Synthesis, Characterization, and Multilayer Assemblies of Acid and Base Polyimides

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Introduction

Interactions of the polymers bearing acid and base functionality with various substances have endorsed the systems with many interesting and potentially applicable properties such as the induced helical backbone structure for probing chirality of small molecules,[1] change of permselectivity and conductivity for fuel cell use,[2] and the improvement of compatibility for blending purposes.[3] The acid and base properties of these polymers have also been explored to enhance interlayer adhesion,[4] to stabilize inorganic nanoparticles[5] and organic dyes[6] in the doped systems, and very recently as driving force to assemble multilayer very thin films.[7]

Polymers having common acid and base units such as carboxylic acid, sulfonic acid, pyridine, and amine can either be ionized into the corresponding polycations and polyanions and interact electrostatically at strong Brønsted acid−base interactions or form a strong hydrogen bonding at relatively weak Lewis acid−base interactions. The acid−base interaction between polymers has recently been utilized as a driving force to assemble multilayer thin films.[7−12] For example, the layer-by-layer (LBL) self-assembly technique developed by Decher et al.[7a,13] is based on the sequential adsorption of polycations and polyanions, derived from their corresponding acid and base polymers. The most substantial advantages of this self-assembly process are the simplicity of the deposition process (solution dipping) and quite accurate control over the average thickness of each polyelectrolyte layers. However, a disadvantage associated with this technique is its rather long processing time,[14] typically over 1 h for each bilayer deposition cycle, which requires the involvement of automation and strictly controlled processing environment. An alternative method for the preparation of multilayer thin films is by alternately spin-coating aqueous solution of two differently charged polyelectrolytes as reported recently by Lee et al.[12] In comparison with the solution-dipping LBL self-assembly process, the spin-coating technique significantly shortens the preparation time and can afford a better film in terms of surface smoothness.

In addition to utilization of the electrostatic interactions as a main driving force in the LBL self-assembly, the interaction due to hydrogen bonding has also been explored for multilayer assembly. Some unique features were reported for these hydrogen-bonding multilayer films, such as film patterning,[10] reversible deposition process,[11] and low or no alkaline salt contamination due to the use of the noncharged acid and base polymers.[15] In principle, any pair of acid and base polymers could be used to form multilayer films as long as they have good electrostatic or hydrogen-bonding interactions and are specifically dissolved in only one of two distinct solvents. The latter requirement is often difficult to be met for many polymers, especially when the target polymers are insoluble in water and have limited solubility in organic solvents. Condensation polyimides are a well-known class of high-performance engineering polymers and commercially used as films, coatings, fibers, and membranes.[16] However, there is no report on the fabrication of multilayer films by spin-coating of acid and base polyimides in organic solvents.

We report herein a rapid assembly of multilayer films by spin-coating of the organic solutions of acid and base polyimides. A series of base polyimides containing a tertiary amine unit were obtained by polymerization of four different aromatic dianhydrides with 1,4-bis(3-aminopropyl)piperazine in acetic acid. These base polyimides were found to be able to bond with an acid polyimide mainly through the hydrogen bonding.

Experimental Section

Materials. All the dianhydrides were purchased from Sigma-Aldrich Canada Ltd. 1,8,4,5-Naphthalenetetracarboxylic dianhydride (NDA), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) were purified by vacuum sublimation. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) was purified by recrystallization from acetic anhydride. 1,4-Bis(3-aminopropyl)piperazine (BAPP) was purified by distillation at reduced pressure. 3,5-Diaminobenzoic acid (DABA) was purified by recrystallization from distilled water. *N*,*N*′-Dimethylacetamide (DMAc) was dried over calcium hydride and vacuum-distilled. Other solvents such as *m*-cresol and acetic acid were purchased from Sigma-Aldrich and used as received.

Characterization. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 or Bruker-400 spectrometer. The chemical shifts relative to tetramethylsilane as internal reference are reported in the ppm scale. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrophotometer. Solubility tests were carried out by dissolving about 10 mg of polymer in 1 mL of studied solvent. Glass transition temperatures (T_gs) were determined on a Seiko 220C DSC at a heating rate of 20 °C/min in nitrogen. The onset temperature for 5% weight loss were determined using a Seiko 120 TG/DTA analyzer at a heating rate of 10 °C/min in nitrogen. Inherent viscosities of polymers were measured with an Ubbelohde capillary viscometer at 30.0 ± 0.1 °C with a concentration of 0.5 g/dL. Absorption spectra were recorded on a Perkin-Elmer Lambda 900 UV−vis−NIR spectrophotometer. Thickness of films was measured using a VASE ellipsometer (J.A. Woollam Co., Inc.) with a WVASE32 analysis software.

1,4-Bis(3-phthalimidopropyl)piperazine (BPIPP). A round-bottomed flask was charged with BAPP (0.8768 g, 4.377 mmol), phthalic anhydride (1.2966 g, 8.754 mmol), and acetic acid (10 mL). The mixture was stirred at 130 °C for 4 h and then poured into aqueous potassium carbonate solution (300 mL, 6 N). The resultant solid was collected by filtration, washed thoroughly with distilled water unitl neutral, and dried at 80 °C in a vacuum oven (ca. 1 mmHg). A fine needlelike crystal was obtained by recrystallization from chlorobenzene: 1.80 g (89.4% yield); mp 166−167 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.77−7.84 (8H, m); 3.57 (4H, t, J = 6.4 Hz, 6.4 Hz); 2.10 (4H, t, J = 6.4 Hz, 6.4 Hz); 1.96 (8H, br); 1.63 (4H, quintet, J = 6.4 Hz, 6.4 Hz, 6.4 Hz, 6.4 Hz). ^{13}C NMR (50 MHz, CDCl$_3$): 168.72, 134.04, 132.59, 123.39, 56.29, 53.22,

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36.92, 25.42. IR (KBr, cm^{-1}): 1770, 1708 ($\upsilon_{C=O}$ of imide). MS (EI, *m*/*z*): 460 (M^+, 16.7%).

General Procedure for the Preparation of Base Polyimides (PI-1−4). A stoichiometric amount of a dianhydride was added to a mixture of BAPP and glacial acetic acid. The solution concentration was kept at 0.15−0.20 g/mL. The solution was stirred at room temperature for 0.5 h and at 130 °C for 12 h. After cooling to room temperature, the resulting viscous solution was poured slowly into a stirred aqueous potassium carbonate solution (6 N). The precipitated product was collected by filtration and washed thoroughly with aqueous sodium bicarbonate solution (1 N), distilled water, and methanol in sequence, and then dried at 120 °C under vacuum (ca. 1 mmHg) for 24 h.

PI-1: light yellow powders; 90.2% yield. ^1H NMR (200 MHz, $CDCl_3$): δ 7.86 (2H, d, J = 7.6 Hz); 7.70−7.75 (4H, m); 3.72 (4H, t, J = 6.8 Hz, 6.8 Hz); 2.27 (12H, m); 1.78 (4H, m). IR (KBr, cm^{-1}): 1768, 1706 ($\upsilon_{C=O}$ of imide).

PI-2: light yellow fibrous powders; 86.9% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (2H, s); 7.88 (4H, s); 3.67 (4H, t, J = 6.8 Hz, 6.8 Hz); 2.25 (12H, m); 1.75 (4H, quintet, J = 6.8 Hz, 6.8 Hz, 6.8 Hz, 6.8 Hz). IR (KBr, cm^{-1}): 1768, 1708 ($\upsilon_{C=O}$ of imide).

PI-3: light yellow powders; 94.2% yield. IR (KBr, cm^{-1}): 1774, 1709 ($\upsilon_{C=O}$ of imide).

PI-4: yellow fibrous powders; 84.6% yield. IR (KBr, cm^{-1}): 1703, 1661 ($\upsilon_{C=O}$ of imide).

Acid Polyimide PI-5. To a solution of 3,5-diaminobenzoic acid (0.3043 g, 2.000 mmol) in *m*-cresol (15 mL) was added 6FDA (0.8885 g, 2.000 mmol). The mixture was stirred at 200 °C overnight. The water produced during reaction was removed though a Dean−Stark trap. After cooling to room temperature, the viscous solution was poured slowly into methanol (500 mL). The precipitated polymer was collected by filtration, washed thoroughly with hot methanol, and dried at 120 °C under vacuum (1 mmHg): 1.09 g (97.3% yield). ^1H NMR (200 MHz, DMSO-d_6): δ 9.41−9.49 (4H, m); 9.23 (2H, d, J = 6.8 Hz); 9.11 (1H, s); 9.05 (2H, s). IR (KBr, cm^{-1}): 1786, 1729 ($\upsilon_{C=O}$ of imide and carboxylic acid).

Preparation of Multilayer Assemblies. Quartz plates were immersed in a mixture of $H_2O/H_2O_2/NH_3$ (5:1:1 by volume) at 80 °C for 15 min, followed by thorough rinsing with distilled water.[17] The quartz plates were first spin-coated with a layer of either acid polyimide (0.5 wt % of **PI-5** in tetrahydrofuran) or base polyimide (0.5 wt % of **PI-2** in chloroform) at a spin speed of 2600 rpm. A more diluted solution (0.4 mg/mL) was prepared for both **PI-2** and **PI-5** in chloroform and tetrahydrofuran (THF), respectively, and then used to build up the acid/base multilayers. To remove insoluble particles, the polymer solutions were filtered through a syringe filter with a pore size of 0.45 μm. Using a spin-coater (model KW-4B, Chemat Technology), a small volume of the acid or base polymer solution was applied onto the substrate, and then the substrate was spun at a speed of 2800 rpm for 30 s. After each coating the polymer film was blow-dried with a gentle stream of nitrogen. No extra care was taken to exclude the moisture and dust in the environment. The layer-by-layer growth of acid/base polymer films was monitored using a UV−vis spectrophotometer. The thickness of each single layer was determined from the UV−vis absorption data of their corresponding polymer films, which were calibrated using a spectral ellipsometer. The corresponding calibration equations obtained by measuring UV−vis absorption at 222 nm of polymer films with different thickness (8−20 nm) are $A = 0.0225T - 0.075$ for **PI-2** and $A = 0.0241T + 0.0662$ for **PI-5**, where A is absorption at 222 nm and T is thickness in nm.

Sample Preparation for IR Measurement. Acid polyimide **PI-5** and base polyimide **PI-2** were cast into thin films on a sodium chloride (NaCl) plate from a solution of THF and chloroform, respectively. Thin films on a NaCl plate were cast from a solution of base polyimide **PI-2** doped with benzoic acid and acetic acid in chloroform. The protonated **PI-2** sample was prepared by adding concentrated hydrochloric acid to a solution of **PI-2** in chloroform and collecting the sample at the chloroform−water interface. For IR measurement, a free-standing film was obtained by casting the **PI-2**/HCl sample in a mixture solvent of acetic acid/water (20/1 v/v) on a glass plate, followed by vacuum (ca. 1 mmHg) drying at 100 °C. The hydrochloric salt of model compound (**BPIPP**) was prepared by adding concentrated hydrochloric acid to a solution of **BPIPP** in THF. The white precipitate was collected by filtration and dried at 100 °C under vacuum (ca. 1 mmHg) and then mixed with potassium bromide to make a pellet for IR measurement. All the other IR measurements were carried out using KBr pellets.

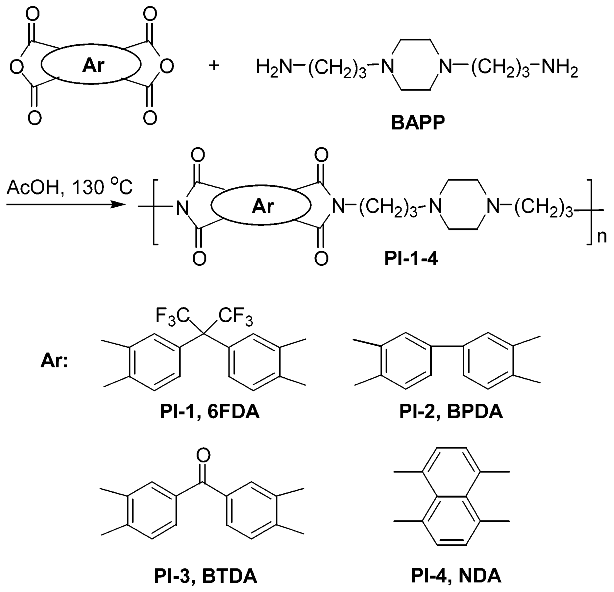
Results and Discussion

Synthesis of Model Compound. Endeavors were initially made to polymerize BAPP and 6FDA by either one-step (e.g., *m*-cresol) or two-step (e.g., first in DMAc and then chemical imidization with acetic anhydride) solution polymerization but failed to obtain a high molecular weight polyimide by both methods. The difficulty of obtaining high molecular weight polyimides from the polycondensation of a dianhydride and an aliphatic diamine with a high basicity, such as of BAPP in our case, has been well recognized. The same is true for making small imide molecules. For example, Teressa et al.[18] tried to condense tertiary amine-containing diamines with β-carbolinedicarboxylic anhydride in toluene and obtained the diimide compounds in a low yield after a long period of reaction time (2 weeks). Mahboobi et al.[19] modified the reaction by heating in a microwave oven a mixture of similar diamines and β-carbolinedicarboxylic anhydride in the presence of $TaCl_5$. Although the reaction time was shortened, the reaction still did not go to completion. The major cause for difficulty in imidization is believed to be the salt formation between amine and the intermediate amic acid during condensation reaction, namely, the salt formation from the basic piperazine moiety and the amic acid in our case. The common methods that have been used to circumvent this problem include the reversed addition (i.e., adding diamine into a solution of dianhydride), use of nonamide solvent, and increase of the reaction temperature. Polymerization in an acidic medium as a means to break up the acid−base interaction between reactants and thus afford high molecular weight polyimides has not been well investigated to date, although organic acid (e.g., *m*-hydroxybenzoic acid) has been reported as an imidization accelerator.[20]

Thus, a model reaction was carried out to study various reaction conditions for making the diimide from BAPP and phthalic anhydride. The reverse addition procedure, use of nonamide solvents (e.g., dimethyl sulfoxide), and increase of reaction temperature (e.g., up to 200 °C in *m*-cresol) were attempted but failed to give the diimide product in reasonable yields. Considering the relative acidity of the amic acid and basicity of BAPP, acetic acid was selected as a solvent in the model reaction. It was found that after reflux at 130 °C for 4 h no trace of any reactants in the reaction using a stoichiometric amount of BAPP and phthalic anhydride was shown by thin-layer chomatography. The corresponding diimide product (**BPIPP**) was isloated in 89% yield, and its structure was consistent with its NMR, IR, and mass spectra.

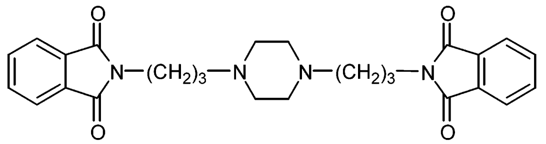
Polymer Synthesis. The polymerizations of BAPP and various aromatic dianhydrides were carried out in glacial acetic acid at a concentration of 0.15−0.20 g/mL to afford a series of polyimides **PI-1−4** (Scheme 1). These base polyimides remained soluble in acetic acid

Scheme 1. Synthesis of Base Polyimides PI-1−4

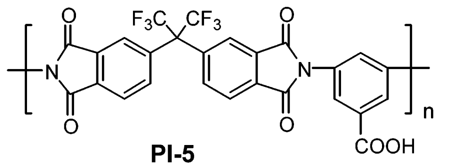


during the course of polymerization, due to the acid−base interaction between the piperazine unit in the polymer backbone and acetic acid. After reflux for 12 h, the viscous polymer solution was poured into aqueous potassium carbonate solution in order to break acid−base interactions between the polymers and acetic acid. The absence of carboxyl hydrogen in the ^{1}H NMR spectrum and the characteristic vibration bands of the imide at around 1770 and 1710 cm^{-1} in the IR spectrum verify the complete imidization in acetic acid. The inherent viscosities of these polymers were measured in acetic acid at 30 °C and ranged from 0.48 to 0.67 dL/g (Table 1), indicating a high molecular weight for these polymers.

To make an acid-containing polyimide (**PI-5**), one-step polycondensation of 6FDA and 3,5-diaminobenzoic acid in boiling *m*-cresol was carried out. The polymer **PI-5** was obtained as white powders in 97% yield. Its inherent viscosity was found to be 0.76 dL/g as measured at 30 °C in DMAc.



BPIPP



PI-5

Solubility Study. The acid and base polyimides **PI-1−5** showed unique solubility in various solvents (Table 2). Owing to the formation of hydrogen bonding, acid polyimide **PI-5** displays a good solubility in a wide range of solvents and even in THF and acetone. When a tertiary amine such as triethylamine was added to a solution of **PI-5** in THF, the precipitate was immediately formed. All the base polyimides **PI-1−4** are soluble in organic acids such as acetic acid and trifluoroacetic acid and even in a mixture of these acids and water. The solubility of **PI-1−4** showed a strong dependence on the corresponding diimide moiety in the polymer backbone. **PI-1** based on 6FDA was readily soluble in polar aprotic solvents such as DMAc, *N,N′*-dimethylforamide (DMF), and dimethyl sulfoxide (DMSO) and partially soluble in chloroform. In contrast, **PI-2** derived from BPDA was found to be quite insoluble in those polar aprotic solvents but very soluble in chloroform. **PI-3** was less soluble than **PI-2** when being tested for the same solvents, and **PI-4** was not soluble in all the solvents tested except for organic acids.

Table 1. Characterizations of Acid and Base Polyimides

polymer	diamine	dianhydride	$[\eta]_{\text{inh}}$ (dL g^{-1})	T_g[c] (°C)	T_d[e] (°C)
PI-1	BAPP	6FDA	0.48[a]	163.7	385.7
PI-2	BAPP	BPDA	0.67[a]	148.4	379.6
PI-3	BAPP	BTDA	0.50[a]	142.9	342.6
PI-4	BAPP	NDA	0.53[a]	ND[d]	291.1
PI-5	DABA	6FDA	0.76[b]	ND[d]	402.6

[a] Inherent viscosity measured in acetic acid at 30 ± 0.1 °C with a concentration of 0.5 g/dL. [b] Inherent viscosity measured in DMAc at 30 ± 0.1 °C with a concentration of 0.5 g/dL. [c] Glass transition temperature by DSC in nitrogen at a heating rate of 20 °C/min. [d] Not detectable. [e] Onset temperature for 5% weight loss measured by TGA in nitrogen with a heating rate of 10 °C/min.

Thermal Property. The base polyimides **PI-1−3** showed glass transition temperatures (T_gs) in the range 142−164 °C (The DSC thermograms of **PI-1−4** are available in the Supporting Information.) The relatively low T_gs of these polymers compared to that of aromatic polyimides are due to the aliphatic moieties in the polymer backbone. This chain flexibility is desirable for achieving a good interlayer diffusion and chain entanglement during the multilayer assembly. **PI-4** based on NDA displayed no glass transition in the temperature up to 260 °C (prior to its thermal degradation temperature of 290 °C), due to its rigid naphthalene diimide moieties. The onset temperatures for 5% weight loss for base polyimides **PI-1−4** were assessed by thermogravimetric analysis in nitrogen with a heating rate of 10 °C/min (Table 1). **PI-1** and **PI-2** were thermally stable up to 380 °C, while **PI-3** and **PI-4** showed relatively poor thermal stability.

DSC measurement did not reveal a glass transition temperature for acid polyimide **PI-5** under 380 °C, probably due to the rigid aromatic backbone and the hydrogen bonding between the carboxylic acid groups. For **PI-5**, its onset temperature for 5% weight loss was about 400 °C in nitrogen, indicating that no dehydration reaction could occur thermally below 400 °C.

Acid−Base Interaction. The acid−base interactions between **PI-1−4** and **PI-5** were investigated in solution and in the solid state. First observed is gel formation of the acid and base polyimide complex in DMSO solution. When a solution of **PI-1** in DMSO was mixed at room temperature with a solution of **PI-5** in DMSO, the mixture turned turbid quickly. This cloudy mixture became clear at elevated temperatures (e.g., above 70 °C) and resumed upon cooling to room temperatures. After being at room temperature for ca. 1 h, a transparent gellike precipitate was formed. However, turbidity of the same polymer mixture in polar aprotic amide solvents such as DMF, DMAc, and 1-methyl-2-pyrrolidinone (NMP) could not be realized.

The acid−base interaction of these acid and base polyimides in solution was first studied by using a model system involving base polyimide **PI-2** and benzoic acid.

Table 2. Solubility of Acid and Base Polyimides in Various Solvents[a]

polymer	DMSO	DMAc	DMF	$CHCl_3$	THF	acetone	AcOH	aq AcOH (70%)
PI-1	+	+	+	±	−	−	+	+
PI-2	−	−	−	+	−	−	+	+
PI-3	−	−	−	±	−	−	+	+
PI-4	−	−	−	−	−	−	+	+
PI-5	+	+	+	−	+	+	−	−

[a] Note: "+" = soluble, "±" = partially soluble, and "−" = insoluble. The solubility of polymer in various solvents was examined visually by dissolving ca. 10 mg of sample in 1 mL of solvent at room temperatures.

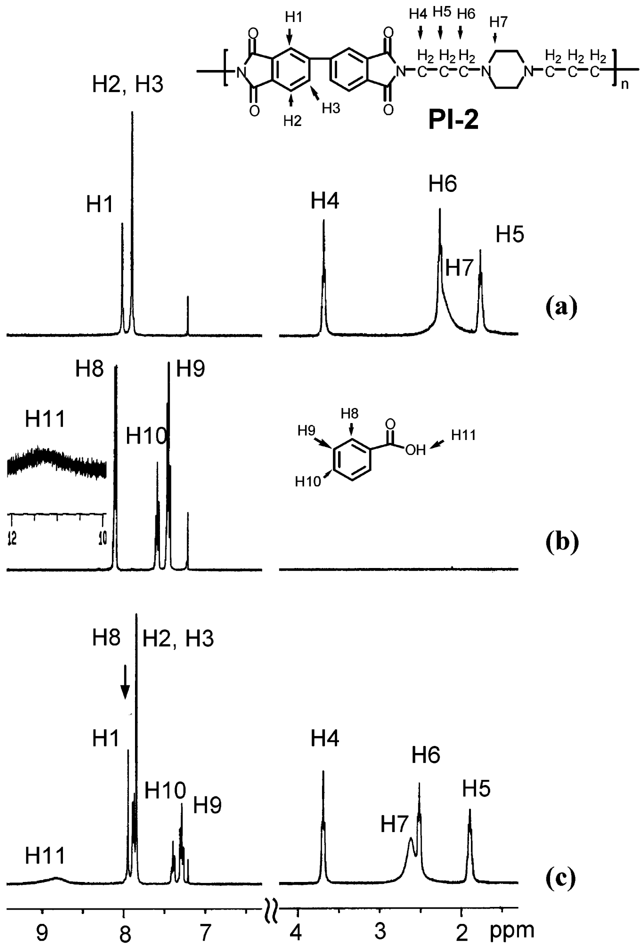


Figure 1. ^{1}H NMR spectra of (a) base polyimide **PI-2**, (b) benzoic acid, and (c) the mixture of **PI-2** and benzoic acid (in 1:1 mole ratio, as calculated with the repeat unit of **PI-2**).

Figure 1 displays the ^{1}H NMR spectra of **PI-2**, benzoic acid, and their mixture (1:1 molar ratio calculated according to the repeat unit of **PI-2**) in deuterated chloroform. Although the mixture of **PI-2** and benzoic acid tends to precipitate slowly out of the chloroform solution, the resulting gellike solid can be redissolved by heating, which allows for the NMR measurement in time. A number of interesting observations were made from this NMR study, which mainly relates to the changes of chemical shifts. For the mixture of **PI-2** and benzoic acid, a large upfield shift and downfield shift were observed for the protons (H-8,9,10) of benzoic acid and the protons close to the tertiary nitrogen atoms in **PI-2** (i.e., H-6,7), respectively. This change in chemical shifts indicates a certain degree of the deprotonation of benzoic acid and protonation of **PI-2**. The upfield shift of carboxyl hydrogen (H-11) from 11.5 ppm (spectrum b, Figure 1) in benzoic acid to 8.8 ppm (spectrum c, Figure 1) in the mixture also denotes a strong acid−base interaction. The nature of the acid−base interaction of **PI-2** and acids (i.e., Brønsted or Lewis) was studied by IR spectroscopy. The O−H band of benzoic acid at 2400−3200 cm^{-1} disappeared, and a new weak broad band showed up at around 2500 cm^{-1} for the mixture of benzoic acid and **PI-2** (1:1 molar ratio based on the repeat unit of **PI-2**). The IR spectra of **PI-2**, benzoic acid, and their mixture are available in the Supporting Information. The latter new band, although being rather weak, is characteristic for a protonated tertiary amine (2200−3000 cm^{-1}). To verify this, the protonated model compound (**BPIPP**) and base polyimide **PI-2** doped with various acids were obtained and characterized by IR (Figure 2). In comparison with **BPIPP** (spectrum d, Figure 2), the hydrochloric salt of **BPIPP** gives rise to a new, strong band at 2200−2800 cm^{-1} (spectrum e) that is assigned to the protonated piperazine moiety. Similar bands can be seen for the hydrochloric salt of base polyimide **PI-2** (spectrum c), although the relative intensity is lower with respect to that of the hydrochloric salt of **BPIPP**. The acid−base systems consisting of **PI-2** and weak benzoic acid and acetic acid showed similar IR features (spectra a and b). The characteristic O−H peak of carboxylic acid vanished and a weak band appeared in the 2200−2800 cm^{-1} region, confirming that base polyimide **PI-2** could only partially protonated by a weak acid like benzoic acid, and thus the major acid−base interaction in this case should be attributed to hydrogen bonding (Lewis acid−base interaction) rather than the electrostatic interaction (Brønsted acid−base interaction). As expected, a polyimide blend prepared from **PI-1** and **PI-5** (1:1 weight ratio) by precipitating a solution of **PI-1** and **PI-5** in DMAc into methanol did not display any

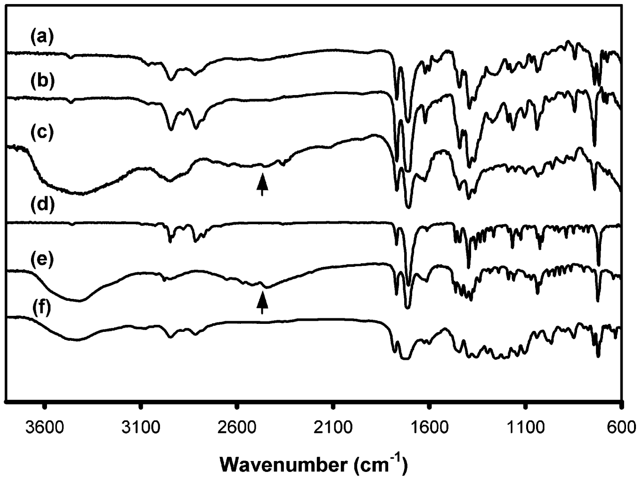


Figure 2. Comparison of IR spectra of various acid−base systems: (a) **PI-2**/benzoic acid (as film on NaCl plate), (b) **PI-2**/acetic acid (as film on NaCl plate), (c) **PI-2**/hydrochloric acid (free-standing film), (d) **BPIPP** (KBr pellet), (e) **BPIPP**/hydrochloric salt (KBr pellet), and (f) **PI-5**/**PI-1** blend (1:1 by weight) (KBr pellet).

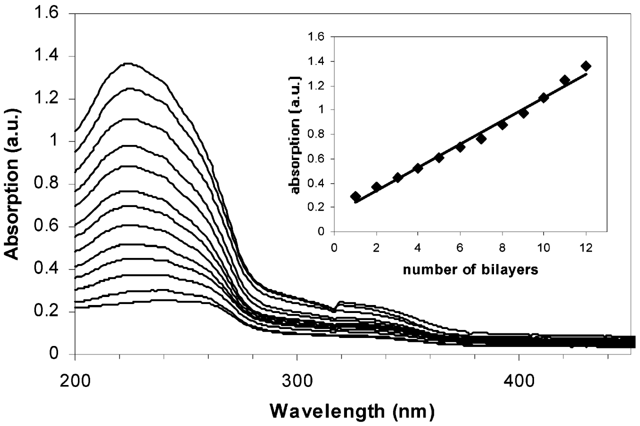


Figure 3. Absorption spectra of 12 **PI-2**/**PI-5** bilayers spin-coated on a quartz plate precoated with a layer of acid−polyimide **PI-5**. The spectra were obtained after each deposition cycle (the bottom absorption curve is from the precoated **PI-2** layer). The inset displays the dependence of the UV−vis absorbance on the number of bilayers.

observable peak that is attributed to the protonated piperazine unit (spectrum f, Figure 2).

The interaction between acid and base polyimides in the solid state was studied by DSC. To prepare a polymer blend, acid polyimide **PI-5** and base polyimide **PI-1** in a different weight ratio were first dissolved in DMAc. The polymer solution was then poured into methanol, and the precipitate was washed with methanol and dried in a vacuum oven at 120 °C. A figure that displays the DSC traces of these polymer blends is available in the Supporting Information. A single T_g was found for each of five blends and increased with the increase of the amount of acid polyimide in the blends, thus indicating that a homogeneous polymer blend without phase separation was obtained. In comparison, the blend derived from **PI-1** with other aromatic polyimide bearing no acid functionality (e.g., polyimide from 6FDA and 4,4′-oxydianiline) is clearly phase separated as examined by microscope and DSC. Therefore, the excellent miscibility between **PI-1** and **PI-5** can be attributed to their unique acid−base interactions.

Multilayer Assembly. The acid−base interaction between polymers and between polymer and various dopants have been widely studied in terms of interfacial adhesion,[4] acid−base doping systems,[5,6] and induction of chiral conformational structure.[1] Our studies have demonstrated that base polyimides containing piperazine rings interact strongly with acid polyimide **PI-5**. This interaction is deemed to be a driving force for the fabrication of multilayer thin films from the acid and base polyimides by the rapid spin-coating process.

Figure 3 displays the typical UV−vis absorption spectra of acid−base polyimide multilayers that were spin-coated on quartz from solutions of **PI-2** in chloroform and **PI-5** in THF. A steady increase of UV−vis absorption is observed with an increase of the number of film layers, confirming the successive and uniform growth of the multilayer film. The inset shows a good linear dependence of UV−vis absorption on the number of bilayers deposited. Microscopic investigation also indicated a smooth surface of multilayer film after 12 deposition cycles. A free-standing transparent film can be peeled off from the substrate by immersing in water and appeared to be flexible and tough. The average thickness of each bilayer was about 3.4 nm as calculated from the UV−vis absorption (i.e., 1.8 nm per **PI-2** layer and 1.6 nm per **PI-5** layer). The thickness of each layer can be easily controlled by adjusting the spin speed and the concentration of polymer solutions. The multilayer films with a thickness per layer ranging from 2 to 150 nm were obtained. The deposition time was ca. 2−4 min for each bilayer on a substrate with a size about 1 in.^{2}, which represents a significant fast process relative to the solution dipping process.

For the multilayer deposition by spin-coating, the affinity of acid or base polymer to the previous layer is critical for a steady buildup of the uniform multilayer. Hydrogen bonding between acid and base polymers is believed to be a driving force in our process. The sharp difference in solubility for the acid and base polymers is also important to the successful deposition of multilayer films by spin-coating. The solvent for acid polymer or base polymer should dissolve no or very little the counter polymer, so that the previously deposited layer will not be washed off during the subsequent spin-coating process. **PI-2** and **PI-5** have very different solubility in chloroform and THF; therefore, these two polymers form a good pair for making a multilayer film by spin-coating deposition. Conceivably, any polymer pairs that meet the solubility requirement should be able to be used to fabricate multilayer films by the spin-coating technique. For example, other base polyimides, i.e., **PI-1**, **PI-3**, and **PI-4** that have poor solubility in chloroform, were also spin-coated into multilayer films together with acid polyimide **PI-5** when using the solution of these three polyimides in acetic acid that is a nonsolvent for **PI-5**.

Conclusions

Acetic acid was first successfully used as solvent in one-step polymerization of aromatic dianhydrides and a piperazine-containing aliphatic diamine. Owing to the strong acid−base interaction, these base polyimides showed unique solubility in organic acids, including acetic acid and trifluoroacetic acid. The acid−base interaction between acid and base polyimides has been demonstrated to be a driving force to form multilayer thin films by a rapid spin-coating process. The strong acid−base interaction and different solubility of acid and base polymers warrant a steady growth of a uniform multilayer film.

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Supporting Information Available: DSC traces of polyimides **PI-1**−**4**; IR spectra of polyimide **PI-2**, benzoic acid, and their mixture in 1:1 mole ratio; DSC traces of base polyimide **PI-1**, **PI-5**/**PI-1** blend (1/10 by weight), **PI-5**/**PI-1** blend (1/4 by weight), **PI-5**/**PI-1** blend (1/2 by weight), **PI-5**/**PI-1** blend (1/1 by weight), and **PI-5**/**PI-1** blend (2/1 by weight). This material is available free of charge via the Internet at http://pubs.acs.org.

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