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Synthesis and characterization of new alkali-soluble polyimides and preparation of alternating multilayer nano-films therefrom

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Abstract

New alkali-soluble aromatic polyimides were prepared by a direct one-step polycondensation of 3,6-di(4-carboxyphenyl)pyromellitic dianhydride with common aromatic diamines in the presence of isoquinoline at 170 °C. The obtained polymers with inherent viscosities of the 0.62–1.01 g/dl range were all amorphous and highly soluble in dilute aqueous NaOH and tetramethylammonium hydroxide. Upon heating in TGA, the carboxylic acid groups degraded away at lower temperatures and the chain backbone did at higher temperatures. In DSC, no glass transition could be detected before decomposition. The alternating multilayer nano-films from the polyimides and poly(ethyleneimine) were prepared by the molecular self-assembly method and characterized by ellipsometry and X-ray reflectivity.

Keywords: Aromatic polyimides; Alkali-soluble polyimide; Self-assembled multilayer film

1. Introduction

Aromatic polyimides have been steadily widening their application fields from the conventional heat-stable structural materials to functional polymers such as photosensitive resists [1], gas-permeation membranes [2], nanoporous materials with low dielectric constant [3] and liquid crystal-aligning films [4]. In most of the applications the polyimide products are processed through the poly(amic acid) precursors, because they have extremely low solubility in organic solvents. The precursor processing procedures are often tied up with formation of the undesirable structures and properties such as micro-void generation, shrinkage or deformation in the final products [5]. To obtain highly soluble polyimides, their chain structure should be appropriately designed and synthesized [6].

To our best knowledge, only a few aromatic polyimides soluble in aqueous solvents have been reported [7–9]. In the present article, two carboxy groups were incorporated onto the aromatic polyimide backbones and investigated their solubility in aqueous alkalis or tetrametylammonium hydroxide (TMAH). The polyimides' solubility in alkali is advantageous not only in direct processing to the final products in imide form but also in improving the environmental friendliness by replacing polluting organic solvent. The solubility in TMAH solution is of particular interests since it is the developing solvent in microlithography for integrated semiconductor circuits, and such polyimides could be used as photoresist material [7].

The carboxy functionality is desirable in developing new applications such as fabrication of nano-structures by molecular self-assembly [10,11], ion exchange membranes, polymer electrolytes or ionomers [6]. The multilayer nanofilms are recently drawing a lot of attention for constructing polymeric nano-structures simply by alternative dipping in two polymer solutions. In these structures, the carboxy group forms the basis of the multi-layer generation via its strong attraction with the polymers with basic functionality.

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Thus, ultrathin films by self-assembly have been extensively investigated for decades [12–14].

In the present work, new aromatic polyimides having carboxy functional groups in side branch were prepared and characterized and their multilayer films with commercial poly(ethyleneimine) (PEI) were made by sequential dipping in a polyimide solution in NMP and PEI in water.

2. Experimental

2.1. Materials and measurements

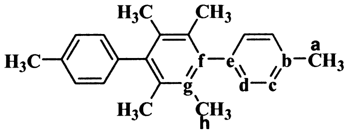
Tetrakis(triphenylphosphine)palladium and potassium permanganate were used without further purification. *N*-Methylpyrolidone (NMP) was distilled over CaH_2. Oxy-*p*-dianiline (ODA) and *p*-phenylenediamine (*p*-PDA) were purified by sublimation. Methylene-*p*-dianiline (MDA), 4,4′-diaminobenzophenone (DABP) and hexafluoroisopropylidene-*p*-dianiline (6FDA) were recrystallized from ethanol. Poly(ethyleneimine) (PEI, 50 wt% in aqueous solution, Sigma Co.) and other commercially available chemicals were used as received.

Melting points (m.p.) were determined using Haake–Bücheler melting point apparatus without correction. Infrared spectra were taken on a Mattson FT-IR spectrometer of infinite gold series and ^{1}H- and ^{13}C-NMR spectra were obtained from a 300 MHz Bruker Fourier Transform DPX 300 spectrometer at room temperature. Thermal analyses of the polymers were carried out at a heating rate of 20 °C/min under nitrogen using Perkin–Elmer Series TGA7 and PEPC Series DSC7. Elemental analyses were performed by an Elementar Vario EL microanalyzer. Wide-angle X-ray diffractograms were obtained in transmission mode with Ni-filtered Cu Kα radiation on a Rigaku Geiger Flex D-Max X-ray diffractometer. Inherent viscosities were determined with an Ubbelhode type viscometer at 25 °C for 0.2 g/dl solutions in NMP. A single wavelength null-type ellipsometer (Rudolf Research; AutoEL) was used to measure the film thickness and X-ray reflectivity measurements for the thin films on both SiO_x/Si substrates were carried out with the synchrotron radiation at Pohang Accelerator Laboratory (PAL), Korea.

2.2. Synthesis of 4,2′,3′,5′,6′,4″-hexamethyl-p-terphenyl (3)

A 500 ml two-neck flask was charged under nitrogen with 4.67 g (16 mmol) dibromodurene, 100 ml toluene, 1.1 g (0.96 mmol) $Pd(PPh_3)_4$ and 100 ml 2 M Na_2CO_3 solution. After addition of 4.7 g (35 mmol) *p*-tolylboronic acid in 30 ml ethanol, the mixture was refluxed for 24 h. After cooled to room temperature, 12.5 ml of H_2O_2(30%) were carefully added under vigorous stirring and the mixture was stirred for an additional hour. When the stirring was stopped, it was separated into two layers. The organic layer was separated out and the aqueous layer was extracted twice with ether and added to the organic phase. After the combined organic phase was dried with $MgSO_4$, the solvent was evaporated to obtain crude product, which was washed by cold ethanol to remove by-products and recrystallized from ethyl acetate.

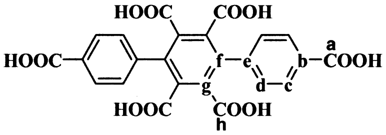
Yield: 66%; m.p.: 284–285 °C; IR (KBr, cm^{-1}): 530(para-subst. oop), 1514(C=C, Ar), 1560, 1655, 1799, 1900 (para-subst.), 2910–3040(C–H, Ar and methyl); ^{1}H-NMR ($CDCl_3$, ppm): $\delta = 1.95$(s, 6H, CH_3), 2.42(s, 12H, CH_3), 7.05–7.09(d, 4H, Ar), 7.22–7.25(d, 4H, Ar); ^{13}C-NMR ($CDCl_3$, ppm): $\delta = 17.6$(h), 20.7(a), 128.4(d), 128.8(c), 131.4(e), 135.2(g), 139.0(b) and 140.5(f).



2.3. Synthesis of 3,6-di(4-carboxyphenyl)pyromellitic acid (4)

In a 250 ml three-necked flask fitted with magnetic stirrer and condenser were placed 3.14 g (0.01 mol) of 1,4-ditolyldurene, 120 ml of pyridine, and 10 ml of water. The mixture was heated to 120 °C and then 28.4 g (0.18 mol) of $KMnO_4$ were added portionwise. After refluxed for 12 h at that temperature, the hot reaction mixture was vacuum filtered over a glass funnel to remove MnO_2. Evaporation of the filtrate produced a solid residue. This solid was put into a 250 ml three-necked flask with stirrer and condenser and then treated with 100 ml of 4% aqueous NaOH solution under agitation. After the flask content was heated to 100 °C, 9.48 g (0.06 mol) of $KMnO_4$ were added and refluxed for 12 h. Excess $KMnO_4$ was destroyed using ethanol until the $KMnO_4$ color disappeared. The reaction mixture was hot-filtered to remove MnO_2 and the filtrate was acidified with HCl to obtain crude product, which was purified by recrystallization in water.

Yield: 67%; IR (KBr, cm^{-1}): 1612(C=C, Ar), 1692(C=O, acid), 3530–2500(O–H, acid); ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 7.37$–7.40(d, 4H, Ar), 7.95–7.98(d, 4H, Ar), 13.3(b, 6H, COOH); ^{13}C-NMR (DMSO-d_6): $\delta = 128.8$(b, d), 130.3(c), 134.3(g), 135.4(f), 141.5(e), 166.9(a) and 167.4(h). Neutralization value: calc. 680.8, found 678.5 mg/g.



*2.4. Synthesis of 3,6-di(4-carboxyphenyl)pyromellitic dianhydride (**5**)*

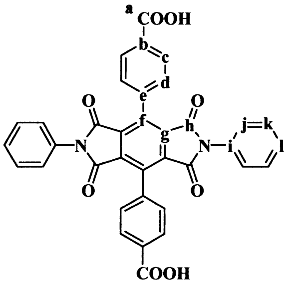
Under nitrogen a 100 ml 2-neck flask was charged with white crystal of 3,6-di(4-carboxy)phenylpyromellitic acid (4.58 g, 10 mmol) and 50 ml of acetic anhydride. After refluxed for 5 h, acetic anhydride was evaporated out to obtain yellow solids, which were recrystallized from dried DMAc.

Yield: 92%; IR (KBr, cm^{-1}): 1681(C=O, acid), 1857 and 1788(C=O, anhydride), 3500–2500(O–H, acid); ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 7.71-7.74$(d, 4H, Ar), 8.08–8.11(d, 4H, Ar), 13.1(b, 2H, acid); elemental analysis ($C_{24}H_{10}O_{10}$), (458.33) calc. C 62.83, H 2.18, O 34.90; found C 62.96, H 2.27, O 34.77.

*2.5. Synthesis of 3,6-di(4-carboxyphenyl)-N,N′-diphenylpyromellitdiimide (**6**)*

Model reaction was conducted in the conventional one-pot condition. Into a 100 ml 3-neck flask were added under nitrogen 0.93 g (10 mmol) of aniline, 2.29 g (5 mmol) of the dianhydride and 32 ml of NMP to keep solid content to 10%(w/v). After addition of catalytic amount (2–3 drops) of isoquinoline, the mixture was stirred at room temperature for 1 h, then gradually heated up to 170 °C and further stirred for 24 h at that temperature. After cooled to room temperature, the solution was poured into excess amount of methanol, whereby yellow solids were precipitated out. The solids were separated by filtration, recrystallized from DMAc/H_2O mixture and dried in vacuo.

Yield: 86%; IR (KBr, cm^{-1}): 1383(C–N, imide II), 1680(C=O, acid), 1774 and 1723(C=O, imide I), 3456–2500(OH, acid); ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 7.50-7.37$(m, 10H, Ar), 7.71–7.68(d, 4H, Ar), 8.04–8.01(d, 8H, Ar), 13.09(b, 2H, acid); ^{13}C-NMR (DMSO-d_6, ppm): $\delta = 127.2$(j), 128.1(l), 128.2(d), 128.7(k), 130.0(b), 130.8(c), 131.3(f), 133.9(g), 135.6(i), 136.0(e), 164.25(h) and 167.2(a).



2.6. Polymer synthesis

Polymerization was conducted exactly by the same method as the model reaction. The viscous polyimide solutions obtained were diluted with NMP and dropped into 400 ml of methanol under vigorous stirring. The precipitates formed were filtered, washed several times with hot methanol, and dried at 200 °C for 24 h in vacuo. The yields were nearly quantitative in all polymerizations.

2.6.1. Poly[p-phenyleneoxy-p-phenylene-3,6-di(4-carboxyphenyl)pyromellitdiimide] (ODA-PI)

FT-IR (KBr, cm^{-1}): 1380(C–N, imide II), 1609 and 1503(C–H, Ar), 1775 and 1722(C=O, imide I), 3650–2500(O–H, acid); ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 7.12-7.10$(d, 4H, Ar), 7.41–7.39(d, 4H, Ar), 7.69–7.66(d, 4H, Ar), 8.02–7.99(d, 4H, Ar), 13.1(b, 2H, COOH); elemental analysis: $(C_{36}H_{19}O_9)_n$, $(622.54)_n$ calc. C 69.46, H 2.91, N 4.50; found C 69.21, H 2.93, N 4.52.

2.6.2. Poly[p-phenylenemethylene-p-phenylene-3,6-di(4-carboxyphenyl)pyromellitdiimide] (MDA-PI)

FT-IR (KBr, cm^{-1}): 1376(C–N, imide II), 1609 and 1514(C–H, Ar), 1772 and 1726(C=O, imide I), 3650–2500(OH, acid); ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 4.01$(s, 2H, methylene), 7.28(b, 8H, Ar), 7.66–7.64(d, 4H, Ar), 7.99–7.97(d, 4H, Ar), 13.1(b, 2H, COOH); elemental analysis: $(C_{37}H_{20}O_8)_n$ $(620.56)_n$ calc. C 71.61, H 3.25, N 4.51; found C 71.41, H 3.27, N 4.49.

2.6.3. Poly[p-phenylenehexafluoroisopropylidene-p-phenylene-3,6-di(4-carboxyphenyl)pyromellitdiimide] (6FDA-PI)

FT-IR (KBr, cm^{-1}): 1376(C–N, imide II), 1613 and 1518(C–H, Ar), 1782 and 1726(C=O, imide I), 3650–2500(O–H, acid); ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 7.44-7.42$(d, 4H, Ar), 7.55–7.52(d, 4H, Ar), 7.69–7.66(d, 4H, Ar), 8.02–7.99(d, 4H, Ar), 13.1(b, 2H, COOH); elemental analysis: $(C_{39}H_{18}O_8)_n$, $(756.56)_n$ calc. C 61.91, H 2.40, N 3.70; found C 61.02, H 2.61, N 3.68.

2.6.4. Poly[p-phenylenecarbonyl-p-phenylene-3,6-di(4-carboxyphenyl)pyromellitdiimide] (DABP-PI)

FT-IR (KBr, cm^{-1}): 1373(C–N, imide II), 1602 and 1510(C–H, Ar), 1655(C=O, benzophenone), 1779 and 1729(C=O, imide I), 3650–2500(O–H, acid); ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 7.60-7.58$(d, 4H, Ar), 7.72–7.69(d, 4H, Ar), 7.83–7.81(d, 4H, Ar), 8.03–8.00(d, 4H, Ar), 13.1(b, 2H, COOH); elemental analysis: $(C_{37}H_{18}O_9)_n$, $(634.55)_n$ calc. C 70.03, H 2.86, N 4.41; found C 69.81, H 2.91, N 4.50.

2.6.5. Poly[p-phenylene-3,6-di(4-carboxyphenyl)pyromellitdiimide] (PDA-PI)

FT-IR (KBr, cm^{-1}): 1376(C–N, imide II), 1613 and 1510(C–H, Ar), 1772 and 1726(C=O, imide I), 3650–2500(O–H, acid); elemental analysis: $(C_{30}H_{14}O_8)_n$ $(530.46)_n$ calc. C 67.93, H 2.66, N 5.28; found C 67.91, H 2.81, N 5.21.

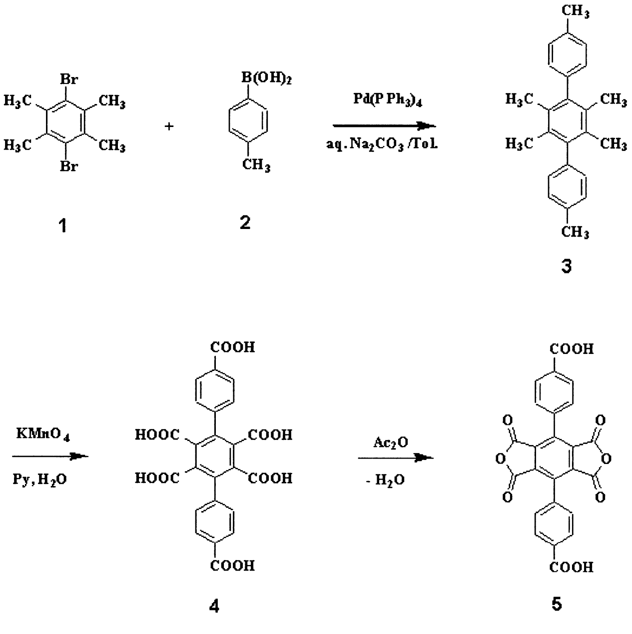
2.7. Preparation of multilayer nano-film

The substrate of silicon (Si) wafer for the deposition was immersed into a 30:70 mixture of 30% H_2O_2 and concentrated H_2SO_4 at 80 °C for 15 min, extensively rinsed with deionized water and dried with nitrogen gas. A cleaned Si-substrate was immersed into the aqueous PEI solution (0.01 M) for 15 min, rinsed extensively with water and dried with nitrogen gas. Then the slide was dipped into the NMP solution (2×10^{-4} M) of the ODA-PI for 15 min, washed thoroughly and dried. This two-step process was repeated in a cyclic fashion to obtain the layer-by-layer self-assembled multilayer films.

3. Results and discussions

3.1. Monomer synthesis

The monomer 3,6-di(4-carboxyphenyl)pyromellitic dianhydride 5 was prepared over a three-step reaction path consisting of Suzuki cross coupling of 3,6-dibromodurene 1 with *p*-tolylboronic acid 2, extensive oxidation of the six methyl groups of 3 to hexa-acid 4 and cyclodehydration, as shown in Scheme 1. The Suzuki coupling reaction was conducted in a heterogeneous system of toluene and aqueous Na_2CO_3 solution in the presence of $Pd(PPh_3)_4$ catalyst. *p*-Tolylboronic acid 2 was readily prepared by reaction of *p*-tolyl magnesium bromide with trimethyl borate followed by hydrolysis. The desired coupled product 3 was obtained in 66% yield after recrystallization from ethyl acetate. Formation of small amount of biphenyl by-product was detected, which could be removed easily by washing with cold ethanol.



Scheme 1. Synthetic route to monomer.

To obtain 3,6-di(4-carboxyphenyl)pyromellitic acid 4, 3,6-ditolyldurene was oxidized with $KMnO_4$ in two steps, in the first in a mixture of 120 ml pyridine and 10 ml water and in the second in 4% aqueous NaOH. The complete oxidation giving the hexa-acid 4 was confirmed not only by spectroscopic characterization but also by neutralization equivalent. The monomer 5 was obtained by cyclodehydration with Ac_2O. Thermal cyclization by heating 4 to 200 °C for 24 h was also conducted, but this product had to be purified by recrystallization. The completion of thermal cyclodehydration of 4 was traced by TGA. The overall yield based on 3,6-dibromodurene was about 41%.

3.2. Polymer synthesis

From the one-pot polymerizations described in Section 2 the fully imidized polymers were obtained always with nearly quantitative yields. The presence of imide rings was confirmed by the characteristic IR bands at 1775 cm^{-1} (asymmetrical C=O stretching vibration), 1726 cm^{-1}-(symmetrical C=O stretching vibration), 1376 cm^{-1}(C–N stretching) and 725 cm^{-1}(ring-carbonyl bending). Since the polymers except PDA-PI were fairly soluble in DMSO, ^{1}H-NMR spectroscopic characterization could be undertaken in DMSO-d_6. In Fig. 1 is reproduced the ^{1}H-NMR spectrum of ODA-PI. As to see from Fig. 1, all the spectral assignments supported the polymer structures as proposed and the chemical shift at 13.1 ppm lets confirm that the –COOH groups remain in the polymer molecules. No other signals due to unreacted monomers or poly(amic acid)s could be detected (Scheme 2).

3.3. Polymer properties

The polyimides obtained had inherent viscosities in the 0.62–1.01 dl/g range in NMP at 25 °C, indicating that the polymers have moderate to high molecular weights. Solubility in common organic solvents and aqueous alkali solutions was investigated qualitatively and the results are summarized in Table 1. The most of obtained polymers are highly soluble in polar aprotic solvents such as NMP, DMSO, DMAc as well as aqueous 0.5% NaOH and 2.38% TMAH solution. PDA-PI having fully rod-like structure was not soluble in any organic solvents but completely soluble in aqueous alkali solution. The high solubility in aqueous NaOH and TMAH solution is attributable for COOH groups incorporated. It is well known that 2.38% TMAH solution is a developing solution mostly used in industry for micro-patterning integrated circuits. Thus, these polymers may be applicable to alkali-developable positive-working photoresist polyimide system [1,7]. A study for this application with photo reactive group is in progress.

Thermal properties of the obtained polyimides were evaluated by TGA and DSC measurements. As summarized in Table 2, they showed two-step pyrolysis patterns and were thermally stable up to 495–523 °C from the 10%

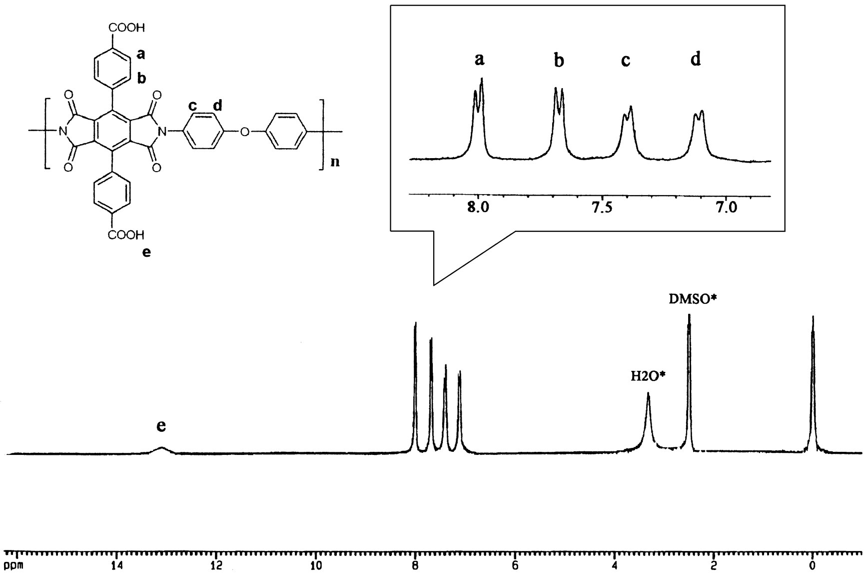
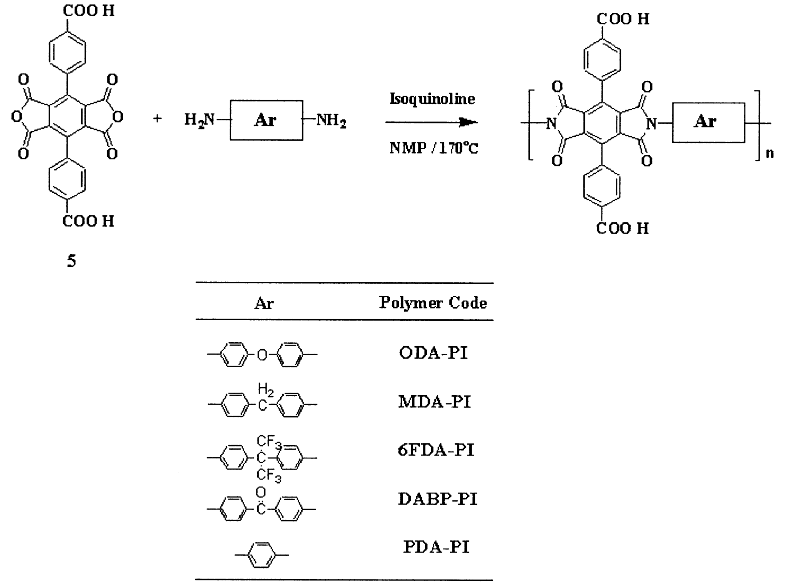


Fig. 1. ^{1}H-NMR-spectrum of ODA-PI(DMSO-d$_6$).

Table 1
Solution properties of polymers

Polymer code	η_{inh}. (dl/g)	Solubility[a]						
		$CHCl_3$	THF	DMSO	NMP	Conc. H_2SO_4	0.5% aq. NaOH	2.38% aq. TMAH
ODA-PI	1.01	−	+	+++	+++	+++	+++	+++
MDA-PI	−	−	−	++	++	+++	+++	+++
6FDA-PI	0.62	−	+	+++	+++	+++	+++	+++
DABP-PI	0.62	−	−	++	+++	+++	+++	+++
PDA-PI	−	−	−	−	−	+++	+++	+++

[a] + : Slightly soluble, ++: soluble on heating, +++: soluble at room temperature, −: insoluble.



Scheme 2. Synthesis of polyimides.

Table 2
Thermal behaviors of polymers measured by TGA and DSC

Polymer code	T_g[a]	Thermal stability[b]			Decomposition behavior[c]			
		T_5 (°C)	T_{10} (°C)	R_{900} (%)	T_{Deh}	T_{max1}	T_{max2}	R_{Cal}/R_{Fnd}(%)
ODA-PI	Indefinite	479	518	60.8	–	510	635	85.5/85.4
MDA-PI		466	500	57.5	375	498	625	85.3/84.3
6FDA-PI		469	523	53.2	361	505	589	88.1/87.9
DABP-PI		442	495	55.4	366	500	640	85.8/84.0
PDA-PI		429	503	48.9	388	519	662	83.0/79.1

[a] Measured by DSC.

[b] T_5 : temperature of 5% wt loss, T_{10} : temperature of 10% wt loss, R_{900} : residual wt% at 900 °C.

[c] T_{Deh} : dehydration temperature, T_{max1}: 1st maximum decomposition temperature, T_{max2}: 2nd maximum decomposition temperature, $R_{Cal,}$: calculated wt% of acid group in repeating unit, R_{Fnd}: found residual wt% after 1st decomposition step.

weight loss temperatures (T_{10}). The lost weights after first degradation step were well coincident with the theoretical content of two COOH groups in a repeating unit of the polymers. Thus, it may predictable that the first step is decarboxylation and the ensuing one corresponds to the decomposition of polyimide backbone. The polymers showed dehydration behavior in TGA near 361–388 °C with weight loss of 2–3%. This behavior disappeared when the samples were dried at 200 °C in reduced pressure, but a few weeks later the dehydration step was observed again. This may result from the water absorbed in the polymers. Such high rate of water absorption must be ascribable for the –COOH groups incorporated in the polymers. In DSC all the polymers showed no phase transitions before decomposition. It is presumable that the polymers have higher T_gs than their decomposition temperature due to the strong interchain interaction of acid-to-acid hydrogen bond.

In X-ray diffractograms, most of the polymers showed no noticeable peak but typical amorphous halos (Fig. 2). Only PDA-PI having fully rodlike structure showed very weak crystalline absorption. It can be supposed that too strong interaction between acid groups disturbs chain packing rather than builds up a regular structure, probably because the chain mobility is restricted by strong interaction between –COOH groups. The presence of bulky phenyl substituent in the side branch may also take a share of being an amorphous nature.

3.4. Multilayer nano-film

The alternating multilayer films of the synthetic polyimide with PEI were prepared by conventional self-assembly method. The first layer on pre-treated Si-wafer was PEI layer and the following was ODA-PI on PEI. This alternating bilayer was accumulated repeatedly. The deposition of each layer was monitored by the film thickness measurement for every dipping step using ellipsometer. The results are shown in Fig. 3. The initial thickness at zero point of X-axis indicates the oxide layer on Si-wafer thus the total thickness of five-double layers was about 193 Å and the average thickness of each layer was 21.2 Å of PEI and 17.1 Å of ODA-PI, respectively. The deviation of linearity at initial stage can be regarded as substrate effect, for it turns to linear relationship just hereafter.

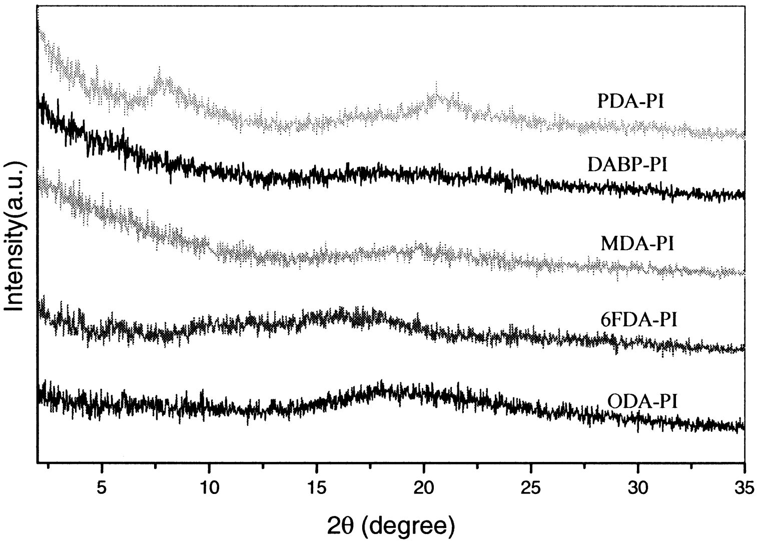


Fig. 2. Wide angle X-ray diffractograms of polyimides.

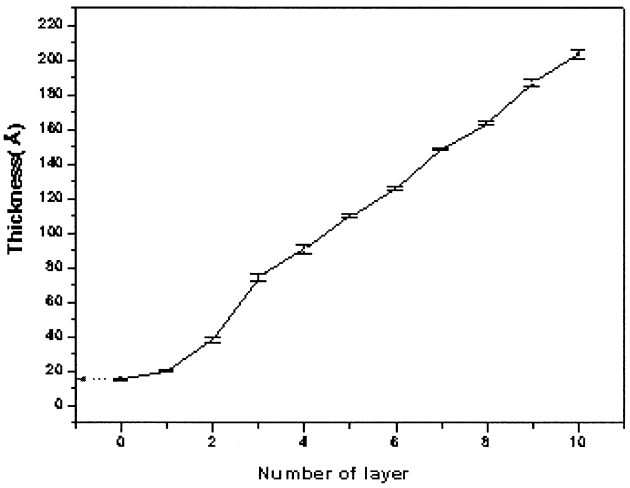


Fig. 3. Ellipsometer measurement of film thickness for each dipping.

In Fig. 4, the X-ray reflectivity is modulated by oscillations reflecting the interference of the substrate/film and film/air interface. The calculated total thickness from periodicity of oscillation was in good agreement with the ellipsometer result, and the oscillations seem to be smearing out quite quickly. Therefore, it is believable that the multilayers have somewhat rough interface or contain some diffusive region. Generally, the interface tends to anneal with elapse of time through intermixing due to inherent charge reversal, as reported for polyelectrolyte self-assembled films [15,16]. Analogous feature was observed also in hydrogen bonding polymers showing high level of phase mixing [17].

The first report on preparation of polyimide multilayer films appeared in Ref. [18], but their fabrications were performed using precursor poly(amic acid) with various polycations such as poly(allyl amine hydrochloride), polyaniline and poly(*p*-phenylenevinylene) precursor. Thus, they were subsequently imidized by thermal treatment or chemical methods using acetic anhydride/pyridine. Generally, the thermal imidization of the poly(pyromellitdiimide) precursors needs to raise the temperature up to 300 °C, but common partner polybases are not sufficiently stable at that temperature. Therefore, the thermal imidizations had to be conducted at lower temperature (185 °C) for longer time (16–18 h) and the chemical imidizations were carried out at room temperature for 18 h. However, the degree of imidizations of polymers were just 92% for the thermally imidized sample and 68% for chemically imidized sample. The fully imidezed polymers were finally obtained by 70 h-treatment by chemical method. This is the detrimental drawback when poly(amic acid) precursor is used. In this system, we used fully cyclized synthetic polyimide.

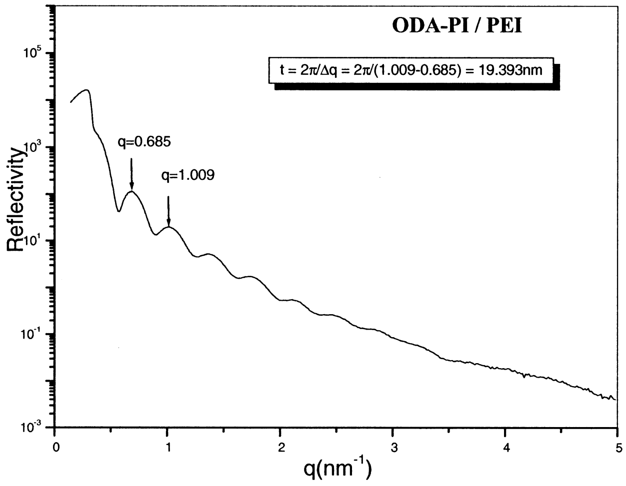


Fig. 4. X-ray reflectivity profile of the multilayer film.

According to the previous report on poly(acrylic acid)/poly(allylamine hydrochloride) multilayer films, fully charged polyelectrolytes formed very thin layers in the 3–5 Å range and partially ionized one showed dramatic change up to 80 Å depending on their degree of ionization [15]. It was also reported that if the multilayer films have hydrogen bonding interaction with the partner polymers, it contributes to the film stability a great deal and the obtained multilayer films shows somewhat increased layer thickness than layers from electrostatic self-assembly [17]. The analogous inference indicates that our multilayer films, though not determined experimentally, were fabricated firmly on the basis of fairly strong hydrogen bonding interaction. But, we should not pass over the chance of polymeric salt formation because the alternating layers buildup was based on the polyacid and polybase. Aromatic carboxylic acids in general have sufficient acidity ($pK_a = 3-5$) for donation of proton to secondary amine of PEI in aqueous solution and acid–base reactions under equilibrium condition in single phase always favors the formation of the most stable species of conjugated acid and base. Detailed studies on state of interface are under way now and these results will be published later.

4. Conclusions

New dianhydride monomer having both pendent phenyl and acid functional group was successfully synthesized via Suzuki coupling, oxidation and cyclodehydration reaction. A series of amorphous aromatic polyimides therefrom were prepared by its polycondensation with common aromatic diamines. They were highly soluble in polar aprotic solvents as well as aqueous alkali solutions. They were thermally stable up to 495–523 °C, as judged by 10% weight loss temperatures measured by TGA and no phase transition was observed before decomposition in DSC measurements. Their multilayer nano-films with poly(ethylene imine) were successfully prepared and characterized by ellipsometry and X-ray reflectivity.

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