

# Facile modifications of polyimide *via* chloromethylation: II. Synthesis and characterization of thermocurable transparent polyimide having methylene acrylate side groups

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**Abstract:** From chloromethylated polyimide, a useful starting material for modification of aromatic polyimides, a thermocurable transparent polyimide having acrylate side groups was prepared. In the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene, chloromethylated polyimide was esterified with acrylic acid to synthesize poly(imide methylene acrylate). The polymer was soluble in organic solvent, which makes it possible to prepare a planar film by spin coating. The polymer film became insoluble after thermal treatment at 230 °C for 30 min. Optical transparency of the film at 400 nm (for 1 μm thickness) was higher than 98 % and not affected by further heating at 230 °C for 250 min. Adhesion properties measured by the ASTM D3359-B method ranged from 4B to 5B. Preliminary results of planarization testing showed a high degree of planarization (DOP) value (>0.53). These properties demonstrate that poly(imide methylene acrylate) could be utilized as a thermocurable transparent material in fabricating display devices such as TFT-LCD.

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**Keywords:** polyimides; functionalization of polymers; high temperature materials; transparency; curing of polymers

## INTRODUCTION

In recent years, many advances in liquid crystal display (LCD) technology have been achieved by the introduction of new materials. Many materials besides the liquid crystal itself are important to the operation of an LCD, and therefore are receiving increasing attention. As a state-of-the-art high-technology product, an overcoat layer to the color filter is a key to fabricating thin film transistor liquid crystal display (TFT-LCD) panels. The overcoat layer not only protects the color filter layer, but also provides a planar surface between the non-smooth color filter patterns and the anode indium-tin oxide (ITO) layer.<sup>1</sup> For large panels, greater than 45 cm, the black matrix is replaced by a resin material, which is relatively thick compared to a chrome black matrix. In such cases the overcoat layer becomes essential for the enhancement of the planarization in the color

filter panel. To fabricate a TFT-LCD with high performance, a spin-coatable overcoat layer with high optical transmittance, high thermal stability and good adhesion to the color filter is required.

As a high-performance polymer with extraordinary thermal and mechanical properties, polyimides have been used in various fields, such as the electronics and aerospace industries.<sup>2</sup> Much effort has been devoted to modifying polyimides to provide them with enhanced solubility, higher optical transparency, photosensitivity, photorefractivity, or nonlinear optical properties.<sup>3–7</sup> A novel modification method of polyimides *via* chloromethylation has been developed in our previous work.<sup>8,9</sup> In a series of modifications of polyimides, *via* chloromethylated polyimide (CMPI), a thermally crosslinkable and transparent polyimide with methylene acrylate side groups has been prepared by facile esterification. In this paper,

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we report the synthesis of poly(imide methylene acrylate) (PIMA) from CMPI in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU). The solubility change before and after heat treatment, the adhesion properties and the optical transmittance of PIMAs were investigated in terms of potential application as an overcoat material in TFT-LCD manufacturing.

## EXPERIMENTAL

### Materials

DBU (Aldrich), tin(IV) chloride (99 %, Aldrich) and chloromethyl methyl ether (TCI) were used as received. Tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and acrylic acid (Aldrich Chem. Co.) were purified by drying with CaH<sub>2</sub> and distillation under reduced pressure. Chloroform (Aldrich Chem. Co.) was washed by sulfuric acid and then water, and distilled over CaCl<sub>2</sub> before use. Polyimide (6FOD-PI) used in this experiment was prepared from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 4,4'-oxydianiline (ODA) as described in previous papers.<sup>8,9</sup> The adhesion promoter,  $\alpha$ -aminopropyltriethoxysilane (AMPS) was purchased from Aldrich and used without further purification.

### Measurements

Spectral measurements by proton nuclear magnetic resonance (<sup>1</sup>H-NMR), UV-vis, and fourier-transform infrared FTIR were performed by using a JEOL Model 400 (400 MHz), a Shimadzu UV-2100S spectrometer, and a Jasco 300E spectrometer, respectively. The <sup>1</sup>H-NMR spectra were obtained from dimethylsulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) solutions with tetramethylsilane as an internal standard. FTIR spectra of polymer films were taken in transmission mode at 2 cm<sup>-1</sup> resolution. Differential scanning calorimetry (DSC) measurements were made on a DSC2010 (TA Instruments) at a scanning speed of 10 °C min<sup>-1</sup>. All the samples were scanned from 50 to 150 °C on the first passage and then cooled to 50 °C before the actual measurements were made on the second cycle.

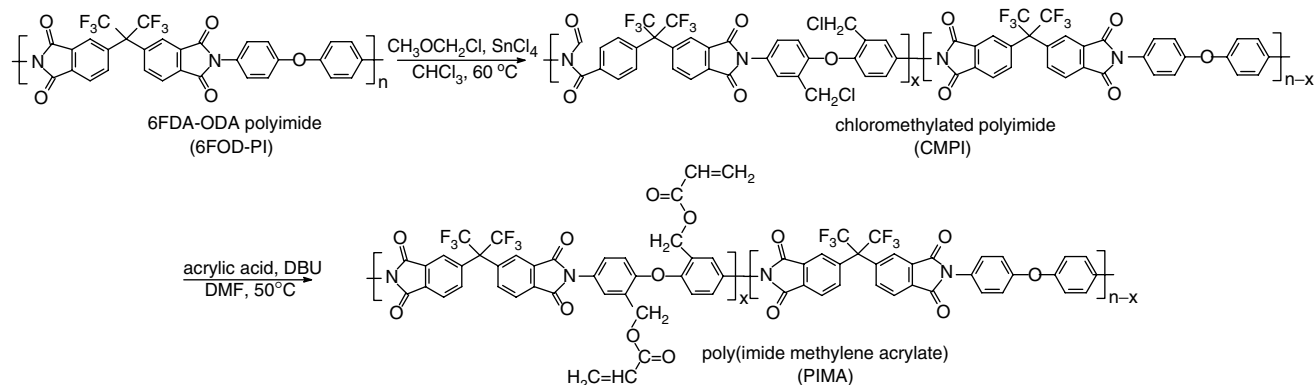
Thermogravimetric analyses (TGA) were carried out on a TGA2050 (TA Instruments) under N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup> up to 600 °C.

### Synthesis of PIMAs

The synthetic scheme of CMPI and PIMA is shown in Scheme 1. The synthetic procedure for CMPI was described in detail in our previous papers.<sup>8,9</sup> Firstly, CMPIs with degree of substitution (DS) of 47, 89 and 192 % (chloromethyl groups per repeating unit of 6FOD-PI) were synthesized from the reaction of 6FDA-ODA polyimide (6FOD-PI) and chloromethyl methyl ether in the presence of tin(IV) chloride in chloroform. These polymers were denoted as CMPI-1, CMPI-2 and CMPI-3, respectively. The chloromethylation ratio (mol% based on one ODA unit) of each sample was calculated by comparing the proton integration value at 8.19 ppm with that at 4.89 ppm. These peaks correspond to two aromatic ring protons of 6FDA (a position) (Fig 1) and two methylene protons in chloromethyl group, respectively. The typical reaction of CMPI with acrylic acid was as follows: With DBU (2 equivalents to -CH<sub>2</sub>Cl) as a catalyst, 0.5 g of CMPI was dissolved in DMF (25 ml) in a 50 ml flask, and then acrylic acid (5 equivalents to -CH<sub>2</sub>Cl) was added. The reaction mixture was stirred for 24 h at 40 °C under nitrogen. The solution was poured into methanol, and the polymer precipitate was reprecipitated from DMF into water. The resulting polymer was dried in a vacuum oven for 48 h at 40 °C to obtain white fibrous particles with a 98 % yield. The reaction between acrylic acid and chloromethyl groups in CMPI were almost quantitative as evidenced in the <sup>1</sup>H-NMR spectra. The PIMAs obtained from CMPI-1, CMPI-2 and CMPI-3 were denoted as PIMA-1, PIMA-2 and PIMA-3, respectively.

### Adhesion and transparency measurement

To obtain polymer films with various thicknesses, PIMAs dissolved in DMAc were spin cast on a silicon wafer or a quartz substrate with varying spin speeds, and used for measurement of FTIR and UV-vis spectra. The thickness of films was estimated



**Scheme 1.** Synthetic route to poly(imide methylene acrylate) (PIMA).

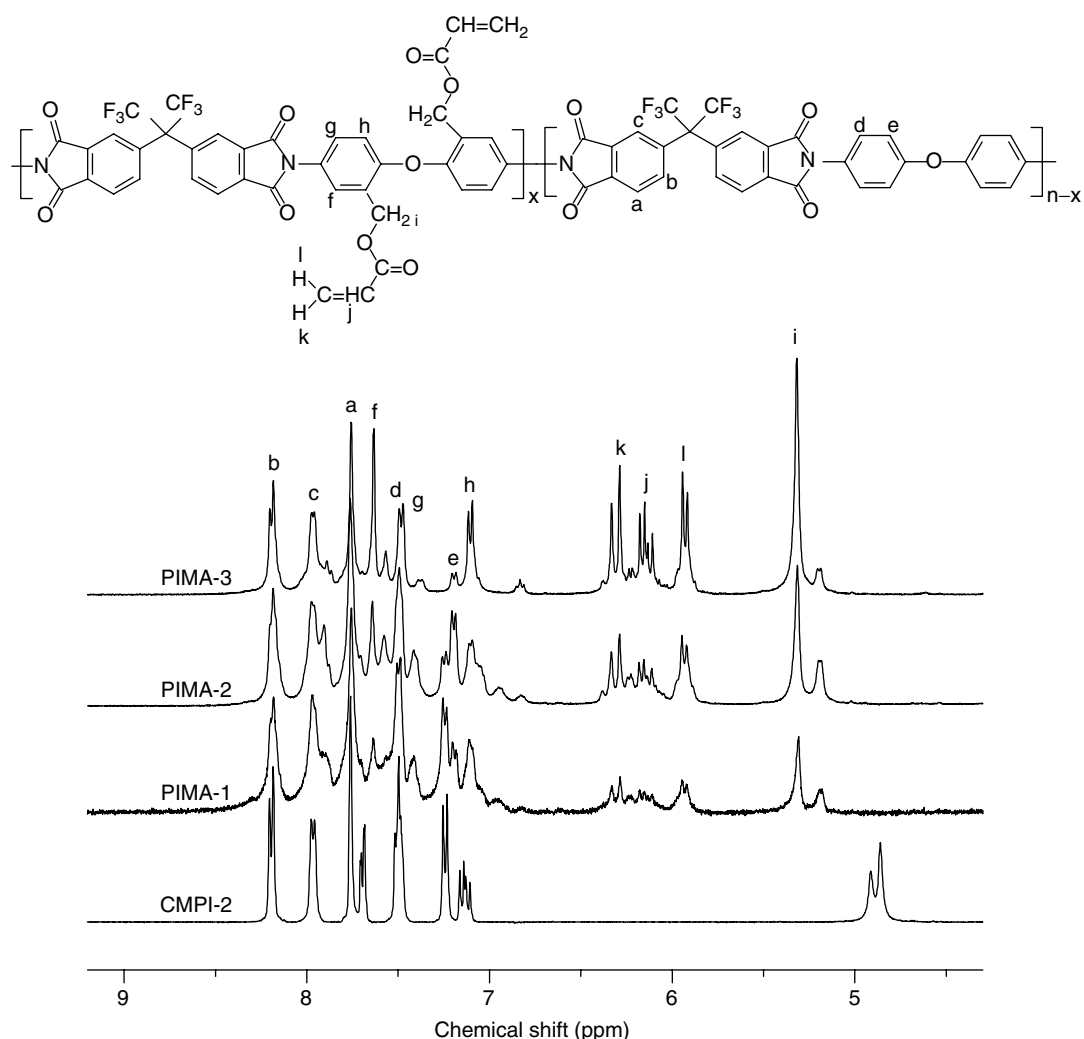


Figure 1.  $^1\text{H-NMR}$  spectra ( $\text{DMSO-}d_6$ ) of PIMAs for various degrees of substitution.

using an alpha-step profiler (Tencor 200, Tencor). The optical transparency was compared by measuring the transmittance of polymer films (*ca* 1  $\mu\text{m}$  thick) at 400 nm by UV-vis spectrometry with subsequent calibration by their thickness. The adhesion of polymer film was measured according to ASTM D3359-B. This test method is similar to the 100/100 crosscut test using 3M tape, but the cracking of the edges of the segments was visually compared with a scale pattern after the test. The classification of this adhesion test ranges from 0B (complete removal of coating film lattices) to 5B (intact lattices with completely smooth edges). DMAc solutions of PIMAs, 6FDA-ODA polyimides and CMPIs were spin cast on 2.5 cm  $\times$  2.5 cm glass substrates (*ca* 1.0  $\mu\text{m}$  film thickness). An adhesion promoter, AMPS, was used (<1 ppm) prior to the polymer coating in some cases.

#### Degree of planarization

After spin coating the polymer solution in cyclohexanone with various concentrations from 5 to 15 wt% on a commercial color filter substrate, the film was heated at 230  $^\circ\text{C}$  for 30 min. The surface profile was measured by using an alpha-step profilometer. The

degree of planarization (DOP) was estimated according to the method in the literature<sup>10</sup> by using the eqn (1):

$$\text{DOP} = 1 - h_f/h_i \quad (1)$$

where  $h_f$  is the final height of the polyimide coating over a step of initial height  $h_i$ .

## RESULTS AND DISCUSSION

### Synthesis and characterization

The route to PIMA is shown in Scheme 1. To compare the properties of polymers with different acrylate contents, three CMPIs with various chloromethylation ratios were prepared. The substitution ratios of chloromethyl groups per repeat unit of CMPIs were 47, 89 and 192 % for CMPI-1, CMPI-2 and CMPI-3, respectively. Esterification of CMPIs with acrylic acid was performed in the presence of DBU as a reaction catalyst. In the NMR spectra (Fig 1), the peaks at 4.85 and 4.91 ppm corresponding to the protons of the  $-\text{CH}_2\text{Cl}$  group of CMPI were completely shifted to 5.31 and 5.19 ppm, respectively. This indicates a quantitative esterification of chloromethyl groups of CMPI. Therefore, the degrees of methacrylate

substitution per repeating unit of PIMAs were estimated to be 47, 89 and 192 % for PIMA-1, PIMA-2 and PIMA-3, respectively. Detailed peak assignments are shown in Fig 1.

The esterification of CMPI with acrylic acid was also confirmed by FTIR spectra of the resulting polymers. As shown in Fig 2, the absorption band at  $790.7\text{ cm}^{-1}$  due to  $\text{CH}_2\text{-Cl}$  stretching of CMPI was not observed in the spectra of PIMAs, implying the complete esterification of chloromethyl group. New bands corresponding to

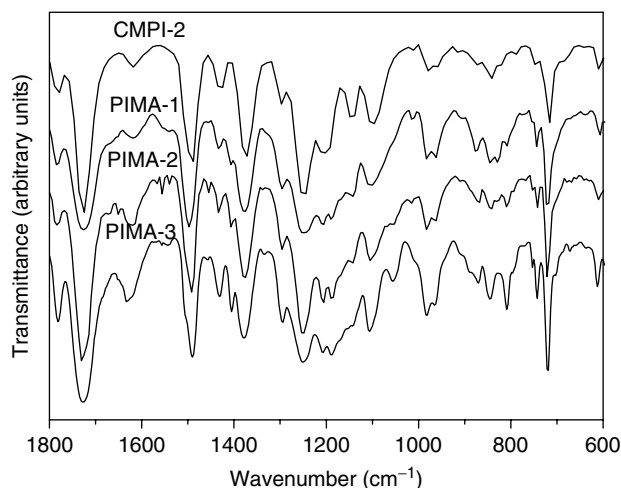


Figure 2. FTIR spectra of PIMAs for various degrees of substitution.

$-\text{CH}=\text{CH}-$ stretching ( $1629\text{ cm}^{-1}$ ),  $=\text{CH}_2$  deformation ( $1408\text{ cm}^{-1}$ ) and  $=\text{C}-\text{H}$  out-of-plane bending ( $809\text{ cm}^{-1}$ ) were observed. Absorbances of the peak centered at *ca*  $1193$  and  $1056\text{ cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$  symmetric and asymmetric stretching) indicated the formation of ester linkage in PIMA. The intensities of peaks related to acrylic ester increased with the increase of substitution degree.

### Solubility

The resulting PIMAs were all soluble in most of the organic solvents as summarized in Table 1. It should be noted that PIMA is already an imidized form so that the high-temperature imidizing process was not required. All PIMAs exhibited good solubility not only in polar aprotic solvents such as DMAC, *N*-methylpyrrolidone (NMP), DMF or DMSO, but also in weakly polar solvents such as THF,  $\text{CHCl}_3$  or cyclohexanone. After PIMA film was heat-treated at  $230^\circ\text{C}$  for 30 min, however, the film did not dissolve in any solvents described above owing to thermal crosslinking of acrylates. The solubility change induced by thermal treatment seems to be useful for making a multi-layer thin film structure in TFT-LCD without affecting the lower layer.

### Adhesion properties

Good adhesion is crucial for the thin film overcoat material in TFT-LCDs. The overcoat should adhere

Table 1. The solubility of PIMA films; none of the PIMA films were soluble in any of the solvents after heating at  $230^\circ\text{C}$  for 30 min in air

Sample	Acetone	Ethyl acetate	Cyclohexanone	$\text{CHCl}_3$	THF	DMF	DMSO	NMP
6FOD-PI	◐	×	○	○	○	○	○	○
CMPI-2	◐	×	○	○	○	○	○	○
PIMA-1	◐	×	○	○	○	○	○	○
PIMA-2	◐	×	○	○	○	○	○	○
PIMA-3	◐	×	○	○	○	○	○	○

○ soluble; ◐ partially soluble; × insoluble

Table 2. Results of adhesion testing for PIMA films by ASTM method D3359-B

Adhesion promoter	6FOD-PI	CMPI-2	PIMA-1	PIMA-2	PIMA-3
Before thermal treatment					
No	0B	0B	4B	4B	4B
Yes <sup>a</sup>	—	—	4B	4B	4B
After thermal treatment <sup>b</sup>					
No	0B	3B	4B	4B	5B
Yes <sup>a</sup>	1B	4B	5B	5B	5B

<sup>a</sup> Pretreated with 1 wt%  $\alpha$ -aminopropyltriethoxysilane in toluene.

<sup>b</sup> Sample was heated at  $230^\circ\text{C}$  for 30 min. ASTM D3359-B

5B — The edges of the cuts are completely smooth: none of the squares of the lattice are detached.

4B — Detachment of flakes of the coating at the intersections of the cuts. A cross cut area not significantly greater than 5 % is affected.

3B — The coating has flaked along the edges and/or at the intersections of the cuts. A cross cut area significantly greater than 5 %, but not significantly greater than 15 % is affected.

2B — The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly in different parts of the squares. A cross cut area significantly greater than 15 %, but not significantly greater than 35 % is affected.

1B — The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross cut area significantly greater than 35 %, but not significantly greater than 65 % is affected.

0B — Any degree of flaking beyond classification 1B.

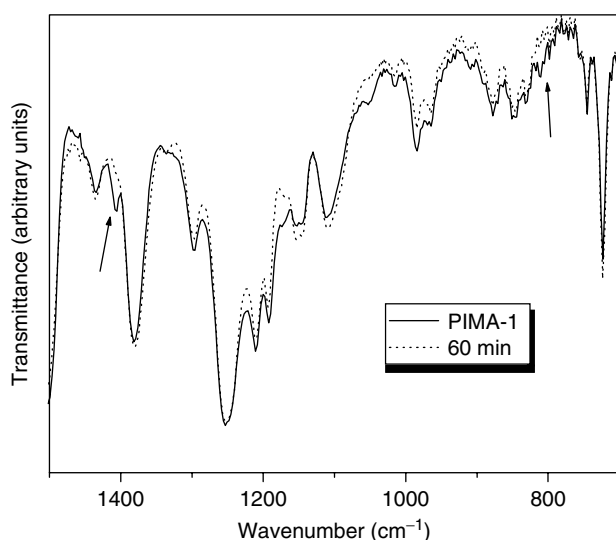
to upper and lower layers well. PIMA was derived from 6FDA-ODA polyimide which is notorious for its poor adhesion. However, PIMA films showed excellent adhesion properties compared with 6FDA-ODA polyimide and CMPI, as summarized in Table 2. The adhesion of PIMA films on a glass substrate was tested according to the ASTM D3359-B method. 6FDA-ODA polyimide showed almost no adhesion to the substrate regardless of adhesion promoter pre-treatment or thermal treatment. In contrast, CMPI showed improved adhesion properties after thermal treatment probably due to the chloromethyl side groups. All of the PIMA films regardless of substitution degree showed significantly better adhesion than 6FDA-ODA polyimide or CMPI. After pre-treatment with a 1% solution of AMPS in toluene, and heating at 230 °C for 30 min, PIMA film showed completely smooth cut edges and none of the squares of the lattice were detached. It is interesting that the adhesion properties of fluorinated polyimides can be considerably improved by the introduction of appropriate side chains.

### Thermal properties

The thermal properties of PIMAs were tested by TGA and DSC at a heating rate of 10 °C min<sup>-1</sup> and the results are summarized in Table 3. 6FDA-ODA polyimide decomposed at around 500 °C, while two decomposition temperatures were observed in the TGA curves for PIMAs. The first at *ca* 250 °C

**Table 3.** Results of thermal analyses for PIMAs

Sample	Decomposition temperature (°C)		$T_g$ (°C)
	First step	Second step	
PIMA-1	254.4	497.7	237.5
PIMA-2	247.9	496.0	222.8
PIMA-3	244.7	498.7	198.3



**Figure 3.** FTIR spectra of PIMA-1 film before, and, after thermal treatment at 230 °C for 60 min.

**Table 4.** Changes in optical transparency measured at 400 nm with respect to heat treatment time at 230 °C for various films

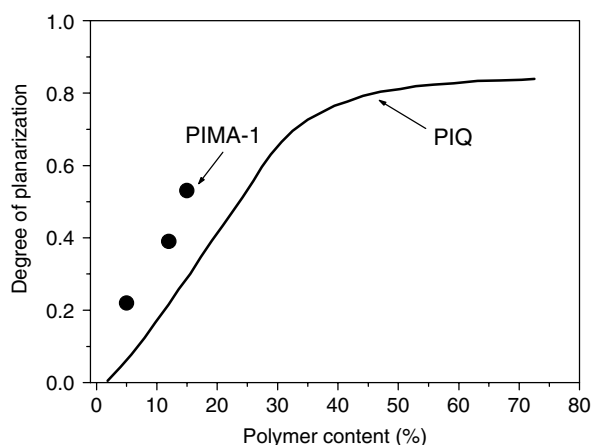
Heat treatment time (min)	CMPI-2	PIMA-1	PIMA-2	PIMA-3	Commercial overcoat <sup>a</sup>
0	99.11	99.00	98.72	98.25	98.67
30	97.41	97.81	98.25	97.00	95.39
60	96.94	97.27	97.87	96.62	92.71
120	96.77	97.00	96.90	96.32	89.98
180	96.45	96.61	96.89	96.11	87.97
240	96.24	96.54	96.54	95.64	85.12

<sup>a</sup> Commercial acrylate-based overcoat material for TFT-LCD fabrication.

was attributed to the decomposition of the methylene acrylate group. The amount of weight loss in the first degradation was in agreement with the acrylate content calculated by the NMR integration values. The decomposition of the polyimide main chain occurred at around 500 °C. The glass transition temperature ( $T_g$ ) of the PIMAs decreased slightly from 237 to 198 °C with the increase of acrylate content. This result coincided with the decrease of the first decomposition temperature with the increase of acrylate content. Compared with the commercial overcoat material OCE-10 (ADMS Technology Co.,  $T_g = 110$  °C), which is based on an acrylate polymer, PIMAs show much higher  $T_g$ . In addition to the glass transition, an exothermic reaction was observed in the DSC thermogram starting at 220 °C that attributed to the thermal crosslinking of acrylate side groups. Thermal crosslinking of PIMA was also monitored by FTIR spectra as shown in Fig 3. When PIMA-1 film was heated at 230 °C for 1 h, the peaks centered at *ca* 1406 cm<sup>-1</sup> (=CH<sub>2</sub> deformation) and 809 cm<sup>-1</sup> (=C-H out-of-plane bending) disappeared, which indicated the double bond of acrylate group participated in a crosslinking.

### Thermal stability of optical transparency

Polymer films for TFT-LCD fabrication should maintain a high transmittance under a high-temperature environment for an extended period of time. For example, typical ITO deposition requires temperatures of the order of 230 °C for several tens of minutes. To investigate the thermal stability of optical transparency, a polymer film of 1 μm thickness was heated at 230 °C for various periods of time. After heat treatment, transmittance at 400 nm was measured. These results were compared with those of a commercial acrylate-based overcoat material (OCE-10, ADMS Technology Co.). Whereas the aromatic polyimides generally show poor optical transparency in the visible light region, PIMA films showed high optical transparency (over 98%), as shown in Table 4. Furthermore, they had excellent thermal stability with respect to optical transparency. After heating for 240 min at 230 °C, PIMA films maintained high optical transparency (>95%) with only a small decrease. CMPI also showed good thermal stability of optical



**Figure 4.** Degree of planarization for PIMA-1 compared to PIQ (Hitachi),<sup>6</sup>.

transparency with 3.5 % transmittance loss. Compared to these, 15 % transmittance loss was observed after 240 min in the case of the commercial overcoat (OCE-10).

#### Planarization properties

To enhance the planarization of color filter panels, an overcoat layer with high planarizability is essential in TFT-LCD fabrication. To investigate the planarization properties of PIMA, the DOP<sup>6</sup> of PIMA-1 was measured with respect to polymer solid content. As shown in Fig 4, the DOP of PIMA-1 ranged from 0.22 to 0.53 for the polymer solutions of 5–15 wt% concentration. PIMA-1 showed an improved planarization property with respect to that of PIQ (Hitachi),<sup>6</sup> a commercial polyimide used in electronic applications. The DOP of PIMA-1 is comparable to that of the OCE-10, which ranges from 0.3 to 0.7 at *ca* 10 % solid content depending on the molecular weight. Considering that the molecular weight of PIMA was not controlled, PIMA showed comparable planarizability to that of the commercial acrylate-based overcoat material. DOP could be increased with an optimum concentration and molecular weight of PIMA.

#### CONCLUSION

In this study, PIMA, a transparent and thermally crosslinkable polyimide comprising methylene acrylate side groups, was synthesized, and its thermal,

physical and optical properties were investigated. The chemical structure of PIMA was confirmed by <sup>1</sup>H-NMR and FTIR spectroscopy. PIMA was soluble in common organic solvents and could be spin coated on a glass or silicon substrate. When heated for 30 min at 230 °C, PIMA films became insoluble due to the thermal crosslinking reaction of acrylate side groups. The FTIR spectra had no characteristic peak of C=C double bonds after 60 min of heating. The resulting polyimides showed high optical transparency, excellent thermal stability, and planarization properties comparable with a commercial overcoat material. In addition, adhesion testing of the polymer films revealed that the adhesion was improved drastically after thermal treatment at 230 °C. In conclusion, we demonstrated PIMA is a good candidate for a thin film material in TFT-LCD fabrication, with high thermal stability of optical transparency and good adhesion.

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