Synthesis of Polyfluoroesters, Polyfluoroamic Acid, Polyfluoroimide, and Polyfluoroacrylates: Formation and Characterization of Their Ultrathin Films

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Fluorine-containing polymers were synthesized using three main synthetic approaches: First, polyamic acid (PA-1) and polyimide (PI-1) were produced from direct polycondensation of 4,4′-hexafluoroisopropylidenediphthalic anhydride and 4,4′-hexafluoroisopropylidenedianiline in *N*-methyl-2-pyrrolidinone (NMP). Second, a novel polyester (PEMPFTDE) with fluorine side chains was synthesized from poly(maleic anhydride-*co*-ethylene). Finally, novel fluorine-containing acrylate (PTFPM) was synthesized by bulk and gas-phase polymerizations. Novel monolayer and ultrathin films of the polymers were prepared by the Langmuir−Blodgett technique. They formed a stable monolayer. The collapse pressure of PA-1 was 62 mN/m, and the area per repeat unit (RU) was 0.12 nm^2. The PI-1 has a collapse pressure of 60 mN/m with an area per RU of 0.23 nm^2. PI-1 films formed a stable monolayer, too. Multilayer depositions onto substrates were possible for all of the polymers except for PEMPFTDE. LB films were characterized by infrared (IR), ultraviolet (UV), and dielectric constant spectroscopies. Further characterizations were carried out using surface plasmon resonance (SPR) and atomic force microscopy (AFM). The dielectric constant for the PI-1 is 1.5, which is the lowest so far reported to my knowledge.

Introduction

Microelectronics has a dominant influence in our lives. This industrial revolution was originally driven by the need for very small and lightweight electronic circuits for military and aerospace applications. With the development of, first, the transistor and, later, the integrated circuit (IC), microelectronics has now grown into a multibillion dollar industry, and its application is ubiquitous. Device miniaturization has brought us from small-scale (SSI) and medium-scale (MSI) to large-scale integration (VLSI) with 10^5 or more components per chip.[1] The next stage may be very large-scale integration (VVLSI).

Research has been going intensively in all areas of microelectronics to provide for ever higher performance (speed) and density at very low cost.[1−7] Active foci include the scaling of devices and the search for novel materials and processing technologies for interconnects and packaging.[8−15] The development of new insulators for interconnects and packaging is one approach to increase the speed.[1,16−31] Compatibility with thin-film

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fabrication techniques, low-dielectric losses, good adhesion to a variety of substrate materials, and thermal, mechanical, and chemical stability have made polymer materials attractive choices as the interlayer dielectric (ILD) and intermetal dielectric (IMD). In its simplest form, the multilevel interconnect structure comprises a metal pattern on a substrate, a polymer layer on top with metalized vials, and a second metal pattern on top of the polymer.

As operating frequencies of electronic devices enter the gigahertz range and as the dimensions of electronic devices approach the submicrometer level, dielectric media with low dielectric constants (<3) become increasingly more important for the reduction of signal coupling among transmission lines. Therefore, there is a clear need to understand the chemistry of materials used in these applications to evaluate better their effects on the electrical and physical performance of devices.

For a material to be suitable as an interconnect dielectric, in addition to having a low dielectric constant, it should be able to withstand temperatures higher than the 470 °C necessary for the subsequent heating steps without the evolution of volatile byproducts. Other important considerations are compatibility with other materials, long-term thermal, chemical, and electrochemical stability, ease of fabrication, and low cost. SiO_2, which has a dielectric constant of 3.5−4.0, has been used as an interlayer dielectric in the industry. Further breakthroughs in high-performance chips hinge critically on the development of new insulators with dielectric constants much lower than that of SiO_2. It is generally believed that, to achieve such a low dielectric constant, organic polymeric materials must be considered instead of the traditional inorganic materials.[1]

Fluoropolymers, especially fluoropolyimides, because of their unique features such as low permittivity, low friction, and high resistance to chemical attack, especially oxidation, have a central position in this current drive toward the development of low-dielectric-constant organic polymeric materials to replace traditional inorganic insulators.[2,3,23,31] Maier et al.[23] and Houghman[31] have had extensive reviews on different polymers that have potential of being used as ILD and IMD. They include poly(benzoxazole)s, poly(phenylquinoxaline)s, polynorbornene, poly(silsesquioxane), etc.

These polymers may have high thermal stability and can be used as IMD and ILD, but many of them are very rigid and cannot be easily processed.[23] In addition, their dielectric constants are 2 and above. Where lower dielectric constants are required, they are difficult to apply.

Aromatic polyimides have excellent thermal stability in addition to their good electrical properties; they are lightweight, flexible, and easy to process. Polyimides, since the invention of integrated circuits (ICS), have been applied to insulation materials in electronic devices. This is because of their relatively low fabrication cost and high performance. However, conventional polyimides have disadvantages as dielectrics for use in microelectronics, like a high coefficient of thermal expansion (CTE) compared to those of Si and SiO_2.[1] The difference in CTE between polyimides and other materials produces peeling, bending, and cracking in electronic devices. Low-thermal-expansion polyimides can be achieved by a linear polymer and molecular construction with only rigid groups such as phenyl rings and imide rings.[5,6]

High water absorption is another problem with insulation materials, because it causes corrosion of metal wiring and instability of electrical properties such as the dielectric constant. Conventional polyimides have relatively high water absorption because of the presence of polar imide rings. However, the water absorption decreases when fluorine is introduced into polyimide molecules because of their hydrophobic nature.[1−7,31]

Apart from new low-dielectric materials, a good method to deposit the dielectric as a uniform film is also required. Owing to the way fabrication technology in the microelectronics industry has developed, and because larger silicon wafers are being used (currently, the technical difficulty of controlling thin-film uniformity for larger wafers has been a challenging area for spin coating), a methodology with the ability to deposit polymers with appropriate properties as conformal films, like the Langmuir−Blodgett (LB) technique[2,3,13−15] and chemical deposition,[1,16] would be useful. Through multilayer formation, thicknesses in the micrometer range can be reached.

However, it is generally considered difficult to fabricate LB films of fluoropolymers or fluorine-containing polymers directly because of their rigidity and hydrophobicity.[17] As a result, there are only a few reports in the literature on monolayers and LB films of fluoropolymer or fluorine-containing polymers made by direct fabrication.[17−19] Direct fabrication is the method whereby synthesized polymers are spread in water from their solution and deposited on the substrate by its movement vertically or horizontally. Indirect fabrication is a method whereby a precursor like polyamic acid is synthesized and deposited through the LB technique. The imidization process then takes place on the substrate by heating. Direct fabrication of LB films of fluoropolyimides has not yet been published. The indirect method has been used on conventional polyimide.[20−22]

Gas-phase deposition is also used to fabricate films of polymers. The polymers are deposited from solvent by a method called chemical vapor deposition (CVD). It has the advantage of being solvent-free. However, there is a problem of internal stress within the polymers, especially if they are deposited below the glass transition temperature. This can be avoided if the polymers are synthesized on the substrate at lower temperature

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in the presence of a macroinitiator. This is a new enhanced method of gas-phase polymerization developed at the Institute of Polymer Research (IPF), Dresden, Germany.

The main objective of the work described herein is to design and synthesize organic dielectric materials and develop new techniques to deposit these materials as thin films with low dielectric constants for use as ILDs and IMDs. In this work, the focus will be on synthesis of fluoropolymers (imide, amide, esters) and their film fabrication using the LB technique. The fluoropolyimides may not be the typical amphiphiles used in the LB technique, but we felt the need to try them because other polymers which are not typical amphiphiles have been deposited, too.[17−19] The rigidity of such polymers sometimes permits them to be fabricated as films through the LB technique. The polymers obtained from modification of poly(ethylene-*co*-maleic anhydride) can form LB films because the main chain has hydrophilic groups. LB films of Teflon AF will be fabricated because it has the lowest dielectric constant of organic compounds. Acrylate, because it can undergo chain polymerization in the presence of an initiator, is going to be used for gas-phase polymerization. In this work we will try to fabricate films from these polymers and select those that can easily form LB films for further characterization to be used in microelectronics. The development of low-dielectric-constant materials as ILDs is crucial to achieve low power consumption, reduce signal delay, and minimize interconnect cross-talk for high-performance VLSI devices.

Materials and Methods

Materials. Poly(maleic anhydride-*co*-ethylene), with M_w 36 000 g/mol, and poly(maleic anhydride-*co*-octadecene), M_w 30 000−50 000 g/mol), were purchased from Polysciences Inc. Perfluorotetradecanol was bought from ABCR as 97% pure. 4,4′-Hexafluoroisopropylidenediphthalic anhydride (6FDA) and 4,4′-hexafluoroisopropylidenedianiline were purchased from Aldrich Chemical Co. as 98% pure. *N*-Methyl-2-pyrolidinone (NMP) and *β*-picoline (*β*) were purchased from Fluka as 99.8% pure. Acetic anhydride, 99% pure, was purchased from Merck. Tetrafluoropropyl methacrylate was purchased from ABCR as 98% pure. 4,4′-Azo-bis(isobutylnitrile) (AIBN) was purchased from Fluka as more than 98% pure. All reagents were used without further purification.

The water used for the monolayer experiments was purified using a Milli-Q Plus system (18.2 MΩ). Hot concentrated chromic acid was used for preparing the substrate. All the substrates were made hydrophobic in the presence of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (Aldrich, 98%). Substrates used included silicon wafer, gold, glass, quartz, and mica (Good Fellow). They were made hydrophobic by exposure to vapors of HMDS. Spreading solvents were THF (Fluka, 99.5%) and chloroform (Fluka, 99.5%). The gold substrates for film deposition were prepared as metal films on glass (76 mm × 26 mm × 1 mm) from 99.9% pure granulated gold.

Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker DRX 500 spectrometer operating at 500.13 MHz for ^{1}H NMR and 125.77 MHz for ^{19}F NMR, using tetramethylsilane as internal standard for ^{1}H NMR and trichlorofluoromethane as internal standard for ^{19}F NMR. Infrared spectroscopy was performed using a Bruker IFS 66 V/S. All readings for the IR measurement were done on a film on ATR crystal or diamond. The size exclusion measurements were carried out with modular chromatographic equipment, a single-column Hibar PS 40 (Merck) containing a refractive index detector at ambient temperature. Thermogravimetry was done on a TGA 7 (Perkin-Elmer).

Monolayer Formation and Deposition of LB Films. A computer-controlled KSV 3000 system (KSV Instruments Finland) LB trough was used in a dust-free box (microelectronic room) with the temperature controlled to 20 ± 1 °C. After the LB trough was thoroughly cleaned, it was filled with 18.2 mΩ cm deionized water. The surface was cleaned again by moving barriers toward the dipping well and sucking away any surface-active agents with a capillary glass tube connected to suction. The final level of the subphase was about 1.0 mm above the rim of the trough. Since the polymers could not dissolve in a well-known spreading solvent such as chloroform, a mixture of solvents was used. The PEMPFTDE and PI-1 (1.0 mg) were dissolved in 100 μL of TFA and made up to 1.0 mL with perfluoro(methylcyclohexane). A mixture (100 μl, 1.0 mg/mL) was used as the spreading solution on the subphase surface, and the solvent was evaporated for about 20−30 min.

The LB films were prepared by the vertical deposition method. After the surface pressure reached 10.0 mN/m, about 30 min was spent to establish equilibrium of the monolayer. From the $\pi-A$ isotherm, the spread monolayer is found to be a solid condensed film at this surface pressure. The monolayers were transferred onto an appropriate substrate (gold and hydrophobic quartz, 76 mm × 26 mm × 1 mm; mica, 10 mm × 10 mm × 1 mm). Usually the first layer was deposited at a speed of 0.2 mm/min and subsequent layers at a speed ranging from 0.5 mm/min to 1.0 mm/min.

Film Thickness Measurement. Film thickness determinations were done on a gold substrate using a surface plasmon resonance instrument put together in our laboratory using the Kretschmann configuration:[1] Under favorable conditions, electromagnetic surface waves can be incident along the interface between two media. The basic requirement is a combination of a lossless medium with a positive permittivity and another of negative real part and positive imaginary part. Under this condition, modes are excited. The modes are called surface plasmons or surface plasmon polaritons (SPPs). Optical excitation of SPPs requires matching of both energy (i.e., optical frequency) and momentum, where h is Planck's constant:

$$P = h/\lambda \tag{1}$$

The momentum can also be expressed in terms of the wave vector K, where

$$\mathrm{K} = 2\pi/\lambda = 2\pi P/h \tag{2}$$

In a typical experiment (Figure 1a), monolayers were deposited onto a thin (50 nm) gold film that was deposited onto a 1-mm-thick rectangular (76 × 26 mm^2) glass by the LB technique. This sample was brought into optical contact with a 40-mm-diameter BK7 glass triangular prism using a thin layer of oil. A 3-mW HeNe laser, model 1300 series (uniphase), at 632.8 nm was used to obtain reflectivity measurements from the prism−sample assembly as a function of incident angle θ. The laser beam was mechanically chopped at a frequency of 930 Hz (Stanford Research System SR540) and polarized parallel to the plane of incidence (p-polarization) with a calcite polarizer (Newport Corp.). The beam is polarized because only p-polarized light will excite surface plasmons at the gold−air interface. The laser beam was collimated onto the gold surface by a lens and the prism, creating a narrow range of incidence angles on the gold film. The entire reflected beam was then collected and focused onto a photodiode (Spindler & Hoyer).

The incident angle was varied by rotating the prism sample on a fine rotation stage with a stepper motor such that one step corresponds to 0.001°. The collection lens and detector were rotated at an angle of 2θ in order to catch the reflected beam, and the output of the photodiode circuit was sent to a lock-in amplifier (EG & G Instruments, model 5105) to demodulate the signal voltage. This reflective signal was then recorded as a function of incidence angle. In this manner, reflectivity versus incident angle curves were obtained first for the bare gold surface and for the coated surfaces (Figure 1b).The shift in angle was used to determine the film thickness by complex Fresnel calculation: for gold (Au), $\epsilon = -17.784 +$

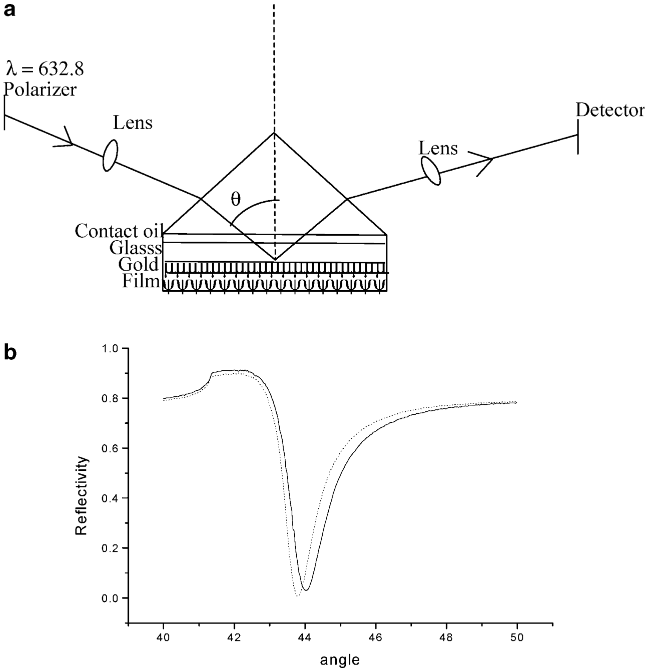


Figure 1. (a) Kretschmann configuration for exciting surface plasmons. (b) Reflectivity vs incident angle curves on bare gold (- - -) and on the coated surface (—).

0.597. This was then fitted on the values of empty gold to obtain the film thickness.

Reflection Absorption Infrared Spectroscopy (RAIR). The gold substrates for RAIR were prepared as metal films on glass (76 mm × 26 mm × 1 mm) at a pressure of $<10^{-5}$ mbar in a leybold Univex 300 evaporator from 99.9% pure granulated gold. The films were prepared by the LB technique.

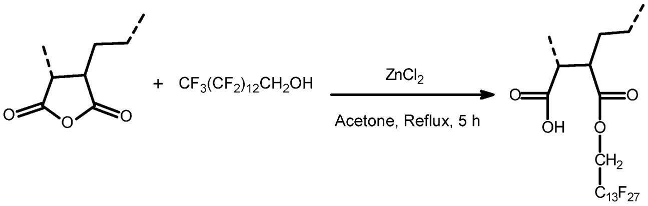
Atomic Force Microscopy. The films were deposited on fresh mica substrate (10 mm × 10 mm × 1 mm) by the LB technique already described. The film was then imaged at ambient temperature using an atomic force microscope (Nanoscope Digital Instruments, Inc.) having a pyramidal Si_3Na tip with radius of curvature approximately 20 nm.

Gas-Phase Polymerization. The gas-phase polymerization of TFPM was carried out in the presence of macroinitiator, poly(octadecene-*co*-maleic anhydride), modified with *tert*-butylhydroperoxide. The macroinitiator was coated onto different hydrophobic substrates (quartz, gold, glass, etc.) by the LB technique. Tetrafluoropropyl methacrylate (TFPM) (2.18 g, 0.01 mol, 1.55 mL) was added into a thick glass and the reaction allowed proceeding under pressure at 80 °C.

Dielectric Spectroscopy. The dielectric measurement was carried out on LB films and spin-coated films with a Novocontrol dielectric interface and a Solartron impedance analyzer, SI 1260. This analyzer is cleaned by heating in chromic acid and washed with a Millipore water system. After it has been thoroughly rinsed with water, it is blown dry in a stream of N_2. An electrode of aluminum stripes is evaporated on the substrate using a Leybold metal coater, as already described. The LB films prepared on hydrophobic glass (26 mm × 24 mm × 1 mm) substrate were used.

Synthesis. *Poly(maleic acid perfluorotetradecanoate-co-ethylene) (PEMPFTDE).* This was synthesized by refluxing a mixture of 1.65 g (5 mmol) of poly(maleic anhydride-*co*-ethylene) and 1.80 g (5 mmol, 1.0 equiv) of 1*H*,1*H*-perfluorotetradecanol in acetone (50 mL) for 5 h in the presence of 100 mg of anhydrous $ZnCl_2$ using the principle of Ringsdorf et al. (Scheme 1).[32] The mixture was concentrated and precipitated from DMSO as a white solid.

Scheme 1. Synthesis of Poly(ethylene-*co*-maleic acid) Perfluorotetradecyl Ester (PEMPFTDE)



Yield: 52%; mp = 267.5 °C. ^1H NMR (500 MHz, MeOD, δ): 2.0−2.18 (m, 4H, $-CH_2-CH_2$), 2.8 (d, 1H, $-CH-COO$), 3.15 (d, 1H, $-CH-COOH$), 4.15 (t, 2H, $-CH_2-OOC$). ^{19}F NMR (CD_3COCD_3-d_6, δ): −79.88 (3F, t, $-CF_3$), −120.33 (10F, s, $-CF_2CF_2CF_2CF_2CF_2-CF_3$), 120.5 (4F, m, $-CF_2CF_2-CH_2$-COOC), −120.72 (2F, s, $-CF_2$), −121.37 (2F, s, $-CF_2$), −122.14 (2F, s, $-CF_2$).

Polyamic Acid (PA-1). 4,4′-Hexafluoroisopropylidenediphthalic anhydride (6FDA) (1.12 g, 2.52 mmol) and 4,4′-hexafluoroisopropylidenedianiline (0.842 g, 2.52 mmol, 1.0 equiv) were added into a flask. NMP (30.0 mL) was added, and the mixture was stirred overnight at room temperature under N_2. At this stage a little highly viscous polyamic acid was withdrawn for further study.

IR (cm^{-1}, film): 3357−2500 (OH), 2888 (C−H), 1663 (C═O), 1520 (NH), 1391 (C═C), 1293 (C−F).

Polyimide (PI-1). The polyamic acid was converted into polyimide after stirring overnight in the presence of acetic anhydride (3 mL) and β-picoline (0.3 mL).[14] It was then precipitated out from methanol to yield a white solid quantitatively.

IR (cm^{-1}, film): 2975 (C−H), 1731 (C═O), 1540 (C═C), 1370 (C−N), 1194 (C−F), 748 (C−N).

Homopolymerization of Tetrafluoropropyl Methacrylate (TFPM). The TFPM (2.0 g, 0.01 mol, and 1.52 mL) and AIBN (5.0 mg) were charged into a polymerization tube. The tube was sealed and heated at 60°C for 24 h. The tube was opened and diluted with acetonitrile. The polymer was precipitated by dropwise addition of the acetonitrile solution to excess methanol with stirring. A white polymer was obtained after drying in a vacuum for 24 h at room temperature.

Yield: 1.80 g.

Gas-Phase Polymerization. The gas-phase polymerization of TFPM was carried out in the presence of a macroinitiator, poly(octadecene-*co*-maleic anhydride), modified with *tert*-butylhydroperoxide as reported by Anders et al.[20] using the poly(octadecene-*co*-maleic anhydride) bought from Polysciences Inc. (M_w 30 000−50 000 g/mol). The macroinitiator was coated onto different hydrophobic substrates (quartz, gold, glass, etc.) by the LB technique. Tetrafluoropropyl methacrylate (TFPM) (2.18 g, 0.01 mol, 1.55 mL) was added onto a thick glass, and the reaction was allowed to proceed under pressure at 80 °C.

Gel Permeation Chromatography (GPC). The size exclusion chromatography (SEC) measurements were carried out with modular chromatographic equipment containing a refractive index detector at ambient temperature. A single column, Hibar PS 40 (Merck), was used. Twenty microliters was used as the injection volume. The concentration of sample was c = 2 g/L, and the flow rate was 1.0 mL/min. The molecular weight was evaluated by use of a PS calibration determined with polystyrene standards (KNAUER) using DMAc.

Thermal Analysis. Thermogravimetry was done on a TGA 7 (Perkin-Elmer). Samples were heated with a heating rate of 10 K/min in nitrogen atmosphere. The DSC experiment was performed using DSC-7 (Perkin-Elmer) at a heating and cooling rate of 20 K/min.

Results and Discussion

The PEMPFTDE was synthesized as shown in Scheme 1. The polymer was purified by precipitation from DMSO and dried under vacuum at room temperature

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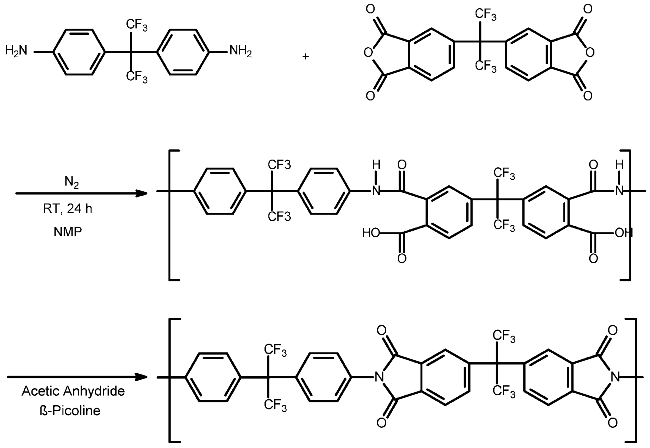
Scheme 2. Synthesis of Polyamic Acid (PA-1) and Polyimide (PI-1)



for 24 h.[1,33] The infrared spectrum showed a strong band at 1717 cm^{-1}. This is characteristic of C=O of an ester.[34,35] The strong bands at 1165−1264 are those of C−O−C and −CF_3 of an ester. The C−F bands are shown at 1003 and 946 cm^{-1}. ^{19}F NMR in deuterated acetone showed triplet peaks at −79.88 ppm, attributed to CF_3, and the multiplet peaks at −120.5 ppm characterized a $-CF_2CF_2CH_2COOC$ group. They are listed in the Materials and Methods. The reaction cannot yield the product without the catalyst, $ZnCl_2$.

The PA-1, the precursor to aromatic polyimide, was obtained by reacting equimolar quantities of the dianhydride and the diamine. The reaction profile is shown in Scheme 2. The reaction mixture was stirred overnight at room temperature under N_2. It was dried in a vacuum overnight, producing the polyamic acid (PA-1) in good yield. The IR spectrum showed characteristic absorptions at 1674 (C=O stretching of amic acid), 1292−1505 (amide 1 and 2 stretching vibrations), and 1292 cm^{-1} (C−N stretching of an amide). The signals in the ^{1}H NMR spectrum in deuterated tetrahydrofuran (THF) of PA-1 are exhibited in Figure 2. The signal at 9.7 ppm is due to the amide proton of the polyamic acid. The phenyl protons are exhibited at 7.2−8.0 ppm. The PA-1 is soluble in acetone, THF, dimethylacetamide (DMAc), dimethylformamide (DMF), and other polar organic solvents. The other peaks which come up around 2−3 ppm are mostly the peaks for solvent used for the measurement and may be end groups. They give no meaning to the spectrum, so they are not shown for all the polymers[2,7,23,32−38] synthesized from 6FDA. For all the ^{1}H NMR figures, the integrations are not shown because the original program used could not transform the integration, but as reported in the Materials and Methods, the integrations were obtained from the NMR program.

The PA-1 was converted into polyimide after stirring overnight at room temperature in the presence of acetic anhydride and β-picoline, as shown in Scheme 2.[1,33] It was then precipitated from methanol and dried in a vacuum overnight to yield the polymer in good yield. It is soluble in aprotic solvents, such as *N*-methylpyrrolidone (NMP), DMF, dimethyl sulfoxide (DMSO), DMAc, etc. The PI-1 is also soluble even in less polar liquids, like pyridine or THF. Its solubility makes the PI-1 a good candidate for fabrication of films. The improved solubility of these polymers can be explained by the presence of voluminous 6F and phenyl groups which prevent strong packing of the chains and thus facilitate the diffusion of small molecules of solvent. In addition, the M_w is within the range to encourage solubility, although that may not be a strong factor, as previous work has shown that fluorine-containing polymers become less soluble with increased fluorine content, even at lower M_w.

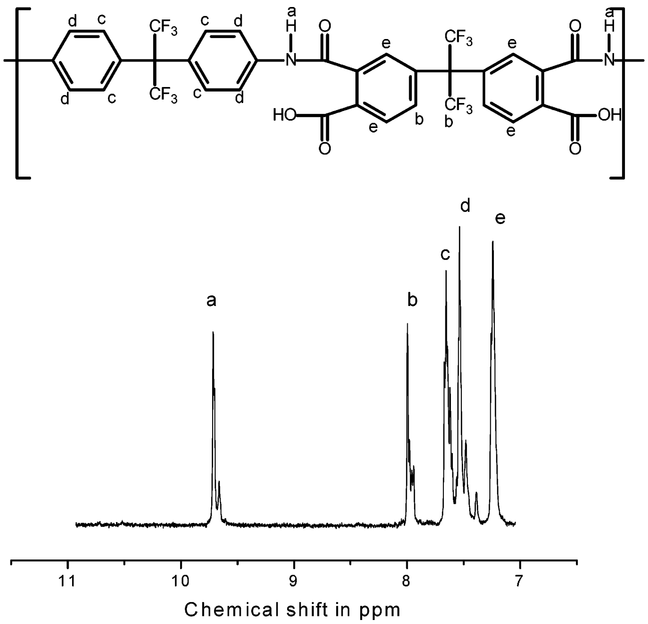


Figure 2. ^{1}H NMR of PA-1 in THF-*d*.

The PI-1 ^{1}H NMR (in deuterated THF) spectrum in Figure 3 indicates peaks at 8.04−7.48 ppm which are characteristic of phenyl protons of the polymer. The IR spectrum of the polyimide showed absorptions in regions 1717−1733, 1582−1618, 1328−1413, 1010−1307, and 691−748 cm^{-1}. The former two bands, 1717−1733 cm^{-1}, are commonly attributed respectively to the symmetric and asymmetric stretching of the carbonyl groups coupled through the five-membered ring. The band at 1328−1413 cm^{-1} has been attributed to the C−N stretch. The strong absorption at 1010−1307 cm^{-1} is attributed to the CF_3 group, both asymmetric and symmetric stretching vibrations. The C−N bending motion in a five-membered imide ring is indicated at 691−748 cm^{-1}. ^{19}F NMR was also used to analyze the polymer. This method has been used to study the reaction intermediates.[39] The ^{19}F NMR spectrum shows no indication of intermediates. This means the polymer was obtained in a clean form. This further confirms the advantage of chemical imidization and that side reac-

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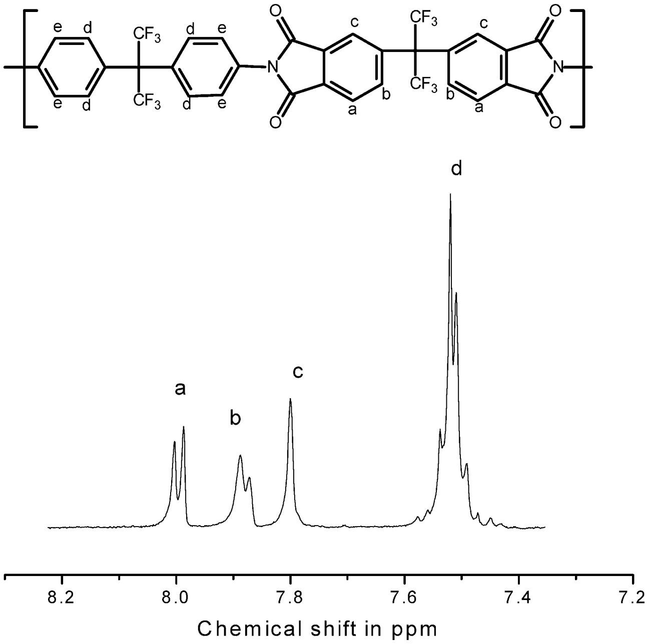
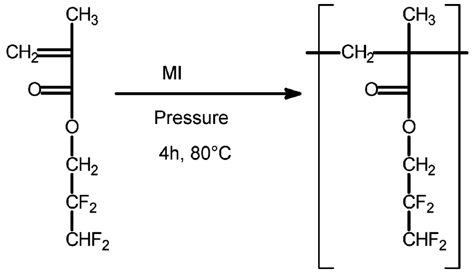


Figure 3. ^{1}H NMR of PI-1 in THF-*d*.

Scheme 3. Gas-Phase Polymerization of Tetrafluoropropyl Methacrylate



tions are very rare. The success of the reaction is probably due to the presence of less sterically hindered diamine. This makes the acylation step simpler. Further, the success of the reaction is also attributed to dehydrative cyclization in the presence of strong dehydrating agents such as acetic anhydride and β-picoline, as shown in Scheme 2.

Poly(tetrafluoropropyl methacrylate) (PTFPM) was synthesized by both radical homopolymerization and chemical vapor deposition (CVD) or gas-phase polymerization,[40−42] as shown in Scheme 3. The radical homopolymerization was carried out in the presence of AIBN as initiator in a dry homopolymerization tube. It was a model experiment for the gas-phase polymerization. The colorless product obtained was soluble in common laboratory solvents such as chloroform, methanol, DMAc, THF, dioxane, DMF, etc. The polymer was analyzed by ^{1}H NMR, and IR confirms the structure of the polymer. The ^{1}H NMR is shown in Figure 4.The ^{1}H NMR spectrum in deuterated chloroform for PTFPM exhibited a triplet peak at 6.1 ppm (1H), multiplets at 4.4 (2H) and 2.00 ppm (2H), and two singlet peaks at 0.8−1.1 ppm (3H). The multiplets at 2.00 ppm are due to the unique tacticity of the polymer.

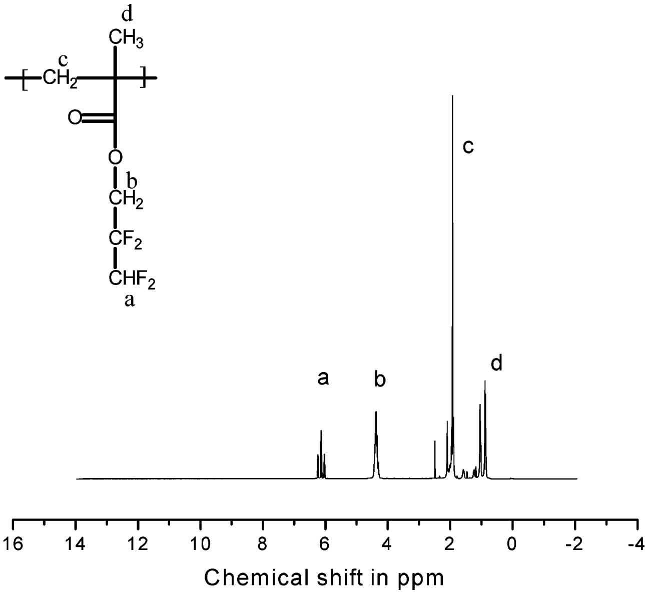


Figure 4. ^{1}H NMR of PTFPM in $CDCl_3$.

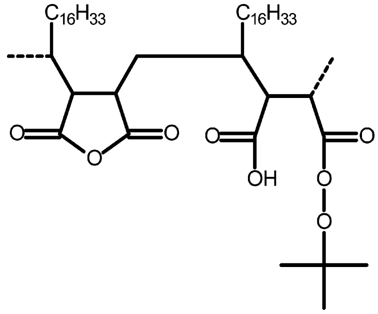


Figure 5. Chemical structure of MI.

Table 1. Molecular Weight Determination by GPC

polymer	M_n (g/mol)	M_w (g/mol)	M_w/M_n
PEMPFTDE	14 100	34 500	2.45
PI-1	17 100	30 600	1.79

The gas-phase polymerization was carried out in the presence of a macroinitiator (MI), poly(octadecene-*co*-maleic anhydride) modified with *tert*-butyl hydroxide. The macroinitiator was brought onto the substrate as a monolayer by the LB technique.The film thickness measurement by ellipsometry (see Table 1) shows that the film thickness increases with reaction time in the presence and in the absence of a macroinitiator. There is a greater increase in thickness in the presence of an initiator, which indicates that the macroinitiator speeds up the reaction, as expected. Structurally, there was no difference between the products obtained from the two processes, except that the product obtained from the gas-phase polymerization is solvent-free and pure, as can be seen from Figure 5. This is a new enhanced method of gas-phase polymerization first reported for the polymer.

The IR spectrum shows characteristic absorptions at 2982 and 1471 cm^{-1}, which are the C−H stretching and bending vibrations, respectively. The characteristic absorptions of C=O, O−C, and C−F are exhibited at 1745 and 1099 cm^{-1}. The characteristic absorption of the CH_2 group at 1653 cm^{-1} is completely absent, as shown in Figure 6, indicating that the product may be obtained pure. The gas-phase polymerization product

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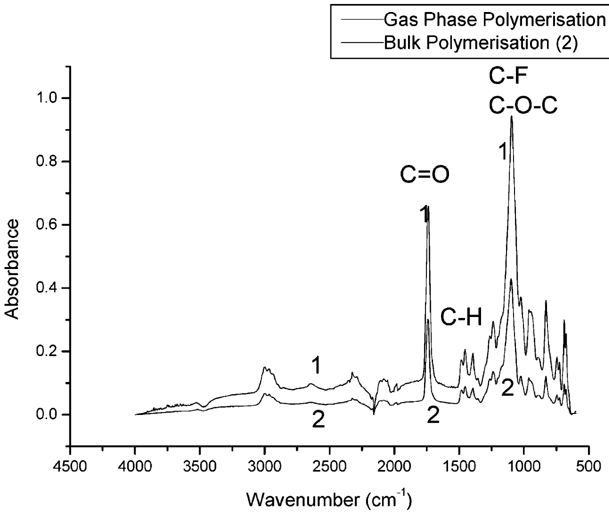

Figure 6. IR of PTFPM from gas-phase and bulk polymerization.

Table 2. Thermal Properties of the Polymers by 1% Weight Loss

		polymer	
	PI-1	PEMPFTDE	PTFPM
TGA (°C)	580	260	265

is of higher purity than the product from bulk polymerization. This can be seen from the increased absorption of the peak at 620 cm^{-1}.

The molecular weight measurements by size exclusion chromatography (SEC) are reported in the Table 1. The SEC showed a number-average molecular weight (M_n) of 85 000 and a weight-average molecular weight (M_w) of 456 000 for PEMPFTDE. The molecular weight distribution (MWD) was 5.37. This may indicate high branching or cross-linking. The M_w of the starting material, poly(ethylene-*co*-maleic anhydride), was 178 000 g/mol. This is an entirely new product. The molecular weights of PI-1 as determined by SEC were 17 100 (M_n), 30 600 (M_w), and 1.79 (M_w/M_n). These values are reasonable for the polyimide obtained from the diamine. It has relatively narrow dispersity, even when it is not a living free radical polymerization. GPC was not done for the rest of the polymers due to their insolubility in the solvents used for GPC.

The thermal properties are reported in Table 2. The polyimide PI-1 had the highest TGA of 480 °C by 1% weight lost. This indicates very high thermal stability. It is a good candidate for use in insulator films in microelectronics. The acrylates, esters, and PAPE showed very low TGA, 260–270 °C. These results show that these compounds do not meet the requirements to be used as insulator films in microelectronics.

The area per repeat unit (RU) of the polymers PAI-1 and PA-1 may be small, as shown in Figure 7 and Table 3.[17] They are probably tightly packed.[11,17] Two possible explanations for the decrease can be suggested: (i) The fluoropolymers tend to have a zigzag orientation on compression, as can be seen in the AFM image (Figure 12, below).[43,44] The helical orientation may not be the case here because that tends to increase collapse area.[45] (ii) The decrease may result from the piling of molecules to form a multilayer;[46] the result may be nonclassical Langmuir–Blodgett films. The hysteresis experiments done on polymers show that there are no hystereses for pressure below the collapse point and for PA-1 there is a perfect reversibility without hysteresis. The steeply inclining parts of the isotherms show the good film-forming behavior of the polymers.[45] The polymers investigated form condensed, stable monolayers on pure aqueous subphases at about 20 °C. They can be deposited on hydrophobic supports without the use of bivalent cations in the subphase.[3] Layers are laid down each time the substrate moves across the phase boundary. For PEMPFTDE, film fabrication was not successful. A single monolayer can be deposited on the upward stroke; however, the deposited monolayer is removed from the substrate on the downstroke.

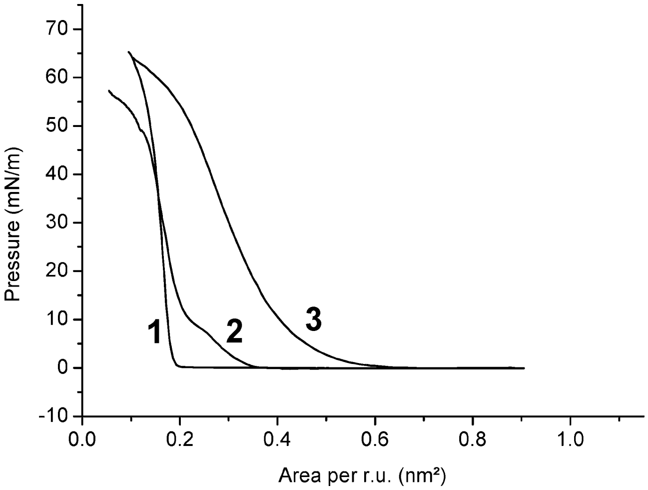

Figure 7. Surface pressure–area isotherms of polymers at 20 °C of PA-1 (1), PTFPM (2), and PI (3).

Table 3. Monolayer and Film Characteristics of Polymers

polymer	collapse pressure (mN/m)	area per RU (nm^2)	monolayer thickness (nm) by SPR
PAPE	62	0.04	1
PTFPM	50	0.20	0.5
PA-1	62	0.20	1.4
PI-1	60	0.23	2.64

The UV–vis spectra of the different numbers of monolayers of PA-1 and PI-1 (Figures 8 and 9, respectively) show that the intensity of the bands is proportional to the number of monolayers at the specific wavelengths, which may indicate the ordered structure of the multilayer.

In addition, the band positions are not shifted with the number of monolayers. This illustrates that there is aggregation which may not be significant for molecules on the adjacent monolayers.[43]

Film thickness measurement, as indicated in Figure 10, was carried out on gold substrate and shows a variation from 1 to 2.6 nm, depending on the polymer. This suggests that some of the orientation of side chains developed in the monolayer by compressing to smaller

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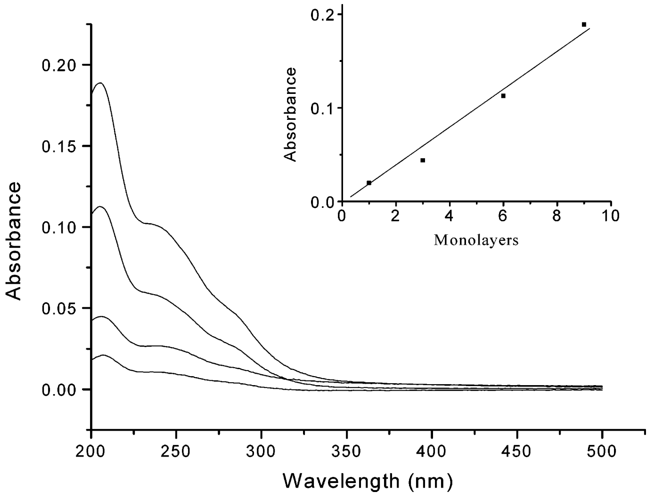

Figure 8. UV−vis spectra of the different numbers of monolayers of the fluoropolyamide, PA-1: changes in UV absorbance at 206 nm.

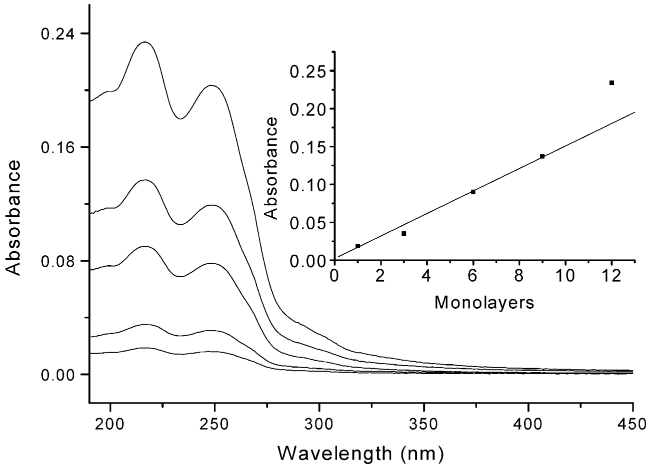

Figure 9. UV−vis spectra of the different numbers of monolayers of the fluoropolyimide, PI-1: changes in UV absorbance at 216 nm.

Table 4. Ellipsometric Film Thickness Measurement at Different Reaction Times on Gold Substrate

	thickness (nm)	
time (h)	with MI	without MI
5	3.28	0.12
15	3.45	0.17
25	10.06	0.84

areas might be preserved during the deposition and in the film.[8]

Assessment of the ordering of the monolayers (PA-1) was obtained by comparison of ATR and reflection−absorption (RAIRS) spectra (Figure 11).[23] While the ATR experiment couples transition dipoles regardless of their orientations, grazing angle reflection only couples transition dipoles perpendicular to the substrate.[23] Changes in intensity between the two spectra (known as dichroism) lead to information about the degree of ordering (in principle of both chains and headgroups). There are "markers" pointing to the well-ordered nature of these molecular multilayers. Most of the bands show strong dichroism, as can be seen from Figure 11. The OH, C═C (phenyl ring), and CF_3 lie perpendicular to the substrate, while the C═O group lies somehow parallel to the substrate.

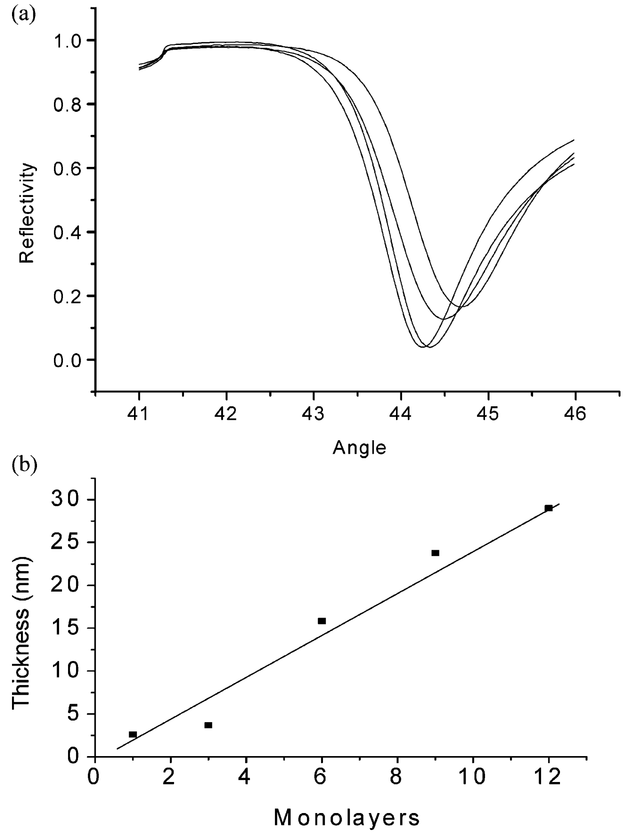

Figure 10. Film thickness measurement by SPR of PI-1: changes in angle with thickness.

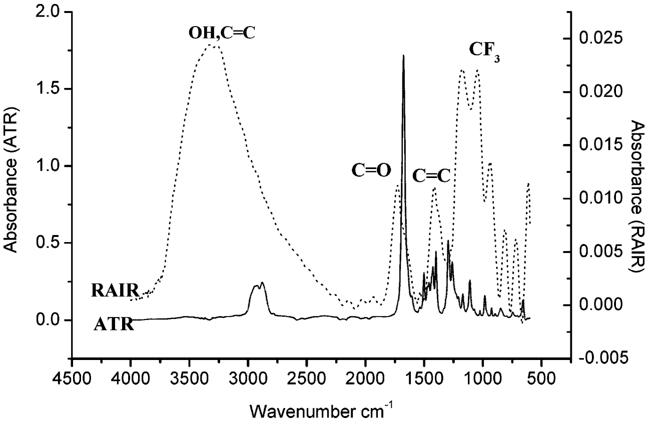

Figure 11. ATR−RAIR of three LB films of PA-1.

The AFM images (Figure 12) of a monolayer on mica are shown. The image (5 × 5 nm^2) obtained is representative of the sample surface. The brighter streak lines are believed to be the polyimide chains, because the main chains of polymer show a slight protrusion above the substrate in height.[44,47] The roughness of the film was less than 1 nm, indicating a homogeneous and well-ordered film.

The real part of permittivity (dielectric constant) for PI-1, as exhibited in Figure 13a, shows decrease at 392.5 K as the frequency is increased from 0 to 10^7 Hz at various temperatures. For the PI-1 LB film thickness of 52 nm, the real part of permittivity is kept constant at 1.5 at the temperatures of 295 and 305 K. This is

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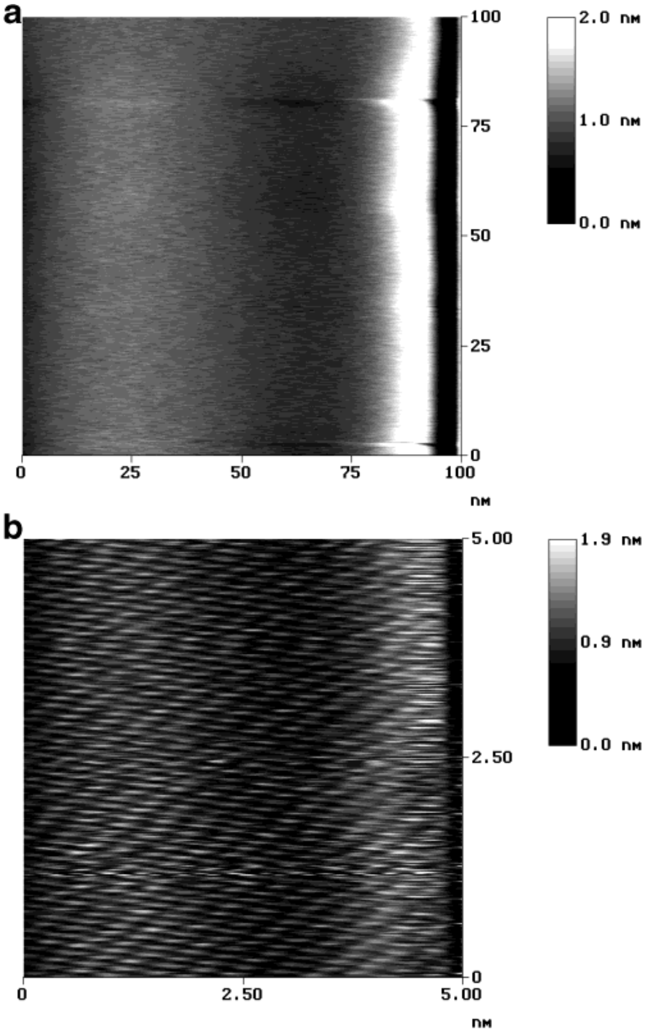

Figure 12. (a) AFM image (100 × 100 nm^2) of monolayer LB film of PI-1. (b) AFM image (5 × 5 nm^2), on the molecular scale, of a monolayer LB film.

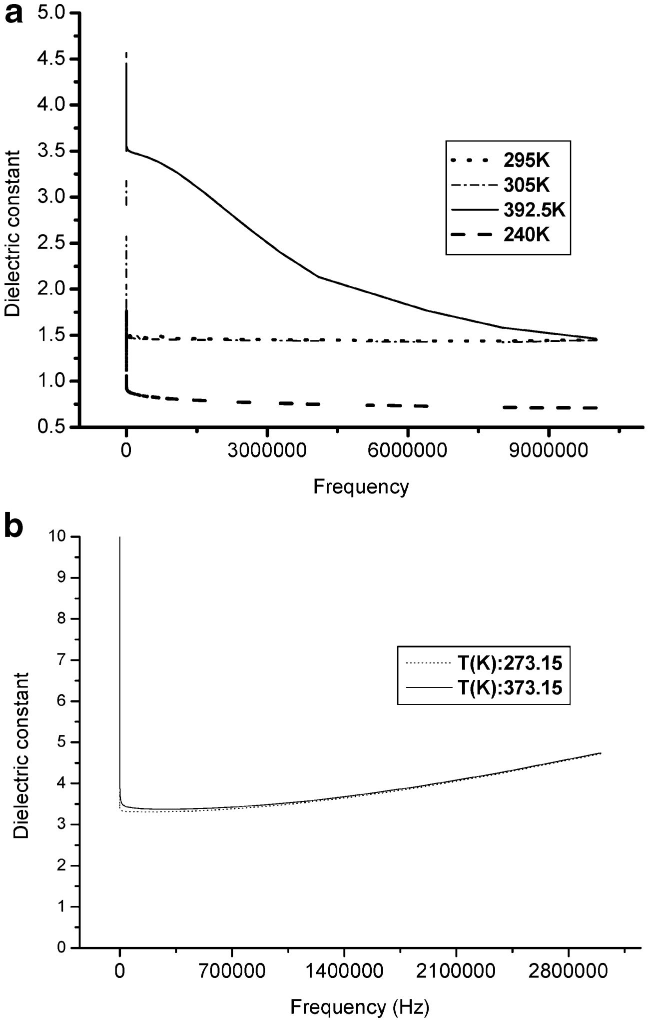

Figure 13. (a) Dielectric spectroscopy of PI-1 (52 nm) at various temperatures. (b) Dielectric spectroscopy on spin-coated layer (100 nm).

the lowest permittivity so far obtained to our knowledge.[23,32] The real part of permittivity for PTFPM (Figure 13b) increases with increasing frequency at the given temperatures (273−373 K) and frequency (0−3 MHz). Controlled polarizations can be obtained in the experiment, leading to different dielectric constants. Decreasing polarization leads to decreasing dielectric constant and vice versa.

In conclusion, the fluoropolymers synthesized form very stable monolayers at the air−water interface. The monolayers can be transferred to different solid supports; film thickness varies proportionally with monolayer number for PAI-1, PA-1, and PI-1. Monolayer thickness varies between 1 and 2.6 nm, depending on the polymer. Atomic force microscopy of the LB film shows an ordered film with a roughness of less than 1 nm. The dielectric constant obtained is as low as 1.5, which is the lowest so far obtained to my knowledge.

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