

# Preparation and Properties of Poly(urethane acrylate) Films for Ultraviolet-Curable Coatings

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**ABSTRACT:** Four different UV-curable poly(urethane acrylate)s were prepared through the reaction of two diisocyanates [i.e., toluene-2,4-diisocyanate (TDI) and isophorone diisocyanate (IPDI)] and two polyols [i.e., polycaprolactone triol (PCLT) and polycaprolactone diol (PCLD)], and they were characterized with Fourier transform infrared spectroscopy. The mechanical properties, thermal properties, and water sorption of the cured poly(urethane acrylate)s were also investigated with respect to the chemical structures of the polyols and diisocyanates. In comparison with linear PCLD-TDI and PCLD-IPDI, crosslinked PCLT-TDI and PCLT-IPDI with trifunctional PCLT showed relatively high thermal decomposition temperatures. The hardness and modulus of the UV-cured poly(urethane acrylate) films, which were measured by a nanoindentation technique, were in the following increasing order: PCLD-IPDI  $\sim$  PCLD-TDI < PCLT-IPDI

$\sim$  PCLT-TDI. The pencil hardness was 3H for PCLT-IPDI and PCLT-TDI and HB for PCLD-IPDI and PCLD-TDI. Two urethane acrylates prepared from the trifunctional polyol showed better acid and alkali resistances than those made from the bifunctional polyol. These mechanical properties and chemical resistances may have been strongly dependent on the chain flexibility of the molecules and crosslinking density. Regardless of the functionality in the polyol, the change in the yellowness index showed a lower value in the poly(urethane acrylate) coating containing the aliphatic diisocyanate IPDI in comparison with the corresponding poly(urethane acrylate) with the aromatic diisocyanate TDI. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2454–2460, 2010

**Key words:** coatings; crosslinking; morphology; photopolymerization; polyurethanes

## INTRODUCTION

Growing concerns about environmental protection have driven industry toward the use of solvent-free polymerization systems, and UV curing has become a viable alternative to the conventional thermal curing of solvent-containing polymer formulations. Added benefits of UV-curable materials, such as fast curing speeds, energy conservation, high efficiency, and less pollution, have led to their increased use in various applications such as paints, thin-film coatings, adhesives, packaging overcoat films, and inks.<sup>1–4</sup> During use, a low viscosity and a high curing speed are two important properties pursued for UV-curable oligomers. Acrylate oligomers are some of the most important UV-curable resins.

However, traditional acrylate oligomers are commonly linear molecules containing two double bonds; their viscosity is usually higher, and this causes difficulties in use, so reactive diluents must be used.<sup>5–7</sup> Highly crosslinked polymers have attracted increasing attention for UV coating and adhesive applications because of the special molecular structures, such as the large number of end groups, compact molecular shape, and reduced chain entanglement.<sup>8–10</sup> The physical and chemical properties of highly crosslinked polymers are rather different from those of their conventional linear counterparts.

Crosslinked polymers have offered very intriguing properties of great potential value for applications, such as high solubility and reactivity. One possible application of highly crosslinked polymers is their use in coatings due to their low solution viscosity and high functionality. One of the most promising fields of application of highly crosslinked polymers in coating technologies is UV-curable coatings.<sup>5,11,12</sup> As is well known, poly(urethane acrylate)s are widely used as oligomers for UV coatings, and they provide excellent physical and mechanical properties, such as good adhesion to various substrates, high flexibility, and excellent impact strength. However, few studies have been

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TABLE I  
Compositions of the Urethane Acrylate Oligomers

Sample	NCO/ OH ratio	Excess OH (%)	PCLD (g)	PCLT (g)	IPDI (g)	TDI (g)	HEA (g)	DBT (g)	MMA (g)	TMPTA (g)	CH <sub>2</sub> CHCO <sub>2</sub> / NHCO <sub>2</sub> ratio
PCLD-IPDI	1.1	10	18	–	8.0	–	4.6	0.06	100.1	23.7	0.056
PCLD-TDI	1.1	10	18	–	–	6.3	4.6	0.06	100.1	23.7	0.056
PCLT-IPDI	1.1	10	–	25	11.1	–	5.8	0.08	140.2	23.7	0.059
PCLT-TDI	1.1	10	–	25	–	8.7	5.8	0.08	140.2	23.7	0.059

performed to prepare highly crosslinked urethane acrylates for the practical application of UV-curing systems.

In this work, two highly crosslinked poly(urethane acrylate)s were prepared through the reaction of trifunctional polycaprolactone triol (PCLT) with toluene-2,4-diisocyanate (TDI) or isophorone diisocyanate (IPDI), and two linear poly(urethane acrylate)s were prepared through the reaction of difunctional polycaprolactone diol (PCLD) with TDI or IPDI; they were characterized with Fourier transform infrared (FTIR) spectroscopy. The mechanical properties, thermal properties, and chemical resistance of the UV-cured poly(urethane acrylate)s for practical applications as coating materials were also investigated with respect to the chemical structures of the polyols and diisocyanates.

## EXPERIMENTAL

### Materials

PCLT [average number-average molecular weight ( $M_n$ ) = 900 g/mol] and PCLD (average  $M_n$  = 1250 g/mol) as polyols, 2-hydroxyethyl acrylate [HEA; weight-average molecular weight ( $M_w$ ) = 116.12 g/mol] as a reactive monomer, and dibutyltin dilaurate (DBT;  $M_w$  = 631.56 g/mol) as a reaction catalyst were purchased from Aldrich Chemical Co. (St. Louis, MO) IPDI ( $M_w$  = 222.28 g/mol) and TDI ( $M_w$  = 174.16 g/mol) as diisocyanates were purchased from Bayer Co. (Berlin, Germany). Methyl methacrylate (MMA;  $M_w$  = 524.51 g/mol) and trimethylolpropane triacrylate (TMPTA;  $M_w$  = 296.32 g/mol) as reactive diluents were purchased from Miwon Commercial Co., Ltd. (Anyang City, Korea). 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184D;  $M_w$  = 204.26 g/mol), purchased from Ciba Specialty Chemicals Co. (Basel, Switzerland), was used as a photoinitiator. All the reagents were used as received without further purification.

### Synthesis of the urethane acrylate oligomers

The highly crosslinked urethane acrylate oligomer PCLT-IPDI was prepared as follows. PCLT and IPDI (1 : 2.5 mol/mol) were charged into a 500-mL, four-necked flask in an ice bath equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a reflux condenser with a drying tube and were mixed perfectly. Then, approximately 200 ppm DBT was

added. After the urethane-forming reaction proceeded at 80°C for over 3 h, the reaction mixture was cooled to 60°C, and HEA was added dropwise. Tipping of the NCO-terminated prepolymer with HEA was done for 1 h below 60°C. Other urethane acrylate oligomers (PCLT-TDI, PCLD-IPDI, and PCLD-TDI) with different compositions are summarized in Table I and were prepared by a similar method.

### Sample preparation

A mixture of urethane acrylates, a photoinitiator (Irgacure 184D; 7 wt %), and dipentaerythritol hexa acrylate (DPHA) and TMPTA as reactive diluents was heated slightly above the ambient temperature to ensure homogeneous mixing, and this was followed by casting onto a glass plate. The thickness of the films was kept around 15–20  $\mu\text{m}$  for the evaluation of their properties. UV curing was carried out through the exposure of the samples to three different lamps in the following sequence: a metal-halide UV lamp (1000 W/cm), a high-pressure mercury UV lamp (1000 W/cm), and a metal-halide UV lamp (1000 W/cm) for 30 s. After they were peeled from the glass plate, the cured films were stored in a desiccator at room temperature for further studies.

### Measurement

#### FTIR spectroscopy

The FTIR spectra of the UV-cured poly(urethane acrylate)s were collected with an Excalibur series FTIR instrument (Digilab Co., California). The transmission mode was used, and the wave-number range was set from 4000 to 650  $\text{cm}^{-1}$ .

#### Thermogravimetric analysis (TGA)

The decomposition profile of the UV-cured poly(urethane acrylate)s was thermogravimetrically analyzed with a TA Instrument (Utah) Q50 instrument. Film samples ranging from 4 to 6 mg were placed in a platinum sample pan and heated from 30 to 600°C under an N<sub>2</sub> atmosphere at a heating rate of 10°C/min, and the weight loss was recorded as a function of temperature.

#### Mechanical properties

The pencil hardness of the UV-cured poly(urethane acrylate) films was determined by ASTM 3363. The

crosscut adhesion test and RCA abrasion test were performed according to ASTM D 3359 and ASTM D 1242, respectively. The pendulum hardness of the UV-cured films was determined with a pendulum hardness rocker (Sheen Instrument, Ltd., Teddington, United Kingdom) according to ASTM 4366 (pendulum weight =  $200 \pm 0.2$  g, amplitude limitation angle =  $6-3^\circ$ ).

Additionally, the modulus and hardness of the UV-cured poly(urethane acrylate) films were measured with an MTS XP nanohardness tester (MTS Co., Minnesota) and a Berkovich (three-sided pyramidal) diamond indenter. Multiple indentations were made at five different locations on the film surface under fixed and applied loads. At different locations, the load–displacement curve was recorded; from this, the effective modulus and hardness could be calculated with standard formulas.<sup>13,14</sup>

#### Chemical and solvent resistance

The chemical resistance was checked according to ASTM D 1647-89. Glass panels coated with samples of poly(urethane acrylate)s were allowed to dry for 3 days. The periphery of the glass panels was coated with wax to restrict the migration of water under the film from open ends. The panels were then dipped into a 3% (w/w) sulfuric acid solution and a 3% (w/w) NaOH solution, and the change in the appearance was monitored after 3 days. The solvent resistance was determined by the double-rub method with a piece of white cotton cloth (ASTM D 5402-93). The solvent was methanol. The result was reported as the minimum number of double rubs at which the films were observed to fail or else 250, which was the maximum number of double rubs carried out. The salt fog spray performance was also determined according to ASTM B117.

#### Thermal shock test

For the UV-cured poly(urethane acrylate) coating, the resistance at a high humidity (JESD22-A100C) was measured via the treatment of the coating samples at the relative humidity (RH) of 95% and at the temperature of  $50^\circ\text{C}$  for 72 h. Also, the resistance to sudden changes in temperature ( $-40$  to  $85^\circ\text{C}$ ) was measured according to JESD22-A104C. After the final cycle was performed, the coatings were inspected for delamination, cracking, and changes in color.

#### Weatherability

For the weatherability (ASTM G53) of the UV-cured poly(urethane acrylate) films, UV-exposure tests were conducted through the exposure of the cured films at a distance of 20 cm from a mercury–tungsten phosphor lamp with a CT-UVT UV-exposure tester (Core-

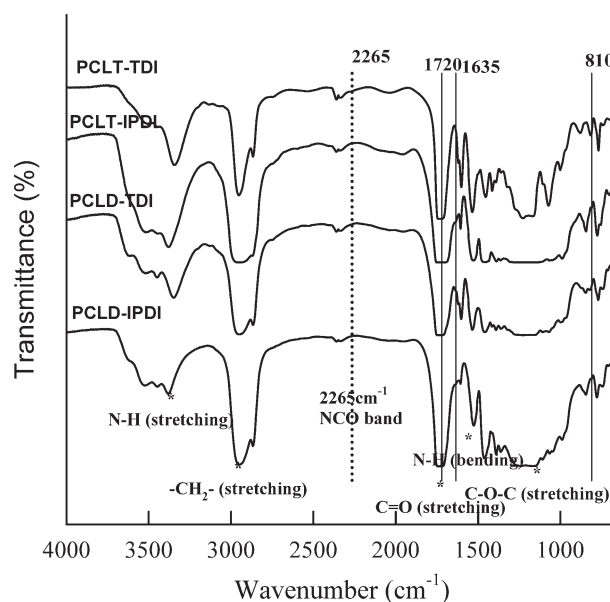
tech Co., Annyang City, Korea). The change in the yellowness index ( $\Delta\text{YI}$ ) was calculated from the yellowness indices (YIs) of the UV-treated film and the corresponding untreated film, which were measured with an A6830 colorimeter (BYK-Gardner Co., Gertsried, Germany).

## RESULTS AND DISCUSSION

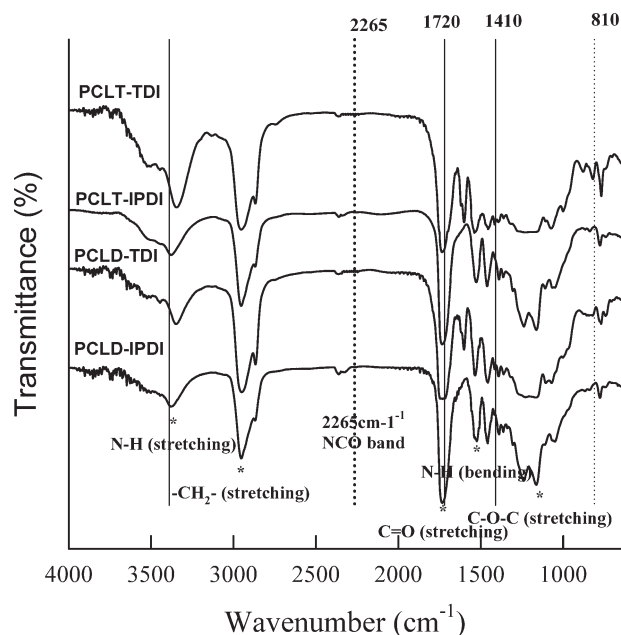
### Synthesis of the UV-cured poly(urethane acrylate)s

In this study, two types of poly(urethane acrylate) films, that is, linear and highly crosslinked films, were prepared by a two-step reaction: (1) the synthesis of urethane acrylate oligomers through the reaction of a difunctional or trifunctional polyol with diisocyanates and then tipping with HEA and (2) the UV curing of the synthesized urethane acrylate oligomers and reactive diluents with a photoinitiator. In particular, the products obtained from the diisocyanates (IPDI and TDI) and the trifunctional polyol PCLT were described as  $A_2+B_3$ -type highly crosslinked or hyperbranched polymers with high degrees of branching.<sup>8,9,15</sup>

Typical FTIR spectra of four different urethane acrylate oligomers and UV-cured poly(urethane acrylate)s are depicted in Figures 1 and 2, respectively. The spectral analysis was mainly used to check the completion of the polymerization reaction in terms of the disappearance of the NCO band at  $2265\text{ cm}^{-1}$  and the appearance of the N–H band at  $3000\text{--}3400\text{ cm}^{-1}$ , which could be ascribed to the hydrogen bonding between N–H and carbonyl groups.<sup>2,4,5</sup> The completion of the reaction was confirmed with the following analysis. As shown in Figure 1, the



**Figure 1** FTIR spectra of four different urethane acrylate oligomers.

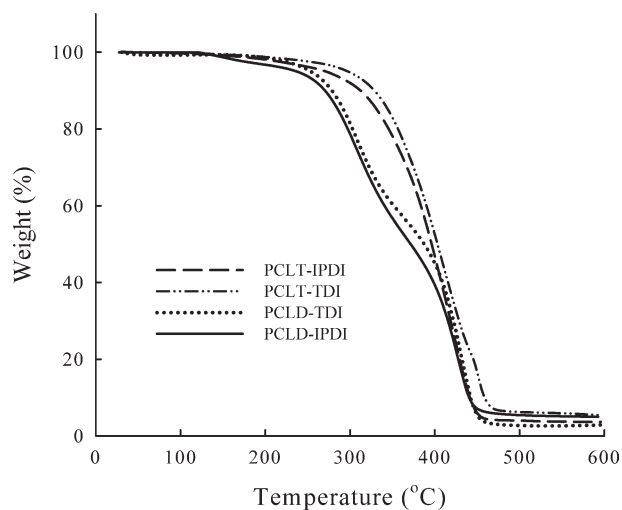


**Figure 2** FTIR spectra of four different poly(urethane acrylate) films.

spectra of the four urethane acrylate oligomers did not show any detectable band at  $2265\text{ cm}^{-1}$  but did show strong absorption bands at  $1720\text{ cm}^{-1}$  (amide I, stretching of the ester  $\text{C}=\text{O}$  bond) and around  $3390\text{ cm}^{-1}$  (stretching vibration of the urethane  $\text{N}-\text{H}$  bond). The results in Figure 1 indicate that the reaction between the difunctional or trifunctional polyol and diisocyanates had occurred. A comparison of Figures 1 and 2 shows that the UV-cured poly(urethane acrylate) films had FTIR spectra similar to those of the corresponding urethane acrylate oligomers, except for the disappearance of the band at  $810\text{ cm}^{-1}$  (out-of-plane bending of  $\text{C}-\text{H}$  in  $>\text{CH}=\text{CH}_2$ ) in the UV-cured poly(urethane acrylate) films. The TDI-based urethane acrylate showed a relatively low decrease in the  $810\text{-cm}^{-1}$  band, and this may be due to the fact that the aromatic rings readily absorbed more UV light than the aliphatic ones did. The results in Figure 2 indicate that the urethane acrylate oligomers reacted with reactive diluents well and the double bonds disappeared; consequently, the polymerization reaction was completed through UV curing.

### Thermal properties of the UV-cured poly(urethane acrylate)s

TGA is one of the commonly used techniques for the rapid evaluation of the thermal stability of different materials, and it also indicates the decomposition of polymers at various temperatures. Figure 3 shows the TGA thermograms of the UV-cured poly(urethane acrylate)s from 30 to  $600^\circ\text{C}$ .



**Figure 3** TGA curves of four different UV-cured poly(urethane acrylate) films.

As shown in Figure 3, the degradation process and thermal stability were dependent on the chemical structures of the polyols and diisocyanates. The degradation process of PCLD-IPDI and PCLD-TDI could be divided into three steps: the thermal degradation of the poly(urethane acrylate) films with bifunctional PCLD occurred in the temperature range of  $160\text{--}280^\circ\text{C}$  for the first step, at  $280\text{--}390^\circ\text{C}$  for the second step, and at  $390\text{--}450^\circ\text{C}$  for the third step. This low degradation temperature, especially for PCLD-IPDI, was mainly attributable to the less stable urethane functional groups in the aliphatic poly(urethane acrylate)s, which could decompose to form alcohol and isocyanate groups. This result agrees with the literature.<sup>16</sup> Additionally, the weight loss of PCLD-IPDI and PCLD-TDI was more pronounced than that of PCLT-IPDI and PCLT-TDI. As shown in Table II, the temperatures of 5% and 10% weight loss increased in the order of PCLD-IPDI < PCLD-TDI < PCLT-IPDI < PCLT-TDI, and both PCLD-IPDI and PCLD-TDI with the bifunctional polyol showed slightly lower thermal stability than

**TABLE II**  
Thermal Properties of Four Different UV-Cured Poly(urethane acrylate) Films

	Linear poly(urethane acrylate)		Crosslinked poly(urethane acrylate)	
	PCLD-IPDI	PCLD-TDI	PCLT-IPDI	PCLT-TDI
Decomposition temperature $^\circ\text{C}$				
5 wt % weight loss	237	253	271	297
10 wt % weight loss	271	279	313	329
Residual weight (%)	5.0	2.9	3.7	5.5



**TABLE III**  
**Properties of the UV-Cured Poly(urethane acrylate) Films**

	Linear poly(urethane acrylate)		Crosslinked poly(urethane acrylate)	
	PCLD-IPDI	PCLD-TDI	PCLT-IPDI	PCLT-TDI
<b>Mechanical properties</b>				
Pendulum hardness (count)	17	18	54	56
Adhesion (crosshatch)	100%	100%	100%	100%
Pencil hardness	HB	HB	3H	3H
RCA abrasion (count)	<30	–	>100	–
Maximum load (mN) <sup>a</sup>	4.78	5.01	5.89	5.77
Modulus (GPa) <sup>a</sup>	4.035	4.447	6.302	5.743
Hardness (GPa) <sup>a</sup>	0.214	0.219	0.248	0.245
<b>Chemical resistance</b>				
3% H <sub>2</sub> SO <sub>4</sub>	Affected	Affected	Unaffected	Unaffected
5% NaOH	Affected	Affected	Unaffected	Unaffected
Solvent resistance: ethanol <sup>b</sup>	220	200	>250	>250
Salt fog spray	Affected <sup>c</sup>	Affected	Unaffected	Unaffected
Resistance in humidity (95% RH/50°C/72 h)	Unaffected	Unaffected	Unaffected	Unaffected
Thermal shock (–40 to 85°C)	Unaffected	Unaffected	Unaffected	Unaffected
Yellowness ( $\Delta YI$ ) <sup>d</sup>	5	53	8	61

<sup>a</sup> Measured with a nanoindenter.

<sup>b</sup> Rub test (indicating the number of double rubs passed without film damage).

<sup>c</sup> Delamination and blister.

<sup>d</sup>  $\Delta YI = (YI \text{ in the final state}) - (YI \text{ in the initial state})$ .

the corresponding PCLT-TDI and PCLT-IPDI with the trifunctional polyol. Also, the TGA results indicated that the poly(urethane acrylate) with the aromatic diisocyanate had a higher decomposition temperature than the corresponding poly(urethane acrylate) with the aliphatic diisocyanate.

In general, the thermal degradation of the polymer poly(urethane acrylate) is associated with changes in C=O and C–N urethane groups, and some urea compounds may be formed during the thermal degradation of poly(urethane acrylate) at a high temperature.<sup>5,17</sup> The enhancement of the thermal stability can be attributed to the higher overall crosslink density. The crosslinking density of the UV-cured films increased with increasing functionality of the polyol, and this may have induced higher thermal stability in PCLT-TDI and PCLT-IPDI with the trifunctional polyol

### Mechanical properties

For coating applications, the mechanical properties of four different UV-cured poly(urethane acrylate) films were measured with several different methods: pendulum hardness, pencil hardness, adhesion (cross hatch), and RCA abrasion. The results are summarized in Table III.

The pendulum hardness of the UV-cured poly(urethane acrylate) films was in the following increasing order: PCLD-IPDI  $\sim$  PCLD-TDI < PCLT-IPDI  $\sim$  PCLT-TDI. The pencil hardness was 3H for PCLT-IPDI and PCLT-TDI and HB for PCLD-IPDI and PCLD-TDI. The RCA abrasion showed the same trend as the

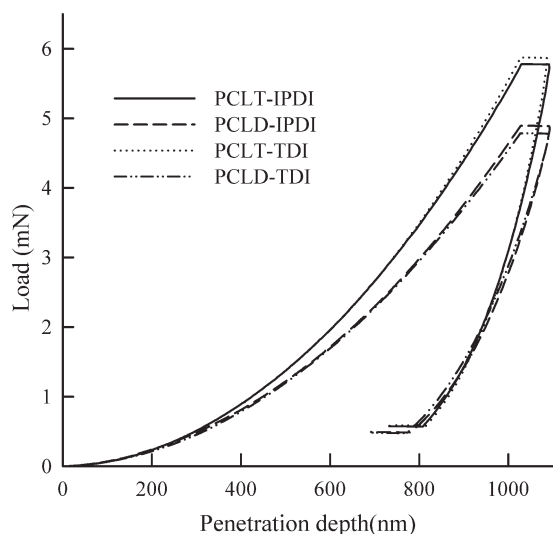
pendulum and pencil hardness: under 30 counts for PCLD-IPDI and over 100 counts for PCLT-IPDI. The pendulum hardness, pencil hardness, and RCA abrasion of the UV-cured films containing the trifunctional polyol showed higher values than the corresponding films containing the bifunctional polyol.

The hardness and effective modulus of the UV-cured poly(urethane acrylate) films were calculated from the nanoindentation load–displacement curves with the Berkovich indenter (Fig. 4). Both the hardness and modulus were in the following increasing order: PCLD-IPDI  $\sim$  PCLD-TDI < PCLT-IPDI  $\sim$  PCLT-TDI. They showed the same trends as the pendulum hardness and pencil hardness. This indicated that the UV-cured poly(urethane acrylate) with the highly crosslinked structure, that is, the trifunctional polyol, showed better mechanical resistance than those with a linear structure. These mechanical properties may be attributed to differences in the chain flexibility of the molecules and crosslinking density.

In general, a trifunctional polyol provides a high degree of crosslinking and low flexibility to a coating and consequently induces high surface hardness.<sup>18</sup> This explanation well fits the results for mechanical resistance in this study.

### Chemical and solvent resistance

To evaluate the overall performance of the coatings, the UV-cured polyurethane films were subjected to acidic and alkali action. The data summarized in Table III reveal that the two urethane acrylates made from the



**Figure 4** Load–displacement relationship of four differently structured UV-cured poly(urethane acrylate) films at a maximum penetration depth of 1000 nm.

trifunctional polyol showed better acid and alkali resistance than those made from the bifunctional polyol.

In general, poly(urethane acrylate) films show excellent solvent resistance.<sup>19</sup> The solvent resistance is expected to decrease as the crosslinking density decreases. Table III shows that, in the case of ethanol resistance, the highly crosslinked poly(urethane acrylate)s showed no variation up to 250 double rubs, whereas the linear poly(urethane acrylate) were seen to fail in the range of 200–220 double rubs. This indicates that the solvent resistance results agree with our expectations.

The better chemical and solvent resistance in the highly crosslinked poly(urethane acrylate)s was associated with the increased crosslinking density of the UV-cured films due to the increased acrylic double bonds of the UV-curable coating. Additionally, the same trend with the solvent resistance could be identified in the salt fog spray test.

#### High humidity and thermal shock resistance

The thermal shock test was quite encouraging. Table III shows that all the UV-cured poly(urethane acrylate) films in this study displayed good resistance to sudden changes in temperature (–40 to 80°C) under high RH. In addition, all the UV-cured poly(urethane acrylate) films showed good resistance under the conditions of high humidity and high temperature.

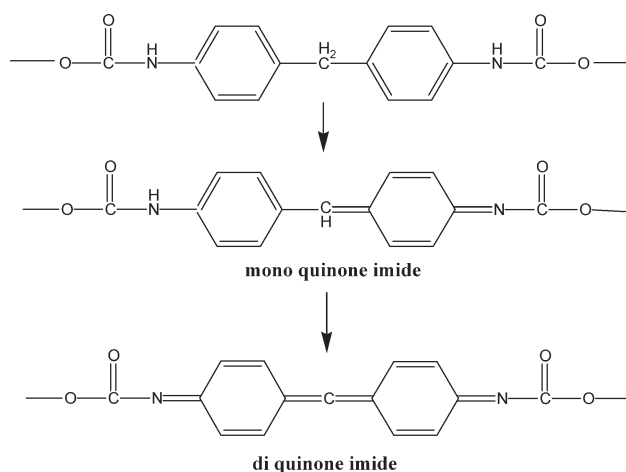
#### Weatherability

The weatherability of the UV-cured poly(urethane acrylate) films with different polyol and diisocyanate types was investigated in terms of  $\Delta YI$ , which has been widely used as a semiquantitative expression

of the weatherability; that is, the smaller  $\Delta YI$  is, the better the weatherability is in coatings.<sup>2</sup> Regardless of the functionality in the polyol,  $\Delta YI$  showed a lower value in a poly(urethane acrylate) coating containing the aliphatic diisocyanate IPDI than the corresponding poly(urethane acrylate) with the aromatic diisocyanate TDI. This indicates higher UV stability and good yellowing resistance with the aliphatic diisocyanate. The poly(urethane acrylate) films derived from the aromatic diisocyanate TDI showed poor yellowing resistance because of quinonization in the presence of UV light, as shown in Figure 5.<sup>20</sup> PCLD-IPDI and PCLT-IPDI with the aliphatic diisocyanate showed good yellowing resistance, as expected, because the quinonization reaction could be avoided.

#### CONCLUSIONS

Four different UV-curable poly(urethane acrylate)s were successfully prepared through the reaction of two diisocyanates (i.e., TDI and IPDI) and two polyols (i.e., PCLT and PCLD). In comparison with the linear PCLD-TDI and PCLD-IPDI, the highly crosslinked PCLT-TDI and PCLT-IPDI with trifunctional PCLT showed relatively high thermal decomposition temperatures. The surface hardness and modulus (measured by a nanoindentation technique) of the UV-cured poly(urethane acrylate) films were in the following increasing order: PCLD-IPDI  $\sim$  PCLD-TDI  $<$  PCLT-IPDI  $\sim$  PCLT-TDI. The pencil hardness was 3H for PCLT-IPDI and PCLT-TDI and HB for PCLD-IPDI and PCLD-TDI. The UV-cured poly(urethane acrylate) with the highly crosslinked structure showed better mechanical resistance than those with the linear structure. Two poly(urethane acrylate) films made from the trifunctional polyol showed better acid and alkali resistance than those made from the bifunctional polyol. These mechanical properties and chemical resistances may be



**Figure 5** Structure of quinone imide in urethane acrylate.

strongly dependent on the chain flexibility of the molecules and crosslinking density. Of the four poly(urethane acrylate) films in this study, PCLT-IPDI showed not only good mechanical and chemical resistance but also good weatherability.

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