

# Liquid UV Curable Cyclohexanedimethanol Diacrylate Monomers

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## Abstract

UNOXOL™ Diol is a *liquid* cycloaliphatic diol based on a unique composition of (*cis,trans*)-1,3/1,4 cyclohexanedimethanol, and is a starting material for synthesis of acrylate monomers for use in ultraviolet (UV) and electron beam (EB) cured coatings, inks, and adhesives. Diacrylate monomers prepared from this unique diol and containing less than 15 wt.% *trans*-1,4-cyclohexanedimethanol diacrylate, are liquid at room temperature and readily soluble in other acrylate monomers and oligomers (in contrast to diacrylates prepared from 1,4-cyclohexanedimethanol, which are solid). More importantly, UV cured coatings based on (*cis,trans*)-1,3/1,4 cyclohexanedimethanol diacrylates show superior hardness, scratch resistance, abrasion resistance, and chemical resistance, compared to common diacrylate monomers used in the UV coating industry, such as tripropylene glycol diacrylate, hexanediol diacrylate, dipropylene glycol diacrylate, and propoxylated neopentyl glycol diacrylate. Thus, this new monomer appears to be a promising material for enhancing the performance of radiation cured coatings, inks, and adhesives. This paper will summarize the synthesis of novel liquid cyclohexanedimethanol diacrylates, as well as, the performance properties of the corresponding UV cured coatings.

## Introduction

Acrylate monomers are low molecular weight ( $100 < MW < 500$  amu) reactive diluents, which are used primarily to reduce the viscosity of radiation curable formulations, but also to impart additional benefits, such as improved adhesion, reactivity, hardness, or flexibility. Due to their good balance of properties, the most commonly used aliphatic diacrylate monomers in UV curable coatings are tripropylene glycol diacrylate (TPGDA), hexanediol diacrylate (HDDA), dipropylene glycol diacrylate (DPGDA), and propoxylated neopentyl glycol diacrylate (2PO NPGDA). However, aliphatic diacrylates with improved hardness, scratch resistance, abrasion resistance, chemical resistance, and weatherability are still desired for the next generation of UV curable coatings, and cyclohexanedimethanol diacrylates (CHDMDA) are a class of monomers that can potentially offer these benefits, due to the presence of the cyclohexyl ring.

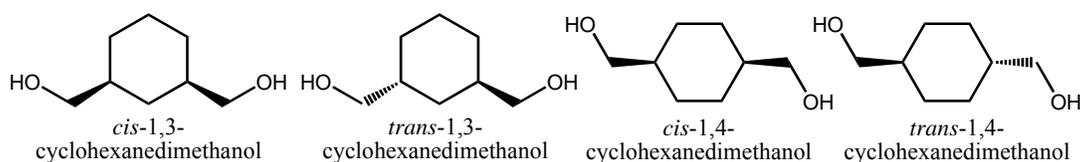
## Overview of Commercially Available Acrylates Prepared from 1,4-Cyclohexanedimethanol

Commercially available cyclohexanedimethanol diacrylates are prepared from 1,4-cyclohexanedimethanol, which is a solid diol at room temperature. 1,4-Cyclohexanedimethanol diacrylate is touted for its abrasion resistance, hardness, and chemical resistance. However, this monomer is a solid at room temperature and insoluble in most acrylates, thus significantly limiting its use in UV/EB curable formulations.<sup>1</sup>

To alleviate this problem, the solid diol (1,4-cyclohexanedimethanol) can be alkoxyated with either ethylene oxide or propylene oxide and then reacted with acrylic acid to form alkoxyated cyclohexanedimethanol diacrylates. These products are commercially available liquids at room temperature and are readily soluble in acrylates used in UV curable formulations. According to supplier

literature, these monomers exhibit enhanced scratch resistance, impact strength, and abrasion resistance compared with industry standard monomers, such as TPGDA and HDDA.<sup>2</sup> However, alkoxylation leads to increased molecular weight (MW) and less defined structures of the monomers, since the length of side chains is difficult to control. Thus, the specific MW of these monomers (ratio of MW to the number of reactive functional groups) is higher than that of the parent 1,4-cyclohexanedimethanol diacrylate, resulting in reduced crosslink density and lower hardness of the cured coating. As a result, the objective of the present work was to synthesize a diacrylate monomer that retains or improves upon the valuable properties of 1,4-cyclohexanedimethanol diacrylate, but is liquid at room temperature and free of alkoxylation.

Recently, a new, *liquid* cycloaliphatic diol consisting of a unique composition of (*cis, trans*)-1,3-cyclohexanedimethanol and (*cis, trans*)-1,4-cyclohexanedimethanol has been commercialized.<sup>3</sup> In contrast to 1,4-cyclohexanedimethanol, UNOXOL™ Diol (henceforth referred to as 1,3/1,4 CHDM) is a liquid, and can be used to synthesize liquid cyclohexanedimethanol diacrylate monomers.



**Figure 1:** Chemical structure of UNOXOL™ Diol (1,3/1,4 CHDM), which is a liquid cycloaliphatic diol mixture.

This paper will summarize the synthesis of novel liquid (*cis,trans*)-1,3/1,4 cyclohexanedimethanol diacrylates (henceforth, referred to as 1,3/1,4 CHDMA), as well as, the performance properties of the corresponding UV cured coatings.

## Experimental

### Gas Chromatography (GC) Analysis

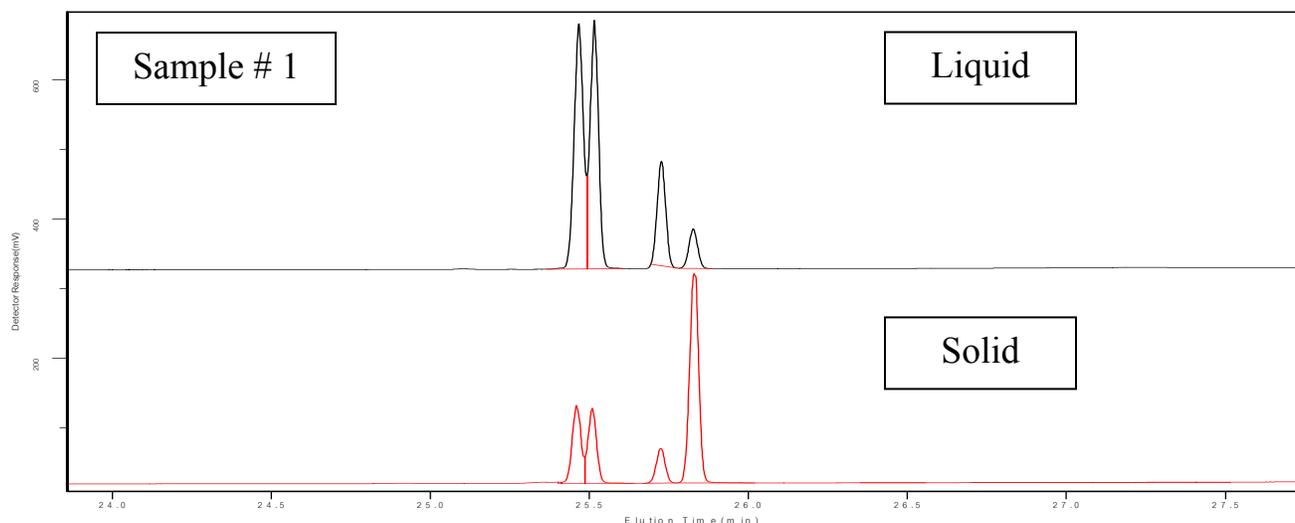
Diol samples were analyzed on a HP 5890 gas chromatograph with an FID using a DB-1 column (60m x 0.32mm x 1.0µm), helium as a carrier gas at 1.5 ml/min constant flow, 300°C injector and detector temperatures, and split ratio 50:1. The oven program was as follows: 80°C for 5 min, 5°C/min for 36 min, and 260°C for 12 min.

Diacrylate samples were analyzed on a HP 6890 gas chromatograph with an FID using a ZB-1 column (60m x 0.32mm x 1.0µm), helium as a carrier gas at 1.5 ml/min constant flow, 300°C injector and detector temperatures, and split ratio 100:1. The oven program was as follows: 50°C for 2 minutes, 10°C/min for 25 min, and 300°C for 6 minutes.

### Preparation of Cyclohexanedimethanol Diacrylates from Standard 1,3/1,4 CHDM (Sample #1)

A mixture of (*cis, trans*) 1,3/1,4-cyclohexanedimethanol (100 g; 0.694 mol of UNOXOL™ Diol) was mixed with toluene (400 ml) and di(isopropyl)ethylamine (252 g; 1.95 mol) and was cooled to 0°C using an ice bath. Acryloyl chloride (153 g; 1.7 mol) in toluene (200 ml) was added slowly over 1 hour while stirring. After the addition, the mixture was stirred for one more hour and then warmed to room temperature. GC analysis revealed that the reaction was complete. The mixture was filtered and the solid residue was washed with toluene (200 ml). The combined filtrate was washed with water (2 x 300 ml), 0.1 M citric acid (5 x 300 ml), saturated NaHCO<sub>3</sub> (300 ml), saturated NaCl (300 ml), and then dried over MgSO<sub>4</sub>. Toluene was removed using a rotovap, and the residue was additionally kept in oil pump vacuum (~0.7 mm Hg) at 60°C for 2 hours. The resulting crude product (180 g) was chromatographed

on silica gel using hexane-ethyl acetate (from 40:1 to 10:1). The pure fractions were combined, 4-methoxyphenol (MEHQ) polymerization inhibitor (100 ppm) in hexane was added, the solvent was evaporated, and the residue was kept in oil pump vacuum to get the constant weight. The pure material (138 g, 79% yield) was characterized by GPC and GC.  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 20.37, 24.84, 25.20, 28.06, 28.73, 29.26, 30.22, 31.82, 32.58, 34.37, 36.60, 36.96 (cyclohexane ring); 67.10, 67.38, 69.27, 69.29 ( $\text{CH}_2\text{O}$ ); 128.41, 128.42, 130.45, 130.49 ( $\text{C}=\text{C}$ ), 166.13, 166.15, 166.16, 166.17 ( $\text{C}=\text{O}$ ). GC/MS: 180 ( $\text{M}^+ - \text{CH}_2=\text{CHCOOH}$ ), 108 ( $\text{M}^+ - 2\text{CH}_2=\text{CHCOOH}$ ), 93, 79, 67, 55. The sample separated into solid and liquid phases at room temperature and the GC scans of both of these phases are shown in Figure 2 below. The isomer composition of each phase, as well as, the overall reaction scheme are highlighted in the Results and Discussion section (see Table 6 and Figure 6).



**Figure 2:** GC scans for the liquid and solid phases of Sample #1 (upper GC: liquid sample; lower GC: solid sample). The isomer elution sequence is *cis*-1,3-; *trans*-1,3-; *cis*-1,4-; *trans*-1,4- as determined by NMR. The *trans*-1,4-diacrylate is the minor isomer in the liquid sample and the major isomer in the solid sample.

### High Efficiency Fractional Distillation of 1,3/1,4 CHDM

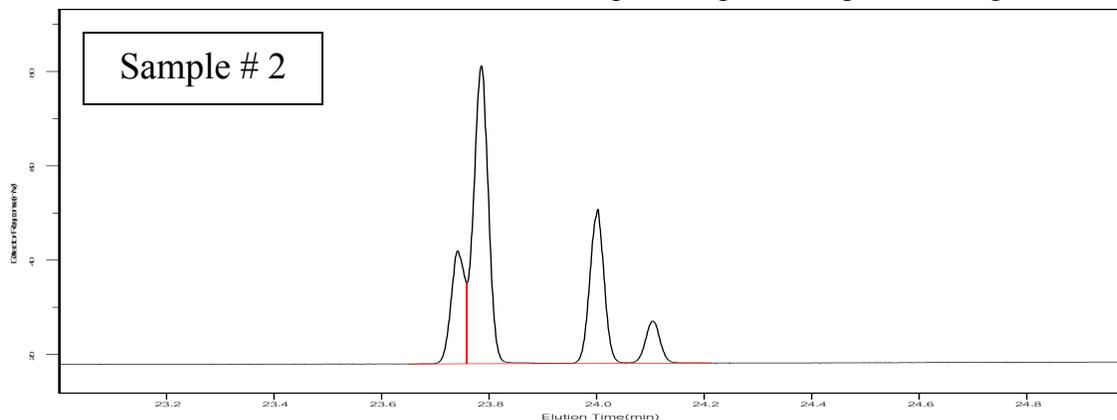
1,3/1,4 CHDM was distilled at 123-131°C and 0.3-0.4 mm Hg using a 50 cm Oldershaw column:

**Table 1:** Scale-up of 1,3-/1,4-Cyclohexanedimethanol Fractional Distillation (2,536 g)

Initial and Distilled Diol Fractions	Amount in Grams (% Initial Material)	<i>Cis</i> -1,3 isomer (%)	<i>Trans</i> -1,4 isomer (%)	<i>Trans</i> -1,3 isomer (%)	<i>Cis</i> -1,4 isomer (%)
Starting Material	2,536 (100)	25.3	30.7	29.9	14.1
Fraction 1B	325 (12.8)	29.0	33.8	24.7	12.5
Fraction 2B	551 (21.7)	28.3	32.7	26.2	12.9
Fraction 3B	1,078 (42.5)	26.4	30.7	28.4	14.6
Fraction 4B	281 (11.1)	23.6	27.3	32.7	16.4
Fraction 5B	129 (5.1)	21.5	24.6	36.0	18.0
Fraction 6B	65 (2.3)	19.3	22.7	37.8	20.2
Fraction 7B	65 (2.3)	16.6	18.3	43.7	21.4
Residue	40 (1.6)	13.1	14.5	48.2	24.1

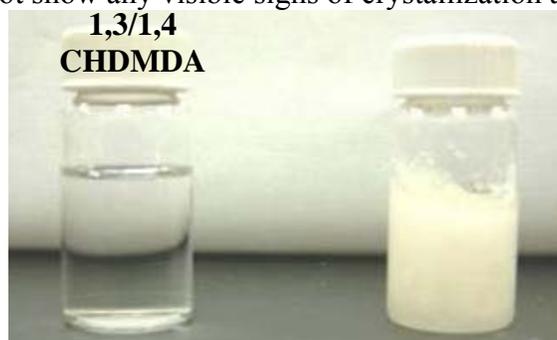
### Preparation of Liquid 1,3-/1,4-Cyclohexanedimethanol Diacrylate (Sample #2)

Sample #2 was prepared by acrylating a late distillation cut (Table 1, Fraction 7B) containing 65 g of 1,3/1,4-cyclohexanedimethanol. The cloudy acrylated sample was filtered to give 56 g of clear liquid cyclohexanedimethanol diacrylate with the composition presented in Table 6 (Sample #2) in the Results and Discussion section. GC scans for this liquid sample are depicted in Figure 3.



**Figure 3:** GC scans for liquid cyclohexanedimethanol diacrylate (Sample #2). The isomer elution sequence is the same as in Figure 2.

Figure 4 shows the difference in appearance between liquid 1,3/1,4 CHDMDA (Sample #2) and the current commercially available solid product: 1,4 cyclohexanedimethanol diacrylate. The liquid diacrylate (containing less than 15% of the trans-1,4-isomer) remains completely liquid when stored at room temperature, and does not show any visible signs of crystallization after 1 year of storage.

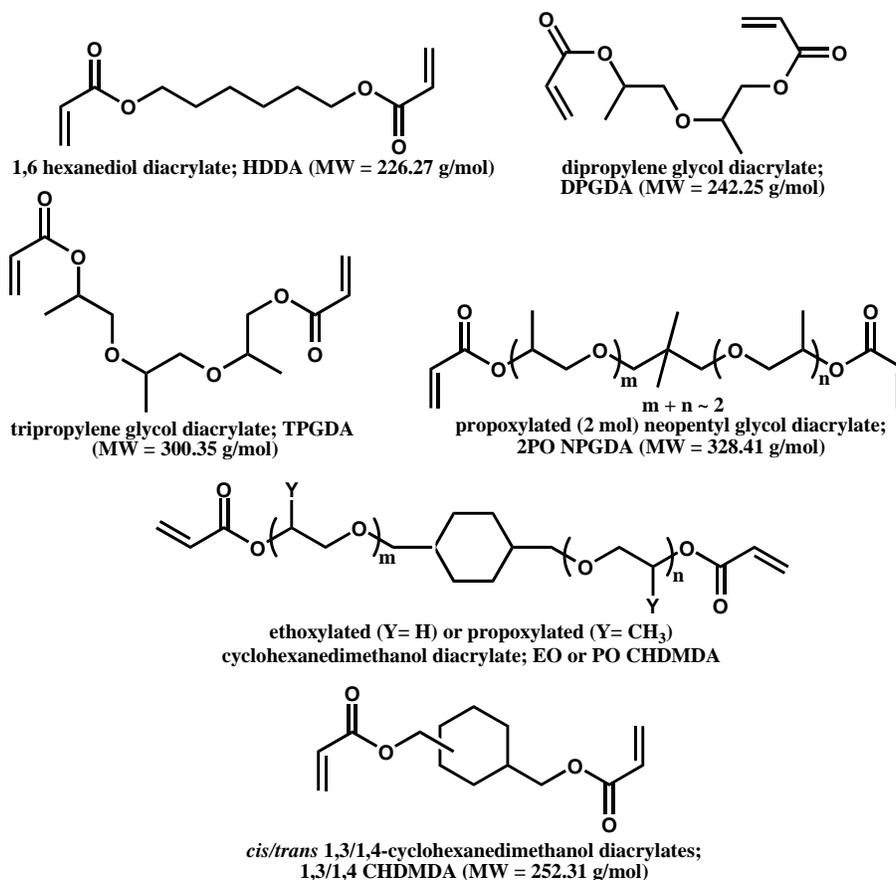


**Figure 4:** Appearance of liquid 1,3/1,4 CHDMDA (left) vs. solid 1,4 cyclohexanedimethanol diacrylate (right).

### Coating Materials

The synthesized liquid (*cis,trans*)-1,3/1,4 cyclohexanedimethanol diacrylate (1,3/1,4 CHDMDA) was then compared to commonly used diacrylate monomers, as well as, alkoxyated cyclohexanedimethanol diacrylates. Three alkoxyated cyclohexanedimethanol diacrylate monomers were evaluated: (i) 3 mole ethoxylated cyclohexanedimethanol diacrylate (3EO CHDMDA), (ii) 5 mole ethoxylated cyclohexanedimethanol diacrylate (5EO CHDMDA), and (iii) 5 mole propoxylated cyclohexanedimethanol diacrylate (5PO CHDMDA). Diacrylate monomers were used as received from the supplier (Sartomer) and without further purification. Chemical structures of the monomers under evaluation are shown in Figure 5.

In addition, the performance of the monomers was evaluated in conjunction with an aliphatic urethane diacrylate (AUDA) oligomer (EBECRYL™ 8402, Cytec). To initiate polymerization, the photoinitiator, 1-hydroxycyclohexyl phenyl ketone (IRGACURE® 184, Ciba), was used.



**Figure 5:** Chemical structures of aliphatic diacrylate monomers used in UV coatings.

### UV Curable Coating Formulations

Coating formulations (~15 grams) were prepared by mixing the acrylates with photoinitiator in a FlackTek SpeedMixer™ (Model DAC 150 FV-K, FlackTek Inc) using a Max 60 Cup and mixing for 5 minutes at 3000 RPM. Specific compositions are shown in Tables 2 and 3.

**Table 2:** Composition of UV Curable Coatings applied on Glass and Polycarbonate

Component	Wt.% of Component
Diacrylate monomer	95.24%
1-hydroxycyclohexyl phenyl ketone photoinitiator	4.76%
TOTAL=	100.00%

**Table 3:** Composition of UV Curable Coatings with Aliphatic Urethane Diacrylate Oligomer and Diacrylate Monomer applied on Polycarbonate

Component	Wt.% of Component
Aliphatic urethane diacrylate (AUDA) oligomer	47.62%
Diacrylate monomer	47.62%
1-hydroxycyclohexyl phenyl ketone photoinitiator	4.76%
TOTAL=	100.00%

### Coating Application and UV Curing

Coating formulations were applied on glass and polycarbonate substrates using wire wound rods. Coatings were applied on glass substrates using a #8 wire wound rod to yield ~10 micron (dry film

thickness) coatings, whereas coatings were applied on polycarbonate substrates using a #20 wire wound rod to yield 35-40 micron coatings. Coatings were UV cured in air using a microwave-powered Fusion UV System (Model DRS-10/12QNH with VPS/I600 lamp system) at a conveyor speed of 10 feet/minute and a 600 W/inch Fusion H electrodeless bulb (100% lamp power). The corresponding irradiance and energy density were measured with a Power Puck<sup>®</sup> radiometer from EIT, Inc. and are shown in Table 4:

**Table 4:** Irradiance and Energy Density used for UV Curing

	<b>UV A</b> <b>(320 – 390 nm)</b>	<b>UV B</b> <b>(280 – 320 nm)</b>	<b>UV C</b> <b>(250 – 260 nm)</b>	<b>UV V</b> <b>(395 – 445 nm)</b>
Irradiance (mW/cm <sup>2</sup> )	1347	1252	154	900
Energy Density (mJ/cm <sup>2</sup> )	1381	1274	151	914

## Property Testing

### *Viscosity*

Viscosities of the liquid materials were measured with a Brookfield DV III+ Rheometer equipped with the Small Sample Adapter (#31 spindle and SC4-35Y sample chamber; 10.5 ml sample volume). Viscosities were measured at 25°C and 20 RPM.

### *Appearance – Initial Haze*

To characterize the appearance of the coatings, the initial haze of the coatings was measured with a haze meter (Haze-Gard Plus, Byk-Gardner), in accordance with ASTM D1003 and D1044. All initial haze data were acquired in total transmittance mode (between 400 and 700 nm) with a port hole size of 1 inch. For coatings on transparent substrates, initial haze values less than 1.0% are desired.

### *Abrasion Resistance Test*

All abrasion tests were performed on coatings applied on polycarbonate using a Taber Abraser (Model 5150, Taber Industries, Inc.) equipped with CS-10F abrasive wheels at a total load of 1000 grams, in accordance with ASTM D1044. Coated samples were abraded for 100 cycles and the percent change in haze (% ΔHaze) was determined by measuring the difference in haze between the unabraded and abraded areas of the coating. A lower % ΔHaze indicates better abrasion resistance.

### *Microindentation Hardness Test*

To assess the hardness of the coatings, a FISCHERSCOPE<sup>®</sup> H100C ultra-low load dynamic microindentation system was used. In this test, a Vickers indenter was pressed into the surface of the coating with an applied force of 5 mN (rate = 5 mN/20 seconds). The maximum load is then held for 20 seconds (creep step) followed by the releasing of the load (rate = 5 mN/20 seconds). A final creep step of 20 seconds completes the test cycle. By taking into account the geometry of the indenter and the penetration depth for the applied force, a universal hardness measurement, HU, is obtained. A higher universal hardness number indicates higher coating hardness.

### *Pencil Hardness*

To assess the hardness and scratch resistance of the coatings, the pencil hardness was measured according to ASTM D3363. In this test, a number of pencil leads of varying hardness are pressed across the surface of the coating and the hardest pencil lead that fails to scratch the coating down to the substrate is reported. The pencil hardness scale is as follows (softest to hardest):

6B < 5B < 4B < 3B < 2B < B < HB < F < H < 2H < 3H < 4H < 5H < 6H

## ***Adhesion***

Adhesion of the UV cured coatings to polycarbonate was measured according to ASTM D3359 (cross-hatch adhesion). Double coated paper tape (3M No. 410) was applied on the scribed cross-hatch area, pressed down, and then stripped away sharply in a direction perpendicular to the surface of the coated sample. The coating was then visually inspected to see whether any of the coating was removed from the substrate by the tape. Specific ASTM ratings for the adhesion test are shown in Table 5. Based on the ASTM rating system, adhesion ratings of 4B and 5B are desired.

**Table 5:** ASTM D3359 Classification for Adhesion

<b>ASTM D3359 Rating</b>	<b>Percent of Coating Removed</b>
5B	0% (Perfect adhesion)
4B	< 5%
3B	5 – 15%
2B	15 – 35%
1B	35 – 65%
0B	> 65%

## ***Solvent Resistance***

Solvent resistance of the UV cured coatings was tested according to ASTM D5402, using methyl ethyl ketone (MEK). In this test, a piece of cotton cheesecloth attached to a 1.5 lb. hammer and saturated with MEK is placed on the coating. The hammer is pushed forward and then back in approximately one second (one double rub). Testing is continued over the same test area for a total of 100 or 200 double rubs. The number of double rubs required to damage the coatings and penetrate to the substrate is reported. Higher double rubs indicate better solvent resistance and surface curing.

## ***Chemical and Stain Resistance***

Chemical and stain resistance of the UV cured coatings was tested by exposing the coatings to various chemicals, according to ASTM D1308. The list of chemicals included: tap water, ethanol, 4% acetic acid, black Rit<sup>®</sup> dye, 5% sodium hydroxide, yellow mustard, Betadine<sup>®</sup> (10% povidone-iodine), and 4% ammonium hydroxide. Several drops of each chemical were placed on the coating and covered with a watch glass for 24 hours. After 24 hours, the chemicals were washed away with water and the coatings were dried. Coatings were visually inspected for any signs of chemical attack or staining and were ranked on a 0-5 scale, from 0 (no effect) through 5 (severe chemical attack or staining).

## ***Accelerated Weathering***

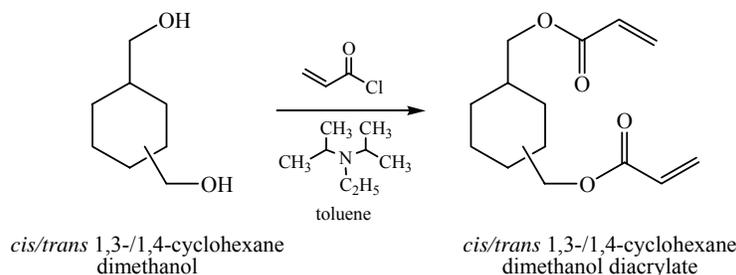
To evaluate the weatherability of the diacrylate monomers, UV cured coatings (~18 microns) applied on poly(methyl methacrylate), PMMA, substrates were placed into a QUV Accelerated Weathering Tester (Q-Lab Corporation). The QUV test was performed in accordance with ASTM G-154, using eight UVB-313 lamps (4 on each side). Irradiance was set at 0.70 W/m<sup>2</sup> and no filters were used. The weathering cycle was four hours of light at 60°C followed by four hours of dark condensation at 50°C. At periodic intervals, the coated samples were taken out of the weathering tester in order to measure the haze and yellowness index.

## **Results and Discussion**

### **Synthesis of Diacrylates from 1,3/1,4 CHDM**

Two options have been explored for making liquid cyclohexanedimethanol diacrylates from 1,3/1,4 CHDM. In the first approach, a standard sample of 1,3/1,4 CHDM was acrylated with acryloyl

chloride in toluene in the presence of di(isopropyl)ethylamine (Figure 6). Aqueous work-up and purification by column chromatography on silica gel resulted in a mixture of the corresponding diacrylates, consisting of both solid (major) and liquid (minor) phases. The desired liquid product was separated by filtration.



**Figure 6:** Acrylation of 1,3/1,4 CHDM with acryloyl chloride in toluene.

GC analysis revealed that the compositions of the liquid and solid phases were strikingly different, as shown in Figure 2 (in Experimental section) and Table 6 below. Based on the analysis, *trans*-1,4-cyclohexanedimethanol diacrylate is the predominant isomer in the solid phase, with the content more than 50%. This isomer was actually isolated by crystallization as a solid material at ambient temperature.

**Table 6:** Isomer Distribution and Physical State of 1,3-/1,4-Cyclohexanedimethanol Diacrylate Samples

Sample	Amount (g)	Physical state	<i>Cis</i> -1,3 isomer (%)	<i>Trans</i> -1,3 isomer (%)	<i>Cis</i> -1,4 isomer (%)	<i>Trans</i> -1,4 isomer (%)
1	138	Solid (major)	18.9	17.4	8.4	<b>52.3</b>
		Liquid (minor)	40.8	37.4	8.4	<b>6.1</b>
2	56	Liquid	17.5	50.4	24.9	<b>7.1</b>

*Note: Percentages of the trans-1,4-cyclohexanedimethanol diacrylate are below 15% in each of the liquid samples.*

Conversely, the concentration of *trans*-1,4-diacrylate in the liquid phase was the lowest among the isomers, as shown in Table 6. Since each diol isomer converts to the same diacrylate isomer (for example, *cis*-1,3-diol → *cis*-1,3-diacrylate, etc.), it was assumed that decreasing the concentration of the *trans*-1,4-diol isomer in the starting 1,3/1,4 CHDM would result in generation of a single phase liquid diacrylate. Therefore, in the second approach, 1,3/1,4 CHDM was first fractionally distilled in vacuum with a 50 cm Oldershaw column containing ~10 trays to produce a number of cuts with noticeably different isomer ratios and reduced concentration of the *trans*-1,4-diol isomer (Table 1).

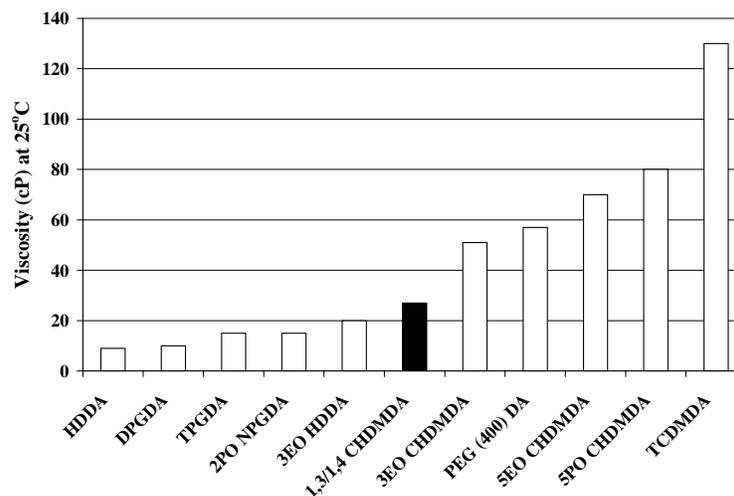
Upon acrylation, the diacrylate mixture showed clear signs of a solid phase when the concentration of the *trans*-1,4-diacrylate exceeded 15%. The appearance of the solid phase varied from haziness when the *trans*-1,4-diacrylate content only slightly exceeded 15% to a substantial crystalline precipitate for a significantly larger percentage of this isomer. However, acrylation of the distillation residue containing less than 15% of the *trans*-1,4-diol results in exclusively a liquid product.

Note that the distillation residue represents only a small percentage of the starting diol, and therefore the industrial distillation will bring very little changes to the combined fractions of the distilled 1,3/1,4 CHDM, so it can most likely be used for regular applications. Thus, sequestering the specific diol composition needed for the liquid diacrylate, which is a specialty product, should not practically affect consistency of the bulk 1,3/1,4 CHDM, which is a commodity chemical.

## Property Testing

### Viscosity

Viscosity is a primary consideration in selecting acrylate monomers, since their diluency can dictate the rheological behavior of the final formulation. Figure 7 compares the viscosity of (*cis,trans*)-1,3/1,4 cyclohexanedimethanol diacrylate (1,3/1,4 CHDMDA) to viscosities reported in supplier literature for commonly used diacrylate monomers. In this figure, polyethylene glycol (400) diacrylate is represented by “PEG (400) DA”; tricyclodecane dimethanol diacrylate is represented by “TCDMDA”.



**Figure 7:** Viscosity comparison of diacrylate monomers

As shown in Figure 7, the viscosity of 1,3/1,4 CHDMDA is ~27 cP, which is higher than HDDA, DPGDA, TPGDA, and 2PO NPGDA, but significantly lower than the alkoxyated cyclohexanedimethanol diacrylates (3EO, 5EO, or 5PO CHDMDA). Moreover, Table 7 illustrates the viscosity reducing power of 1,3/1,4 CHDMDA, when blended with a high viscosity aliphatic urethane diacrylate oligomer (50:50 blend by weight). As Table 7 shows, 1,3/1,4 CHDMDA can significantly reduce the viscosity of the formulation and has superior reducing power compared to the alkoxyated cyclohexanedimethanol diacrylate, 3EO CHDMDA; however, it does not reduce the viscosity to the same extent as HDDA, DPGDA, and TPGDA (most likely due to the bulkier cyclohexyl ring).

**Table 7:** Viscosity Reducing Power of Selected Diacrylate Monomers Blended with Aliphatic Urethane Diacrylate Oligomer (50:50 Blend by Weight)

<i>Formulation</i>	<i>Viscosity (cP) at 25°C</i>
Aliphatic urethane diacrylate (AUDA)	15,000 cP (supplier literature)
AUDA + HDDA	172.0 ± 3.0 cP
AUDA + DPGDA	332.5 ± 1.5 cP
AUDA + TPGDA	416.0 ± 1.0 cP
<b>AUDA + 1,3/1,4 CHDMDA</b>	<b>596.5 ± 1.5 cP</b>
AUDA + 3EO CHDMDA	970.5 ± 1.5 cP

### Performance Properties of UV Cured Coatings

In conjunction with viscosity, the desired performance properties (i.e. hardness, scratch resistance, abrasion resistance, and chemical resistance) of the final UV cured coating are key factors in selecting monomers for a particular application. Table 8 summarizes the performance properties of 10 micron coatings applied on glass, while Table 9 summarizes the results for 35 micron coatings applied

on polycarbonate (PC). *These results are for coatings containing only the diacrylate monomer and photoinitiator.* Henceforth, each entry in the tables below represents the average of three samples and the error is indicated by one standard deviation above and below the mean.

**Table 8:** Properties of 10 Micron UV Cured Coatings with Diacrylate Monomer and Photoinitiator applied on Glass

<u>Diacrylate</u>	<u>Universal</u>	<u>Initial</u>	<u>Pencil</u>	<u>MEK</u>
<u>Monomer</u>	<u>Hardness (N/mm<sup>2</sup>)</u>	<u>Haze (%)</u>	<u>Hardness</u>	<u>Double Rubs</u>
<b>1,3/1,4 CHDMDA</b>	<b>193.44 ± 1.39</b>	<b>0.15</b>	<b>3H</b>	<b>Pass 100 rubs</b>
HDDA	113.85 ± 4.81	0.07	H	Pass 100 rubs
TPGDA	116.41 ± 4.47	0.06	B	Pass 100 rubs
DPGDA	156.40 ± 5.46	0.05	H	Pass 100 rubs
2PO NPGDA	61.07 ± 2.88	0.06	B	Fail 50 rubs
3EO CHDMDA	36.38 ± 3.21	0.04	B	Pass 100 rubs
5EO CHDMDA	18.93 ± 3.73	0.02	< B	Fail 30 rubs
5PO CHDMDA	16.86 ± 2.07	0.08	H	Fail 30 rubs

**Table 9:** Properties of 35 Micron UV Cured Coatings with Diacrylate Monomer and Photoinitiator applied on PC

<u>Diacrylate</u>	<u>Universal</u>	<u>Initial</u>	<u>Abrasion Resist.</u>	<u>Pencil</u>	<u>MEK</u>	
<u>Monomer</u>	<u>Hardness (N/mm<sup>2</sup>)</u>	<u>Haze (%)</u>	<u>(% ΔHaze)</u>	<u>Hardness</u>	<u>Double Rubs</u>	<u>Adhesion</u>
<b>1,3/1,4 CHDMDA</b>	<b>180.04 ± 1.80</b>	<b>0.61 ± 0.02</b>	<b>18.93 ± 4.77</b>	<b>HB</b>	<b>Pass 200 rubs</b>	<b>5B</b>
HDDA	103.82 ± 1.18	0.67 ± 0.03	19.95 ± 4.14	HB	Pass 200 rubs	5B
TPGDA	104.77 ± 2.00	0.68 ± 0.03	36.77 ± 6.31	2B	Pass 200 rubs	1B
DPGDA	141.83 ± 2.08	0.62 ± 0.03	26.58 ± 3.97	2B	Pass 200 rubs	0B
2PO NPGDA	74.29 ± 3.71	0.63 ± 0.03	47.05 ± 5.58	2B	Pass 200 rubs	1B
3EO CHDMDA	49.12 ± 0.58	0.60 ± 0.03	32.51 ± 4.15	3B	Pass 200 rubs	0B
5EO CHDMDA	9.32 ± 0.45	0.63 ± 0.03	26.30 ± 0.35	3B	Pass 200 rubs	0B
5PO CHDMDA	6.80 ± 0.18	0.60 ± 0.01	50.79 ± 0.36	3B	Pass 100 rubs	0B

Both Tables 8 and 9 demonstrate that UV cured coatings derived from 1,3/1,4 CHDMDA have significantly higher hardness (both universal and pencil) compared to the other diacrylates. The higher hardness of 1,3/1,4 CHDMDA can be attributed to the higher crosslink density, as well as, the presence of the cyclohexyl ring. As expected, the alkoxyated cyclohexanedimethanol diacrylates have significantly lower hardness (due to their higher molecular weight and the resulting lower crosslink density of cured coatings), compared to 1,3/1,4 CHDMDA. Moreover, the abrasion resistance of 1,3/1,4 CHDMDA is significantly better than the other diacrylates. As a result, the use of 1,3/1,4 CHDMDA results in coatings that are *both hard and abrasion resistant*. Finally, only the coatings prepared from 1,3/1,4 CHDMDA or HDDA pass the adhesion test on polycarbonate and have 100% adhesion. Coatings based on the other diacrylate monomers show either very poor adhesion or complete adhesion failure to the polycarbonate substrate.

Similar enhancements in performance are seen when 1,3/1,4 CHDMDA is used in conjunction with an aliphatic urethane diacrylate (AUDA) oligomer, as shown in Table 10.

**Table 10:** Properties of 40 Micron UV Cured Coatings with Aliphatic Urethane Diacrylate (AUDA) Oligomer, Diacrylate Monomer, and Photoinitiator applied on Polycarbonate

<u>Diacrylate:</u>	<u>Universal</u>	<u>Initial</u>	<u>Abrasion Resist.</u>	<u>Pencil</u>	<u>MEK</u>	
<u>Hardness (N/mm<sup>2</sup>)</u>	<u>Haze (%)</u>	<u>(% ΔHaze)</u>	<u>Hardness</u>	<u>Double Rubs</u>	<u>Adhesion</u>	
AUDA	9.28 ± 1.08	0.69 ± 0.03	30.90 ± 3.23	3B	Pass 100 rubs	2B
<b>AUDA + 1,3/1,4 CHDMDA</b>	<b>150.74 ± 2.14</b>	<b>0.63 ± 0.05</b>	<b>14.14 ± 2.17</b>	<b>B</b>	<b>Pass 100 rubs</b>	<b>5B</b>
AUDA + HDDA	101.63 ± 3.59	0.58 ± 0.07	27.12 ± 2.87	2B	Pass 100 rubs	5B
AUDA + TPGDA	94.74 ± 6.36	0.59 ± 0.01	42.68 ± 0.91	2B	Pass 100 rubs	5B
AUDA + DPGDA	129.61 ± 2.36	0.60 ± 0.03	40.01 ± 0.13	2B	Pass 100 rubs	5B

When used alone, the aliphatic urethane diacrylate is very soft and shows poor adhesion to the polycarbonate substrate. However, when a 50:50 blend of AUDA with 1,3/1,4 CHDMDA is used, the resulting UV cured coating exhibits tremendous improvement in hardness, abrasion resistance, and adhesion. The other diacrylate monomers also improve the hardness and adhesion of the coatings, but they do not simultaneously improve the abrasion resistance, as does 1,3/1,4 CHDMDA.

### ***Chemical and Stain Resistance***

Coatings with improved chemical and stain resistance are required for demanding applications in which there is a high probability of exposure to harsh environments (i.e. automotive, marine, and aerospace applications). Table 11 illustrates the excellent chemical resistance of UV cured coatings made from 1,3/1,4 CHDMDA (a lower number indicates better chemical resistance). Coatings prepared from 1,3/1,4 CHDMDA were largely unaffected by the tested chemicals, whereas coatings prepared from the other diacrylate monomers were very susceptible to attack by bases, black dye, and mustard. Improved chemical and stain resistance is due to a number of contributing factors, including increased crosslink density, the presence of the cyclohexyl ring, and the hydrophobicity of 1,3/1,4 CHDMDA.

**Table 11:** Chemical Resistance of 35 Micron UV Cured Coatings with Diacrylate Monomer and Photoinitiator on PC.

<i>Chemicals &amp; Stains</i>	<i>1,3/1,4 CHDMDA</i>	<i>HDDA</i>	<i>TPGDA</i>	<i>DPGDA</i>	<i>2PO NPGDA</i>	<i>3EO CHDMDA</i>	<i>5EO CHDMDA</i>	<i>5PO CHDMDA</i>
Tap water	0	0	1	0	2	0	2	1
Ethanol	1	0	2	1	2	1	1	2
4% Acetic acid	0	0	1	0	0	1	0	2
Black RIT <sup>®</sup> dye	0	2	3	2	4	4	5	5
5% NaOH	0	0	2	1	1	1	2	1
Yellow mustard	0	1	1	1	1	2	2	2
Betadine <sup>®</sup>	0	0	0	0	0	2	5	1
4% NH <sub>4</sub> OH	0	1	1	1	4	3	2	3
<b>Total Score=</b>	1	4	11	6	14	14	19	17

### ***Accelerated Weathering***

Accelerated weathering testing is used to assess the influence of ultraviolet light, temperature, and moisture on coatings, in order to simulate outdoor weathering conditions and predict exterior durability. Coatings that show minimal changes in color, adhesion, and coating properties during the course of accelerated weathering are desired for a host of exterior applications (i.e. automotive). Figure 8 compares the QUV performance of 1,3/1,4 CHDMDA versus HDDA, a monomer known for its excellent weatherability in UV cured coatings.<sup>4</sup> *The following results are for coatings containing only the diacrylate monomer and photoinitiator (no light stabilizers were included).* The performance of uncoated PMMA substrates is also included for comparison.

As shown in Figure 8, coatings made from 1,3/1,4 CHDMDA, as well as, HDDA show less than 0.5% change in haze or yellowness index, compared to the uncoated PMMA substrate after exposure to 1000 hours in the QUV, which is indicative of excellent weathering performance. It is important to note that the observed change in yellowness index is largely due to the change in color of the underlying PMMA substrate. Moreover, the coatings did not show any signs of delamination or micro-cracking (which would have been evident by significant changes in the haze of the coatings). Based on this initial investigation, the weathering performance of 1,3/1,4 CHDMDA appears to be quite good and very comparable to the highly weatherable monomer, HDDA. The excellent weatherability of both of these monomers is due to a number of factors, including the aliphatic backbone, hydrophobicity (i.e. resistance to hydrolysis), crosslink density, and lack of alkoxylation.

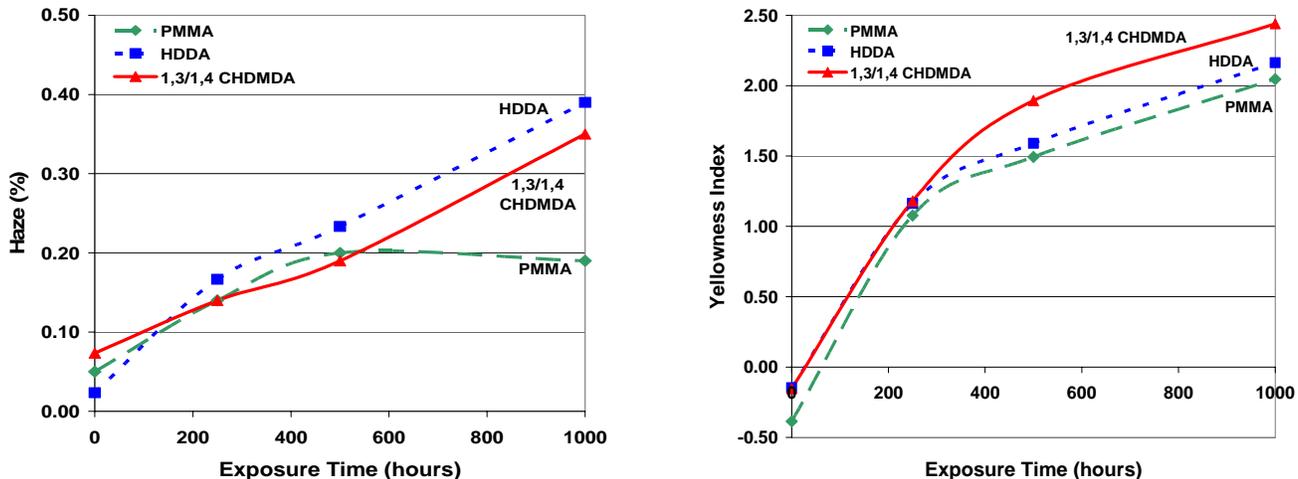


Figure 8: Effect of QUV exposure time on haze and yellowness index of UV coatings applied on PMMA.

## Conclusions

Liquid (*cis,trans*)-1,3/1,4-cyclohexanedimethanol diacrylates are readily soluble in acrylates used in typical UV/EB curable formulations and impart superior hardness, scratch resistance, abrasion resistance, and chemical resistance to the final coatings. This monomer, alone or in combination with acrylated oligomers, appears promising for enhancing performance of UV/EB coatings, inks, and adhesives for a number of substrates, including plastic, paper, wood, metal, and glass.

Acrylation of 1,3/1,4 CHDM with acryloyl chloride in toluene, and in the presence of di(isopropyl)ethylamine, resulted in a mixture of diacrylates consisting of both solid and liquid phases. The liquid product was separated by decantation. Alternatively, high efficiency distillation of 1,3/1,4 CHDM gave late cuts and distillation residue with reduced percentages of the *trans*-1,4-isomer. Acrylation of the obtained 1,3-/1,4-cyclohexanedimethanol compositions (containing less than 15 wt% of the *trans*-1,4-cyclohexanedimethanol isomer) resulted in novel liquid (*cis,trans*)-1,3/1,4-cyclohexanedimethanol diacrylate monomers.

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