbones and polystyrene (PS) or poly(pentafluorostyrene) (PFS) brushes, were synthesized by atom transfer radical polymerization from the FPI macrorinitiators. The PS and PFS side chains in the comb-shaped copolymers were of well-defined length. The chain length of the PS and PFS side chains could be regulated by varying the ATRP time. The FPI-cb-PS copolymer macromolecules were shown to self-assemble into ordered arrays on the hydrogen-terminated silicon surface. The macromolecular assembly, consisting of aligned and uniformly spaced rigid rods of 20-30 nm in length, was revealed by AFM images. In addition to good solution processability, the FPI-cb-PFS copolymer with its unique macromolecular architecture and high molecular weight up to 3,600,000 also exhibited good thermal stability, improved mechanical property and very low dielectric constant (κ~2.1). These fluoropolymers are thus a potential ultra-low-κ material for sub-micron and nano-level electronics.

In Chapter 4 block copolymers of PFS and poly(methylmethacrylate) (PMMA) (PFS-b-PMMA), were synthesized by ATRP. The copolymers were cast into thin films, followed by UV irradiation to photo-degrade the PMMA block. The porosity of the PFS film can be regulated by changing the PMMA content of the PFS-b-PMMA copolymer. A dielectric constant of 1.8 can be achieved in the nanoporous PFS film with a pore volume above 0.3 ml/g.
In Chapter 5, core-shell structured poly(pentafluorostyrene)-block-poly(divinyl benzene) (SiO$_2$-g-PFS-b-PDVB) nanospheres were prepared via consecutive surface-initiated ATRPs of pentafluorostyrene and divinyl benzene on SiO$_2$ nanoparticles. SiO$_2$-g-PFS-b-PDVB nanospheres of about 80-150 nm in diameter were allowed to agglomerate on a silicon substrate to form a film of about 2-4 µm in thickness. Under UV irradiation, PDVB outer layer with residual double bonds on the core-shell nanospheres underwent inter- and further intra-sphere crosslinking to strengthen the film. Removal of the silica cores of the crosslinked nanospheres by HF etching gave rise to the nanoporous fluoropolymer film. The high porosity contributed by both the interstitial spaces among the nanospheres and the hollow cores of the nanospheres led to a dielectric constant as low as 1.7 for the resulting film.

In Chapter 6, amphiphilic block copolymers of PFS and poly(acrylic acid) (PAAC) (PFS-b-PAAC) were obtained by hydrolysis of the block copolymers of PFS and poly(tert-butyl acrylate) (PtBA), or the PFS-b-PtBA copolymers prepared via consecutive ATRP’s. The PFS-b-PAAC copolymers were cast into membranes by phase inversion in aqueous media. The presence of well-defined hydrophilic and hydrophobic blocks of controlled proportions in the amphiphilic block copolymers allowed the formation of stable reverse micelles of controlled dimension when the copolymers underwent phase inversion. The resulting membranes with
three-dimensionally ordered pores and with pore sizes in the micrometer range were obtained from self-assembly and reverse micelle formation of the amphiphilic block copolymers. The pore sizes can be regulated by changing the content of PAAC in the PFS-\(b\)-PAAC copolymers and the pH of the medium used for phase inversion.

In Chapter 7, well-defined and tadpole-shaped block-graft amphiphilic macromolecules with a hydrophilic head of controllable dimension, consisting of designed length and number of PAAC brushes, and a hydrophobic PFS tail of controlled length were synthesized by consecutive ATRP’s. The process involved (i) synthesis of PFS via ATRP, (ii) block copolymerization with glycidyl methacrylate (GMA) via ATRP to give the PFS-\(b\)-PGMA copolymer, (iii) immobilization of the bromoacid initiators on the GMA units of the PGMA block to generate the PFS-\(b\)-PGMA macroinitiators, (iv) ATRP-mediated graft copolymerization with tert-butylacrylate (tBA) to generate the PFS-\(b\)-(PGMA-\(g\)-PtBA) copolymer. Hydrolysis of the PFS-\(b\)-(PGMA-\(g\)-PtBA) block-graft copolymer converted the PtBA side chains into PAAC side chains to produce an amphiphilic PFS-\(b\)-(PGMA-\(g\)-PAAC) macromolecule. The tadpole-shaped structure of the resulting macromolecules was revealed by AFM. The formation of well-defined and uniform micelles from the present well-defined block-graft copolymers was demonstrated.
CHAPTER 2

LITERATURE REVIEW
2.1 Applications and Physicochemical Properties of Fluoropolymers

Fluoropolymers, arising from strong bonding between carbon and fluorine atoms and the shielding of carbon backbone by fluorine atoms, exhibit unique physicochemical properties, such as, high thermal stability, enhanced chemical resistance, aging and weather resistance, oil and water repellence, excellent inertness and low flammability and refractive index [Améduri et al., 2001; Scheirs, 1997]. As a family of high-performance materials, fluoropolymers are widely used in various aggressive environments such as in chemical processing, oil well, motor vehicle engines, nuclear reactor, aerospace, aeronautics, optics, microelectronics, paints and coatings, engineering and biomaterial applications [Dorobny, 2000].

However, fluoropolymers, especially perfluoropolymer such as polytetrafluoroethylene (PTFE), polyhexafluoropropylene(PHFP) etc., have various disadvantages, such as poor solubility in common organic solvents and poor processibility [Améduri et al., 2001]. The synthesis of fluoro-copolymers has gained much attentions, because these copolymers not only exhibit improved physicochemical properties of fluoropolymers, but also exhibit various functionality by introducing different functional segments [Souzy et al., 2004]. Functional fluoro-copolymer have found applications in biomedical areas, due to the special physicochemical properties of fluoropolymers, such as chemical and biological inertness, high gas solubility, high fluidity and spreading coefficients and low surface tensions [Riess, 2002].
2.2 Macromolecular Architecture Design and Synthesis.

The interest in the synthesis of complex polymeric architectures, including linear di-, tri-, or multiblock copolymers, and nonlinear architectures, such as multi-arm, comb-shaped, star-shaped, palm-tree, dumbbell, umbrella-shaped and dendritic polymers, has increased enormously. Combining two or more chemically heterogeneous polymeric fragments by covalent bonds, the resulting architectures can exhibit unique properties in solution and solid state arising from the physicochemical properties of each segment. Complex polymeric architectures can be prepared by anionic polymerization, cationic polymerization, free radical polymerization, group transfer polymerization, ring opening metathesis polymerization, chemical modification, and combination of different polymerization methods [Hadjichristidis et al., 2003]. Recent development in control living radical polymerization including reversible addition fragmentation chain transfer processes (RAFT), nitroxide mediated polymerization (NMP) and atom transfer radical polymerization (ATRP), provides an alternative approach to synthesis complex polymeric architectures [Pyun et al., 2001; Kamigaito et al., 2001; Hawker et al., 2001]. The mechanism of living free radical polymerization, which involves a rapid dynamic equilibrium between a minute amount of growing free radicals and a large majority of dormant species, can give rise to well-defined (nearly monodispersed) macromolecules with ‘active’ or ‘living’ chain ends. These ‘active’ or ‘living’ molecules can, in turn, be used to synthesize complex macromolecules with well-defined structure and complex molecular structures [Kamigaito et al., 2001].
2.2.1 Macromolecular Architectures via ATRP

Since the atom transfer radical polymerization (ATRP) was first reported by Sawamoto and Matyjaszewski groups, it is among the most rapidly developing areas in polymer chemistry [Kato et al., 1995; Wang et al., 1995]. The increased tolerance of functional group and impurities make ATRP a key tool for synthesizing complex polymeric architectures with well defined structures and various functional segments [Matyjaszewski et al., 2001]. ATRP has shown to be an effective approach to synthesize various complex polymeric architectures.

Due to the absence of the chain-termination reactions and equal opportunity in polymer chain’s growth, ATRP can be used to copolymerize monomers to synthesize the gradient copolymers. Gradient copolymer is polymer with the composition along the chain varying smoothly in a statistical sense or the composition of polymer has a gradient. The first gradient copolymer from copolymerization of styrene and MMA was reported by Matyjaszewski’s group [Wang et al., 1995]. The molecular weight was predictable and the polydispersity less 1.25. From then on, a series of gradient copolymers such as, of n-butyl acrylate and styrene, epoxystyrene and styrene, trimethyilsilylstyrene and styrene, and MMA and n-butyl acrylate have been synthesized via ATRP [Arshart et al., 1999; Jones et al., 1999; McQuillan et al., 2000; Ziegler et al., 2001].
The wide variety of monomers, conservation of end groups, and control over molecular weights and polydispersity can facilitate ATRP to synthesize di- or tri-copolymers [Wang, U.S. Pant. 5,763,548]. Di-or tri-block copolymer is a polymer with two or three different macromolecular segments. Since the first di-block polystyrene-\(b\)-poly(methyl acrylate) copolymer was synthesized by Matyjaszewski’s group [Wang et al., 1995], numerous di-block copolymers, such as poly(butyl methacrylate)-\(b\)-poly(methyl methacrylate) [Granel et al., 1996], poly(methyl methacrylate)-\(b\)-poly\((N,N\)-dimethylacrylamide) [Senoo et al., 2000], poly(methyl methacrylate)-\(b\)-poly(4-vinylpyridine) [Yamamoto et al., 2000], and polystyrene-\(b\)-poly(hydroxylethyl methacrylate) [Wang and luo et al, 1999] have been prepared via ATRP. Tri-block copolymers such as, poly(methyl methacrylate)-\(b\)-poly(n-butyl methacrylate)-\(b\)-poly(methyl methacrylate) [ship, 1998], poly\((N,N\)-dimethylacrylamide)-\(b\)-poly(methyl methacrylate)-\(b\)-poly\((N,N\)-dimethylacrylamide) [Beers et al., 1999], and polystyrene-\(b\)-poly(4-acetoxy)styrene-\(b\)-polystyrene [Chen et al., 1999] have been prepared by either two-step block copolymerization with bifunctional initiators or by three-step block copolymerization from monofunctional initiators.

Star polymers can be prepared via ATRP from a multifunctional initiator. The number of arms of the multiarmed/star polymers is predetermined by the number of the carbon-halogen bonds of the initiator. A series of tetra-, hexa- and octa-armed star polymers of MMA have been prepared from corresponding initiators via ATRP.
Star block copolymers can also be prepared by block copolymerization of different monomers from multifunctional initiators via ATRP [Percec et al., 2000].

Comb-shaped and graft copolymers can also be prepared either by ATRP of macromonomers or by ATRP graft polymerization of monomers and macroinitiators with the reactive carbon-halogen bonds along the main chains. For example, comb-shaped polymers were prepared by ATRP of poly(oxyethylene glycal) macromonomers with varying molecular weights between 400 and 2000 [Mecerreyes et al., 2000]. Comb-shaped poly(hydroxylethyl methacrylate)-cb-polystyrene copolymers have been prepared via ATRP of styrene from the bromoisobutyrate immobilized poly(hydroxylethyl methacrylate) macroinitiators [Beers et al., 1998]. Random copolymerization of macromonomers and with a low molecular weight comonomer can be used to prepare graft copolymers. Graft copolymers such as, of n-butylacrylate and methacryloxy-capped poly(MMA) [Roos et al., 1999], and of n-butyl methylmethacrylate and methacryloxy-capped poly(ethylene oxide) [Hedrick et al., 1998] with narrow distributed molecular weights have been prepared via ATRP.

Hyperbranched polymers were synthesized from ATRP of monomers that have an initiating group along with a vinyl group [Frechet, 1995; Gaynor et al., 1996]. In addition, more complex polymeric architectures, such as dumb-bell-shaped, palm-tree-shaped and block graft copolymer could be also be synthesized via ATRP.
2.2.2 Functional Copolymers Prepared via ATRP

Comparing to ionic polymerization, ATRP, as a radical polymerization techniques exhibits more tolerance for polar functional group. Thus, this advantage of ATRP leads to direct synthesis of functional polymers with well-defined structure and controllable molecular weights. Polymers with functional groups at the chain ends can be prepared by ATRP of monomers and initiators, having various functional groups, such as hydroxyl-functionalized group, amine-functionalized group, amide-functionalized group, double bond-functionalized group, and epoxy-functionalized group [Kamigaito et al., 2001].

First of all, ATRP can be used to polymerize a wide range of functional monomers directly to produce polymers with functionalized pendent group and with well-defined structure and molecular weight. Epoxy groups, for example, could remain intact under the ATRP process. Glycidyl acrylate was polymerized to high molecular weight polymers ($M_n=50,000$) in bulk using CuBr and dNbp as catalyst and the molecular weight distribution is quite narrow < 1.25 [Matyjaszewski et al., 1997]. Hydroxyl functional monomer is readily polymerized via ATRP in bulk or in water at room temperature. ATRP of 2-hydroxyethyl methacrylate using n-propanol as the solvent can produce a polymer with molecular weight up to $M_n=40000$, and with...
polydispersity index less than 1.5 [Beers et al., 1999]. Amino- and
amido-functionalized monomers can also be polymerized directly by ATRP using
CuBr as catalyst. However, the successful polymerization of these monomers requires
polydentate ligands to avoid the displacement of the ligand on the copper complex by
the polymer chain [Coessens et al., 2001].

Polymers of carboxylic acid as a type of weak polyelectrolytes can be used as
environmental and biological materials for their special physicochemical properties
[Mori, 2003]. However, acrylic acid and methacrylic acid cannot be polymerized by
ATRP directly because of the interaction of the carboxylic acid functional groups with
the Cu catalyst [Matyjaszewski et al., 2001]. Therefore, group-protected acrylic acid
or methacrylic acid, such as (t-butyl acrylate), trimethylsilyl methacrylate,
terahydropyrabnyl methacrylate, and benzyl methacrylate were polymerized via ATRP
to produce well-defined polymers. After removal of the protecting groups, the
polymers of acrylic acid or methacrylic acid with well-defined structure were obtained
[Coessens et al., 2001]. Polymers of acrylic acid or methacrylic acid can also be
produced from hydrolysis of their corresponding sodium-salt polymers. Ionic
monomers carrying carboxylic salt, such as sodium methacrylate [Ashford et al., 1999]
and sodium 4-vinylbenzonate [Wang and Jackson, 2000] were polymerized with a
water-soluble bromide initiator in aqueous media to give rise to polymers with
moderately controlled molecular weights and molecular weight dispersity (<1.3).
After hydrolysis, the block copolymers with acrylic acid blocks were obtained.
2.2.3 Flouro-Block Copolymers Prepared via ATRP

Combining the unique properties of fluoropolymer and the special physicochemical properties of another polymeric block, fluorinated copolymers have attracted much attention recently [Reisinger et al., 2002; Imae, 2003]. Fluoro-block polymer would exhibit unique solution and physicochemical properties arising from the themodynamic incompatible of fluorinated polymers and other blocks, which can lead to self-assembly of the macromolecules into ordered nano-scale-structures with periodicity. Thus, fluoro-block copolymers were expected to find applications in nano-objects fabrication and biomedical areas.

There are two types of fluorinated monomers, fluorinated acrylate monomers, such as perfluoroalkyl (meth)acrylate and fluorinated aromatic monomers, such as pentafluorostyrene, can be polymerized via ATRP. Homopolymers of perfluoroheptyl (meth)acrylate were firstly synthesized by Matyjaszewski’s group via ATRP in scCO₂ using fluorinated ligand system [Xia et al., 1999]. Di-block copolymers of fluorinated (meth)acrylates and (2-dimethylamino)ethyl methacrylate or butyl methacrylate were prepared via ATRP under heterogeneous conditions [Li, 2002]. Fluorinated di-block copolymer poly(vinylidenedifluoride-co-hexafluoropropylene)-b-polystyrene and poly(vinylidenedifluoride-co-hexafluoropropylene)-b-P(methyl methacrylate) were prepared by ATRP of styrene and MMA monomer from chlorine-terminated
poly(vinylidenedifluoride-co-hexafluoropropylene) macroinitiator, respectively. [Shi et al., 2004].

Aromatic fluoropolymers have gained much attention because of their excellent thermal stability and good mechanical properties. Di-block copolymer of pentafluorostyrene and polystyrene was synthesized via ATRP of pentafluorostyrene from Br-terminated polystyrene or styrene from Br-terminated poly(pentafluorostyrene) macroinitiators [Jankova et al., 2003]. Highly fluorinated poly(pentafluorostyrene)-block-poly(2,3,5,6-tetrafluoro-4-(2,2,3,3,3-pentafluoropropoxy) styrene) and poly(pentafluorostyrene)-block-poly(2,3,5,6-tetrafluoro-4-(2,2,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctaoxy) styrene) were prepared by consecutive ATRP from Br-terminated poly(pentafluorostyrene) macroinitiators. These highly fluorinated block copolymers exhibit ultra-low surface energy [Borkar et al., 2004].

Complex fluorinated block copolymer architectures, such as ABA tri-block, and star-shaped have also been prepared via ATRP. ABA-shaped triblock fluorinated block copolymers were prepared by ATRP of pentafluorostyrene and bi-bromo-terminated poly(ethylene oxide) macroinitiator [Zhang et al., 2002; Jankova et al., 2004]. More complex polymeric architectures, such as four-arm star-like fluorinated block copolymer of methyl ether poly(ethylene glycol) methacrylate and heptadecafluorodecyl methacrylate, were also prepared by consecutive ATRP
[Shemper et al., 2004]. Functional fluorinated di-block copolymers containing sulfonic or carboxylic segments were synthesized from sulfonated of aromatic group of polystyrene-\textit{b}-poly((perfluorononeyl)oxylethyl methacrylate) or hydrolysis of t-butyl group of the poly(t-butyl acrylate)-\textit{b}-poly((perfluorononeyl)oxylethyl methacrylate) copolymers. Each precursor block copolymer with well-defined structure was prepared via ATRP [Li et al., 2003; Wang et al., 2004].

2.3 Ultra-low-\(\kappa\) Materials

Dielectric is any insulating medium, which intervenes between two conductors and permits electrostatic attraction and repulsion to take place across it. Dielectric constant is the property of a dielectric which determines the electrostatic energy stored per unit volume for unit potential gradient. Therefore, the materials with dielectric constant less than 2.5, or in the other word, materials having very good insulating properties, are called ultra-low-\(\kappa\) materials. [Websites: ttp://www.electronicconcepts.ie/news_updates.asp]

The increasing demands for miniaturization in the microelectronics industry force the continual development of high-performance materials used in the fabrication of semiconductor devices. Using the ultra-low dielectric constant (ultra-low-\(\kappa\)) interlayers can reduce the resistance-capacitance (RC) time delay, cross talk, and power dissipation in the new generation of higher-desity integrated circuits[Maier, 2001; Maex et al., 2003]. According to the Semiconductors Industry Association (SIA)
roadmap, a dielectric constant of interlays would be less than 2.0 to when the feature dimension in integrated circuits decrease to less than 0.13 µm [Maex et al., 2003]. High temperature polymers, including aromatic polyimides, poly(aryl ether)s, poly(ether ketone)s, heteroaromatic polymers and fluoropolymers, have been suggested for use as intermetal insulating dielectric materials.

### 2.3.1 Preparation of Fluoropolymer-based Dielectrics

Fluoropolymers are potential candidate for interlay dielectric applications because of their low dielectric constants and good chemical and thermal properties. Perfluorinated aliphatic polymers exhibit the lowest dielectric (2.0-2.1) constant among all bulk polymeric materials. However, most of fluoropolymers such as poly(tetrafluoroethylene), are highly crystalline, insoluble in common organic solvent, and with a decomposition temperature not far above the melting temperature [Maier, 2001]. Thus, these polymers can not process through common method such as melt processing and solvent casting. The difficulties in processing hinder their applications in sub-micrometer and nanometer-scale electronics.

Plasma polymerization is a convenient way to prepare fluoropolymer films. A variety of fluoropolymer films such as, tetrafluoromethane, hexafluoropropeneoxide [Savage et al., 1991], perfluoroallybenzne [Han et al., 2000], etc., have been prepared by plasma polymerization. However, the fluoropolymer films prepared from plasma polymerization, in most case, are insoluble and crosslinked, and lack defined chemical
Fluorinated polymer films can also be obtained by fluorination of hydrocarbon films. Fluorocarbon gas treated polymer films, such as poly(4-hydroxystyrene), poly(benzocyclobutene), poly(1,3-butadiene) and amorphous carbon, resulted in the decrease in dielectric constant of the film to 2.0-2.4. However, the thermal stability of the films was destroyed greatly. Thus, preparation of fluoropolymer with good thermal property, low dielectric constant and good solubility is still of great interest.

2.3.2 Nanoporous Low-κ Materials

In recent years, the introduction of air gaps into interconnect structures [Loo et al., 2001; Kohl et al., 2000] and nanopores into polymers [Hedrick et al., 1999; Nguyen et al., 1999; Padovani et al., 2001; Gagliani et al., 1979] to reduce their dielectric constants have been demonstrated. The incorporating of air, which has a dielectric constant of about 1, can greatly reduce the dielectric constant of the resulting porous structure. An approach of generating nanoporous film with pore size in nanometer range involves the use of block or graft copolymers. These copolymers were composed of a high-temperature, high glass transition temperature polymeric matrix and a second component that phase separates and can subsequently undergo clean thermal decomposition with evolution of volatile by-products to form a closed-cell structure. The pore size and pore volume of the resulting porous films can be tuned by controlling the molecular structure and molecular weight of labile segment. By this
end, nanoporous polyimide films have been prepared from block copolymers of polyimide and PMMA [Hedrick et al., 1995a], polyimide and PS [Hedrick et al., 1995b; Kim et al., 2001], fluorinated polyimide and poly(propylene oxide) [Carter et al., 2001; Fodor et al., 1997] and fluorinated polyimide and poly(methyl styrene) [Charlier et al., 1995]. Alternative methods for preparing graft copolymers and related nanoporous low-κ polyimide films have been reported [Fu et al., 2003b; Wang et al., 2004; Chen et al., 2004]. Furthermore, nanoporous poly(silsesquioxane)s [Su et al., 2002; Kim et al., 2002], and organosilicate films [Nguyen et al., 1999; Padovani et al., 2001] have been prepared by selective thermal decomposition of the sacrificial templates from the matrix films. This method provides an approach to produce porous film with controllable pore size and pore volume by using sacrificial template with different molecular weight. However, this method requires the matrix polymer having a higher $T_g$ than the decomposition temperature of the labile block. This limitation has hindered its extensive application.

Krause et al. developed an alternative approach to produce nanoporous polyimide films by supercritical foaming [Krause et al., 2001a; Krause et al., 2001b]. Firstly, the polyimide film is saturated with CO$_2$ at an elevated pressure. Then, the polymer/gas mixture is quenched into a super-saturated state by reducing the pressure and increasing the temperature. Finally, the nucleation and growth of the gas cells results in the formation of porous film. However, the poor control of the pore sized and pore volume in the resulting film, as well as the high $T_g$ requirement in the polymeric
matrix hindered its application.

It is possible to prepare fluoropolymer films with $\kappa$ less than 2.0 by introducing nanopores into fluoropolymeric matrix. Nanoporous fluoropolymer films can not be prepared by the methods described above because of the difficulty in processing. Ultra-low- $\kappa$ nanoporous fluoropolymer films ($\kappa < 1.9$) can be prepared by plasma polymerization of $C_4F_8$ and extraction of the non-crosslinked polymers with tetrahydrofuran [Takahashi et al., 2003], or from nanoporous composites consisting of plasma-polymerized allylpentafluorobenzene nanospheres and magnetron sputtering-deposited poly(tetrafluoroethylene) [Fu et al., 2004]. However, the uncontrollable pore size and open pore structure make these fluoropolymer films unsuitable for microelectronic applications [Maier, 2001]. Therefore, the preparation of nanoporous fluoropolymer with close-celled pore and controllable pore size is still of great interested.

### 2.4 Amphiphilic Block Copolymers

The interest in the synthesis and characterization of amphiphilic block copolymers has increased enormously in the recent years due to their unique molecular structure, consisting of both hydrophobic and hydrophilic blocks. The immiscibility between different blocks and the competing thermodynamic effects can give rise to spherical, spindly, gyroid, and lamellar molecular architecture, depending on the volume fraction, chemical composition, segmental interaction and molecular weight of the block.
copolymers [Lazzarri et al., 2003]. Amphiphilic block copolymer can be synthesized from conventional free radical polymerization [Nagamune et al., 1996; Lieske et al., 1998; Tauer et al., 1995], anionic polymerization [Calderara et al., 1993; Hirao et al., 1998; Webster et al., 1983], cationic polymerization [Charleux et al., 1999; Faust, 1999] and coupling reactions [Berger et al., 1996; Esselborn et al., 1996]. Furthermore, amphiphilic block copolymer with well-defined structure can be synthesized by ATRP process. These works have been reviewed by Jagur-Grodzinski [2001], Cossens [2001] and Mori [2003], respectively.

The segmental incompatibility endows the amphiphilic block copolymers with unique solution properties, as well as surfactive and self-associative characteristics, leading to the formation of micellar systems [Riess, 2003]. The micellization of amphiphilic copolymers in a selective solvent is a typical aspect of their colloidal properties. When an amphiphilic copolymer dissolved in a solvent that is a thermodynamic good solvent for one block and a precipitant for the other, the copolymer chains may self-assemble into micellar systems. The shape and size of these micelles are determined by the molecular structure and the solution conditions [Tuzar, 1993]. The micelles of the block copolymers formed in selective solvents, are potentially useful in nanotechnology, biomediacal area and industrial emulsification.

2.4.1 Application of Amphiphilic Block Copolymers as Emulsifiers
Amphiphilic block copolymers used as emulsifiers or dispersion stabilizers in emulsion polymerization have aroused increasing interest over the last decades [Riess,
Comparing with the traditional low-molecular-weight surfactants, amphiphilic block copolymer exhibits lower diffusion coefficients and lower critical micelle concentrations [Müller et al., 1997; Bouix et al., 1998]. Most important of all, the micelles formed from amphiphilic block copolymers can act as the seeds for creation of particles and remains long-term stability than those from traditional surfactants [Rager et al., 1999].

Since the amphiphilic block copolymer was first used in emulsion polymerization in 1950s by Wyandottes Chemical Corp for the preparation of PVAc dispersion [French, 1958], this research area has attracted increasing attentions. As emulsifiers, amphiphilic block copolymers including (i) nonionic block copolymers, such as block copolymers containing hydrophilic poly(ethylene oxide)s or poly(propylene oxide) blocks [Guyot et al., 2002; Jialanella et al., 1992] (ii) carboxylate block copolymers such as block copolymers containing poly(acrylic acid) or poly(methyl acrylic acid) blocks [Rager et al., 1999; Burguiere et al., 2003], (iii) sulfonate block copolymers [Müller et al., 1997; Tauer et al., 2000] and (iv) cationic block copolymer [Leemans et al., 1998; Schipper et al., 1995] have been studied for emulsion polymerizations.

Amphiphilic block copolymer can also be used as the emulsifiers in the inverse emulsion polymerization (water-in-oil polymerization). Amphiphilic block copolymer was reported by Wormuth et al. [2001] for the preparation of superparamagnetic latex by encapsulation of ion oxide in acrylic polymers. Furthermore, amphiphilic block
copolymers have been extensively used in the multiple emulsions, such as water-in-oil-in-water and oil-in-water-in-oil systems [Adam et al., 1989; Kanouni et al., 2002]. Furthermore, the use of the amphiphilic block copolymer as the stabilizers instead of traditional low-molecular-weight surfactants can improve the polymerization rate [Bognolo et al., 1991].

2.4.2 Application of Amphiphilic Block Copolymers in Drug Delivery.

Amphiphilic block copolymers have been used extensively in pharmaceutical applications ranging from sustained-release technologies to gene delivery [Adams et al., 2003]. In aqueous solution, amphiphilic block copolymers associate into micelles. The hydrophobic core regions of the resulting micelles can serve as reservoirs for hydrophobic drugs. Micelles based on amphiphilic block copolymers such as, poly(ethylene oxide)-block-poly(L-amino acid)s [Kwon et al., 1994; Yokoyama et al., 1998; lavasanifar et al., 2001], poly(ethylene oxide)-block-poly(ester)s [Kim et al., 1998; Stolnik et al., 2001; Burt et al., 1999] and poly(ethylene oxide)-block-poly(propylene oxide)-block- poly(ethylene oxide) [Kozlov et al., 2000; Venne et al., 1996; Batrakova et al., 1999], have been used for drug delivery. Amphiphilic block copolymer micelles are interest for drug delivery applications for a number of reasons. Firstly, hydrophobic drugs can be physically entrapped in the core of block copolymer micelles and transported at a concentration higher than that in intrinsic water. Secondly, hydrophilic blocks, which can form hydrogen bonds with the aqueous surrounding, produce a tight shell around the micellar core. As a result,
the contents of the hydrophobic core are effectively protected against hydrolysis and enzymatic degradation. Finally, the size and morphology of micelles for drug delivery application can be easily tuned by changing the chemical composition, the total molecular weight and block length ratio of the original amphiphilic block copolymers.

2.4.3 Application of Amphiphilic Block Copolymers in Structure-controlled Nanomaterials

Micelles with shapes from spherical to cylindrical, rod-like or plate-like can be formed from self-assembly of amphiphilic block copolymers by carefully choose conditions of micellar formation [Hamley, 2003]. Thus, amphiphilic block copolymer can be used to fabricate well-defined polymeric objects with various shapes such as polymeric spheres, rod or fibers, tunable sizes, and controllable compositions [lazzari et al., 2003].

Firstly, amphiphilic block copolymers can be used as the templates to prepared spherical nano-objects. Well-defined carbon nanospheres have developed by Tang et. al. [2004] through pyrolysis of shell cross-linked nanoparticles prepared by micellization and crosslinking of amphiphilic poly(acrylic acid)-block-poly(acrylonitrile) block copolymers in aqueous systems. Nanoparticle consisting of interlocked core about 10s nm in diameter and a corona with two well-separated hemispheres were prepared from poly(styrene)-block-poly(2-vinylpyridine)-block-poly(butylmethacrylate) through crosslinking poly(2-vinylpyridine) block [Saiti et al., 2000].
It is worth mentioning that polymeric nanofibers have also been prepared from self-organizing of amphiphilic block copolymers. Poly(4-vinylpyridine)-block-poly(styrene) diblock copolymers were combined with an amphiphile pentadecylphenol to yield macromolecules. Proper selection of conditions allowed the formation of morphology of PS cylinders inside a poly(4-vinylpyridine)(pentadecylphenol) matrix. Subsequent removal of pentadecylphenol yields polystyrene nanofibers [de Moel et al., 2001]. Self assembly of a low molecular weight poly(ethylene oxide)-block-poly(butadiene) gave rise to the formation of worm-like micelles at a low concentration in water. After crosslinking of the double bonds in the poly(butadiene), structure-stabled polymeric nanofibers were obtained [Won et al., 1999].

Amphiphilic block copolymers can also be used to prepare nanostructured organic/inorganic hybrids. These works have been reviewed by Förster et al. [1998].

In summary, there are few reports on the preparation of amphiphilic block fluoropolymer with well-defined macromolecular structure via ATRP. The high incomparability between the fluoropolymer block and the hydrophilic block would afford the copolymer a good property of micelle formation. The preparation of the complex fluoropolymeric architectures such as comb-shaped and tadpole-shaped is still something new and interesting.
Chapter 3

Rigid Fluorinated Polyimides with Well-defined Polystyrene/Poly(pentafluorostyrene) Side Chains from Atom Transfer Radical Polymerization
3.1 Introduction

Polyimides have been widely used as dielectric and encapsulation materials in microelectronics industry [De Abajo et al., 1999; Ohya et al., 1996; Maier, 2001]. Methods for improving the dielectric, mechanical and physicochemical properties of polyimides, which included the incorporation of pendant fluoro- or perfluoroalkyl groups [Miyagawa et al., 2003; Banerjee et al., 2003] and alteration of microstructure and morphology through block and graft copolymerizations have been developed [Martin et al., 2000]. The design and synthesis of fluoropolyimides with unique macromolecular architecture, high molecular weight, good thermal stability and solubility, and low dielectric constant are of great interest.

The work described in this chapter involves the synthesis of comb-shaped copolymers, consisting of fluorinated polyimide (FPI) backbones and polystyrene or poly(pentafluorostyrene) brushes by atom transfer radical polymerization from the FPI macroinitiators. The synthesis route is shown schematically in Figure 1. The resulting comb-shaped copolymers with rigid backbones (arising from the aromatic structure of polyimides) and nearly monodispersed polystyrene or poly(pentafluorostyrene) brushes were characterized by GPC, NMR, XPS, TGA, AFM, and dielectric constant measurements.
3.2. Experimental

3.2.1 Materials

2,4-Dinitrophenol (97%), 4,4’-hexafluoroisopropylidene (99%), triethylamine (99.5%), and tetrahydrofuran or THF (Anal. Grade), magnesium sulfate (99%) were purchased from Aldrich Chemical Company of Sternheim, Germany. CuBr (99%), 2-bromoisobutyryl bromide (98%), Sn\text{II}Cl_2·2H_2O (99.99%), ethyl acetate (Anal. Grade), methanol (Anal. Grade), N,N,N’N’N’-pentamethyldiethylenetriamine (99%), styrene (99%) and pentafluorostyrene (FS) (98%) were purchased from Aldrich Chemical Company of Milwaukee, WI. 2,4-Dinitrophenol and 4,4’-hexafluoroisopropylidene were thoroughly dehydrated before use by heating at 80°C in an oven for 12 h. THF was dried by heating at 80°C over 24 h with pristine sodium. The styrene and FS monomer was passed through a ready-to-use disposable inhibitor removal column (Aldrich Chem. Co.) prior to use.

3.2.2 Chemical Synthesis

3.2.2.1 Synthesis of 2,4-dinitrophenyl-2-bromoisobutyrate

2,4-Dinitrophenol (3.0 g, 16 mmol), triethylamine (2.8 mL, 20 mmol), and THF (40 mL) were introduced into a 100 mL three-neck round-bottom flask equipped with a condenser, a dropping funnel and a nitrogen inlet/outlet. After cooling to 0°C, 2-bromoisobutyryl bromide (5.0 mL, 41 mmol) in 10 mL of THF was added slowly, with continuous stirring, to the mixture over a period of 1 h under a nitrogen atmosphere. The temperature was allowed to rise to room temperature. The reaction
runs 24 h under stirring. The \((\text{C}_2\text{H}_5)_3\text{N}\cdot\text{HBr}\) was removed by filtration and the solvent removed by rotary evaporation. The product was isolated as an orange brown liquid, which crystallized upon standing. The solid was washed three times with 20 mL of ethanol to give a pale yellow crystalline product. Yield = 48%; m.p.: 79°C (DSC). \(^1\)H NMR (CDCl\(_3\), \(\delta/\text{ppm}\)): 8.98 (d, 1H, aromatic ring), 8.57 (dd, 1H, aromatic ring), 7.59 (d, 1H, aromatic ring) and 2.10 (s, 6H, CH\(_3\)) \(^{13}\)C NMR (CDCl\(_3\), \(\delta/\text{ppm}\)): 168.44 (C=O), 148.27 (aromatic ring), 145.33 (aromatic ring), 141.50 (aromatic ring), 129.16 (aromatic ring), 126.11 (aromatic ring), 121.74 (aromatic ring), 53.96 (C-Br) and 30.25 (CH\(_3\)). FTIR (solid, ATR cell): 1335 cm\(^{-1}\) (NO\(_2\)) and 1760 cm\(^{-1}\) (C=O).

### 3.2.2.2 Synthesis of 2,4-diaminophenyl-2-bromoisobutyrate

2,4-Dinitrophenyl-2-bromoisobutyrate (5.0 g, 15 mmol) and SnCl\(_2\)·2H\(_2\)O (33.9 g, 150 mmol) were dissolved in 200 mL of ethyl acetate. The mixture was refluxed for 1 h at 80°C, cooled, and the pH adjusted to 8-9 using a 5 wt% aqueous solution of sodium bicarbonate. Distilled water (200 mL) was added to separate the ethyl acetate layer. The organic layer was washed with saturated brine solution (3 × 200 mL), followed by distilled water (2 × 200 mL). The organic layer was then dried with magnesium sulfate, and the solvent was removed under reduced pressure. A light brown crystalline product was obtained. The product was purified by column chromatography with ethyl acetate as the mobile phase. Yield = 55%; m.p. > 200°C. \(^1\)H NMR (CDCl\(_3\), \(\delta/\text{ppm}\)): 7.27 (d, 1H, aromatic ring), 6.63 (d, 1H, aromatic ring), 6.26 (dd, 1H, aromatic ring), 4.56 (s, 4H, NH\(_2\)) and 2.01 (s, 6H, CH\(_3\)). \(^{13}\)C NMR (CDCl\(_3\), \(\delta/\text{ppm}\)): 168.55 (C=O), 140.97 (aromatic ring), 138.04 (aromatic ring), 126.01 (aromatic ring), 115.70 (aromatic...
ring), 110.52 (aromatic ring), 107.26 (aromatic ring), 62.18 (C-Br) and 31.43 (CH₃).

FTIR (solid, ATR cell): 3341, 3283 cm⁻¹ (NH₂) and 1666 cm⁻¹ (C=O).

3.2.2.3 Synthesis of the fluorinated polyimide macroinitiators

Initially, 0.41 g of 2,4-diaminophenyl-2-bromoisobutyrate (1.5 mmol) was dissolved in 3 mL of freshly distilled m-cresol. Then, 4,4’-hexafluoroisopropylidene (6FDA) (0.666 g, 1.50 mmol) and isoquinoline (0.4 mL, as the catalyst) were added at room temperature under a nitrogen atmosphere. The mixture was stirred for 1 h at room temperature. The temperature was slowly raised to 160°C and refluxed for 18 h. The polymerization was performed under flowing nitrogen to remove the water produced during imidization. The resulting viscous solution was poured into 100 mL of methanol with stirring. The precipitate was removed by filtration. The fluorinated polyimide macroinitiators (FPI-Br) so obtained were washed twice with 20 mL of methanol and hexane, respectively, and then dried at 100°C for 12 h under reduced pressure. Yield = 42%. FTIR (solid, ATR cell): 1781, 1713 cm⁻¹ (C=O) and 1366 cm⁻¹ (C-N). \( M_n = 9.4 \times 10^3 \) g/mol and polydispersity index (PDI) = 1.31.

3.2.2.4 Comb-shaped copolymers via ATRP

(a) In a typical copolymerization reaction, 0.067 g (0.007 mmol) of FPI-Br was dissolved in 0.2 mL of DMF. Then, 14.3 mg (0.10 mmol) of CuBr, 0.02 mol of styrene and 0.01 mmol of N,N,N’,N,N’-pentamethyldiethylene triamine were added. After three freeze-evacuate-thaw cycles, the mixture was heated to 110°C for 120 min. The reaction mixture was diluted with THF, eluted through an alumina column to remove the copper complex, and then poured into 200 mL of methanol to induce precipitation.
of the copolymer. The comb-shaped copolymer with the FPI backbone and polystyrene (PS) brushes (side chains) is referred to as the FPI-cb-PS copolymer. About 0.7 g of white powders were obtained (M_n=6.6x10^4 g/mole, PDI=1.41).

(b) In another copolymerization reaction, 0.067 g of FPI-Br was dissolved in 0.2 mL DMF. Then, 14.3 mg (0.1 mmol) of CuBr, 0.02 mol of pentafluorostyrene and 0.01 mmol of N,N,N’,N’,N’-pentamethyldiethylene triamine were added. After three freeze-evacuate-thaw cycles, the mixture was heated to 110°C for 120 min. The reaction mixture was diluted with THF, eluted through an alumina column to remove the copper complex, and then poured into 200 mL of methanol to induce the precipitation of the copolymer. The comb-shaped copolymer with the FPI backbone and poly(pentafluorostyrene) (PFS) brushes (side chains) is referred to as the FPI-cb-PFS copolymer. About 0.9 g of brown powders were obtained (M_n=7.8x10^4 g/mole, PDI=1.46).

### 3.2.2.5 Cleavage of side chains from the comb-shaped copolymers

In a typical reaction, 0.2 g of the FPI-cb-PS copolymer (M_n=6.6x10^4 g/mol and PDI=1.41 from GPC) was dissolved in a mixture of 20 mL of 5 wt% methanol solution of KOH and 30 mL of THF in a 100 mL round-bottom flask. The reaction mixture was refluxed for 1 week. When the solution was cooled to room temperature, concentrated hydrochloric acid was added to adjust the pH value to about 7. The mixture was extracted with chloroform and washed with water. The solvent was evaporated under reduced pressure. The remaining solid was dried by pumping under reduced pressure at room temperature. About 0.14 g of white powders were obtained (M_n=3.7x10^3 g/mol
and PDI=1.41 from GPC).

### 3.2.3 Materials Characterization

The structures of the FPI-Br and the comb-shaped copolymers were characterized by $^1$H NMR spectroscopy on a Bruker ARX 300 MHz spectrometer. CDCl$_3$ was used as the solvent for the FPI-Br and FPI-$cb$-PS copolymers. For the FPI-$cb$-PFS copolymers, tetrahydrofuran-$d_8$ was used instead. Gel permeation chromatography (GPC) was performed on an HP 1100 HPLC, equipped with a HP 1047A refractive index detector and a PLgel MIXED-C 300x7.5 mm column (packed with 5 µm particles of different pore sizes). The column packing allowed the separation of polymers over a wide molecular weight range of 200 to 3,000,000. THF was used as the eluent at a flow rate of 1 mL/min at 35°C. Polystyrene standards were used as the references. Thermal properties of the copolymers were measured by thermal gravimetric analysis (TGA). The samples were heated to 900°C at a heating rate of 10°C/min under a dry nitrogen atmosphere in a Du Pont Thermal Analyst 2100 system, equipped with a TGA 2050 thermal gravimetric analyzer. Differential scanning calorimetry (DSC) studies were conducted on a DSC82ze (Mettler Toledo Co. Zurich, Switzerland) apparatus at a heating rate of 10°C/min under a nitrogen atmosphere. FTIR measurements were carried out on a Bio-Rad FTS 165 spectrophotometer by dispersing the sample in an ATR cell. XPS measurements were carried out on a Kratos AXIS HSi spectrometer (Kratos Analytical Ltd, Manchester, England) with a monochromatized Al Kα X-ray source (1486.6 eV photons). The X-ray source was run at a reduced power of 150 W
(15 kV and 10 mA). The samples were mounted on the standard sample studs using double-sided adhesive tapes. The core-level spectra were obtained at a photoelectron take-off angle (with respect to the sample surface) of 90°. The pressure in the analysis chamber was maintained at 10⁻⁸ Torr or lower during sample measurements. The dielectric constants (κ’s) of the copolymer films were measured on a RF impedance/capacitance material analyzer (Hewlett Packard model 4291B) in the frequency range of 1 MHz to 1.8 GHz and at 50% relative humidity (25°C) under ambient atmosphere. Each film for dielectric constant measurement was obtained by spin-coating from a 10 wt% THF solution of the comb-shaped copolymer on a clean Si(100) substrate at 1000 revolutions/min. The film so-obtained had a thickness in the range of 10-20 µm, depending on the molecular weight of the copolymer. Film density was measured on a top-loading electronic Mettler Toledo balance (model AP250D, equipped with a density kit) according to the Archimedean principle. The mechanical properties of the polymer and copolymer film were measured on an Instron Model 5544 tensile tester from the Instron Corporation.

3.2.4 Macromolecular Structure of the Comb-shaped Copolymers

About 0.01 g of the FPI-cb-PS copolymer (Mₓ=1.4x10⁵ g/mol) was dissolved in 50 mL of THF. The solution was spin-coated on a hydrogen-terminated Si(100) substrate (Si-H substrate) at 2000 revolutions/min until the solvent had evaporated completely. The Si-H substrate was obtained by etching of the oxide-covered Si(100) substrate with 10 vol% HF. In comparison with the hydrophilic nature of the oxide-covered
silicon surface, the hydrophobic nature of the Si-H surface allowed better interactions of the hydrophobic copolymer with the substrate surface. The surface morphology of the film was studied by AFM, using a Nanoscope IIIa AFM from the Digital Instruments Inc. In each case, an area of 500 nm x 500 nm was scanned using the tapping mode. The drive frequency was 330 ±50 kHz, and the voltage was between 3.0 and 4.0 V. A drive amplitude of 300 mV, a set point of 3.34 µV, and a scan rate of 1.0 Hz were used.
3.3. Results and Discussion

3.3.1 Graft Copolymerization of Styrene and Pentafluorostyrene from the FPI Macroinitiators

The process of synthesizing the comb-shaped copolymers of fluorinated imide and styrene (or pentafluorostyrene) is shown schematically in Figure 3.1. Initially, 2,4-diaminophenyl-2-bromoisobutyrate was synthesized by the reduction of 2,4-dinitrophenyl-2-bromoisobutyrate. The latter was prepared from the reaction of 2,4-dinitrophenol with 2-bromoisobutyric acid. The fluorinated polyimide (FPI) macroinitiators (FPI-Br) were prepared from 2,4-diaminophenyl-2-bromoisobutyrate and 4,4’-hexafluoroisopropylidene by a one-step condensation reaction. 4,4’-Hexafluoroisopropylidene was used because the resulting polymer had relatively good solubility in common organic solvents, such as THF and DMF [de Abajo et al., 1999]. The FPI-Br macroinitiator should be completely imidized to prevent the carboxylic group from reacting with the Cu(II) species of the atom radical polymerization (ATRP) catalyst system. The reaction led to the formation of metal carboxylates which could inhibit deactivation in ATRP [Coessens et al., 2001].

The pristine FPI-Br has a number average molecular weight (M_n) of about 9.4x10^3 g/mole (corresponding to an average of 14 repeat units), weight average molecular weight (M_w) of about 1.2x10^4 g/mole, and a polydispersity index (PDI=M_w/M_n) of about 1.31, as indicated by gel permeation chromatography (GPC) results of Figure
Figure 3.1 Schematic illustration of the synthesis of comb-shaped copolymer of fluorinated polyimide and polystyrene (FPI-cb-PS) and of fluorinated polyimide and polypentafluorostyrene (FPI-cb-PFS) copolymer by atom radical polymerization (ATRP)
a: $M_n = 9.4 \times 10^3$ g/mole  \hspace{0.5cm} M_w / M_n = 1.28  (FPI-Br)
b: $M_n = 1.4 \times 10^5$ g/mole  \hspace{0.5cm} M_w / M_n = 1.57  (FPI-cb-PS2)
c: $M_n = 7.3 \times 10^3$ g/mole  \hspace{0.5cm} M_w / M_n = 1.19  (PS2)

Figure 3.2. Gel permeation chromatography (GPC) traces of the (a) brom-contained fluorinated polyimide macroinitiator (FPI-Br), (b) comb-shaped copolymer of fluorinated polyimide and polystyrene (FPI-cb-PS2) in Table 3.1. Synthetic conditions: [Styrene]:[Br]_{FPI-Br}:[CuBr]:[PMDE] = 200:1:1:1 at 110°C for 4 h) comb-shaped copolymer, and (b) polystyrene (PS) side chains hydrolyzed from FPI-cb-PS2.
3.2 (Trace \( a \)). Trace \( b \) shows the GPC results of a comb-shaped copolymer of FPI and polystyrene (FPI-\( cb \)-PS copolymer) from a monomer (styrene) to initiator molar feed ratio of 200 and a reaction time of 4 h (Sample FPI-\( cb \)-PS2 in Table 3.1). After the ATRP of styrene, the \( M_n \) of the resulting FPI-\( cb \)-PS2 copolymer increases dramatically to \( 1.4 \times 10^5 \) g/mol and PDI of the copolymer also increases to 1.57. Trace \( c \) is the GPC result of the PS side chains, cleaved from the FPI-\( cb \)-PS2 copolymer. The side chains have a \( M_n \) of about \( 7.3 \times 10^3 \) (containing about 70 repeat units of styrene) and a PDI of about 1.19. GPC results of the copolymers prepared from other reaction time are also summarized in Table 3.1. The increase in PDI of the FPI-\( cb \)-PS copolymer from that of the starting FPI-Br can be attributed to the fact that there are more initiator sites in the fraction of FPI macroinitiator with a higher molecular weight. Thus, after graft copolymerization with styrene, the large molecules will become even larger, leading to a wider distribution in molecular sizes of the resulting copolymers. The possibility of cross-linking among macromolecule is very low because of the characteristic of ATRP. Table 3.1 also shows that, with the increase in reaction time, the conversion of monomer also increased. The theoretical \( M_n \)’s of comb-shaped FPI-\( cb \)-PS and FPI-\( cb \)-PS copolymers (\( 6.8 \times 10^4 \) and \( 1.1 \times 10^5 \) g/mole for a reaction time of 2 h and \( 2.1 \times 10^5 \) and \( 3.6 \times 10^5 \) g/mol for a reaction time of 10 h) calculated from their respective monomer conversions, are in reasonable agreement with those obtained from GPC measurements. The ATRP of pentafluorostyrene (FS) from the FPI macroinitiators gave rise to the corresponding FPI and poly(pentafluorostyrene) copolymer (FPI-\( cb \)-PFS copolymer). At the given monomer to initiator molar feed ratio of 200:1
<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomer Conversion</th>
<th>Reaction Time (min)</th>
<th>(M_n^{[a]}) (g/mol)</th>
<th>Poly-dispersion Index (PDI)(^{[b]})</th>
<th>(M_n^{[c]}) (g/mol)</th>
<th>(M_n^{[d]}) (g/mol)</th>
<th>Density(^{[e]}) (g/cm(^3))</th>
<th>Dielectric Constant ((\kappa))</th>
<th>PS/PFS Brushes of the Copolymers</th>
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<td></td>
<td>(M_n^{[a,f]}) (g/mol)</td>
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<td></td>
<td></td>
<td></td>
<td>Poly-dispersion Index(^{[b]}) (PDI)</td>
</tr>
<tr>
<td>FPI-Br</td>
<td>20%</td>
<td>120</td>
<td>9.4x10(^3)(^{[i]})</td>
<td>1.31</td>
<td>1.41</td>
<td>6.9x10(^4)</td>
<td>6.8x10(^4)</td>
<td>1.10</td>
<td>3.0</td>
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<td>FPI-cb-PS1(^{[b]})</td>
<td>34%</td>
<td>240</td>
<td>1.4x10(^5)</td>
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<tr>
<td>FPI-cb-PS2(^{[b]})</td>
<td>70%</td>
<td>600</td>
<td>2.6x10(^5)</td>
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<td>FPI-cb-PS3(^{[b]})</td>
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<td>120</td>
<td>7.8x10(^4)</td>
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<td>FPI-cb-PFS1(^{[b]})</td>
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<td>1.8x10(^5)</td>
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<tr>
<td>FPI-cb-PFS3(^{[b]})</td>
<td>64%</td>
<td>600</td>
<td>3.6x10(^5)</td>
<td>1.71</td>
<td>3.7x10(^5)</td>
<td>3.6x10(^5)</td>
<td>1.30</td>
<td>2.1</td>
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</table>

\(^{[a]}\) Determined from gel permeation chromatography (GPC) using polystyrene standards as the reference

\(^{[b]}\) =number molecular weight \(M_n/\) weight average molecular weight (Mw)

\(^{[c]}\) Calculated from \(^{1}\)H NMR spectroscopy results.

\(^{[d]}\) Theoretical values calculated from conversion data

\(^{[e]}\) Determined according to the Archimedean Principle. Density of PS =1.05 g/cm\(^3\) density of PFS =1.43 g/cm\(^3\)

\(^{[f]}\) Cleaved side chains from hydrolysis of the corresponding copolymer. (FS=pentafluorostyrene)

\(^{[g]}\) Corresponding to about 14 repeat units

\(^{[h]}\) The copolymer was synthesized using the bromo-contained fluorinated polyimide macroinitiator (FPI-Br). The molar feed ratio of [Styrene (or Pentafluorostyrene)]:[Br]:[FPI-Br]:[CuBr]:[PMDE] = 200:1:1:1 (PMDE= N,N,N’N’N’-pentamethyldiethylenetriamine)
and at a polymerization time of about 2 h, the $M_n$ of the FPI-cb-PFS copolymer increases markedly from $9.4 \times 10^3$ to $7.8 \times 10^4$. At the same time, the PDI increases from 1.31 to 1.46 (Sample FPI-cb-PFS1 in Table 3.1).

The length of PS (or PFS) side chains in the FPI-cb-PS (or FPI-cb-PFS) copolymers can be regulated by varying the reaction time at the given monomer to initiator feed ratio (200:1). Table 3.1 shows the GPC results of the cleaved PS and PFS side chains from the FPI-cb-PS and FPI-cb-PFS copolymers, respectively. As the reaction time increased from 120 to 600 min, the $M_n$ of the PS side chains increased from $3.7 \times 10^3$ to $1.5 \times 10^4$ g/mol, while the PDI remained at around 1.2. For the corresponding FPI-cb-PFS copolymers, the $M_n$ of the PFS side chains increased from $6.2 \times 10^3$ to $1.8 \times 10^4$ g/mole and the PDI remained at around 1.2. The results indicate that comb-shaped FPI-cb-PS and FPI-cb-PFS copolymers with well-defined, or narrowly monodispersed, PS and PFS side chains have been synthesized from the FPI-Br macroinitiators by ATRP. For the FPI-cb-PFS copolymers prepared under prolonged ATRP time, (for example, FPI-cb-PFS3 in Table 3.1), the $M_n$ and the length of the cleaved PFS side chains obtained from GPC were lower than those determined from NMR spectroscopy or theoretical calculations. The discrepancy probably arose from the difference in hydrodynamic volumes between FPI-cb-PFS (or PFS) and PF standards used as GPC references.

3.3.2 Chemical Structures of the FPI-Br Macroinitiators and the FPI-cb-PS and FPI-cb-PFS Copolymers
The chemical structures of the FPI-Br macroinitiators and the FPI-cb-PS copolymers were studied by $^1$H NMR spectroscopy. Figure 3.3(a) shows the $^1$H NMR spectrum of the FPI-Br macroinitiators described in Table 3.1. The chemical shifts at about 1.8 ppm and in the range of 6.4-8.2 ppm are attributable to the protons of the bromo-esters and aromatic protons of the FPI, respectively. The minor chemical shifts in the range of 2.0-4.1 ppm are probably associated with sec-butyl (-$(\text{CH}_3)_2$CH) or hydroxyl (OH) groups incorporated during the FPI synthesis. Figure 3.3(b) shows the $^1$H NMR spectrum of a FPI-cb-PS copolymer (Sample FPI-cb-PS2 in Table 3.1). The chemical shifts in the range of 6.3-8.2 ppm are attributable to the aromatic protons of FPI and the PS side chains. Grafting of PS from FPI has resulted in the appearance of chemical shifts in the range of 1.6 to 2.4 ppm, attributable to the aliphatic -CH-CH$_2$- of the PS side chains. The chemical shift at about 1.2 ppm is attributable to the C-CH$_3$ group, while the chemical shift at about 4.4 ppm is associated with the -CHBr terminal group. The average length of PS side chains in the FPI-cb-PS copolymer can also be determined from the $^1$H NMR spectrum, using the area of the methylidyne protons in the -CHBr terminal group (k in Figure 3.3(b)) and the areas of the methylene and methylidyne protons (i and j in Figure 3.3(b)) in the backbone of the PS side chain. The NMR-derived copolymer compositions are also given in Table 3.1. The average length of the PS side chains deduced from NMR results is in reasonably good agreement with that estimated from GPC results. The good agreement of $M_n$ of the comb-shaped copolymer from NMR to that from GPC is accidental.
Chemical Shifts (ppm)

(a)

Chemical Shifts (ppm)

(b)
Figure 3.3. 300 MHz $^1$H NMR spectra of the (a) bromine-contained fluorinated polyimide macroinitiator (FPI-Br) having a $M_n$ of about $9.4 \times 10^3$ g/mole, (b) comb-shaped copolymer of fluorinated polyimide and polystyrene (FPI-cb-PS2 in Table 3.1. [Styrene]:[Br]$_{FPI-Br}$:[CuBr]:[PMDE] = 200:1:1:1 at 110°C for 4 h) having a $M_n$ of about $1.4 \times 10^5$ g/mole (c) comb-shaped copolymer of fluorinated polyimide and polypentafluorostyrene (FPI-cb-PFS2 in Table 3.1. [PF]:[Br]$_{FPI-Br}$:[CuBr]:[PMDE] = 200:1:1:1 at 110°C for 4 h) copolymer having a $M_n$ of about $1.6 \times 10^5$ g/mole.
Figure 3.3(c) shows the $^1$H NMR spectrum of a FPI-cb-PFS copolymer (Sample FPI-cb-PFS2 in Table 3.1). The chemical shifts in the range of 6.3-8.2 ppm are attributable to the aromatic protons of the FPI. Grafting of PFS side chains to FPI has resulted in the appearance of chemical shifts in the range of 2.0 to 2.9 ppm, attributable to the aliphatic $-CH-CH_2-$ of the PFS side chains. The chemical shift at about 1.1 ppm is attributable to the C-$CH_3$ group, while the chemical shift at about 4.8 ppm is associated with the $-CH$Br terminal group. The average length of the PFS side chains in the FPI-cb-PFS copolymer can also be determined from the $^1$H NMR spectrum, using the area of the methyl protons in the bromoester group (g in Figure 3.3(c)) and the areas of the methylene and methylidyne protons (i and j in Figure 3.3(c)) in the backbone of the PFS side chain. The average chain length of PFS in each copolymer, deduced from NMR results, is also given in Table 3.1. Again, the average length of PFS side chains obtained from the NMR results is in reasonable agreement with that estimated from the GPC results.

3.3.3 Chemical Composition of the FPI-Br Macroinitiators and the FPI-cb-PS and FPI-cb-PFS Copolymers

Figure 3.4 shows the respective C 1s and Br 3d core-level spectra of (a) the FPI-Br macroinitiators and (b) the FPI-cb-PS copolymer (FPI-cb-PS2 in Table 3.1). The C1s core-level spectrum of the FPI-Br macroinitiators can be curve-fitted with five peak components, having binding energies (BE’s) at 284.6 eV for the $\text{C}-\text{H}$ species, at 285.8 eV for the $\text{C}-\text{N}$, at 286.2 eV for the $\text{C}-\text{O}$ species, at 288.4 eV for the $N(\text{C}=\text{O})_2$ species and at 292.8 eV for the $\text{CF}_3$ species [Zhang et al., 2000]. The BE of the $\text{C}-\text{Br}$ species at
Figure 3.4. C 1s and Br 3d core-level spectra of the (a) brom-contained fluorinated polyimide macroinitiator (FPI-Br) having a $M_n$ of about $9.4 \times 10^3$ g/mole, (b) comb-shaped copolymer of fluorinated polyimide and polystyrene (FPI-cb-PS2 in Table 3.1. [Styrene]:[Br]$_{FPI-Br}$:[CuBr]:[PMDE] = 200:1:1:1 at 110°C for 4 h) having a $M_n$ of about $1.4 \times 10^5$ g/mole (c) comb-shaped copolymer of fluorinated polyimide and polypentafluorostyrene (FPI-cb-PFS2 in Table 3.1. [PF]:[Br]$_{FPI-Br}$:[CuBr]:[PMDE] = 200:1:1:1 at 110°C for 4 h) copolymer having a $M_n$ of about $1.6 \times 10^5$ g/mole.
about 286.3 eV [Beamson, 1992] overlaps with that of the C-O species. The BE’s of the O-C=O species and the N(C=O) imide species cannot be resolved unambiguously. The two species are represented by a single peak component at the BE of about 288.4 eV.

The XPS-derived [Br]/[C] ratio of 0.034 in Figure 3.4(a) for the FPI-Br macroinitiators is in excellent agreement with the theoretical ration of 0.035, based on the chemical structure of FPI-Br. Thus, there is approximately one bromo group (grafting side) per repeated unit of PFI. The substantial increase in intensity of the C-H peak component at the BE of 284.6 eV and the appearance of the π - π* shake-up satellite at the BE of 291.1 eV in Figure 3.4(b) are consistent with the presence of the PS side chains in the FPI-cb-PS copolymer. The intensity of the Br 3d core-level signal in the FPI-Br macroinitiators has decreased substantially after the ATRP of styrene because the relative concentration of Br in the FPI-cb-PS copolymer is lower than that of Br in the FPI-Br macroinitiators. The C1s core-level spectrum (Figure 3.4(c)) of the FPI-cb-PFS copolymer (FPI-cb-PFS2 in Table 3.1) can be curve-fitted with four peak components, having BE’s at 284.6 eV for the C-H species, at 286.1 eV for the –C$_5$F$_5$ species, at 288.4 eV for the CF(aromatic) species, and at 292.4 eV for the π - π* shake-up satellite [Beamson et al., 1992]. The BE’s of the C-Br species at about 286.3 eV and the C-O species at about 286.2 eV overlap with that of the C$_5$F$_5$ species (286.1 eV). The BE’s of the O-C=O species and the N(C=O)$_2$ imide species cannot be resolved unambiguously from that of the CF(aromatic) species.
3.3.4 AFM Characterization of the Comb-shaped FPI Copolymers

The comb-shaped FPI copolymers were further characterized by atomic force microscopy (AFM). Figure 3.5(a) shows an AFM tapping mode image of the FPI-cb-PS copolymer (FPI-cb-PS2 in Table 3.1) on a hydrogen-terminated silicon (Si-H) surface. The latter is more hydrophobic than the pristine (oxide-covered) silicon surface [Xu et al., 2004] and is expected to improve the interaction with the hydrophobic FPI-cb-PS macromolecules. Orderly aligned rigid macromolecular chains are discernible from the AFM image. The FPI-cb-PS molecules were found to self-assemble or align on the Si-H surface. The orderly assembly of the FPI-cb-PS molecules probably has resulted from the stiffness of the FPI backbone arising from the rigid conformation of aromatic rings. The excluded volumes of dense side chains forced the comb-shaped FPI-cb-PS macromolecules to assume a rod-like conformation in a good solvent, e.g. THF. When the dilute THF solution of FPI-cb-PS was cast onto a ‘compatible’ substrate, the rod-like copolymers self-assembled on the Si-H surface into ordered macromolecular arrays to minimize the surface free energy.

With a $M_n$ of about $1.4 \times 10^5$ g/mole, each molecule of FPI-cb-PS2 has, on the average, about 14 repeat units of the fluorinated imide in its backbone and 70 styrene units in each of its 14 side chains. Figure 3.5(b) shows the 3-dimensionally optimized state [Simulation Results from ACD Labs Freeware 5.0] of a FPI-cb-PS copolymer molecule with 4 FPI repeat units in the backbone and 2 PS side chains, each with 4
Figure 3.5. (a) AFM images of the comb-shaped copolymer of fluorinated polyimide and polystyrene (FPI-cb-PS2 in Table 3.1. [Styrene]:[Br]_{FPI-BF}[CuBr]:[PMDE] = 200:1:1:1 at 110°C for 4 h) macromolecular assembly on the hydrogen-terminated Si(100). The overall size of the image is approximately 500 nm x 500 nm. The topographical roughness of the surface with self-assembled macromolecular arrays is also shown. (b) A comb-shaped copolymer of fluorinated polyimide and polystyrene (FPI-cb-PS) model with 4 imide repeat units and two PS chains each having 4 repeat units.
The PS side chain exists as random coil and has a dimension of about 1 nm. Arising from the rigidity of the aromatic rings, the FPI backbone with 4 FPI repeat units has a fully extended length of about 6.7 nm in the presence of torsion among the aromatic rings.

In the AFM image of Figure 3.5(a), the rigid rod-like FPI-\textit{cb}-PS2 macromolecules have lengths in the range of 20-30 nm and widths in the range of 4-6 nm. Since each FPI repeat unit has a calculated length of about 1.7 nm, the observed length of the FPI-\textit{cb}-PS2 backbone (~14 repeat units) is comparable to that of the theoretical dimension (24 nm). As for the PS side chains, they probably exist as random coils around the rigid FPI backbone. The width or the radius of the FPI-\textit{cb}-PS copolymer rod is about 4-6 nm, which is comparable to the unperturbed dimension (~5.7 nm) of PS random coils [Billymer et al., 1984] consisting of about 70 repeat units. The macromolecule assumes the shape of a rigid rod because of the increase in excluded volume arising from repulsion among the PS side chains [Hadjichristidis et al., 2003]. The topographical scan of the surface with self-assembled macromolecular arrays in Figure 3.5(a) reveals well-defined repeating features of 6-7 nm in height. Thus, the side chains were presented in a highly folded state, instead of in the fully extended conformation. The ordered repeating features presented by AFM coincide with the macromolecular arrays, while the feature dimension is comparable to the lateral dimension of the comb-brush structure.
3.3.5 Thermal Stability, Processability, Mechanical Property and Dielectric Constant of the Comb-shaped Copolymers

Thermal stability, processability, mechanical property and dielectric property are the main concerns for polymeric materials used as interlayer dielectrics in the new generation of sub-micron and nano-level electronics [Maier, 2001]. When subjected to thermogravimetric analysis (TGA) (Figure 3.6), the FPI macroinitiator underwent a two-step weight loss process. The first major weight loss at about 260°C was probably associated with the decomposition of the bromoester groups. When heated to a temperature above 600°C, about 50% of the weight remained. The phenomenon suggests that the FPI has been carbonized. The FPI-cb-PS and FPI-cb-PFS copolymers, on the other hand, underwent a clean major weight loss, commencing at about 400°C and 470°C, respectively. These temperatures corresponded to the thermal decomposition temperatures of the PS and PFS side chains. The results suggest that thermal stability of the copolymers is dominated by the PFS and PS brushes. Thus, the FPI-cb-PFS copolymer exhibits an excellent thermal stability owing to the presence of fluorinated aromatic groups.

Both FPI-cb-PS and FPI-cb-PFS copolymers exhibit good solubility in common organic solvents, such as THF, DMF and xylene. For example, 10 wt% THF solutions of FPI-cb-PS and FPI-cb-PFS2 can be prepared readily. Uniform FPI-cb-PS (and FPI-cb-PFS) films up to ten’s of microns in thickness can be obtained by spin-coating
Figure 3.6. Thermal gravimetric (TGA) curves of (a) brom-contained fluorinated polyimide macroinitiator (FPI-Br) having a $M_n$ of $9.4 \times 10^3$ g/mol, (b) comb-shaped copolymer of fluorinated polyimide and polystyrene (FPI-cb-PS2 in Table 3.1. [Styrene]:[Br]_{FPI-Br}:[CuBr]:[PMDE] = 200:1:1:1 at 110°C for 4 h) having a $M_n$ of about $1.4 \times 10^5$ g/mole, and (c) comb-shaped copolymer of fluorinated polyimide and polymer pentfluorostyrene (FPI-cb-PFS2 in Table 3.1. [PF]:[Br]_{FPI-Br}:[CuBr]:[PMDE] = 200:1:1:1 at 110°C for 4 h) copolymer having a $M_n$ of about $1.6 \times 10^5$ g/mole.
a 10 wt% THF solution of the copolymer at different rotation speeds. Thus, good solubility of the comb-shaped FPI-\(cb\)-PS and FPI-\(cb\)-PFS copolymers in common organic solvents has imparted good processability to these copolymers with rigid backbones. The PFS homopolymer film is brittle. The film prepared from the PFS homopolymer, with a \(M_n\) of \(2.7 \times 10^4\) g/mol and PDI of 1.12, has a tensile strength of about 0.6 MPa and a fracture strain of about 2-3%. In comparison, the FPI-\(cb\)-PFS copolymers have improved tensile strength of 0.9-1.1 MPa and fracture strain of about 5-7 %, arising from the contribution of the PFI main chain and the introduction of PFS side chains.

Dielectric constants (\(\kappa\)’s) of the FPI film and the FPI-\(cb\)-PS and FPI-\(cb\)-PFS copolymer films are shown in Table 3.1. The FPI maroinitiator has a dielectric constant of about 3.0. For the FPI-\(cb\)-PS copolymers, relatively low dielectric constants (in the order of 2.6) were obtained. These \(\kappa\) values are comparable to that of the PS homopolymer. The FPI-\(cb\)-PFS3 copolymer with a \(M_n\) of about \(3.6 \times 10^5\) g/mol has a low dielectric constant of only about 2.1, which is lower than that of the PFS homopolymer (\(\kappa\sim 2.2\)) [Han et al., 1998] and is comparable to that of the very inert poly(tetrafluoroethylene) (\(\kappa\sim 2.1\)). This phenomenon can be accounted for by the fact that, in addition to having a high fluorine content, the copolymer with the comb-shaped macromolecular architecture had an increased free volume over those of the FPI and PFS homopolymers. The comb-shaped FPI-\(cb\)-PFS macromolecular architecture has a density of about 1.30 g/cm\(^3\), which is lower than that of 1.43 g/cm\(^3\).
for the PFS homopolymer or that of 1.41 g/cm$^3$ for the FPI, arising probably from the less efficient packing of the rigid comb-shaped structure.
3.4. Conclusions

Comb-shaped FPI-cb-PS and FPI-cb-PFS copolymers were successfully prepared via ATRP of styrene and pentafluorostyrene, respectively, from the FPI-Br macroinitiators. The PS and PFS side chains in the comb-shaped copolymers were of well-defined lengths. The chain length of the PS and PFS side chains could be regulated by varying the ATRP time. The FPI-cb-PS copolymer with a $M_n$ of about $9.4 \times 10^3$ g/mol, having about 14 fluorinated imide units in the rigid backbone (rod) and about 70 styrene units in each of the 14 side chains (coils), were shown to self-assemble into ordered arrays on the hydrogen-terminated (hydrophobic) silicon surface. The macromolecular assembly, consisting of aligned and uniformly spaced rigid rods of 20-30 nm in length and 4-6 nm in lateral dimension, was revealed by AFM images. In addition to good solution processability, the FPI-cb-PFS copolymer with its unique macromolecular architecture also exhibited good thermal stability, improved mechanical properties and very low dielectric constant ($\kappa \sim 2.1$). The FPI-cb-PFS copolymer is thus a potential ultra-low-\(\kappa\) material for sub-micron and nano-level electronics.
CHAPTER 4

Nanoporous Ultra-Low Dielectric Constant Fluoropolymer Films via Selective UV Decomposition of Poly(pentafluorostyrene-block-methylmethacrylate) Copolymers Prepared by ATRP
4.1 Introduction

As mentioned in the literature review, fluoropolymers are potential candidates for interlayer dielectric applications because of their low dielectric constants, chemical inertness and good thermal stability [Sacher, 1994; Souzy et al., 2004]. The introduction of nanopores or air gaps into fluoropolymer is expected to reduce their dielectric constants to below 2. Poly(methylmethacrylate) (PMMA) is a well-known positive photo-resist [Reiser, 1989]. Upon exposure to deep ultra-violet (UV) or electron beam irradiation, PMMA is degraded and depolymerized into small molecular fragments via chain scission or oxidation [Kaczmarek et al., 2000; Osawa et al., 1991; Caykara et al., 1999]. On the other hand, fluoropolymers have good optical and photochemical stability when exposed to deep UV [Forsythe et al., 2000; Ameduri et al., 2001].

In this part of work, block copolymers of poly(pentafluorostyrene) (PFS) and poly(methylmethacrylate) (PMMA) (PFS-\(b\)-PMMA), were synthesized by ATRP. The copolymers were cast into thin films, followed by UV irradiation to photo-degrade the PMMA block. After the decomposed PMMA fragments had been extracted, the resulting nanoporous fluoropolymer films exhibited an ultra-low dielectric constant of about 1.8. The aromatic fluoropolymer was chosen over the more flexible fluorinated aliphatic chains in an attempt to enhance the thermal stability and mechanical properties of the resulting nanoporous films.
4.2. Experimental

4.2.1 Materials

Ethyl bromoisobutyrate (EBB), tetrahydrofuran (THF), 2,2’-bipyridine (bpy), methanol and xylene were purchased from Aldrich Chemical Company of Milwaukee, WI and were used as received. CuBr (Sigma-Aldrich, Seelze, Germany) was purified in acetic acid, washed with methanol and dried under vacuum to afford a white powder. 2,3,4,5,6-Pentafluorostyrene (FS) (Aldrich) was passed through a ready-to-use disposable inhibitor-remover column (Aldrich). Methylmethacrylate (MMA) (Aldrich) was distilled under reduced pressure and stored at -10°C.

4.2.2 Atom Transfer Radical Polymerizations (ATRP)

a. ATRP of FS

The general procedure is as following: A mixture of 0.017 ml (0.1 mmol) of EBB, 14.3 mg (0.1 mmol) of CuBr, 47 mg of bpy and 0.01mol of FS was placed in a 25 ml glass tube. The tube was degassed by three freeze-evacuate-thaw cycles and sealed under vacuum. It was then placed in an oil-bath preheated to 110°C. After a prescribed reaction time, the polymerization mixture was diluted with THF and eluted through an alumina column to remove the copper bromide complex. The polymer was precipitated in excess methanol. The FS polymer (PFS) in white powder form was collected after drying under reduced pressure.

b. Block Copolymerization with MMA

In a typical block copolymerization, 0.8 g of the PFS macroinitiator (PFS-Br) was
Figure 4.1. Schematic illustration of the synthesis of the PFS-\textit{b}-PMMA copolymer from ATRP and the preparation of the corresponding nanoporous PFS film.
dissolved in 7 ml xylene, 2 ml of MMA, 0.0072 g (0.05 mmol) of CuBr and 0.024 g of bpy were added. After three freeze-evacuate-thaw cycles, the mixture was heated to 90°C for 7-12 h. The block copolymer solutions were diluted with THF, eluted through alumina column to remove the copper complex, and then precipitated in methanol. Yields of the powdery block copolymers were determined gravimetrically after drying under reduced pressure.

4.2.3 Preparation of the PFS-\textit{b}-MMA Films

Initially, the block copolymer was dissolved in \textit{N}-methyl-2-pyrrolidone (NMP) to a concentration about 17%. The films with a thickness 1-2 µm were prepared by spin-coating from the solvent at 2000 round/min on a clean Si(100) substrate. The film was kept at 80°C for about 6 h, and then at 170°C for another 12 h, in a vacuum oven.

4.2.4 Photo-decomposition of the Block Copolymer Films.

The main products of the photodegradation of PMMA in vacuum are methyl formate, methanol, methyl methacrylate and, in air, methane, hydrogen, carbon monoxide, and carbon dioxide are formed in addition. The PFS block has high UV resistance as the other fluoropolymer due to the strong C-F bond on the aromatic rings. The selective UV decomposition of the PMMA block in the copolymer film was carried out using a Kratos LH150 xenon arc source. The 150 W xenon source provided an intensity of about $10^{17}$ photons/cm$^2\cdot$s$\cdot$10 nm in the wave length region of 250-350 nm. After 3 h
of UV exposure, the film was extract in excess methanol for 24 hours to remove the
degradation products of PMMA. The film was subsequently dried at 50°C in a vacuum
oven for about 12 h.

### 4.2.5 Materials Characterization

The structures, chemical composition and molecular weights of polymers were
characterized by $^1$H NMR, XPS and GPC, respectively. The thermal properties and
dielectric constant of the fluoropolymer films were studied by TGA and RF
impedance/capacitance material analyzer. The procedures were the same as those
described in Section 3.2.3. Field emission scanning electron microscopy (FESEM)
measurements were carried out on a JEOL JSM-6700 field emission scanning electron
microscope (FESEM) at an accelerating voltage of 1-5 kV and an object distance of 3
mm. The nanoporous film was fractured in liquid nitrogen and mounted on the sample
stud by means of a double-sided adhesive tape for cross-sectional view study. A thin
layer of platinum was sputtered onto the sample surface prior to the FESEM
measurement. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis
was carried out on an ION-TOF SIMS IV instrument (ION-TOF, GmbH, Germany),
using procedures similar to those described earlier.[Yang et al., 2002] The primary ion
beam (10 keV Ar$^+$) with a spot size of ~50 µm was rastered over an area of 500×500
µm$^2$ while keeping the total dose under $10^{13}$ ions/cm$^2$. The Brunauer-Emmett-Teller
(BET) method was applied to the nitrogen adsorption isotherms to determine the pore
volume or porosity of the nanoporous films. The BET measurements were carried out
on a Quantachrome NOVA 1200 system at 77 K. Samples were degassed at 25°C for 12 h before each measurement.
4.3 Results and Discussion

4.3.1 Homopolymerization and Block Copolymerization

Pentafluorostyrene (FS) polymerized readily in the bulk at 110°C under the ATRP conditions. The average molecular weight of the FS polymer (PFS) can be regulated by changing the monomer to initiator feed ratio. The data in Table 4.1 show that as the [monomer]/[initiator] molar feed ratio is increased from 100 to 800, the number-average molecular weight ($M_n$) of the resulting PFS increases from $9.3 \times 10^3$ g/mol to $5.2 \times 10^4$ g/mol, while the polydispersity index (PDI) remains at around 1.2.

In order to obtain a nanoporous PFS film with good physical and mechanical properties, the macroinitiator (PFS-Br) with a relatively high $M_n$ (PFS4 in Table 4.1) was used for the block copolymerization with methylmethacrylate (MMA). The content of the poly(methylmethacrylate) (PMMA) block in the PFS-$b$-PMMA copolymers can also be adjusted by changing the [monomer]/[macroinitiator] molar feed ratio. The PMMA contents in the PFS-$b$-MMA copolymers were revealed by the GPC results (Table 4.1). As the [MMA]/[PFS-Br] molar feed ratio is increased from 600 to 1800, the content of the PMMA block in the copolymer increases from 27% (mole%) to 54%. At the same time, the PDI of the copolymer increases only slightly to 1.3, compare to 1.2 for the starting PFS homopolymer.
Table 4.1 Characteristics of the Poly(pentafluorostyrene) and Poly(pentafluorostyren-\textit{b}-methyl methacrylate) Copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Monomer]/[Initiator] Ratio</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>Polydispersity</th>
<th>$T_g$ (°C)</th>
<th>PMMA Content in PFS-\textit{b}-PMMA</th>
<th>Pore Volume (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFS1</td>
<td>100:1[^{[a]}]</td>
<td>9.3x10(^3)</td>
<td>1.13x10(^4)</td>
<td>1.20</td>
<td>95</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>PFS2</td>
<td>200:1</td>
<td>1.6x10(^4)</td>
<td>1.97x10(^4)</td>
<td>1.22</td>
<td>98</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>PFS3</td>
<td>400:1</td>
<td>2.4x10(^4)</td>
<td>2.68x10(^4)</td>
<td>1.11</td>
<td>100</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>PFS4</td>
<td>800:1</td>
<td>5.2x10(^4)</td>
<td>6.02x10(^4)</td>
<td>1.16</td>
<td>102</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>PFS-\textit{b}-PMMA(^1)[[^{[b]}]^]</td>
<td>600:1[^{[c]}]</td>
<td>6.2 x10(^4)</td>
<td>7.50x10(^4)</td>
<td>1.21</td>
<td>103</td>
<td>16</td>
<td>27</td>
</tr>
<tr>
<td>PFS-\textit{b}-PMMA(^2)[[^{[b]}]^]</td>
<td>1200:1</td>
<td>7.3x10(^4)</td>
<td>1.11x10(^5)</td>
<td>1.31</td>
<td>104</td>
<td>29</td>
<td>44</td>
</tr>
<tr>
<td>PFS-\textit{b}-PMMA(^3)[[^{[b]}]^]</td>
<td>1800:1</td>
<td>8.3x10(^4)</td>
<td>11.7x10(^4)</td>
<td>1.26</td>
<td>104</td>
<td>37</td>
<td>54</td>
</tr>
</tbody>
</table>

\[^{[a]}\] The molar ratio of [FS]:[EBB]:[CuBr]:[bpy] =100:1:1:3

\[^{[b]}\] The copolymer was synthesized using PFS4 as the macroinitiator


\[^{[d]}\] The content of PMMA was calculated from: $(M_{n[PFS-\textit{b}-PMMA]} - M_{n[PFS]})/M_{n[PFS-\textit{b}-PMMA]}$

\[^{[e]}\] The PMMA content corresponds to the first major weight loss in TGA of the PFS-\textit{b}-PMMA copolymer.

\[^{[f]}\] The weight loss of the PFS-\textit{b}-PMMA film after selective UV decomposition.

\[^{[g]}\] Pore volume determined by BET method.
4.3.2 Chemical Structures of the PFS and PFS-b-PMMA

The chemical structures of the PFS homopolymer and PFS-b-MMA block copolymer were studied by $^1$H NMR spectroscopy. Figure 4.2 (a) shows the $^1$H NMR spectrum of the PFS (PFS4 of Table 4.1). The chemical shifts at 1.7-3.0 ppm are attributable to the protons of aliphatic $-\text{CH-CH}_2$ of the PFS. Because of the relatively high $M_n$ of PFS ($M_n \sim 5.2 \times 10^4$), the chemical shift associated with the $-\text{CHBr}$ terminal group of the PFS at 4.9 ppm is not discernible [Jankova et al., 2003].

Figure 4.2(b) shows the $^1$H NMR spectrum of the PFS-b-PMMA copolymer (PFS-b-PMMA2 in Table 4.1, $M_n \sim 7.3 \times 10^4$). The chemical shift in the region of 0.9-1.1 ppm is associated with the C-CH$_3$ group of the PMMA block. The signal in the region of 1.6-1.9 ppm accounts for the -CH$_2$- group of the PMMA block, and is partially obscured by the protons of the aliphatic $-\text{CH-CH}_2$ of the PFS block. The chemical shift at about 3.6 ppm is attributable to the $-\text{OCH}_3$ group of the PMMA block.

4.3.3 Characterization of the Copolymer and Nanoporous Film Composition.

Figures 4.3(a) to 4.3(c) show the respective C 1s core-level spectra of the PFS (PFS4 of Table 4.1), PFS-b-PMMA (PFS-b-PMMA2 of Table 4.1) and the resulting nanoporous fluoropolymer film after selective UV decomposition of the PMMA block. The C 1s core-level spectrum of the PFS homopolymer can be curve-fitted with three peak components, having binding energies (BE’s) at 284.6 eV for the C-H
Figure 4.2. 300 MHz $^1$H NMR spectra of (a) the PFS with a $M_n$ of $5.2 \times 10^4$ g/mol (PFS4 in Table 4.1), and (b) the corresponding PFS-$b$-PMMA block copolymer with a $M_n$ of $7.3 \times 10^4$ g/mol (PFS-$b$-MMA2 in Table 4.1).
species, at 286.1 eV for the −C\textsubscript{5}F\textsubscript{5} species of the aromatic rings, and at 288.4 eV for the C−F (aromatic) species [Han, 2000]. The [C-H]/[C-F] molar ratio, as derived from the C 1s peak component area ratio, is about 0.41, in good agreement with the theoretical ratio of 0.4 for PFS. The O-C\textsubscript{3}H\textsubscript{3} and O-C=O species of the PMMA block have C 1s BE’s at about 286.3 eV and about 288.6 eV, respectively [Beamson et al., 1992] (Figure 4.3(b)). The BE’s of these two species overlap with those of the −C\textsubscript{5}F\textsubscript{5} and C-F(aromatic) species, respectively. The substantial increase in intensity of the C-H peak component at the BE of 284.6 eV in Figure 4.3(b) confirms the existence of the PMMA block in the PFS-\textit{b}-PMMA copolymer. The PMMA content in the PFS-\textit{b}-PMMA copolymer can be deduced from the (\([\text{C-H}]+[\text{C-C}]\)) and (\([\text{C-F}]+[\text{O-C=O}]\)) peak component area ratio in the C 1s core-level spectrum by taking into account of the \([\text{C-H}] : [\text{C-F}]\) stoichiometry in PFS and the (\([\text{C-H}]+[\text{C-C}]\)) : \([\text{O-C=O}]\) stoichiometry in PMMA. Thus, a PMMA content about 56\% is obtained for the PFS-\textit{b}-PMMA2 copolymer. This PMMA content in block copolymer derived from XPS data is slightly higher than that determined from GPC results (Table 4.1).

In Figure 4.3(c), the substantial reduction in the relative intensity of the peak component at the BE of 284.6 eV and the resemblance of the C 1s core-level line shape to that of the PFS homopolymer suggest that the PMMA blocks have been removed almost completely in the nanoporous fluoropolymer films. Scission at the joint between two blocks in the copolymer required a higher energy than the
Figure 4.3 C 1s core-level spectra of (a) the pristine PFS film with a $M_n$ of $5.2 \times 10^4$ g/mol (PFS4 in Table 4.1), (b) the PFS-b-PMMA block copolymer with a $M_n$ of $7.3 \times 10^4$ g/mol (PFS-b-MMA2 in Table 4.1), and (c) the nanoporous PFS film prepared from the PFS-b-PMMA2 copolymer film.
degradation of the PMMA chain [Thurn-Albert et al., 2000], and probably has hindered the complete decomposition of the PMMA blocks in the nanoporous fluoropolymer film. The retention of residual MMA units in the nanoporous fluoropolymer film is also indicated by the higher $[\text{C-H}]/[\text{C-F}]$ intensity ratio in Figure 4.3(c), in comparison to that in Figure 4.3(a).

### 4.3.4 Thermal Analysis of the PFS-\textit{b}-PMMA Copolymers and the Corresponding Nanoporous Fluoropolymer Films

The thermal properties of the PFS homopolymer and the PFS-\textit{b}-PMMA copolymers were studied by thermogravimetric analysis (TGA), and differential scanning calorimeter (DSC) in nitrogen. The results are shown in Table 4.1. The glass transition temperature ($T_g$) of the PFS homopolymer increases from 95°C to 102°C as the $M_n$ increase from 9.3x10$^3$ to 5.2 x10$^4$ g/mol. Thus, after UV decomposition of the PMMA block, the resulting nanoporous fluoropolymer matrices will not collapse during processing, for instance, at 50°C for 24 h under vacuum to remove the degradation products.

The PMMA contents in the PFS-\textit{b}-PMMA copolymers and the UV decomposed films were also characterized by TGA. Figure 4.4 shows the TGA results of the PFS homopolymer (PFS4 in Table 4.1) (curve a), PFS-\textit{b}-PMMA copolymer (PFS-\textit{b}-PMMA2 in Table 4.1) (curve b) and the nanoporous film from selective UV decomposition of the PFS-\textit{b}-PMMA2 (curve c). The PFS homopolymer from living radical polymerization exhibits good thermal stability. In nitrogen, the weight loss of
Figure 4.4. TGA curves of (a) the pristine PFS with a $M_n$ of $5.2 \times 10^4$ g/mol (PFS4 in Table 4.1), (b) the PFS-$b$-PMMA block copolymer film with a $M_n$ of $7.3 \times 10^4$ g/mol (PFS-$b$-PMMA2 in Table 4.1), and (c) the nanoporous PFS film prepared from the PFS-$b$-PMMA2 copolymer film.
the PFS commences at about 450°C. The PFS-\(b\)-PMMA copolymer undergoes a two-step degradation process. The onset of the first major weight loss, which occurs at the temperature of 320°C, corresponds to the onset of decomposition of the PMMA block in the PFS-\(b\)-PMMA copolymer. The second major weight loss commences at about 450°C, which coincides with the decomposition temperature of the PFS. The extent of the initial weight loss (34%) coincides approximately with the PMMA content of the PFS-\(b\)-PMMA2 copolymer (27 wt% from the GPC result).

The nanoporous PFS film also undergoes a two-step weight loss behavior, albeit the initial weight loss (4 wt%) is substantially below that of the PFS-\(b\)-PMMA2 copolymer. Thus, UV decomposition has resulted in an almost complete removal of the PMMA block in the nanoporous PFS film, except probably short segments or units at the block joints. Most importantly, the second major weight loss in the nanoporous film (curve c) also commences at about 450°C. The result readily suggests that thermal stability, and thus the chemical structure, of the PFS matrix in the resulting nanoporous PFS film was well-preserved after selective UV decomposition of the PMMA blocks.

### 4.3.5 Chemical Structure of the PFS-\(b\)-MMA Copolymer and the Corresponding Nanoporous Film

The chemical structure of the PFS-\(b\)-PMMA copolymers and their corresponding nanoporous films were also characterized by time-of-flight secondary ion mass spectrometry (ToF-SIMS). Figures 4.5(a) and 4.5(b) show the respective ToF-SIMS spectra of the PFS-\(b\)-PMMA block copolymer (PFS-\(b\)-PMMA2 of Table 4.1) film
Scheme 4.1: Assignments of Positive Ions in ToF-SIMS
Figure 4.5(a). Positive ion ToF-SIMS spectra of the PFS-\(b\)-PMMA block copolymer with a \(M_n\) of \(7.3 \times 10^4\) g/mol (PFS-\(b\)-PMMA2 in Table 4.1)
Figure 4.5(b) the nanoporous PFS film prepared from the PFS-\(b\)-PMMA2 copolymer film after selective UV decomposition of the PMMA block.
and the corresponding nanoporous film after selective UV decomposition. The assignments of the positive ion fragments of the PFS-\textit{b}-PMMA film and the PFS nanoporous film are shown in Scheme 4.1. In Figure 4.5(a), the fragments at m/z 167 (peak A) is assigned to C\(_6\)F\(_5\)\(^+\), at 181 (peak B) to C\(_6\)F\(_5\)CH\(_2\)\(^+\), at 195 (peak C) to C\(_6\)F\(_5\)CH\(_2\)CH\(_2\)\(^+\), at 205 (peak D) to C\(_6\)F\(_5\)C(CH\(_2\))\(^+\), at 207 (peak E) to C\(_6\)F\(_5\)C(CH\(_2\))CH\(_2\)\(^+\), and at 374 (peak F) to C\(_6\)F\(_5\)CCHCH(C\(_6\)F\(_5\))CH\(_2\)\(^+\) of the PFS block. The fragments at m/z 73 (peak G) is assigned to CH\(_3\)OCOCH\(_2\)\(^+\), at 99 (peak H) to C(CH\(_3\))(OCOCH\(_3\))CH\(^+\), at 199 (peak I) to CH(CH\(_3\))(OCOCH\(_3\))CH\(_2\)C(CH\(_3\))(OCOCH\(_3\))CH\(^+\), at 292 (peak J) to (C\(_6\)F\(_5\))C\(^+\)CHCH\(_2\)C\(^+\)(CH\(_3\))(COOCH\(_3\)) and at 294 (peak K) to (C\(_6\)F\(_5\))CH\(^+\)CH\(_2\)CH\(_2\)C\(^+\)(CH\(_3\))(COOCH\(_3\)). The presence of these fragments indicates that the PFS-\textit{b}-MMA block copolymer has been successfully prepared. Peaks J and K are particularly interesting because they are associated with the pentafluorostyrene and MMA joint in the block copolymer. The relatively low intensity of these two peaks is consistent with the low concentration of block joints in the copolymer film. In Figure 4.5(b), the substantial reduction in intensity of peaks G, H and I suggests that most of the PMMA blocks have been decomposed. On the other hand, the persistence of strong intensities for peaks A, B, C, D, E and F indicates that the PFS blocks are well-preserved in the nanoporous fluoropolymer film. Thus, the ToF-SIMS results are consistent with those obtained from the XPS and TGA analysis. The fact that peaks J and K are well preserved in Figure 4.5(b) indicates that the MMA units at the joints of the block copolymer are retained in the PFS nanoporous
film.

4.3.6 Morphology of the Nanoporous Fluoropolymer Films

For dielectric applications, not only should the nanoporous materials exhibit a low dielectric constant, the pore size should preferably be in the range of 10-50 nm, and the pores must not be interconnected [Maeir, 2001]. In this study, the nanoporous structure of the fluoropolymer film was revealed by the FESEM images. Figure 4.6(a) shows the cross-sectional view of the PFS-\textit{b}-PMMA (PFS-\textit{b}-PMMA2 in Table 4.1) copolymer film at a magnification of 100,000x. The copolymer film exhibits a dense (non-porous) morphology. The microdomain structure arising from the phase separation of the PMMA block PFS block was not clearly revealed because of technical limitation of the FESEM. Figure 4.6(b) shows the cross-section view of the corresponding PFS-\textit{b}-PMMA2 film after UV exposure for 3 h. The dark areas are the voids left behind by the degraded PMMA blocks. The pores are in the range of 30-50 nm and consist of closed-cells. Figures 4.7(a) and 4.7(b) show the respective surface images, at a magnification 50,000x, of the PFS-\textit{b}-PMMA2 copolymer film before and after UV decomposition. The surface of the PFS-\textit{b}-PMMA film shows a dense and none porous morphology. After UV exposure, a small number of pores of irregular size and shape are discernible on the film surface, indicating that aggregates of PMMA blocks were removed from the surface and near-surface regions. The discernable of close-cell pore structure in the Figure 4.7(b) suggests that the interconnectivity in the resulting pores was almost avoided.
Figure 4.6 FESEM cross-sectional images of the PFS-\(b\)-PMMA copolymer film with a \(M_n\) of \(7.3 \times 10^4\) g/mol (PFS-\(b\)-PMMA2 in Table 4.1) (a) before (b) after UV decomposition of the PMMA blocks.
Figure 4.7. FESEM surface images of the PFS-\textit{b}-PMMA copolymer film with a $M_n$ of $7.3 \times 10^4$ g/mol (PFS-\textit{b}-PMMA2 in Table 4.1) (a) before (b) after UV decomposition of the PMMA blocks.
4.3.7 Density and Dielectric Constant of the Nanoporous Fluoropolymer Films

In this study, the density of the resulting nanoporous fluoropolymer film was used to characterize the formation of the porous structure and the porosity. The porosity of the nanoporous PFS film can be determined from the weight loss of the PFS-\textit{b}-PMMA film after selective UV decomposition. The porosity, expressed in term of the pore volume, was also determined by the BET adsorption isotherm method. Satisfactory agreement between the porosity, obtained by the weight loss method, and the pore volume, determined by the BET method, was observed for each nanoporous film (Table 4.1). With the increase in concentration of PMMA blocks in the PFS-\textit{b}-PMMA copolymer film, the density of the resulting nanoporous fluoropolymer film decreases. Thus, the desirable porosity of the fluoropolymer film can be tailored by adjusting the PMMA content in the PFS-\textit{b}-PMMA copolymer. The dielectric constants ($\kappa$'s) of the resulting nanoporous PI films are of the primary concern. For the nanoporous fluoropolymer film, the ultimate $\kappa$ value is governed by the intrinsic $\kappa$ value of the PFS, and the morphology and porosity of the nanoporous structure. Figure 4.8 shows the dielectric constant (measured at 1 MHz) of the nanoporous PFS films, prepared from the PFS-\textit{b}-PMMA block copolymers, as a function of porosity of the films. The dielectric constant of the pristine PFS film is about 2.2, when measured under ambient conditions. As anticipated, all the nanoporous PFS films exhibits considerably lower dielectric constants. Nanoporous PFS film with a low dielectric constant of about 1.8 was obtained from the PFS-\textit{b}-PMMA2 block copolymer with an initial PMMA content of 29 wt% and a
Figure 4.8. Dielectric constant of the nanoporous PFS film as a function of pore volume of the film.
weight loss of 32% (BET pore volume of 0.29 ml/g). With the further increase in weight loss to 39% (BET pore volume of 0.38 ml/g), via the use of the PFS-\textit{b}-PMMA film with a PMMA content of 37 wt\%, the dielectric constant of the nanoporous PFS film decreases only marginally. With the increase in PMMA block content, increasing amount of residual PMMA fragments is retained in the resulting nanoporous film. The situation is aggravated by the fact that interconnected pores and large pores become abundant in films with a porosity near 40%.
4.4 Conclusions

PFS-\textit{b}-PMMA block copolymers have been successfully prepared via ATRP. Most of the PMMA blocks in the PFS-\textit{b}-PMMA copolymer film could be selectively decomposed by UV irradiation. Nanoporous ultra-low-\(\kappa\) PFS films with pore sizes in the range of 30-50 nm were obtained. The porosity of the PFS film can be regulated by changing the PMMA content of the PFS-\textit{b}-PMMA copolymer. A dielectric constant of 1.8 can be achieved in the nanoporous PFS film with a pore volume above 0.3 ml/g. The pore volume over 0.3 ml/g would result in the decrease in the mechanical properties of the fluoropolymer film. In summary, selective UV decomposition of the PMMA blocks in the PFS-\textit{b}-PMMA copolymer films from the ATRP process provided an alternative approach to the preparation of nanostructured ultra-low-\(\kappa\) films with well-preserved fluoropolymer chains.
Chapter 5

Nanoporous Ultra-Low-κ Fluoropolymer Films from Agglomerated and Crosslinked of Hollow Nanospheres

Poly(pentafluorostyrene)-block-Poly(divinyl benzene)
5.1 Introduction

Ultra-low dielectric constant (ultra-low-$\kappa$) interlayers with $\kappa<2.0$ are required to reduce the RC time delay, cross talk, and power dissipation in the next generation of sub-micron and nano-level electronics [Maex, 2003; Maier, 2001]. Inclusion of air ($\kappa\sim1.0$) into interconnect structures [Loo, 2001; Kohl, 2000] and incorporation of nanopores into polymers [Maier, 2001] are attractive approaches to reducing the dielectric constants of materials. Fluoropolymers are potential candidates for interlayer dielectric applications, as described in Section 2.3.1.

When particles agglomerate to form a film, interstitial spaces are formed. Thus, films fabricated from nanospheres are in reality a nanoporous materials [Fu et al., 2004]. In this chapter, an alternative approach to fabricating crosslinked nanoporous fluoropolymer films with $\kappa\sim1.7$ is described. The synthesis strategy is shown schematically in Figure 5.1. Initially, the initiator for atom transfer radical polymerization (ATRP), trichloro(4-chloromethyl-phenyl)silane, was immobilized on the surface of SiO$_2$ nanoparticles of about 25 nm in diameter. Consecutive surface-initiated ATRPs of pentafluorostyrene and divinyl benzene gave rise to the SiO$_2$ nanoparticles with surface-grafted poly(pentafluorostyrene)-block-poly(divinyl benzene) (SiO$_2$-g-PFS-b-PDVB). SiO$_2$-g-PFS-b-PDVB nanospheres of about 80-150 nm in diameter were allowed to agglomerate on a silicon substrate to form a film of about 2-4 $\mu$m in thickness. Under UV irradiation, the PDVB outer layer with residual double bonds on the core-shell nanospheres underwent inter- and further intra-sphere
crosslinking to strengthen the film. Removal of the silica cores of the crosslinked nanospheres by HF etching gave rise to the nanoporous fluoropolymer film. The high porosity contributed by both the interstitial spaces among the nanospheres and the hollow cores of the nanospheres led to a dielectric constant as low as 1.7 for the resulting film.
Figure 5.1. Schematic illustration of the process for preparing crosslinked ultra-low-κ fluoropolymer films from agglomeration and crosslinking of the nanospheres of poly(pentafluorostyrene)-block-poly(divinyl benzene)
5.2 Experimental

Experimental Section:

Formation of nanoporous fluoropolymer films. Dried SiO$_2$ particles of about 25 nm in diameter (2.0 g), trichloro(4-chloromethyl-phenyl) silane (3 g, 97%) and 20 ml of absolutely dried THF were introduced into a two-necked flask. Under an argon environment, triethylamine (1.2 ml) in THF (5 ml) were added drop-wise with stirring. The reaction mixture was left to stand for 8 h, and then exposed to air for another 18 h. After 5 cycles of ethanol/THF rinse and separation by centrifugation, about 1.8 g of the initiator-immobilized SiO$_2$ particles was obtained. About 0.1 g of the initiator-immobilized silica particles, 4.2 ml of pentafluorostyrene, 4 ml of dry DMF and 4 mg of CuCl were introduced into a dry Pyrex® test tube. After purging with argon for 20 min, about 10 µl of $N,N',N''-pentamethyldiethylenetriamine$ (PMDETA) was added, and the tube was sealed with a rubber stop. Surface-initiated ATRP was carried out under continuous stirring at 110°C. The reaction time was varied from 1.5 to 6 h. The SiO$_2$-g-PFS nanospheres were precipitated from 200 ml of methanol, re-dispersed in THF, and centrifuged to remove the absorbed PFS homopolymer. The process was repeated twice. The surface-initiated ATRP of divinyl benzene was carried out using the same procedure described above, except the SiO$_2$-g-PFS particles were used as the macroinitiators and methyl iso-butyl ketone as the solvent instead. The SiO$_2$-g-PFS-$b$-PDVB nanospheres were deposited on a clean Si(100) substrate from a 2 wt% THF dispersion to fabricate the nanostructured films. The resulting film with a thickness of about 2-4 µm was irradiated for 15 min with a
800 W mercury lamp having a maximum emission at about 254 nm, followed by immersing the crosslinked film in 10% HF to dissolve the SiO$_2$ cores.

**Characterization**

The procedures and conditions for XPS, GPC, dielectric constant measurement are similar to those described in Section 3.2.1. The characterization of FESEM and BET are same as those described in section 4.2.5. A JEOL 2010 TEM was used to characterize the morphology of nanoparticles. Energy-dispersive X-ray (EDX) analysis was carried out on a JEOL JSM5600LV scanning electron microscope. The mechanical properties of films were measured on an Instron Model 5544 tensile tester.
5.3 Results and Discussion

Initially, trichloro(4-chloromethyl-phenyl) silane ATRP initiators were immobilized onto the surface of silica particles of about 25 nm in diameter through reaction of the chlorosilyl group with the silanol group. TEM micrograph of the initiator-immobilized silica nanoparticles (Figure 5.2(a)) shows that the surface-modified particles remain unagglomerated. Figure 5.3(a) shows the XPS wide scan spectrum of the initiator-immobilized silica nanoparticles. The peak component at the binding energy (BE) of about 200 eV, attributable to the covalent Cl 2p species, indicated that the benzyl chloride initiators have been successfully immobilized on the silica surface. The relative amount of benzyl chloride on the surface of silica particles was revealed by energy-dispersive X-ray (EDX) analysis. The signals at 2.65 keV and 0.25 keV are attributable to chlorine and carbon, respectively. The chlorine concentration of about 1.28 wt% is in reasonable agreement with that (1.44 wt%) obtained from the elemental analysis result. The corresponding surface benzyl chloride initiator concentration of 2.4 initiators/nm$^2$ is comparable to the reported silane initiator density of 2.6 initiators/nm$^2$ for the silica particle surface [von Timothy, 1999].

The initial silica-\textit{graft}-poly(pentafluorostyrene) (SiO$_2$-g-PFS) nanospheres were prepared via surface-initiated ATRP of pentafluorostyrene from the initiator-immobilized silica nanoparticles, using CuCl and $N,N,N',N'',N''$-pentamethyldiethylenetriamine (PMDETA) as the catalyst system.
Figure 5.2 (a) TEM image of the initiator-immobilized silica particles, (b) TEM image of the SiO$_2$-g-PFS (SiO$_2$-g-PFS1 in Table 1) nanospheres, (b’) FESEM image of the ruptured PFS hollow spheres, (c) FESEM cross-sectional image of a composite film fabricated from agglomerated SiO$_2$-g-PFS-b-PDVB1 nanospheres, and (d) FESEM cross-sectional image of the corresponding crosslinked nanoporous fluoropolymer film.
The characteristics of the SiO$_2$-g-PFS nanospheres are summarized in Table 1. Figure 5.2(b) shows the TEM image of the SiO$_2$-g-PFS1 (Table 5.1) core-shell structure (dark-colored core for SiO$_2$ and light-colored shell for PFS). The appearance of strong C 1s and F 1s signals, and the disappearance of Si 2s and Si 2p signals in the XPS spectrum in Figure 5.3(b), were consistent with a SiO$_2$-g-PFS core-shell structure having a PFS shell thickness greater than the sampling depth of the XPS techniques (~7 nm in a fluoropolymer matrix [Tan et al., 1993]). Figure 5.4(a) shows the EDX results of the SiO$_2$-g-PFS nanospheres. The appearance of the strong carbon and fluorine signals and dramatic decrease in the silicon signal revealed that the SiO$_2$-g-PFS nanospheres have been successfully prepared. The thickness of the PFS shell can be adjusted by changing the polymerization time [von Timothy et al., 2001; Mandal et al., 2000]. The number average molecular weight ($M_n$) of PFS, cleaved via HF etching, from the SiO$_2$-g-PFS nanoparticles increases from 1.8x10$^4$ g/mol to 6.4x10$^4$ g/mol with the increase in polymerization time from 1.5 h to 6 h, while the polydispersity indices remain at around 1.2 (Table 5.1).

Figure 5.2(b’) shows the field-emission scanning electron microscopy (FESEM) image of some ruptured PFS hollow nanospheres (originated from HF-etched SiO$_2$-g-PFS1 of Table 5.1). The disappearance of the Si and oxygen signals, and the predominance of carbon and fluorine signals in the EDX analysis results, confirm that the silica cores have been completely removed from the PFS hollow nanospheres (Figure 5.4(b)). The ruptured nanospheres from SiO$_2$-g-PFS1 have a shell thickness
<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymerization Time (h)</th>
<th>Molecular Weight[^a] (g/mole)</th>
<th>PDI[^a]</th>
<th>Particle Size[^c] (nm)</th>
<th>Shell Thickness[^c] (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}-g-PFS\textsubscript{1}[^b]</td>
<td>1.5</td>
<td>1.8x10\textsuperscript{4}</td>
<td>1.20</td>
<td>88</td>
<td>28</td>
</tr>
<tr>
<td>SiO\textsubscript{2}-g-PFS\textsubscript{2}[^b]</td>
<td>3.0</td>
<td>3.9x10\textsuperscript{4}</td>
<td>1.18</td>
<td>106</td>
<td>39</td>
</tr>
<tr>
<td>SiO\textsubscript{2}-g-PFS\textsubscript{3}[^b]</td>
<td>6.0</td>
<td>6.4x10\textsuperscript{4}</td>
<td>1.13</td>
<td>145</td>
<td>52</td>
</tr>
</tbody>
</table>

[^a] \(M_n\) and PDI of the cleaved PFS chains (from HF acid treatment of SiO\textsubscript{2}-g-PFS).
[^b] Synthesized using a molar ratio of \([\text{pentafluorostyrene}]:[\text{initiator}]:[\text{CuCl}]:[\text{PMDETA}]=800:1:1:1. The amount of initiator on the SiO\textsubscript{2} surface was determined from element analysis.
[^c] Average particle size and shell thickness of 50 nanospheres, from TEM images prior to HF treatment.
Figure 5.3. XPS wide scan spectra of the (a) initiator-immobilized silica particles, (b) SiO$_2$-g-PFS (SiO$_2$-g-PFS3 in Table 5.1) nanospheres, and (c) SiO$_2$-g-PFS-b-PDVB (SiO$_2$-g-PFS-b-PDVB3 in Table 5.2) nanospheres.
Figure 5.4. EDX spectra of the (a) silica-

graft-poly(pentafluorostyrene) nanoparticles (SiO\textsubscript{2}-g-PFS 1 in Table 5.1), (b) poly(pentafluorostyrene) hollow nanospheres, (c) silica-

graft-poly(pentafluorostyrene)-block-poly(divinyl benzene) (SiO\textsubscript{2}-g-PFS-b-PDVB3 in Table 5.2) nanospheres, and (d) crosslinked nanoporous poly(pentafluorostyrene) (PFS) films prepared from SiO\textsubscript{2}-g-PFS-b-PDVB3 in Table 5.2).
of about 30 nm, which is consistent with that obtained from the TEM results (Table 5.1). With the $M_n$ of PFS increases from $1.8 \times 10^4$ g/mol to $6.4 \times 10^4$ g/mol, the average shell thickness of the hollow nanospheres increases correspondingly from about 28 nm to 52 nm.

A thin layer of poly(divinyl benzene) was subsequently grafted on the SiO$_2$-g-PFS nanospheres via ATRP of divinyl benzene, using the Cl-terminated PFS chains as the macroinitiators. Elemental analysis results indicate that 20 min of ATRP gives rise to a divinyl benzene content of about 17 mol% in the copolymer shell of the SiO$_2$-g-PFS-$b$-PDVB1 nanospheres (Table 5.2). The XPS wide scan spectrum of the SiO$_2$-g-PFS-$b$-PDVB nanospheres indicates a substantial decrease in the [F]/[C] ratio (Figure 5.3(c)), consistent with the presence of PDVB shell. The well-preserved nanospheres after HF treatment and washing/extraction in THF (a good solvent of PFS) confirm the formation of a crosslinked PDVB outer layer from the second ATRP process. In comparison with the $^1$H NMR spectra of the SiO$_2$-g-PFS nanospheres, the appearance of chemical shifts at 6.8-7.2 ppm (aromatic H of divinyl benzene) and 5.6-6.6 ppm (vinyl H of divinyl benzene) in the $^1$H NMR spectra of the corresponding SiO$_2$-g-PFS-$b$-PDVB nanospheres not only indicates that the SiO$_2$-g-PFS-$b$-PDVB nanospheres have been successfully prepared, but also confirms the persistence of double bonds on the SiO$_2$-g-PFS-$b$-PDVB nanospheres.

Figure 5.2(c) shows the FESEM cross-sectional image of a composite film on a clean
Table 5.2. Characteristics of the SiO$_2$-graft-Poly(pentafluorostyrene)- block-Poly(divinyl benzene) Nanospheres and the Resulting Nanoporous Films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymerization Time (min)</th>
<th>PDVB Content$^b$ (mol%)</th>
<th>Particle Size$^c$ (nm)</th>
<th>Tensile Strength$^d$ (MPa)</th>
<th>Dielectric Constant$^e$ ($\kappa \pm 0.1$)</th>
<th>Pore Volume$^f$ (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$-g-PFS-b-PDVB$^1[a]$</td>
<td>20</td>
<td>17</td>
<td>92</td>
<td>0.8</td>
<td>1.8</td>
<td>0.31</td>
</tr>
<tr>
<td>SiO$_2$-g-PFS-b-PDVB$^2[a]$</td>
<td>20</td>
<td>18</td>
<td>108</td>
<td>0.8</td>
<td>1.7</td>
<td>0.34</td>
</tr>
<tr>
<td>SiO$_2$-g-PFS-b-PDVB$^3[a]$</td>
<td>20</td>
<td>15</td>
<td>146</td>
<td>0.7</td>
<td>1.7</td>
<td>0.35</td>
</tr>
</tbody>
</table>

$^a$ Block copolymer prepared from the correspond SiO$_2$-g-PFS nanospheres in Table 1. The molar ratio of [divinyl benzene]:[initiator]:[CuCl]:[PMDETA]=100:1:1:1.

$^b$ Determined from element analysis.

$^c$ Average particle size of 50 nanospheres, from SEM images prior to HF treatment.

$^d$ Tensile strength of the nanoporous films.

$^e$ $\kappa$ values of the nanoporous films were measured at 1 MHz and the silica cores were removed by HF etching.

$^f$ Pore volume of the nanoporous films determined by BET method.
Si(100) substrate deposited from a 2 wt% THF dispersion of the SiO$_2$-g-PFS-$b$-PDVB1 (Table 5.2) nanospheres. The nanoporous structure and the agglomeration of well-defined spheres with an average diameter of about 92 nm are clearly discernable. Subsequent UV irradiation induced further crosslinking within the PDVB layers, as well as crosslinking among the SiO$_2$-g-PFS-$b$-PDVB nanospheres via the residual double bonds on the sphere surfaces. The resulting film exhibited good solvent resistance, as well as resistance against re-dispersing of the nanospheres in organic solvents.

Crosslinked nanoporous PFS-$b$-PDVB films, consisting of crosslinked hollow PFS-$b$-PDVB nanospheres, were obtained by HF etching to remove the SiO$_2$ cores of the UV-treated SiO$_2$-g-PFS-$b$-PDVB films. Figure 5.2(d) shows the FESEM cross-sectional image of a fluoropolymer film composed of the PFS-$b$-PDVB1 hollow nanospheres. Pores contributed by both the interstitial spaces among the nanospheres and the voids in the cores of the hollow spheres are discernable. The almost complete disappearance of the Si and oxygen signals, and the predominance of carbon and fluorine signals in the EDX analysis (Figure 5.4(d)) of the films confirmed that the silica cores have been removed. The resulting porous films exhibited good resistance to common organic solvents, such as THF and chloroform. As expected, the crosslinked nanoporous PFS-$b$-PDVB films also exhibit improved mechanical property. The PFS-$b$-PDVB films have a tensile strength of about 0.8 MPa, which is much higher than that of corresponding porous PFS films (~0.2 MPa).
For a nanoporous fluoropolymer film, the ultimate $\kappa$ value is governed by the intrinsic $\kappa$ value of the matrix polymer, and the morphology and porosity of the nanoporous structure. The dielectric constant (measured at 1 MHz) and the porosity (from BET method) of the nanoporous PFS-$b$-PDVB films fabricated from the corresponding SiO$_2$-$g$-PFS-$b$-PDVB nanospheres are shown in Table 5.2. The dielectric constant of the pristine PFS film is about 2.2, when measured under ambient conditions. As anticipated, all the nanoporous PFS-$b$-PDVB films exhibits considerably lower dielectric constants. The nanoporous PFS-$b$-PDVB film, obtained from the SiO$_2$-$g$-PFS-PDVB3 nanospheres, has a dielectric constant as low as 1.7. The higher porosity of the film from SiO$_2$-$g$-PFS-$b$-PDVB3 than that of the film from SiO$_2$-$g$-PFS-$b$-PDVB1 was probably due to the reduced packing efficiency for lager spheres in the former.
5.4 Conclusions

A simple approach to fabricating crosslinked and nanostructured fluoropolymer films with ultra-low-κ has been described. The surface-initiated ATRP process allowed the preparation of well-defined SiO$_2$-g-PFS-$b$-PDVB core-shell structures. PFS-$b$-PDVB hollow nanospheres with different PFS shell thicknesses can be readily prepared by controlling the PFS chain lengths during the surface-initiated ATRP process. Obviously, the dimension of the hollow cores can also be controlled by changing the size of initiator-immobilized silica nanoparticles. The thin outer layer of crosslinked PDVB with residual double bonds helped to (i) maintain a well-defined core-shell structure of the SiO$_2$-g-PFS-$b$-PDVB hybrids initially, (ii) promote crosslinking among the agglomerated nanospheres during UV exposure, (iii) preserve the core void of each hollow nanosphere after SiO$_2$ removal, and (iv) enhance the mechanical properties of the nanoporous fluoropolymer film. The nanoporous fluoropolymer films, with porosity contribution from the interstitial spaces among the nanospheres and the core voids of the hollow spheres, exhibited a dielectric constant as low as 1.7.
CHAPTER 6

Three-Dimensionally-Ordered Porous Membranes Prepared via Self-Assembly and Reverse Micelle Formation from Well-defined of Amphiphilic Block Copolymers
6.1 Introduction

Arising from their excellent physicochemical properties, such as high temperature resistance, excellent chemical inertness and low surface energy [Améduri et al., 2001; Forsythye et al., 2000], fluoropolymers are potentially useful as barrier materials and biomaterials [Kang et al., 2000; Kim et al., 2002]. Membranes, especially fluoropolymer membranes, with three-dimensionally-ordered pores and well-controlled surface (including pore surface) chemical composition are potentially useful as substrates or reservoirs for biocatalyst [Alexandridis et al., 2000], templates for preparing nanoparticles [Li et al., 2000], and media or substrates for cell culture [Nishikawa et al., 1998; Karthaus et al., 2000]. Ordered mesoporous films have been prepared by self-assembly of rod-coil block copolymers [Jenekhe et al., 1999; Widawski et al., 1994], arraying of air bubbles in polymer films[Srinivasarao et al., 2001], stabilization of water droplets in polymer film [Peng et al., 2003; Yabu et al., 2003; Maruyama et al., 1998] and spin coating of polymer solutions[Park et al., 2004]. Accordingly, the preparation and control of three-dimensionally-ordered porous fluoropolymer membrane, by macromolecular design and controlled polymerization and copolymerization via ATRP’s, will be of great interest.

In this part of work, amphiphilic block copolymers of poly(pentafluorostyrene) (PFS) and poly(acrylic acid) (PAAC) (PFS-b-PAAC) were obtained by hydrolysis of the block copolymers of PFS and poly(tert-butyl acrylate) (PtBA), or the PFS-b-PtBA copolymers. The latter copolymers were synthesized by a consecutive ATRP process.
The PFS-\textit{b}-PAAC copolymers were cast into membranes by phase inversion in aqueous media. The resulting membranes with three-dimensionally well-defined pores and with pore sizes in the micrometer range were obtained from self-assembly and reverse micelle formation of the amphiphilic block copolymers. The pore sizes can be regulated by changing the content of PAAC in the PFS-\textit{b}-PAAC copolymers and the pH of the medium used for phase inversion.
6.2. Experimental

6.2.1 Materials

Ethyl bromoisobutyrate (EBB), tetrahydrofuran (THF), 2,2’-bipyridine (bpy), methanol and xylene were purchased from Aldrich Chemical Company, Milwaukee, WI and were used as received. CuBr (CuBr, 99%, Aldrich) was purified in acetic acid, washed with methanol and dried under reduced pressure to afford a white powder. 2,3,4,5,6-Pentafluorostyrene (FS) and tert-butyl acrylate (tBA) (Aldrich Chem. Co.) were passed through a ready-to-use disposable inhibitor-remover column (Aldrich Chem. Co.).

6.2.2 Atom Transfer Radical Polymerization (ATRP)

a. ATRP of FS

A mixture of 0.017 ml (0.1 mmol) of EBB, 14.3 mg (0.1 mmol) of CuBr, 47 mg of bpy and 11.43 ml (0.08 mol) of FS was introduced into a 25 ml glass tube. The tube was degassed by three freeze-evacuate-thaw cycles and sealed under vacuum. It was then placed in an oil bath preheated to 110°C. After an ATRP time of 1.5 h, the polymerization mixture was diluted with THF and eluted through an alumina column to remove the copper bromide complex. The polymer was precipitated in excess methanol. The FS polymer (PFS) in white powder form was collected after drying under reduced pressure. About 8.1 g of white powders (yield ~52%, \( M_n=6.6\times10^4 \) g/mole, PFS3 in Table 6.1) were obtained. The so-prepared PFS with an active chain end (PFS-Br) was used as the macroinitiator for the subsequent ATRP.
b. Block Copolymerization with tBA

In a typical block copolymerization reaction, 1.32 g of the PFS macroinitiator (PFS-Br, \(M_n=6.6 \times 10^4\) g/mole, PFS3 in Table 6.1) was dissolved in 7 ml xylene. 0.8 ml (0.005 mole) of tBA, 0.003 g (0.02 mmol) of CuBr and 0.01 g (0.06 mmol) of bpy were added. After three freeze-evacuate-thaw cycles, the mixture was heated to 90°C for 3 h. The block copolymer solution was diluted with THF, eluted through an alumina column to remove the copper complex, and then poured into 200 ml of hexane to precipitate the copolymer. After drying under reduced pressure, about 0.46 g of the block copolymer powders (\(M_n=7.3 \times 10^4\) g/mole, PFS-\(b\)-PtBA1 in Table 6.1) were obtained.

6.2.3 Preparation of the PFS-\(b\)-PAAC

About 0.4 g PFS-\(b\)-PtBA (PFS-\(b\)-PtBA1 in Table 6.1) copolymer and 10 ml of THF was introduced into a 25 ml round-bottom flask equipped with a spiral condenser. After the copolymer was fully dissolved, 1 ml of concentrated hydrochloric acid was added dropwise. The flask was immersed into an 80°C oil bath. After refluxing for 24 h, the final PFS and poly(acrylic acid) (PAAC) block copolymer was precipitated in hexane. The copolymer powder was washed with copious amounts of ethanol before being dried under reduced pressure.
6.2.4 Preparation of the Membrane

The membranes were prepared by the phase inversion technique. The PFS-\textit{b}-PAAC copolymer was dissolved in THF to a concentration of 20 wt\% at room temperature. The copolymer solution was cast on a glass plate. The glass plate was immediately immersed in doubly distilled water. After the membrane had detached from the glass plates, it was extracted in a second bath of doubly distilled water at 70°C for 30 min. The membrane with a thickness of about 30 µm was obtained after drying by pump under reduced pressure for the subsequent characterization.

6.2.5 Materials Characterization

The procedures and conditions for \textsuperscript{1}H NMR, XPS, GPC and SEM measurements are similar to those described in Section 3.2.3 and Section 4.2.5, respectively.
Figure 6.1. Schematic illustration of the formation of reverse micelle and porous membrane from the amphiphilic PFS-\(b\)-PAAC block copolymer.
6.3. Results and Discussion

6.3.1 Homopolymerization and Block Copolymerization

Pentafluorostyrene (FS) was polymerized in the bulk at 110°C under the ATRP conditions. The number average molecular weight ($M_n$) of the FS polymer (PFS) can be regulated by changing the monomer to initiator feed ratio. The data in Table 6.1 show that as the [monomer]/[initiator] molar feed ratio is increased from 100 to 800, the $M_n$ of the resulting PFS increases from $9.3 \times 10^3$ g/mol to $6.6 \times 10^4$ g/mol, while the polydispersity index (PDI) remains at around 1.2.

Acrylic acid (AAC) cannot be polymerized directly by ATRP because of the interaction of the carboxylic acid functional groups with the Cu catalyst [Coessens, 2001]. Therefore, the amphiphilic block copolymer of PFS and AAC polymer (PFS-\textit{b}-PAAC copolymer) was prepared from hydrolysis of the poly(\textit{tert}-butyl acrylate) (PtBA) block in the PFS-\textit{b}-PtBA block copolymer. In order to obtain copolymer membranes with good physical and mechanical properties, the macroinitiator (PFS-Br) with a relatively high $M_n$ (PFS3 in Table 6.1) was used for the block copolymerization with \textit{tert}-butyl acrylate (tBA). The content of tBA polymer (PtBA) block in the PFS-\textit{b}-PtBA copolymer can also be adjusted by changing the [monomer]/[macroinitiator] feed ratio. The PtBA contents in the PFS-\textit{b}-PtBA copolymers were first deduced from the GPC results (Table 6.1). As the [tBA]/[PFS-Br] molar ratio is increased from 250 to 1500, the content of PtBA block
<table>
<thead>
<tr>
<th>Sample</th>
<th>[Monomer]/[Initiator] Ratio</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>Polydispersity Index (PDI)</th>
<th>PtBA Content in PFS-$b$-PtBA[c] (mol%)</th>
<th>PtBA Content in PFS-$b$-PtBA[d] (mol%)</th>
<th>Mean Diameter $D_m$ (µm)[f]</th>
<th>Standard Deviation $SD$ (µm)[f]</th>
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</thead>
<tbody>
<tr>
<td>PFS1</td>
<td>100:1[a]</td>
<td>9.3 x 10^3</td>
<td>1.1 x 10^4</td>
<td>1.19</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PFS2</td>
<td>400:1</td>
<td>3.4 x 10^4</td>
<td>4.0 x 10^4</td>
<td>1.18</td>
<td>---</td>
<td>---</td>
<td>2.4</td>
<td>0.3</td>
</tr>
<tr>
<td>PFS3</td>
<td>800:1</td>
<td>6.6 x 10^4</td>
<td>8.0 x 10^4</td>
<td>1.21</td>
<td>---</td>
<td>---</td>
<td>2.6</td>
<td>0.4</td>
</tr>
<tr>
<td>PFS-$b$-PtBA1</td>
<td>250:1[b]</td>
<td>7.3 x 10^4</td>
<td>9.3 x 10^4</td>
<td>1.28</td>
<td>13.8</td>
<td>14.6</td>
<td>4.4</td>
<td>0.7</td>
</tr>
<tr>
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<td>500:1</td>
<td>7.6 x 10^4</td>
<td>9.2 x 10^4</td>
<td>1.20</td>
<td>18.6</td>
<td>19.3</td>
<td>2.6</td>
<td>0.4</td>
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<td>PFS-$b$-PtBA3</td>
<td>1000:1</td>
<td>8.0 x 10^4</td>
<td>10.8 x 10^4</td>
<td>1.26</td>
<td>24.3</td>
<td>25.0</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PFS-$b$-PtBA4</td>
<td>1500:1</td>
<td>10.1 x 10^4</td>
<td>12.4 x 10^4</td>
<td>1.24</td>
<td>44.5</td>
<td>44.3</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

[a] The molar ratio of [FS]:[EBB]:[CuBr]:[bpy] = 100:1:1:3. Reaction temperature = 110°C and reaction time = 1.5 h. PFS was also referred to as PFS-Br macroinitiator since it contained the Br-terminated living end group for the subsequent block copolymerization with tBA.

[b] The molar feed ratio of [tBA]:[PFS-Br]:[CuBr]:[bpy] = 250:1:1:3 PFS3 was used as the macroinitiator for all block copolymerizations.

c] The content of PtBA was calculated from: $n_{[tBA]}/(n_{[tBA]} + n_{[FS]})$, in which $n_{[tBA]}=(M_{[PFS-b-PtBA]}-M_{[PFS]})/M_{[tBA]}$ and $n_{[PFS]}=M_{[PFS]}/M_{[FS]}$.

d] The tBA content in the PFS-$b$-PtBA copolymers were determined from $^1$H NMR spectroscopy results, based on the area ratio of the proton of the tertiary butyl group of PtBA (a in Figure 1(a)) and the methylidyne protons in the main chain. (b in Figure 1(a)).

e] The membrane was cast in doubly distilled water (pH~7) at 25°C from 30 wt% THF solution of the hydrolyzed PFS-$b$-PtBA copolymer

[f] From SEM images, using the relationships $D_m = \frac{\sum_{i=1}^{n} D_i}{n}$ and $SD = \sqrt{\frac{\sum_{i=1}^{n} (D_i - D_m)^2}{n}}$ and based on 100 pores (n=100) of diameters $D_i$

[g] Difficult to cast into ordered porous membrane, because of the high content of the hydrophilic blocks and the unstable reverse micelles.
in the copolymer, as determined from GPC results, increases from 13.8 mole% to 44.5 mole%. However, the PDI of the copolymers remains at around 1.2.

6.3.2 Chemical Structure of the PFS-\text{-}b\text{-}PtBA and PFS-\text{-}b\text{-}PAAC copolymers

The chemical structures of the PFS-\text{-}b\text{-}PtBA and PFS-\text{-}b\text{-}PAAC block copolymers were studied first by \textsuperscript{1}H NMR spectroscopy. Figure 6.2(a) shows the \textsuperscript{1}H NMR spectrum of the PFS-\text{-}b\text{-}PtBA block copolymer (PFS-\text{-}b\text{-}tBA1 of Table 6.1). The chemical shifts at 1.7-3.0 ppm are attributable to the protons of the aliphatic $-\text{CH}_2\text{CH}_2$ of the PFS and PtBA in the PFS-\text{-}b\text{-}PtBA block copolymer. The chemical shifts at about 1.4 ppm and 4.3 ppm are attributed to the $-\text{C(CH}_3)_3$ of the PtBA block and the $-\text{CH}\text{Br}$ terminal group in the PFS-\text{-}b\text{-}PtBA block copolymer, respectively. The NMR results are thus consistent with the structure of the PFS-\text{-}b\text{-}PtBA block copolymer. The tBA content in the PFS-\text{-}b\text{-}PtBA copolymer can be determined from the \textsuperscript{1}H NMR spectrum, using the relative proton areas of the tertiary butyl group of PtBA and the areas of the methylidyne protons in the main chain. (a and b, respectively, in Figure 6.2(a)) The NMR-derived compositions of the copolymers are given in Table 6.1. For each copolymer, the composition derived from NMR analysis agrees well with that obtained from GPC molecular weight measurement.

Figure 6.2(b) shows the \textsuperscript{1}H NMR spectrum of the PFS-\text{-}b\text{-}PAAC copolymer obtained from the hydrolysis of the PFS-\text{-}b\text{-}PtBA1 sample in Table 6.1. The chemical shifts in the region of 1.7-3.0 ppm are associated with the protons of the aliphatic $-\text{CH}_2\text{CH}_2$ of
Figure 6.2 300 MHz $^1H$ NMR spectra of (a) the PFS-$b$-PtBA copolymer with a $M_n$ of $7.3 \times 10^4$ g/mol (PFS-$b$-PtBA1 in Table 6.1), and (b) the corresponding PFS-$b$-PAAC block copolymer from hydrolysis of the PFS-$b$-PtBA1 copolymer.
the PFS and PAAC in the PFS-b-PAAC block copolymer. The hydrolysis of PtBA into PAAC is consistent with the disappearance of the peak at the chemical shift of 1.4 ppm which is attributable to the \(-C(CH_3)_3\) of the PtBA block. The NMR results are thus consistent with the hydrolysis of PFS-b-PtBA block copolymer into the PFS-b-PAAC block copolymer.

6.3.3 Chemical Composition of the PFS-b-PtBA and PFS-b-PAAC copolymers

The hydrolysis of the PFS-b-PtBA into PFS-b-PAAC was also verified by the XPS analysis results. Figure 6.3 shows the curve-fitted C 1s core-level spectra of (a) the PFS-b-PtBA (PFS-b-PtBA2 in Table 6.1) copolymer and (b) the corresponding PFS-b-PAAC copolymer obtained from hydrolysis of the PFS-b-PtBA2 copolymer. The C 1s core-level spectrum of the PFS-b-PtBA block copolymer can be curve–fitted with four peak components, with the binding energies (BE) at 284.6 eV for the \(\text{CH}\) species, at 286.2 eV for the \(-\text{CC}_3\text{F}_3\) and \(-\text{CO}\) species, at 288.4 eV for the aromatic \(-\text{CF}\) and the \(-\text{(O)}\) species, and at 292.4 eV for the \(\pi-\pi^*\) shake-up satellite [Fu et al., 2003]. The COOH species of the PAAC block in the PFS-b-PAAC copolymer has a C 1s BE’s at about 288.4 eV (Figure 6.3(b)). The substantial reduction in the relative intensity of the peak component at the BE of 284.6 eV suggests that the PtBA block has been successfully hydrolyzed into PAAC. Furthermore, the hydrolysis of PtBA block into PAAC is also indicated by the increase in the \([F]/[C]\) intensity ratio in PFS-b-PAAC block copolymer, in comparison to that of the PFS-b-PtBA block copolymer. XPS results are thus consistent with the NMR results.
Figure 6.3 C 1s core-level spectra of (a) the PFS-\textit{b}-PtBA copolymer with a $M_n$ of $7.3 \times 10^4$ g/mol (PFS-\textit{b}-PtBA1 in Table 6.1), and (b) the corresponding PFS-\textit{b}-PAAC block copolymer hydrolyzed from the PFS-\textit{b}-PtBA1 copolymer.
6.3.4 Morphology of the PFS-\(b\)-PAAC Membrane

The resulting amphiphilic PFS-\(b\)-PAAC block copolymers were cast into membranes by phase inversion in aqueous media at 25°C from 20 wt% THF solutions. The surface morphology of the membranes was studied by scanning electron microscopy (SEM). Figure 6.4(a) shows surface morphology of the PFS-\(b\)-PAAC membrane (PAAC content ~ 14 mole%, hydrolyzed from PFS-\(b\)-PtBA1 in Table 6.1), cast in doubly distilled water of pH~7. The pores are well-defined and have a mean diameter \(D_m\) of about 2.4 µm and a standard deviation in pore diameter of about 0.3 µm. The plausible process of formation of uniform and well-defined pores is shown in Figure 6.1. The PFS-\(b\)-PAAC amphiphilic copolymer has a highly hydrophobic PFS block and a hydrophilic PAAC block. In THF, the whole amphiphilic block copolymer molecules remain well extended, because both of the hydrophobic and hydrophilic blocks have good solubility in THF. During the process of phase inversion in an aqueous medium, the FPS blocks associate hydrophobically and precipitate out from aqueous medium, while the PAAC blocks remain fully extended in the aqueous medium. The strong repulsion arising from the incomparability of the two blocks in the block copolymer molecule forces the macromolecules to undergo partial phase separation between the hydrophobic blocks and the hydrophilic blocks in an aqueous medium. Due to the good solubility of PAAC blocks in an aqueous medium, a large amount of water was trapped within the hydrodynamic volume of the self-assembled PAAC chains in the reverse micelles within the polymer matrix of increasing
Figure 6.4. SEM images of (a) surface view of the PFS-b-PAAC copolymer membrane hydrolyzed from PFS-b-PtBA1 in Table 6.1, (b) cross-sectional view of the PFS-b-PAAC copolymer membrane hydrolyzed from PFS-b-PtBA1 in Table 6.1.
hydrophobicity. After drying, the hydrophilic PAAC block collapse on the hydrophobic PFS surface, leaving behind well-structured or well-defined pores. The basic structural feature (pore size) of the membrane is determined by the size of the micelle and, thus, the length of the amphiphile’s blocks. The well-defined nature of amphiphilic PFS-\(b\)-PAAC block copolymers, with narrow PDI’s for the hydrophobic blocks and hydrophilic blocks from consecutive ATRP’s, in turn, lead to the formation of reverse micelles with narrow pore sized distribution. Thus, the resulting membranes have well-defined and uniform pores. Figure 6.4(b) shows the cross-sectional view of the membrane cast from the PFS-\(b\)-PAAC copolymer obtained from hydrolysis of PFS-\(b\)-PtBA1 in Table 6.1. The separated and spherical pores of sizes in range of 2-3 µm in the bulk of the film are similar to those on the surface. Thus, the presence of well-defined porous structure throughout the film is consistent with their origin from the reverse micelles.

Figure 6.5(a) shows the surface morphology of a membrane from the PFS-\(b\)-PAAC copolymer (PAAC content \(\sim\) 24 mole%, hydrolyzed from PFS-\(b\)-PtBA3 in Table 6.1), cast in doubly distilled water at pH~7. The pores remain well-defined, with a \(D_m\) of about 4.4 µm and a \(SD\) in pore diameter of about 0.7 µm. The increase in pore size with the increase in PAAC content in the PFS-\(b\)-PAAC block copolymer is consistent with the reverse micelle formation during membrane casting by phase inversion. The core diameter of conventional micelles is determined by the chain length of the hydrophobic hydrocarbon block [Gelbart et. al, 1994]. Thus, the pore sizes of the
Figure 6.5. SEM images of (a) surface view of the PFS-\textit{b}-AAC copolymer membrane hydrolyzed from PFS-\textit{b}-PtBA3 in Table 6.1 and (b) surface view of the PFS-\textit{b}-AAC copolymer membrane hydrolyzed from PFS-\textit{b}-PtBA1 in Table 6.1 and cast in an aqueous medium at the PH of 2.
present membrane from reverse micelle formation are influenced by the chain length of the PAAC hydrophilic block. The longer the hydrophilic block, the greater the hydrodynamic radius of the reverse micelle core. With a $M_n$ of about $7.3 \times 10^4$ g/mole, each molecule of the PFS-$b$-PAAC block copolymer hydrolyzed from PFS-$b$-PtBA1 block copolymer has, on the average, about 340 repeat units of FS in hydrophobic block and about 55 repeat units of AAC in hydrophilic block. For the PFS-$b$-PAAC block copolymer hydrolyzed from PFS-$b$-PtBA3, the number of PAAC repeat units has increased to about 110. Thus, during the phase inversion process, the latter molecules can retain more aqueous solvent among the hydrophilic PAAC block, leading to the formation of a larger reverse micelle. Further increase in chain length of the hydrophilic PAAC block will lead to unstable reverse micelles. As a result, the PFS-$b$-PAAC copolymer with a PAAC content of about 45 mole%, hydrolyzed from PFS-$b$-PtBA4 in Table 6.1, failed to form an ordered porous membrane when cast under similar conditions.

The pH value of the aqueous medium for membrane casting by phase inversion also influences the pore size of the membranes cast from the present amphiphilic block copolymers. Figure 6.5(b) shows the surface morphology of the PFS-$b$-PAAC membrane (PAAC content~14 mole%, hydrolyzed from PFS-$b$-PtBA1 in Table 6.1), cast in an aqueous medium of pH 2. The well-defined and uniformly distributed pores have a reduced $D_m$ of about 0.6 μm and a $SD$ in pore diameter of about 0.1 μm, in comparison to a $D_m$ of 2.4 μm and $SD$ of 0.3 μm for the corresponding membrane cast
at pH~7 (Figure 6.4(a)). As a weak acid (pK$_a$=4.3) [Zhai et al., 2002], the carboxylic groups of the PFS-$b$-PAAC block copolymer are readily ionized to become negatively charged. When the pH of the casting medium is increased to 4.3, the carboxylic groups are transformed into carboxylic ions. Strong electrostatic repulsion among the carboxylic anions and their interactions with the aqueous environment force the PAAC blocks to adopt a highly extended conformation, and thus giving rise to larger pore sizes in the resulting membrane (Figure 6.4(a)). However, at a low pH, the PAAC blocks assume a more compact helical conformation [Ito et al., 1997]. The change in conformation and the reduced interaction with the aqueous environment will give rise to smaller reverse micelles, leading to a substantial reduction in pore size of the resulting membrane.
6.4 Conclusions

PFS-\(b\)-PtBA block copolymers have been successfully prepared via consecutive ATRP’s. Amphiphilic PFS-\(b\)-PAAC block copolymer was obtained from the hydrolysis of the corresponding PFS-\(b\)-PtBA block copolymer. The content of the hydrophilic PAAC block in the PFS-\(b\)-PAAC copolymer can be regulated during synthesis by varying the PtBA content in the PFS-\(b\)-PtBA block copolymers through the change in monomer to initiator feed ratio. The presence of well-defined hydrophilic and hydrophobic blocks of controlled proportions in the amphiphilic block copolymers allowed the formation of stable reverse micelles of controlled dimension when the copolymers underwent phase inversion (The hydrophobic PFS block changed from liquid phase to solid). The process, in turn, can be used to prepare materials systems with well-ordered and potentially useful structures, such as membranes with three-dimensionally-ordered micro and nano-pores of uniform size.
CHAPTER 7

Tadpole-shaped Amphiphilic Block-Graft Copolymers Prepared via Consecutive Atom Transfer Radical Polymerizations
7.1 Introduction

Polymers with unique structures, such as block, graft, star, gradient, hyperbranched and comb structures, have found applications in colloids stabilization, crystal growth modification, induced micelle formation, and intelligent drug carrier systems [Ishizu et al., 2003; Hadjichristidis et al., 2003; Lazzari et al., 2003; Mori et al., 2003]. Micelle and reverse micelle formation of amphiphilic block copolymers in selected solvents has been well studied, because the colloidal systems can be applied as nanoreservoirs in controlled drug delivery, gene therapy and phase transfer catalysis [Riess, 2003], as templates for the fabrication of nanostructured hybrids [Lazzari et al., 2003] and nanoparticles [Tang et al., 2004], and as reaction media for biocatalyst in liquid phase[Carvalho et al., 2000; Walde et al., 2001]. Rod-coil (or tadpole-shaped) block-graft amphiphilic copolymers with a hydrophobic head and a hydrophilic tail have been synthesized by metallocene-initiated polymerization of macromonomers [Neiser et al., 2004], and ATRP of macronomers from macroinitiators [Kurjata et al., 2004; Hong , 2003]. Arising from the special physicochemical properties of fluoropolymers, the amphiphilic fluorcoopolymers with tad-pole structure are expected to exhibit very special solution and colloidal property.

In this part of work, well-defined and tadpole-shaped block-graft amphiphilic macromolecules with a hydrophilic head of controllable dimension, consisting of designed length and number of poly(acrylic acid) (PAAC) brushes, and a
hydrophobic poly(pentafluorostyrene) (PFS) tail of controlled length were synthesized by consecutive ATRP’s (Figure 7.1). The process involved (i) synthesis of PFS via ATRP, (ii) block copolymerization with glycidyl methacrylate (GMA) via ATRP to give the PFS-\textit{b}-PGMA copolymer, (iii) immobilization of the bromoacid initiators on the GMA units of the PGMA block to generate the PFS-\textit{b}-PGMA macroinitiators, (iv) ATRP-mediated graft copolymerization with \textit{tert}-butylacrylate (tBA) to generate the PFS-\textit{b}-(PGMA-\textit{g}-PtBA) copolymer. Hydrolysis of the PFS-\textit{b}-(PGMA-\textit{g}-PtBA) block-graft copolymer converted the PtBA side chains into PAAC side chains to produce an amphiphilic PFS-\textit{b}-(PGMA-\textit{g}-PAAC) macromolecule.
7.2 Experimental Section

7.2.1 Materials

The monomers, 2,3,4,5,6-pentafluorostyrene (FS, 99%), glycidyl methacrylate (GMA, 97%) and tert-butyl acrylate (tBA, 99%), were purchased from Aldrich Chemical Co, of Milwaukee, WI. They were used after removal of the inhibitors in a ready-to-use disposable inhibitor-removal column (Aldrich). Analytical grade tetrahydrofuran (THF) was purchased from Tedia Co., Fairfield, OH. Copper(I) bromide (CuBr, 99%, Aldrich) was purified with acetic acid [Shinoda, 2001]. 2-Bromo-2-methyl propionic acid (BMPA, 98%), ethyl 2-bromoisobutyrate (EBB, 98%), 2-2′-bipyridine (bpy, 99%), N,N,N′,N′,N”-pentamethyldiethylenetriamine (PMDETA, 99%), trifluoroactic acid and tetrabutylammonium hydroxide (TBAH, 99%) were also purchased from Aldrich Chemical Co. and were used as received. High purity argon was used in all reactions.

7.2.2 Synthesis of the Poly(pentafluorostyrene) (PFS) Macroinitiators

A dry Pyrex® test tube equipped with a magnetic stirrer was charged with 0.029 g (0.2 mmol) of CuBr and 5.7 ml (0.04 mol) of FS. The reaction mixture was degassed by bubbling argon through the solution for 20 min, after which, 0.141 g (0.9 mole) of bpy ligand (0.141 g, 0.9 mmol) was added dropwise into the mixture under an argon atmosphere. The reaction mixture was flushed with argon for another 10 min. Finally, 29.4 µL (0.2 mmol) of EBB initiator was added and the test-tube was fitted tightly with a rubber stopper under an argon atmosphere. Polymerization was carried out
Figure 7.1 Consecutive atom transfer radical polymerizations (ATRP’s) for the preparation of the block-graft amphiphilic macromolecule of poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft-poly(acrylic acid)) (PFS-b-(PGMA-g-PAAC)).
under continuous stirring at 110°C. After 80 min, the reaction mixture turned viscous and the reaction was stopped by diluting with THF. The catalyst complex was removed from the reaction mixture by passing it through an alumina column. The PFS homopolymer was precipitated in an excess volume of methanol. The resulting polymer was filtered and dried in vacuo overnight. About 4.6 g of white powders (yield ~60%, \( M_n = 2.5 \times 10^4 \) g/mole) were obtained.

7.2.3 Synthesis of the PFS-\( b \)-PGMA Diblock Copolymers

A dry Pyrex\textsuperscript{®} test-tube equipped with a magnetic stirrer was charged with 0.5 g PFS (\( M_n = 2.5 \times 10^4 \) g/mole) and 1 mL of THF. The PFS macroinitiator was expected to assume a more fully extended conformation in THF, minimizing steric hindrance to the active chain-end. GMA (0.55 mL, 4.0 mmol) was then added. The mixture was degassed by bubbling argon through it for 15 min. After degassing, the catalyst, 6 mg (0.04 mmol) of CuBr, was added carefully into the reaction mixture. The latter was degassed by bubbling argon through it for another 15 min. Finally, 10 \( \mu \)L (0.04 mmol) of PMDETA ligand was added and the test-tube was sealed under an argon atmosphere with a rubber stopper. The reaction mixture was stirred at 60°C for 60 min. The reaction mixture was then diluted with THF and passed through an alumina column to remove the metal complex. The resulting copolymer (PFS-\( b \)-PGMA) was precipitated in hexane, filtered, and dried by pumping overnight under reduced pressure. About 0.51 g of white powders (\( M_n = 2.9 \times 10^4 \) g/mole) were obtained. The block copolymerization was also carried out with reaction time of 90 min and 150
7.2.4 Immobilization of the Bromoacid Initiators onto PFS-b-PGMA

A dry 25 mL round-bottom flask equipped with a magnetic stirrer was charged with 0.5 g of the PFS-b-PGMA copolymer (M_n=2.9x10^4 g/mole, containing 20.6 mole% GMA units) and 10 ml of THF. BMPA (0.1 g, 1.2 times in molar excess relative to the concentration of GMA repeat units in the copolymer) and TBAH (0.062 g, half the amount of BMPA) were then added under vigorous stirring. The flask was subsequently fitted with a condenser and stirred at 80°C for 24 h. When the solvent was cooled to room temperature, the product was precipitated in methanol. The filtered product was rinsed thoroughly with ethanol to remove the BMPA residue in the polymer. The macroinitiator was finally obtained after drying overnight under reduced pressure. The macroinitiator had a M_n of 3.0x10^4 g/mole and degree of functionalized ([bromoester]/[GMA] ratio) of about 1.08. The [bromoester]/[GMA] ratio was determined from the sensitivity factor corrected bromine and carbon X-ray photoelectron spectroscopy (XPS) core-level spectral area ratios.

7.2.5 Synthesis of the PFS-b-PGMA-g-PrBA Block-Graft Copolymers

The macroinitiator (0.6 g, M_n=3.0x10^4 g/mole) was dissolved in a test tube containing 1 ml of THF. tBA (3.6 ml, 0.025 mol) was then added. The reaction mixture was degassed with argon for 15 min. The CuBr catalyst (0.072 g, 0.5 mmol) was added carefully into the mixture and the reaction mixture was degassed for another 15 min.
Finally, the ligand PMDETA (110 µL, 0.5 mmol) was added and the reaction tube was sealed under an argon atmosphere. The reaction was carried out at 80°C for 180 min. The increase in reaction temperature improved the ATRP-mediated graft polymerization rate of the second acrylate. THF was added to stop the reaction and the catalyst complex was removed by passing the reaction mixture through an alumina column. The product was precipitated in hexane, filtered, and then dried overnight under reduced pressure. About 1.2 g of white powders were obtained (Mₙ=6.6x10⁴ g/mole, PDI=1.41, with 55 wt% PtBA content).

7.2.6 Hydrolysis of the PFS-b-(PGMA-g-PrBA) Copolymers

A dry 25 mL round-bottom flask equipped with a magnetic stirrer was charged with 0.5 g of the PFS-b-(PGMA-g-PrBA) copolymer (Mₙ=6.6x10⁴ g/mole) and 5 mL of THF. Trifluoroacetic acid (five times in molar excess relative to the amount of tert-butyl acrylate repeat units in the copolymer, or about 0.03 mol) was added. The reaction mixture was stirred continuously at room temperature for 36 h. The product was precipitated in hexane, filtered and dried overnight by pumping under reduced pressure. About 0.3 g of white powders were obtained.

7.2.7 Polymers Characterization

The procedures and conditions for ¹H NMR, XPS, GPC, AFM and TGA measurements are similar those described in Section 3.2.3 and Section 4.2.5, respectively. About 0.05 g the PFS-b-(PGMA-g-PAAC) copolymer (Mₙ=6.4x10⁴
g/mole) was dissolved in 50 ml of THF with stirring. About 50 ml of doubly-distilled water was added slowly, with stirring, over a period of 3 h using a syringe pump. The mixture was stirred for an additional 2 h to yield a micelle suspension. The micelle suspension was then transferred into a cellulose dialysis membrane tubing (Sigama-Aldrich Chem. Co., St. Louis, Mo.). The latter was placed in a 1 L beaker filled with deionized water and dialyzed for about 2 days under gentle stirring. Field emission scanning electron microscopy (FESEM) measurements were carried out on a JEOL JSM-6700 field emission scanning electron microscope (FESEM) at an accelerating voltage of 1-5 kV and an object distance of 2 mm. The micelle solution was spin-coated on a clean Si(100) substrate at 1000 round/min until the solvent had evaporated completely. A thin layer of platinum was sputtered onto the sample surface prior to the FESEM measurement.
7.3 Results and Discussion

7.3.1 Synthesis of PFS and PFS-b-PGMA Block Copolymer

Pentafluorostyrene (FS) polymerizes readily in the bulk at 110°C under ATRP conditions. The average molecular weight of the FS polymer (PFS) can be regulated by changing the monomer to initiator ratio or by controlling the extent of monomer conversion. In this work, PFS homopolymers with different molecular weights were synthesized by changing the [FS]/[initiator] ratio. Earlier studies had suggested that the end-group functionality was well-preserved in the polymer when the conversion of monomer was kept below 95%. [Patten, 1998] Thus, in this work, the ATRP of FS was kept below 90% conversion in order to obtain PFS macroinitiators (PFS-Br) with well-preserved end-group functionality. The PFS-Br macroinitiator, obtained from an [FS]/[EBB initiator] ratio of 200 (Table 7.1) was used for the subsequent block copolymerization.

PFS and poly(glycidyl methacrylate) (PGMA) block copolymers (PFS-b-PGMA) were subsequently prepared via ATRP of glycidyl methacrylate (GMA) from the PFS-Br macroinitiators. PFS-b-PGMA copolymers with different PGMA contents were synthesized by controlling the degree of GMA conversion. Table 7.1 summarizes the GPC results of PFS-b-PGMA block copolymers, obtained via ATRP of GMA from the PFS-Br macroinitiators ($M_n=2.5x10^4$ g/mole, $M_w/M_n=1.16$) at a [GMA]/[PFS-Br] ratio of 200, as a function of polymerization time. With the increase in reaction time from 60 min to 150 min, the number average molecular
Table 7.1 Preparation of poly(pentafluorostyrene) (PFS) and poly(pentafluorostyrene)-block-poly(glycidyl methacrylate) (PFS-b-PGMA) block copolymers by atom transfer radical polymerization (ATRP)

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Monomer]/[initiator]</th>
<th>Reaction Time (min)</th>
<th>$M_n$ (g/mole)</th>
<th>Polydispersity (PDI)</th>
<th>NMR$^c$ mole%</th>
<th>GPC$^d$ mole%</th>
<th>TGA$^e$ mole%</th>
<th>Repeat Units [FS]:[GMA]</th>
<th>Theoretical Molecular Weight (g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFS$^a$</td>
<td>200:1</td>
<td>80</td>
<td>2.5x10$^4$</td>
<td>1.16</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>129:0</td>
<td>3.0x10$^4$</td>
</tr>
<tr>
<td>PFS-b-PGMA1$^b$</td>
<td>200:1</td>
<td>60</td>
<td>2.9x10$^4$</td>
<td>1.26</td>
<td>20.6</td>
<td>17.8</td>
<td>12.8</td>
<td>129:28$^{[f]}$(34)$^{[g]}$</td>
<td>3.2 x10$^4$</td>
</tr>
<tr>
<td>PFS-b-PGMA2$^b$</td>
<td>200:1</td>
<td>90</td>
<td>3.0x10$^4$</td>
<td>1.20</td>
<td>26.1</td>
<td>21.3</td>
<td>17.5</td>
<td>129:35 (46)</td>
<td>3.5 x10$^4$</td>
</tr>
<tr>
<td>PFS-b-PGMA3$^b$</td>
<td>200:1</td>
<td>150</td>
<td>3.3x10$^4$</td>
<td>1.24</td>
<td>34.3</td>
<td>30.3</td>
<td>31.7</td>
<td>129:56 (67)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Prepared from a molar ratio of [FS]:[EBB]:[CuBr]:[bpy] =200:1:1:3 at 110°C for 80 min. FS=pentafluorostyrene, EBB=2-bromoisobutyrate and bpy=2,2'-bipyridine

$^b$ The copolymer was synthesized using PFS as the macroinitiator and a molar feed ratio [GMA] : [PFS-Br] : [CuBr] : [PMDETA] =200:1:1:1 at 60°C for 60 min. GMA = glycidyl methacrylate, PFS-Br = bromine-terminated poly(pentafluorostyrene) macroinitiator, and PMDETA = N,N',N'',N'''-pentamethyl diethylenetriamine

$^c$ The content of PGMA was determined from the area ratio of the methyldiaryle protons in the epoxy group (f in the $^1$H NMR spectrum of Figure 1(a)) and the methylene and methyldiaryle protons (b, and c in the $^1$H NMR spectrum of Figure 1(a)) in the main chain.

$^d$ The content of PGMA was calculated from: $M_n$[PFS-b-PGMA] $\approx$ $M_n$[PFS]$/M_n$[PFS-b-PGMA]

$^e$ The PGMA content calculated from the first major weight loss in TGA of the PFS-b-PGMA copolymer.

$^f$ Determined from GPC results. Molecular weights of FS=194 g/mole and GMA=142 g/mole

$^g$ Determined from NMR results. Molecular weights of FS=194 g/mole and GMA=142 g/mole
weight (M<sub>n</sub>) of the PFS-<i>b</i>-PGMA copolymer increases from 2.9x10<sup>4</sup> to 3.3x10<sup>4</sup> g/mole, while the polydispersity index (PDI) remains at around 1.2.

The chemical structure of the PFS-<i>b</i>-PGMA block copolymer was characterized by <sup>1</sup>H NMR spectroscopy. Figure 7.2(a) shows the <sup>1</sup>H NMR spectrum of the PFS-<i>b</i>-PGMA copolymer (PFS-<i>b</i>-PGMA1 in Table 7.1, M<sub>n</sub>=2.9x10<sup>4</sup> g/mole, PDI=1.26). The chemical shifts at 0.9-1.7 ppm are attributable to the methyl protons of ethyl 2-bromoisobutyrate initiator and PGMA. The chemical shifts at 1.8-2.9 ppm are attributed to the methylene protons of aliphatic –CH<sub>2</sub>-CH<sub>2</sub> of PFS and –CH<sub>2</sub>-C of PGMA. The chemical shifts in the region of 2.6-4.2 ppm are associated with the methylidyne protons of glycidyl groups of PGMA. The <sup>1</sup>H NMR results are thus consistent with the presence of both PFS and PGMA blocks in the copolymer structure. The GMA content in the PFS-<i>b</i>-PGMA copolymer can be determined from the <sup>1</sup>H NMR spectrum, using the area of the methylidyne protons in the epoxy group (f in Figure 7.2(a)) and the areas of the methylene and methylidyne protons (b and c in Figure 7.2(a)) in the main chain. The NMR-derived compositions of the copolymers are given in Table 7.1.

Curves a and b in Figure 7.3 are the GPC traces of the PFS homopolymer (PFS-Br) and the PFS-<i>b</i>-PGMA block copolymer (PFS-<i>b</i>-PGMA1 in Table 7.1), respectively. The PFS prepared by ATRP has a M<sub>n</sub> of about 2.5x10<sup>4</sup> g/mole and a PDI of about 1.16. After block copolymerization, the M<sub>n</sub> of the PFS-<i>b</i>-PGMA has increased to
Figure 7.2 300 MHz $^1$H NMR spectra of (a) the poly(pentafluorostyrene)-block-poly(glycidyl methacrylate) (PFS-$b$-PGMA) copolymer with a $M_n$ of 2.9x10$^4$ g/mol (PFS-$b$-PGMA1 in Table 7.1), (b) the corresponding macroinitiator with a $M_n$ of 3.0x10$^4$ g/mol (Macroinitator1 in Table 7.2).
a $M_n = 2.5 \times 10^4$ g/mole; $M_w/M_n = 1.16$ (PFS in Table 1)
b $M_n = 2.9 \times 10^4$ g/mole; $M_w/M_n = 1.26$ (PFS-$b$-PGMA1 in Table 1)
c $M_n = 3.0 \times 10^4$ g/mole; $M_w/M_n = 1.23$ (Macroinitiator1 in Table 2)
d $M_n = 6.6 \times 10^4$ g/mole; $M_w/M_n = 1.41$ (PFS-$b$-(PGMA-g-PtBA)1 in Table 3)
e $M_n = 5.0 \times 10^4$ g/mole; $M_w/M_n = 1.38$ (hydrolyzed from PFS-$b$-(PGMA-g-PtBA)1 in Table 3)

![Log (Molar Mass)](image)

**Figure 7.3** GPC traces of the (a) the pristine poly(pentafluorostyrene) (PFS) homopolymer (PFS in Table 7.1), (b) the poly(pentafluorostyrene)-block-poly(glycidyl methacrylate) copolymer (PFS-$b$-PGMA1 copolymer in Table 7.1), (c) the corresponding Macriniitiator1 in Table 7.2, (d) the poly(pentafluorostyrene)-block-(poly(glycidylmethacrylate)-graft-poly(tert-butylacrylate)) copolymer (PFS-$b$-(PGMA-g-PtBA)1 in Table 7.3), and (e) the corresponding amphiphilic poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft- poly(acrylic acid)) (PFS-$b$-(PGMA-g-PAAC)) copolymer hydrolyzed from PFS-$b$-(PGMA-g-PtBA)1.
about $2.9 \times 10^4$ g/mole, while the PDI increases slightly to 1.26. The PGMA content in the PFS-$b$-PGMA block copolymer can be calculated from the GPC results. For the PFS-$b$-PGMA1 copolymer with a PGMA content of about 16.8 mole% (13.7 wt%), there are about 129 FS repeat units and about 28 GMA repeat units in the block copolymer. The copolymer compositions derived from GPC results are shown in Table 7.1. The higher value of GMA content obtained from NMR (Table 7.1) than that from GPC probably arose from the difference in hydrodynamic volume of PGMA and the PS standards used for GPC measurements. The chemical composition of the PFS-$b$-PGMA block copolymer was studied by XPS. Figure 7.4(a) shows the C 1s core-level spectrum of PFS-$b$-PGMA1 in Table 7.1. The spectrum was curve-fitted with four peak components, having binding energies (BE’s) at 284.6 eV for the $\text{C}-\text{H}$ species, at 286.1 eV for the $-\text{CC}_5\text{F}_5$ species of the aromatic rings, at 288.4 eV for the $\text{C}-\text{F}$(aromatic) species, and at about 294.8 eV for the $\pi - \pi^*$ shake-up satellite associated with the aromatic rings of PFS [Beamson, 1992; Muilenberg, 1978]. The $\text{O-CH}_n$ (n=1 or 2) and the $\text{O-}\text{C}=\text{O}$ species of the PGMA block have C 1s BE’s at about 286.4 eV and 288.6 eV, respectively [Kang, 2000]. The BE’s of these two species overlap with those of the $-\text{CC}_5\text{F}_5$ and $\text{C}-\text{F}$(aromatic) species, respectively. The XPS-derived molar ratio of the $[\text{CH}] + [\text{C}=\text{C}]$ species to the $[\text{O-}\text{C}=\text{O}] + [\text{C}-\text{F}]$(aromatic) species for the PFS-$b$-PGMA1 copolymer was about 0.44, comparable to the theoretical ratio of 0.48 for the copolymer ([FS]:[GMA]=129:34, Table 7.1). The PGMA content in the PFS-$b$-PGMA copolymer can also be estimated from the thermogravimetric analysis (TGA) results. The extent of the initial weight
Figure 7.4 C 1s core-level spectra of (a) the PFS-\textit{b}-PGMA1 copolymer in Table 7.1, (b) the corresponding macroinitiator Macroinitiator1 in Table 7.2, (c) the PFS-\textit{b}-(PGMA-\textit{g}-PtBA)1 block-graft copolymer in Table 7.3, and (d) the corresponding amphiphilic PFS-\textit{b}-(PGMA-\textit{g}-PAAC) copolymer hydrolyzed from PFS-\textit{b}-(PGMA-\textit{g}-PtBA)1.
loss (12.8 mole%), associated with the PGMA content of the PFS-\textit{b}-PGMA1 block copolymer, is comparable to the PGMA content deduced from GPC results (17.8 mole% or NMR results 20.6 mole%). The copolymer composition estimated from the TGA results is also included in Table 7.1.

### 7.3.2 Immobilization of ATRP Initiators on the PFS-\textit{b}-PGMA Block Copolymers

The ATRP initiators were immobilized onto the PFS-\textit{b}-PGMA block copolymers through the TBAH-catalyzed addition reaction of 2-bromo-2-methyl propionic acid (PMBA) and the epoxy ring of the GMA units in the PFS-\textit{b}-PGMA copolymers. The results are summarized in Table 7.2. The structure of the resulting macroinitiators was first studied by $^1$H NMR spectroscopy. Figure 7.2(b) shows the $^1$H NMR spectrum of the macroinitiator prepared from PFS-\textit{b}-PGMA1 in Table 7.1. The chemical shift at about 1.7 ppm is associated with the $\text{-CH}_3$ protons in the bromoester groups. The chemical shifts in the region of 2.8-4.5 ppm (e, f, g, h, i, j, and k) are attributable to the protons resulting from the reaction of the epoxy group with the carboxylic acid group. The NMR results thus indicate that the initiator has been successfully immobilized onto the PFS-\textit{b}-PGMA block copolymer. It is difficult to quantify the extent of esterification from NMR results because the methyl protons of the bromoester group overlap with the methylene protons of PGMA in the main chain.
Table 7.2 Immobilization the atom transfer radical polymerization (ATRP) initiator on the poly(pentafluorostyrene)-block-poly(glycidyl methacrylate) (PFS-b-PGMA) copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (g/mole)</th>
<th>Polydispersity (PDI)</th>
<th>Degree of Functionalization [Br]/[C][d]</th>
<th>[Bromoester]/[GMA][c] (mole%)</th>
<th>Theoretical Molecular Weight (g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroinitiator1[a]</td>
<td>3.0 $\times 10^4$</td>
<td>1.23</td>
<td>2.0</td>
<td>1.08</td>
<td>3.7 $\times 10^4$[f]</td>
</tr>
<tr>
<td>Macroinitiator2[b]</td>
<td>3.2 $\times 10^4$</td>
<td>1.22</td>
<td>2.7</td>
<td>1.18</td>
<td>4.1 $\times 10^4$</td>
</tr>
<tr>
<td>Macroinitiator3[c]</td>
<td>3.5 $\times 10^4$</td>
<td>1.25</td>
<td>3.1</td>
<td>0.93</td>
<td>4.5 $\times 10^4$</td>
</tr>
</tbody>
</table>

[a] Prepared from PFS-b-PGMA1 in Table 1 with a GMA and BMPA molar feed ratio of about 1.2 in THF at 80°C for 24 h. GMA = glycidyl methacrylate and PMBA = 2-bromo-2-methyl proionic acid.

[b] Prepared from PFS-b-PGMA2 in Table 1 with a GMA and BMPA molar feed ratio of about 1.2 in THF at 80°C for 24 h.

[c] Prepared from PFS-b-PGMA3 in Table 1 with a GMA and BMPA molar feed ratio of about 1.2 in THF at 80°C for 24 h.

[d] Determined from XPS results.

[e] The molar ratio of bromoester in the macroinitiator molecule to the GMA content of the corresponding PFS-b-PGMA copolymer.

[f] The theoretical molecular weight of the macroinitiator was calculated from the degree of functionalization of the corresponding poly(pentafluorostyrene)-block-poly(glycidyl methacrylate) (PFS-b-PGMA) copolymer.
The chemical composition of the PS-\textit{b}-PGMA macroinitiators was also studied by XPS. Figure 7.4(b) shows the Br 3d and C 1s core-level spectra of the macroinitiator prepared from PFS-\textit{b}-PGMA1 in Table 7.1. After immobilization of the initiator, a Br 3d peak component at the BE of 70 eV has appeared (compare Figure 7.4(b) to Figure 7.4(a)). The amounts of the bromo-initiator immobilized, defined as the number of bromoester groups/GMA moiety and calculated from the XPS-derived [Br]/[C]_{total} molar ratio, are shown in Table 7.2. Under the given conditions, almost all of the epoxy groups have reacted with PMBA. In addition, one epoxy group may react simultaneous with two bromoester units [Matyjaszewski, 2000] to give rise to a [bromoester]/[GMA] ratio slightly greater than 1 in some macroinitiators (Table 7.2). The coupling of the PMBA molecules with the epoxy groups is also supported by the GPC results. Curve c in Figure 6.3 show the GPC trace of the Macroinitiator1. The $M_n$ has increased slightly to $3.0 \times 10^4$ g/mole, while the PDI remains at around 1.2, in comparison with that of the starting PFS-\textit{b}-PGMA1 copolymer (Curve b in Figure 7.3).

\textbf{7.3.3 The Synthesis of PFS-\textit{b}-(PGMA-\text{g}-PtBA) and PFS-\textit{b}-(PGMA-\text{g}-PAAC) Block-Graft Copolymers.}

Acrylic acid (AAC) cannot be polymerized directly by ATRP because of the interaction of the carboxylic acid groups with the Cu catalyst.[Patten, 1998; Ornatska, 2004] Thus, the amphiphilic PFS-\textit{b}-(PGMA-\text{g}-PAAC) block graft copolymer was prepared by hydrolysis of the tert-butyl acrylate (tBA) polymer
(PtBA) side chains of the FPS-\textit{b-(PGMA-g-PtBA)} copolymers. PFS-\textit{b-(PGMA-g-PtBA)} copolymers with PtBA brushes (side chains) of different lengths were synthesized by controlling the degree of tBA conversion. Table 7.3 shows the GPC results of PFS-\textit{b-(PGMA-g-PtBA)} block copolymers, synthesized via ATRP of tBA from Macroinitiator1 in Table 7.2 at a molar feed ratio of about 1200, as function of reaction time. With the increase in reaction time from 180 min to 600 min, the number average molecular weight ($M_n$) of PFS-\textit{b-(PGMA-g-PtBA)} increases from $6.6 \times 10^4$ to $9.5 \times 10^4$ g/mole, while the polydispersity index (PDI) remains at about 1.4. The growth of the PtBA side chains is thus consistent with a controlled or ‘living’ process.

The chemical structure of the PFS-\textit{b-(PGMA-g-PtBA)} block-graft copolymers and the resulting PFS-\textit{b-(PGMA-g-PAAC)} amphiphilic macromolecules were characterized by $^1$H NMR spectroscopy. Figures 7.5(a) and 7.5(b) show the $^1$H NMR spectra of PFS-\textit{b-(PGMA-g-PtBA)}1 in Table 7.3 and the resulting amphiphilic PFS-\textit{b-(PGMA-g-PAAC)} macromolecule, respectively. The chemical shift at about 1.4 ppm is attributable to the protons of tertiary butyl group (C(CH$_3$)$_3$ of the PtBA (Figure 7.5(a)). The length of PtBA side chains can also be determined from the relative proton areas of the tertiary butyl group of PtBA(a”” in Figure 7.5(a)) and the methyl and methyldyne groups of epoxy. The higher DP of PtBA obtained from the NMR results than that from the GPC results (Table 7.3) can probably be accounted by the fact that the hydrodynamic volume of the densely grafted sample would be
Table 7.3 Characterization of poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft-poly(tert-butylacrylate)) (PFS-b-(PGMA-g-PtBA)) and poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft-poly(acrylic acid)) (PFS-b-(PGMA-g-PAAC)) copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Times (min)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (g/mole)</th>
<th>Polydispersity (PDI)</th>
<th>PtBA Content&lt;sup&gt;b&lt;/sup&gt; wt%</th>
<th>tBA Repeat Units&lt;sup&gt;c&lt;/sup&gt;</th>
<th>tBA Repeat Units&lt;sup&gt;d&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (g/mole)</th>
<th>Polydispersity (PDI)</th>
<th>PAAC Content&lt;sup&gt;e&lt;/sup&gt; wt%</th>
<th>AAC Repeat Units&lt;sup&gt;f&lt;/sup&gt;</th>
<th>AAC Repeat Units&lt;sup&gt;g&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFS-b-(PGMA-g-PtBA)&lt;sup&gt;1[a]&lt;/sup&gt;</td>
<td>180</td>
<td>6.6x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.41</td>
<td>55</td>
<td>10</td>
<td>16(1.1x10&lt;sup&gt;5&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.0x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.38</td>
<td>40</td>
<td>10</td>
<td>16(7.6x10&lt;sup&gt;4&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>PFS-b-(PGMA-g-PtBA)&lt;sup&gt;2[a]&lt;/sup&gt;</td>
<td>360</td>
<td>8.6x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.38</td>
<td>65</td>
<td>16</td>
<td>28(1.6x10&lt;sup&gt;5&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6.4x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.39</td>
<td>53</td>
<td>17</td>
<td>28(1.1x10&lt;sup&gt;5&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>PFS-b-(PGMA-g-PtBA)&lt;sup&gt;3[a]&lt;/sup&gt;</td>
<td>600</td>
<td>9.5x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.42</td>
<td>69</td>
<td>18</td>
<td>36(1.9x10&lt;sup&gt;5&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>7.1x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.42</td>
<td>58</td>
<td>20</td>
<td>36(1.3x10&lt;sup&gt;5&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Prepared from a molar ratio of [tBA]:[Macroinitiator1:Table2]:[CuBr]:[PMDETA] =1200:1:24:24 in THF at 80°C for 180 min. tBA=tert-butyl acrylate and PMDETA=N,N,N’,N’,N’’-pentamethyldiethylenetriamine.

<sup>b</sup>The content of PtBA was calculated from: (M<sub>n</sub>[PFS-b-(PGMA-g-PtBA)]-M<sub>n</sub>[Macroinitiator1])/M<sub>n</sub>[PFS-b-(PGMA-g-PtBA)].

<sup>c</sup>The average number of tBA repeat units in each side chain was calculated base on the fact that all the GMA repeat units had coupled with the bromoester, a [FS]:[GMA] ratio of 129:28 (Table 1) and molecular weight of tBA=128 g/mol.

<sup>d</sup>The average number of AAC repeat units in each side chain was calculated from the relative proton areas of tertiary butyl group of PtBA(a’’’’’ in the 1H NMR spectrum of Figure1(c) and the methyl and methilidyne groups of epoxy. AAC=acrylic acid.

<sup>e</sup>The content of PAAC was calculated from: (M<sub>n</sub>[PFS-b-(PGMA-g-PAAC)]-M<sub>n</sub>[Macroinitiator1])/M<sub>n</sub>[PFS-b-(PGMA-g-PAAC)]

<sup>f</sup>The average number of AAC repeat units in each side chain was calculated as in [c], except that the molecular weight of AAC (72 g/mol) was used.

<sup>g</sup>The average number AAC repeat units in each side chain was calculated as in [d], except that all the tBA units had been hydrolyzed into AAC units.

<sup>h</sup>Theoretical molecular weights of the block-graft copolymer.
Figure 7.5 300 MHz $^1$H NMR spectra of (a) the poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft-poly(tert-butylacrylate)) (PFS-b-(PGMA-g-PtBA)) copolymer with a $M_n$ of $6.6 \times 10^4$ g/mol (PFS-b-(PGMA-g-PtBA)1 in Table 7.3), and (b) the corresponding amphiphilic poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft-poly(acrylic acid)) PFS-b-(PGMA-g-PAAC) copolymer hydrolyzed from PFS-b-(PGMA-g-PtBA)1.
much smaller than the random coil equivalent of the polystyrene standards. The almost complete disappearance of the chemical shift at 1.4 ppm in Figure 7.5(b) is consistent with the hydrolysis of PFS-\(b\)-(PGMA-g-PtBA) to PFS-\(b\)-(PGMA-g-PAAC). The chemical composition of the PFS-\(b\)-(PGMA-g-PtBA) and PFS-\(b\)-(PGMA-g-PAAC) copolymers was again studied by XPS. The chemical composition of the PFS-\(b\)-(PGMA-g-PtBA) and PFS-\(b\)-(PGMA-g-PAAC) copolymers was studied by XPS. Figures 7.4(c) and 7.4(d) show the C 1s core-level spectrum of PFS-\(b\)-(PGMA-g-PtBA)\(1\) in Table 7.3 and its resulting amphiphilic PFS-\(b\)-(PGMA-g-PAAC) copolymer. The C 1s core-level spectra of PFS-\(b\)-(PGMA-g-PtBA)\(1\) and the corresponding PFS-\(b\)-(PGMA-g-PAAC) copolymer are curve-fitted with three peak components, having binding energies (BE’s) at 284.6 eV for the C-H and C-C species, at 286.1 eV for the \(\text{–CC}_3\text{F}_5\) species of the aromatic rings and at 288.4 eV for the C-F (aromatic) species. The O-\(\text{CH}_n\) (n=1 or 2), C-Br and O-\(\text{C(CH}_3)_3\) species in the PFS-\(b\)-(PGMA-g-PtBA) copolymer have BE’s at about 286.4 eV, which cannot be distinguished unambiguously from the \(\text{–CC}_3\text{F}_5\) species.[Beamson, 1992; Muilenberg, 1978] The BE of the O\(\text{C}\equiv\text{O}\) species with a BE at about 288.6 eV overlaps with that of the C-F(aromatic) species. The presence of PtBA in the PFS-\(b\)-(PGMA-g-PtBA) copolymer is confirmed by the increase in peak intensity ratio of the components at 284.6 eV and 288.4 eV to about 1.8, in comparison to only about 0.5 for the starting macroinitiator. The decrease in peak intensity ratio of the components at BE’s of 284.6 eV and 288.4 eV to 0.94 in Figure 7.4(d) suggests that the PFS-\(b\)-(PGMA-g-PtBA) block-graft copolymer has
been successfully hydrolyzed into the amphiphilic PFS-\textit{b}-(PGMA-\textit{g}-PAAC)
block-graft copolymer.

Curves d and e in Figure 7.3 show the GPC traces of PFS-\textit{b}-(PGMA-\textit{g}-PtBA)\textsubscript{1} in
table 7.3 and the corresponding PFS-\textit{b}-(PGMA-\textit{g}-PAAC) copolymer. After the
ATRP of tBA, the M\textsubscript{n} of PFS-\textit{b}-(PGMA-\textit{g}-PtBA)\textsubscript{1} block-graft copolymer has
reached 6.6\times 10^4 g/mole, in comparison to a M\textsubscript{n} of 3.0\times 10^4 g/mole for the
Macroinitiator\textsubscript{1} of Table 7.2. The PDI has also increased to about 1.41 from 1.23.
The M\textsubscript{n} of the PFS-\textit{b}-(PGMA-\textit{g}-PAAC) copolymer hydrolyzed from
PFS-\textit{b}-(PGMA-\textit{g}-PtBA)\textsubscript{1} in Table 7.3 decreases to 5.0\times 10^4 g/mole, while the PDI
remains at around 1.4. The hydrolysis of PFS-\textit{b}-(PGMA-\textit{g}-PtBA) into
PFS-\textit{b}-(PGMA-\textit{g}-PAAC) was also revealed by the TGA results. For the
PFS-\textit{b}-(PGMA-\textit{g}-PAAC) block copolymer hydrolyzed from
PFS-\textit{b}-(PGMA-\textit{g}-PtBA)\textsubscript{1} in Table 7.3, the PFS content increases to about 55 wt%
from about 40 wt% prior to hydrolysis. The result is consistent with the fact that the
tert-butyl groups in the PFS-\textit{b}-(PGMA-\textit{g}-PtBA) copolymer have been removed
during the hydrolysis.

\textbf{7.3.4 AFM Characterization of the Tadpole-shaped PFS-\textit{b}-(PGMA-\textit{g}-PAAC)
Block-Graft Copolymer}

The resulting rod-coil amphiphilic copolymers should exhibit novel solution
properties and nanostructures. The macromolecular architecture was studied by
AFM. Figure 7.6(a) shows an AFM tapping mode image of the PFS-\textit{b}-(PGMA-\textit{g}-
Figure 7.6 (a) AFM image of the rod-coil poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft-poly(acrylic acid)) (PFS-b-(PGMA-g-PAAC)) (hydrolyzed from PFS-b-(PGMA-g-PtBA)2 in Table 7.3) copolymer assembly on the oxides-covered Si(100) surface. The overall size of the image is approximately 1 µm x 1 µm, and (b) the plausible macromolecular structure of the poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft-poly(acrylic acid)) (PFS-b-(PGMA-g-PAAC)) copolymer on the Si(100) surface.
-PAAC) block-graft copolymer (PFS-\textit{b}-(PGMA-g-PAAC)\textsubscript{2} in Table 7.3) macromolecules dispersed on an oxides-coved Si(100) substrate surface. According to the GPC and NMR results, the copolymer sample has a hydrophobic tail consisting of about 129 FS repeat units and a rod-shaped hydrophilic head comprising of about 34 GMA repeat units, and 34 PAAC bristles (side chains), each with a length of about 28 AAC repeat units. The bright spot (Arrow 1) at the end of each cylindrical brush, is probably associated with a PFS coil. The coils have dimensions in the order of 25-30 nm. The cylindrical brush (Arrow 2) is probably associated with the aggregate of hydrophilic PGMA-g-PAAC blocks of the macromolecules on the hydrophilic SiO\textsubscript{x} surface. The plausible structure of a PFS-\textit{b}-(PGMA-g-PAAC) block-graft macromolecule on the Si(100) surface is shown in Figure 7.6(b). On the hydrophilic (oxides-covered) Si(100) surface, the hydrophilic PGMA-g-PAAC block of the PFS-\textit{b}-(PGMA-g-PAAC) copolymer assumes a more extended conformation. Under the driving force of surface tension and good polymer-substrate interaction, the hydrophilic PGMA-g-PAAC block also has a feather-like appearance. Thus, the AFM image of the macromolecular assembly on the Si(100) surface is consistent with the presence of a rod-coil structure in the present amphiphilic block-graft copolymers.

### 7.3.5 Micelles Formation

The tadpole-shaped amphiphilic PFS-\textit{b}-(PGMA-g-PAAC) block copolymer, consisting of a hydrophilic PGMA-g-PAAC block and a hydrophobic PFS coil,
Figure 7.7 (a) FESEM image of the micelles from 1 g/L solution of the poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft-poly(acrylic acid)) copolymer (PFS-b-(PGMA-g-PAAC)2 in Table 7.3), and (b) the plausible mechanism of micelle formation from the copolymer.
provides possibility for unique micellar formation in aqueous media. The size and shape of the micelles formed from the PFS-b-(PGMA-g-PAAC) block-graft copolymers were studied by FESEM. Figure 7.7(a) shows the surface morphology of the micelles formed from a 1 g/L aqueous solution of the PFS-b-(PGMA-g-PAAC)2 copolymer (M_n=6.4x10^4 g/mole). Each molecule has 129 FS repeat units and 34 PAAC bristles (side chains), consisting of about 28 AAC repeat units. The micelles are well-defined, spherical and uniform in size, and have a diameter in the range of 180-200 nm. The plausible process for the micelle formation is shown in Figure 7.7(b). The driving force for the micelle formation from the amphiphilic copolymer probably involves strong repulsion between the highly hydrophilic PGMA-g-PAAC block and the high hydrophobic PFS coil [Matsumoto, 2004]. In the THF solution, the entire amphiphilic tadpole-shaped copolymer molecule remains well extended. During the process of micelle formation or with increasing water content, the hydrophilic PGMA-g-PAAC will become even more extended, while the PFS segments associate hydrophobically by phase inversion to reduce the contact area with the mixed solvent. Thus, well-defined spherical micelles, which assume the conformation of the lowest Gibbs free energy, are formed. The diameter of the micelle is determined by the chain length of the hydrophobic hydrocarbon block.[Gelbart, 1994] Thus, the well-defined uniform micelles observed can be attributed to the well-defined amphiphilic macromolecular structure of the PFS-b-(PGMA-g-PAAC) block-graft copolymer obtained via the consecutive ATRP’s.
7.4 Conclusions

Tadpole-shaped block-graft copolymers or rod-coil amphiphilic macromolecules, PFS-\(b\)-(PGMA-\(g\)-PAAC), have been successfully prepared via consecutive ATRP’s. The PFS-\(b\)-(PGMA-\(g\)-PAAC) macromolecules have a hydrophilic ‘head’, comprising of a PGMA-\(g\)-PAAC cylindrical ‘brush’ (rod), and a PFS hydrophobic tail (coil). The length of the hydrophilic head and the length of the PAAC bristles, can be regulated by controlling the monomer to initiator feed ratio or the degree of monomer conversion during each ATRP. This multiple-ATRP approach allows the design and synthesis of macromolecules with specific and interesting architectures. For instance, a rod-coil block-graft amphiphilic copolymer with a hydrophobic head and a hydrophilic tail can be expected from the reversal of the polymerization sequence. The amphiphilic nature of the macromolecules may further allow the fabrication of functional materials with unique morphologies, such as porous membranes [Ying et al., 2004] and micelle/inverse micelle systems [Matsuoka et al., 2003], via a simple phase inversion process. The formation of well-defined and uniform micelles from the present well-defined block-graft copolymers was demonstrated.
CHAPTER 8

Conclusions and Recommendations for Future Work
The present work has attempted to design and synthesize well-defined fluoropolymers, poly(pentafluorostyrene) in particular, of unique and functional macromolecular architectures and structures. These fluoropolymer structure and architectures exhibited unique physicochemical properties and could be assembled to create nanostructures, such as low-κ nanoporous fluoropolymer dielectrics. In addition, well-defined fluoropolymers with functional segments, such as hydrophilic block, could exhibit special solution properties and could be used for nano-scale fabrications. Atom transfer radical polymerization (ATRP) has been shown to be an effective approach for the synthesis of complex polymeric architectures based on the fluoro-monomer of pentafluorostyrene. The polymeric structures were well-defined and their dimension could be regulated by changing polymerization conditions. First of all, comb-shaped FPI-cb-PS and FPI-cb-PFS copolymers have been successfully prepared via ATRP of styrene and pentafluorostyrene, respectively, from the FPI-Br macroinitiators. The macromolecular assembly, consisting of aligned and uniformly spaced rigid rods of 20-30 nm in length and 4-6 nm in lateral dimension, was revealed by AFM images. In addition to good solution processability, the FPI-cb-PFS copolymer with its unique macromolecular architecture also exhibited good thermal stability, improved mechanical properties and very low dielectric constant (κ~2.1). The FPI-cb-PFS copolymer is thus a potential ultra-low-κ material for sub-micron and nano-level electronics.

Secondly, PFS-b-PMMA block copolymers have been successfully prepared via
ATRP. Most of the PMMA blocks in the PFS-\textit{b}-PMMA copolymer film could be selectively decomposed by UV irradiation. Nanoporous ultra-low-\(\kappa\) PFS films with pore sizes in the range of 30-50 nm were obtained. The porosity of the PFS film can be regulated by changing the PMMA content in the PFS-\textit{b}-PMMA copolymer. A dielectric constant of 1.8 can be achieved in the nanoporous PFS film with a pore volume above 0.3 ml/g. This ultra-low-\(\kappa\) nanoporous fluoropolymer film with good mechanical properties can be potentially used for the future dielectric interlay.

Consecutive surface-initiated ATRPs of pentafluorostyrene and divinyl benzene from silane-coupled silica nanosparticles (25 nm in diameter) gave rise to the core-shell silica-\textit{graft}-poly(pentafluorostyrene)-\textit{block}-poly(divinyl benzene) (SiO\textsubscript{2}-\textit{g}-PFS-\textit{b}-PDVB) nanospheres. SiO\textsubscript{2}-\textit{g}-PFS-\textit{b}-PDVB nanospheres of about 80-150 nm in diameter were allowed to agglomerate on a silicon substrate to form a film of about 2-4 \(\mu\)m in thickness. Under UV irradiation, the PDVB outer layer with residual double bonds on the core-shell nanospheres underwent inter- and further intra-sphere crosslinking to strengthen the film. Removal of the silica cores of the crosslinked nanospheres by HF etching gave rise to the nanoporous fluoropolymer film. The high porosity contributed by both the interstitial spaces among the nanoshpheres and the hollow cores of the nanospheres led to a dielectric constant as low as 1.7 for the resulting film.

Amphiphilic PFS-\textit{b}-PAAC block copolymers were obtained from the hydrolysis of
the corresponding PFS-b-PtBA block copolymers prepared via consecutive ATRP’s. The presence of well-defined hydrophilic and hydrophobic blocks of controlled proportions in the amphiphilic block copolymers allowed the formation of stable reverse micelles of controlled dimension when the copolymers underwent phase inversion. The process, in turn, can be used to prepare material systems with well-ordered and potentially useful structures, such as membranes with three-dimensionally-ordered micro and nano-pores of uniform size.

Finally, tadpole-shaped block-graft copolymers or rod-coil amphiphilic macromolecules, PFS-b-(PGMA-g-PAAC), have been successfully prepared via consecutive ATRP’s. The macromolecular structure of these rod-coil polymeric macro-molecular architectures with a hydrophilic head and a hydrophobic tail has been revealed by AFM. The amphiphilic nature of the macromolecules may further allow the fabrication of functional materials with unique morphologies, such as porous membranes and micelle/inverse micelle systems, via a simple phase inversion process. The formation of well-defined and uniform micelles from the present well-defined block-graft copolymers was demonstrated.

It should be noted that, this thesis has focused mainly on the preparation of the fluoropolymers with novel architectures and structures, and their physicochemical properties. The unique function and potential applications of these novel macromolecular architectures and structures have also been demonstrated. In the
future, other complex fluoropolymer architectures, arising from different structures, such as tri-block, palm-tree, double-bell, hyper-branch and comb-shape, and various functional segments, such as thermo-sensitive, electron-conductive and electron-luminescent block, as well as based on different fluoromonomers, such as perfluorostyrene and fluorinated acrylate monomers, could be synthesized by the controlled living radical polymerization approaches. Furthermore, the unique physicochemical properties and their applications in biomedical and electronic areas for these functional fluoropolymers should be further explored.
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