

# Characterization of UV-Curable Reactive Diluent Containing Quaternary Ammonium Salts for Antistatic Coating

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**ABSTRACT:** Reactive diluent with quaternary ammonium salts (RDQ) for UV-curable antistatic coating was synthesized by reacting glycidyl methacrylate (GMA) and piperazin with dropping the methansulfonic acid. In order to compare the curing behavior of RDQ with commercial monomers, the photopolymerization of RDQ, 1,6-hexandiol diacrylate (HDDA) and 1,6-hexandiol dimethacrylate (HDDMA) were studied by using real-time IR spectroscopy. Surface properties such as surface resistance, pencil hardness, and solvent resistance of the cured films containing RDQ were investigated. When used as a reactive diluent in the UV-curable coating formulation, the RDQ imparted excellent antistatic properties to the final material. The results of an Fourier transform infrared/attenuated total reflectance (FTIR/ATR) depth profile analysis show that RDQ molecules are more concentrated near the surface within a micrometer-thick layer, indicating that existence of the ionic components in the surface layer is responsible for antistatic property. Film cured from the formulation containing 12 wt % of RDQ showed the best mechanical properties with reasonable surface properties. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 132–137, 2002; DOI 10.1002/app.10273

**Key words:** UV curable; photopolymerization; React-IR; antistatic; reactive diluent

## INTRODUCTION

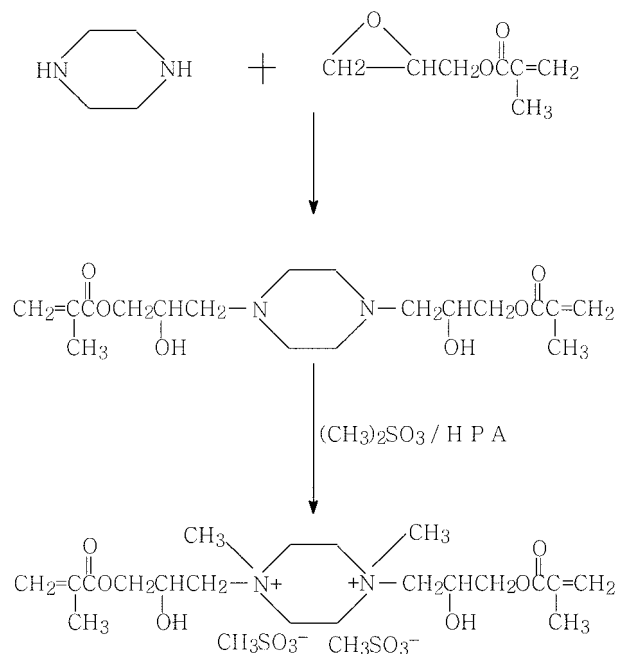
The popularity of environmentally safe coating (ESC) systems is increasing due to global regulations to reduce the volatile organic components in coating formulations. Among ESC systems such as radiation-cured, water-based, high-solid, powder, and supercritical carrier coatings, UV-radiation cured coating systems continue to have the

brightest future.<sup>1–4</sup> The present popularity of UV radiation curing is due to a number of reasons.<sup>5</sup> First, UV curables are comprised of 100% reactive components, which provide an environmentally acceptable coating. Second, UV-curing systems are energetically efficient; they require a small fraction of the power normally consumed by thermally cured coatings. Finally, UV curables can be easily formulated to meet a variety of applications since functionalized monomers and oligomers are available covering a wide range of properties.

The use of radiation curable coatings on plastic substrates is growing rapidly.<sup>6</sup> As a result, there is an increasing demand for UV-curable, anti-

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**Scheme 1** The structure of RDQ.

static, hard coatings with improved durability especially for certain plastic products. The coating's antistatic properties are generally imparted by a low molecular weight antistatic agent added to the formulation. Although the antistatic properties of such coatings are adequate initially, they often do not last long as the antistatic agent is wiped off or somehow lost. This is particularly true when the agent is a low molecular weight material.<sup>7,8</sup> There have been many attempts to introduce the quaternary ammonium salt groups into the UV-curable oligomers for permanent antistatic properties.<sup>9</sup> However, there has been few attempt to produce the UV-curable monomers containing quaternary ammonium salt groups for antistatic property.

In this study, the performance of a UV-curable antistatic diacrylate molecular diluent containing quaternary ammonium salts was prepared and compared to commercially available monomers and its effect on the curing and surface properties of a coating network was investigated.

## EXPERIMENTAL

### Synthesis of RDQ

As shown in Scheme 1, the RDQ was prepared via a two-step reaction. To a 250 mL three-neck flask

equipped with water bath, thermometer, refluxing condenser, dropping funnel, and magnetic stirring bar, 8.6 g (0.1 mol) of piperazine (Aldrich Chemical Co.) and 0.1 g of 4-methoxyphenol (Aldrich Chemical Co.) as a radical polymerization inhibitor were charged and heated to 65°C. 28.4 g (0.2 mol) of glycidyl methacrylate (Aldrich Chemical Co.) was slowly added and the mixture was maintained for 2 h at 65°C. The reaction product was identified with <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 6.1, 5.6 (4H, d, CH<sub>2</sub>=), 5.0 (2H, s, HO—), 3.7 (4H, m, O—CH<sub>2</sub>—), 3.5 (2H, m, —CH—), 2.4–2.6 (12H, m, N—CH<sub>2</sub>—), and 1.95 (6H, s, CH<sub>3</sub>).

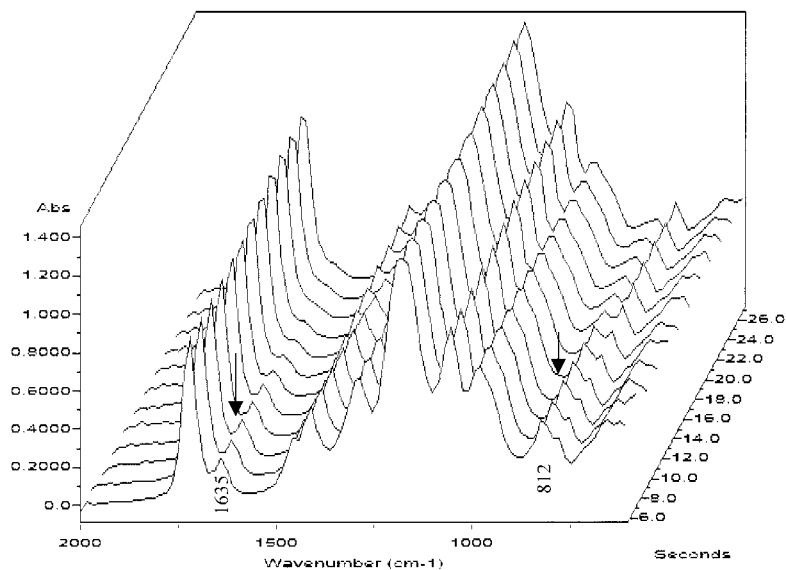
The above reaction product was diluted with 51 hydroxyl propyl acrylate (HPA; OSAK YUKI Co.). After addition of the diluent 0.14 mol of methyl methane sulfonate (MMA; Alrich Chemical Co.) was added dropwise over the course of 30 min at 50°C. The reaction mixture was stirred for 2 h at 50°C, to give a gray liquid and then cooled. The salt group of the final product (RDQ) was identified by the titration of the remaining amine group with 0.1 N HCl solution and potentiometric titrator (Metrohm Co., model: 716 DMS Titrino). Sixty-eight percent of the total amine group was converted into quaternary ammonium group (70%, theoretical).

### Coating Formulation and Curing Procedure

The photocurable resin composition was prepared by thoroughly mixing 40 g of the urethane acrylate oligomer (Ebecry 264; UCB Chemicals), 30 g of trimethylpropane triacrylate (TMPTA; Sartomer), 25 g of 1,6-hexandiol diacrylate (HDDA; BASF), 4 g of 1-hydrophenyl ketone (trademark Iraqure 184; Ciba-Gegy), and 1 g of polyether-modified dimethylsiloxane copolymer (trademark, BYK 307; BYK-Chemic GmbH) as a leveling agent. Different amounts of RDQ (0–24 wt %) were added into the above composition. A 15 μm thick coating of the resin composition was applied on polycarbonate sheets by bar coater (No. 7: RDS) and then cured with 80 W/cm light from a medium pressure mercury lamp of conventional UV equipment.

### Cure Monitoring and Film Properties

Infrared spectra were recorded on a Bruker Aspect 1000 Fourier transform spectrometer. Surface spectra were recorded with the aid of an ATR attachment. Germanium (Ge) and KRS-5 refraction elements were used at nominal angles of



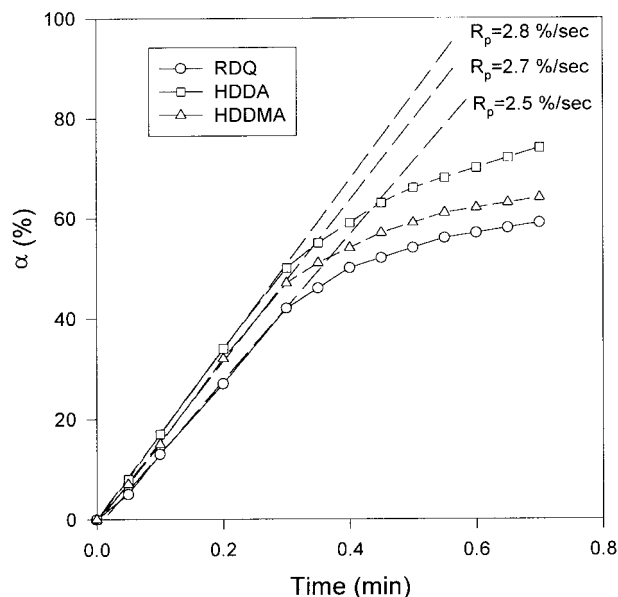
**Figure 1** Real-time FTIR/ATR spectra of UV-exposed RDQ.

incidence of 60° (Ge) and 45° or 60° (KRS-5). Film samples were held against both faces of each reflection element with a sample holder. Each piece of film was backed by a resilient rubber pad (1 mm thick) that was slightly smaller than the film sample. For the photopolymerization of the monomers, 5 wt % of a photo initiator was mixed with each batch of monomers. The photo polymerization of RDQ, HDDA, and 1,6-hexandiol dimethacrylate (HDDMA) (Ancomer) was studied by using real-time infrared spectroscopy (ATS-1000 from ASI Applied Systems). In particular, the decrease of the sharp peak centered at 812  $\text{cm}^{-1}$  (C—H deformation mode of acryl group) was monitored.<sup>11,12</sup> To assess the effect of different amounts of RDQ in the formulation, a number of performance tests were conducted on the cured film samples. The hardness of the cured film was measured by using graphite pencils of increasing hardness as described in ASTM D 3363-74. Solvent resistance was determined by rubbing the cured coating film with a piece of cheesecloth saturated with methyl ethyl ketone (MEK) under finger pressure. The number of back-and-forth rubs require to break through the coating surface was recorded. The surface insulation resistance was measured with a surface resistivity meter (SRM-110 from PINION). Durability of UV-cured coatings was examined after washing with water at 80°C and under relative humidity 85% for 2000 h. The tensile properties of the cured films (tensile strength and elongation at break) were determined by measuring dumbbell samples with

a universal testing machine (AGS-500D from SHIMAZU) operating at a crosshead speed of 10 mm/min. The contact angle of the UV cured films was determined by a SEO 300A from Surface & Electro-Optics Co., Ltd. This system is based on the sessile drop method. Temperature and relative humidity in the laboratory were within the range of 21 and 25°C and 20 and 30%, respectively. Deionized water (DI) water was used as probing liquids.

## RESULTS AND DISCUSSION

The typical real-time Fourier transform infrared/attenuated total reflectance (FTIR/ATR) spectra of UV-exposed RDQ are shown in Figure 1. The spectra are highlighted by the disappearance of the 1635 and 812  $\text{cm}^{-1}$  bands characteristic of the C=C stretching and the C—H deformation modes of the acryl group of RDQ, respectively. Since the decrease in intensity of these peaks is attributable to the gradual disappearance of the acrylic double bond as the cure progresses, the extent of photo polymerization can be spectroscopically recorded in real time.<sup>13,14</sup> The cure profile of RDQ was compared to those of the diacrylate monomers commonly used in UV-curable systems. Figure 2 shows the conversion curves of photopolymerization of HDDA, HDDMA, and RDQ, respectively. The conversion ( $\alpha$ ) was calculated at various intervals using the following equation:



**Figure 2** The conversion curves of homopolymerization of RDQ, HDDA, and HDDMA.

$$\alpha(\%) = \frac{[I_{812}]_o - [I_{812}]_t}{[I_{812}]_o} \times 100 \quad (1)$$

where  $[I_{812}]_o$  and  $[I_{812}]_t$  are the sample absorbances at  $812 \text{ cm}^{-1}$ , before and after UV exposure, respectively. Usually, relative intensity is required because the absolute intensity varies from sample to sample. Since it is difficult to find the reference peak from the infrared spectra of crosslinking system, conversion of photopolymerization was deduced based on the absolute intensities. The kinetics of photopolymerization were

also analyzed using the method described by Decker<sup>12</sup> and the steady state equation given below:

$$R_p(\%/s) = \frac{I_1 - I_2}{I_o(t_2 - t_1)} \times 100 \quad (2)$$

where  $R_p$  is the rate of polymerization in %/s,  $I_1$  and  $I_2$  are the absorbancies in the straight line region of the sigmoid curve, and  $t_1$  and  $t_2$  are times in seconds that correspond to the absorbancies  $I_1$  and  $I_2$ .  $I_o$  is the initial absorbance at the start of the experiment. As shown in Figure 2, for all of the different systems 50% conversion is reached with less than 0.5 min of exposure. However, the overall rate of polymerization ( $R_p$ ) as well as final conversion ( $\alpha$ ) of RDQ are lower than those of HDDA and HDDMA. It is presumably due to the strong steric effect from quaternary ammonium salts and the methyl group of the RDQ. Since cure monitoring was performed at the film-substrate interfaces by ATR and film thickness was 2 mm, it is not surprising to have less than 80% conversion even after 0.6 min of exposure for all the systems studied.

At this point, it is necessary to discuss the effect of RDQ on the surface and bulk properties of the UV-curable coating. The results of the investigations of the UV-cured coating films are summarized in Table I. As the concentration of RDQ in the formulation increases from 0 to 24%, the surface resistance decreases markedly from  $10^{14}$  to  $10^{10} \Omega$ . It is expected that the hydrophilic OH group and quaternary ammonium salts of RDQ will give the antistatic property to the coat-

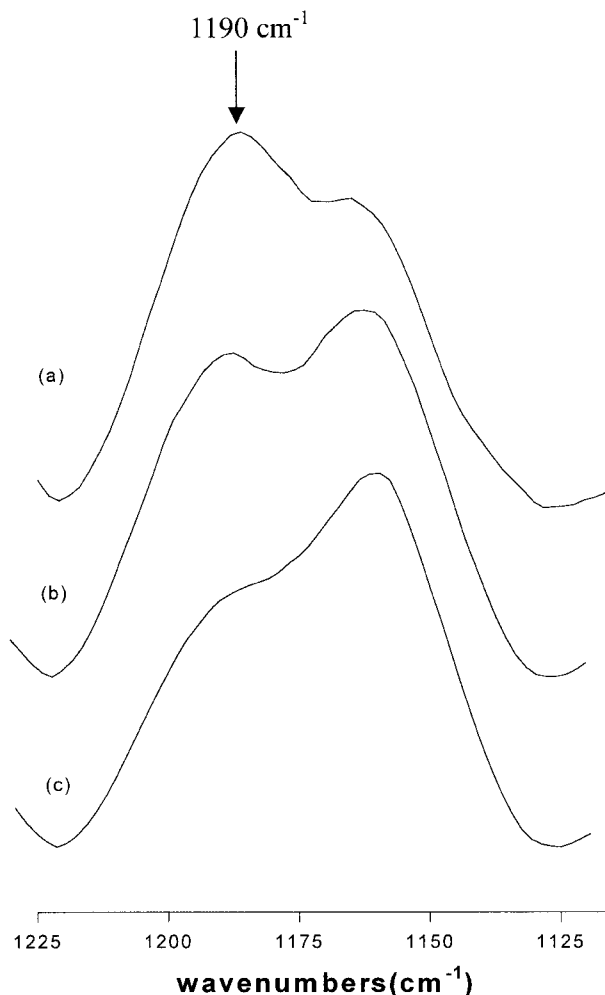
**Table I** Film Properties of UV-Cured Coatings

	Sample				
	A1	A2	A3	A4	A5
Amount of RDQ (%)	0	6	12	18	24
Surface resistance ( $\Omega$ )					
Initial	$10^{14}$	$10^{12}$	$10^{11}$	$10^{10}$	$10^{10}$
After washing	$10^{14}$	$10^{12}$	$10^{11}$	$10^{10}$	$10^{10}$
Pencil hardness	1H	1H	1H	HB	HB
Contact angle ( $^\circ$ )	76	49	35	25	24
Solvent resistance (MEK)	>200	>200	>200	<200	<200
Young's modulus ( $\text{kgf/mm}^2$ )	92.1	90.8	89.8	87.4	85.4
Tensile strength ( $\text{kgf/mm}^2$ )	1.5	1.7	2.2	2	1.8
Elongation (%)	1.7	2.2	3.2	2.7	2.6
Energy (J)	0.008	0.012	0.023	0.020	0.016

ing film because both groups are able to absorb water on the surface. Because of the groups' hydrophilic nature, RDQ decreases the contact angle between water and UV-cured film, thus allowing water to be uniformly distributed on the surface.<sup>15,16</sup> In order to test antistatic durability, a moisture resistance test was conducted with the UV-cured coatings to measure the change in static charge of the film after 2000 h of exposure at 80°C and 85% relative humidity. The results are shown in Table I. It was found that there is no drop of the surface resistivity in the UV-cured film containing the RDQ. It is theorized that the RDQ in the film did not migrate to the surface under the influence of moisture and temperature due to the crosslinking reaction between RDQ and other ingredients (monomer/oligomer).

Table I also shows the relationship between the concentration of RDQ and surface hardness of the film. The pencil hardness remains 1H, independent of the concentration of RDQ, until 12 wt % but decreased to HB when the concentration of RDQ is increased to more than 12 wt %. In light of these results, it is evident that adding RDQ at 12 wt % results in a cured film, which achieves a good balance between the antistatic property and surface hardness, two characteristics that are often difficult to achieve at the same time. The results of the chemical resistance test are also summarized in Table I. It is notable that adding RDQ into the coating formulation provides the permanent antistatic property with improved solvent resistance in the UV-cured film.

In order to rationalize the above observations, it is necessary to address questions concerning the film formation behavior of the coating containing RDQ. The behavior of the surface concentrations of RDQ as a function of increasing penetration depth beneath the film surface has been observed with the aim of better understanding the above experimental results. The series of ATR spectra shown in Figure 3 recorded with the different reflection conditions demonstrate decline pattern of asymmetric  $\text{SO}_3^-$  stretching band ( $1190 \text{ cm}^{-1}$ ) as the penetration depth of the IR beam is increased. A decrease in the peak intensity of  $I$  ( $1190 \text{ cm}^{-1}$ ) with an increase in penetration depth could be interpreted as evidence that RDQ are more concentrated near the surface within a micrometer-thick layer. Hence, existence of ionic components in surface layer is responsible for the improved properties such as antistatic and solvent resistance properties.



**Figure 3** FTIR/ATR spectra of UV-cured film containing the 12 wt % of RDQ: (a) Ge60/60, (b) KRS-5 60/60, and (c) KRS-5 45/60.

In addition to the film's surface properties, the mechanical properties are also dependent on the concentration of RDQ in the coating formulation. Young's modulus decreased and tensile strength and elongation values increased with increasing RDQ concentration. Notable is the high tensile strength and elongation values found in the cured film samples containing the 12 wt % of RDQ. Due to the ionic interaction of the ionic groups, introduced in the crosslinked network, the freedom of movement of the network will be limited because of physical crosslinking. Although the UV-cured film without the RDQ gives a very brittle coating, the film becomes tougher as indicated in energy value ( $J$ ) as RDQ is added into formulation until 12 wt %. It is interesting to see the decrease of mechanical properties above 12 wt %. If ionic



groups physically crosslink the material, more ionic groups should result in the better mechanical properties. This can be explained by the fact that there is a critical ionic concentration for cluster formation that tends to decrease the mechanical properties due to the phase separation. Morphological study of the coating films varying ionic concentration is necessary to explain the mechanical behavior of this crosslinked system. Similar experimental results were observed in the literature.<sup>17</sup>

It has been demonstrated that RDQ is a useful molecular diluent, which can modify the UV-curable coating with covalently bonded functional salt resulting antistatic coating. RDQ can impart increased tensile strength and elongation without sacrificing other desirable properties such as pencil hardness and solvent resistance until the amount of RDQ is less than 12 wt %. This promising UV monomer can be used in many application fields that require the transparency, lightweight, and long-term antistatic property.

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