

# ● Multifunctional Acrylates via Transesterification

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## 1. Introduction

Acrylic esters with multiple acryloyl groups in the molecule are called multifunctional acrylates, and are widely used as raw materials for formulating ultraviolet (UV) curable and thermosetting resins.

Since launching multifunctional acrylate as a UV-curable resin ARONIX in the 1970s, we have cultivated the technology over many years. We have recently established a production technology for multifunctional acrylates using a new manufacturing method (transesterification).

This article introduces the characteristics of the new multifunctional acrylate products that can now be produced using our transesterification method.

- Glycerol triacrylate (ARONIX MT-3547)
- Ultra-high hydroxyl value PETA (ARONIX MT-3548)
- High purity DPHA (ARONIX MT-3549)

## 2. Our new multifunctional acrylate products

### 2.1 Glycerol triacrylate (ARONIX MT-3547)

Most of the multifunctional acrylates that are on the market are manufactured from alcohols derived from petrochemical resources, such as pentaerythritol and trimethylolpropane.

Glycerol, on the other hand, is an alcohol obtained from animal fats and biomass vegetable oils, and is found in large quantities in the form of fatty acid esters.

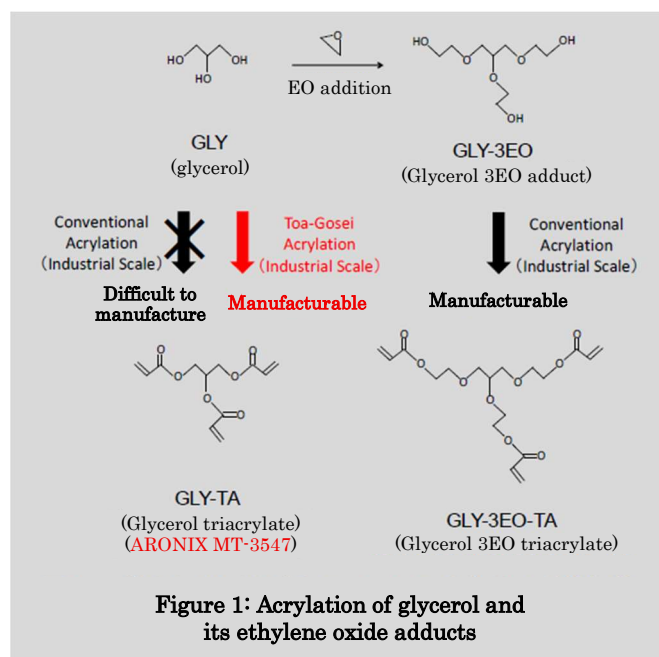
From the standpoint of stable supply of raw-material alcohol and carbon neutrality, there is a need to develop multifunctional acrylates using glycerol as the raw material. However, the multifunctional acrylates derived from glycerol that have been distributed on a commercial scale have so far been limited to acrylates with a structure in which alkylene oxide was added to glycerol, and direct acrylate compounds of glycerol (glycerol triacrylates) have not been available (Figure 1).

The reason for this is that glycerol has a structure in which hydroxyl groups are densely concentrated (1,2-diol structure), and that it is prone to side reactions such as Michael addition during acrylation, which significantly deteriorates the purity of the resulting product. In addition, the glycerol triacrylate produced has a structure with densely packed acryloyl groups, making it highly prone to polymerization and raising concerns about manufacturing difficulties.

Conventionally, alkylene oxide has been added to the hydroxyl groups to increase the distance between functional groups, partly to avoid these technical difficulties.

From a product-performance perspective, the characteristics of multifunctional acrylates, such as rapid curing and the hard coating film formed after curing, are said to be correlated with the concentration of acryloyl groups in the molecule<sup>1)</sup>. Glycerol triacrylate is also an attractive material in terms of performance because it has an even higher concentration of acryloyl groups than pentaerythritol tetraacrylate (PETTA), which is considered a material with high hardness.

While the high viscosity cited as a disadvantage of multifunctional acrylates stems from the large molecular weight of multifunctional acrylates, glycerol triacrylate has a smaller molecular weight than trimethylolpropane triacrylate (TMPTA), which is a low viscosity material, and can achieve even lower viscosity.



Having focused on such potential of glycerol and its direct acrylates, we advanced the development of production technology, and succeeded in industrialization through our proprietary transesterification technology.

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**Table 1** shows the characteristics of glycerol triacrylate (ARONIX MT-3547) that we have launched.

MT-3547 achieved a pencil hardness (a measure of the hardness of the cured coating film) that was comparable to that of PETTA. While PETTA is solid at room temperature and somewhat difficult to handle, MT-3547 has the advantage of being liquid.

Its viscosity is also less than half that of TMPTA, which is a level not previously seen in multifunctional acrylates that are trifunctional or higher.

**Table 1: Comparison between ARONIX MT-3547 and existing acrylates**

	GLY-TA ARONIX MT-3547	GLY- 3EO-TA	PETTA	TMPTA
Acryloyl group concentration (theoretical value, mmol/g)	11.8	7.8	11.4	10.1
Acryloyl group concentration (actual measurement value, mmol/g)	10.7	6.2	10.6	9.4
Pencil hardness <sup>a)</sup> (750 gf)	5H	2H	5H	2H
Viscosity (mPa·s/25°C)	30	117	Wax-like solid <sup>b)</sup>	90

- a) Formulation: Multifunctional acrylate/Irgacure 184 (manufactured by BASF) = 100 parts/5 parts  
 Substrate: Glass  
 Coating: In air, 5 µm film thickness  
 Light source: High-pressure mercury lamp, irradiance 200 mW/cm<sup>2</sup>, dose 5.4 mJ/cm<sup>2</sup> (UV-A)
- b) 75 mPa·s/50°C

An example of a suitable use of MT-3547 is as a reactive diluent for hard-type urethane acrylates<sup>2)</sup>.

Urethane acrylates have high viscosity and are often diluted with solvents or reactive monomers to improve handling during coating. However, the use of solvents requires a drying process after coating, and results in restrictions regarding the coating location due to work environment issues.

In addition, none of the conventional reactive monomers for dilution achieved both low viscosity and sufficient hardness at levels that were required for coating, and a decrease in coating film hardness was unavoidable when a hard-type urethane acrylate was diluted with a reactive monomer.

**Table 2** shows the changes in physical properties of hard-type urethane acrylate when diluted with various reactive monomers.

MT-3547 can maintain the hardness, which is a characteristic of hard-type urethane acrylate, at nearly the same level, while demonstrating a sufficient viscosity reduction effect.

**Table 2: Examples of use of ARONIX MT-3547 (used as a reactive diluent for multifunctional urethane acrylate)**

	Blank	GLY-TA ARONIX MT-3547	TMPTA	TMP- 3EO-TA <sup>a)</sup>
Formulation composition <sup>b)</sup>	100/0	50/50	50/50	50/50
Viscosity (mPa·s/25°C)	18,050	380	1,040	600
Universal hardness <sup>c) d)</sup> (N/mm <sup>2</sup> )	318	302	276	223
Scratch resistance <sup>c) e) f)</sup> Steel wool #0000	No scratch	No scratch	Scratched	Scratched
Flexibility <sup>c) e)</sup> Mandrel test mmø	6	6	6	3

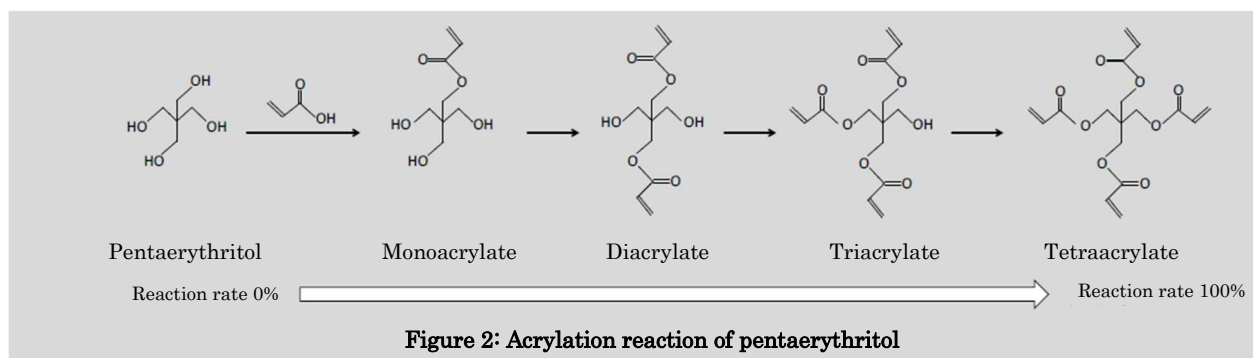
- a) Trimethylolpropane (3EO) triacrylate  
 b) Parts by weight of multifunctional urethane acrylate/parts by weight of reactive diluent  
 c) Formulation: Blended composition/Irgacure 907 (manufactured by BASF) = 100 parts/5 parts  
 Light source: High-pressure mercury lamp, irradiance 500 mW/cm<sup>2</sup>, dose 200 mJ/cm<sup>2</sup> (UV-A)  
 d) Substrate: Glass  
 Coating: In air, 20 µm film thickness  
 e) Substrate: adhesion-modified PET (TOYOBO COSMOSHINE A4300, thickness: 100 µm)  
 Coating: In air, 5 µm film thickness  
 f) 500 gf/cm<sup>2</sup>, 100 cycles

## 2.2 Ultra-high hydroxyl value PETA (ARONIX MT-3548)

By intentionally suppressing the reaction rate in the synthesis of pentaerythritol acrylate and leaving hydroxyl groups, it is possible to obtain a highly functional material with multiple acryloyl groups and hydroxyl groups in the molecule (**Fig. 2**).

These hydroxyl groups are used to impart hydrophilicity to the resin and to produce multifunctional urethane acrylates through reaction with isocyanate. However, the hydroxyl-bearing component content could not be sufficiently increased using existing manufacturing methods.

The reason is that, in dehydration esterification using acrylic acid and acidic catalyst such as sulfuric acid, unreacted acrylic acid and acidic catalyst must be removed by extraction and washing after the reaction completes<sup>3)</sup>. In this step, the hydroxyl-bearing acrylate components tend to partition into the aqueous phase, making them difficult to recover as a product. There is also a transesterification method that does not require extraction and washing, but pentaerythritol is insoluble in most organic solvents and has low reactivity, making it difficult to obtain practical reaction rates with known transesterification catalysts.



Recognizing the potential of hydrophilic curing materials, we pursued the development of highly active, practical transesterification catalysts to overcome this technological challenge. We finally succeeded in obtaining a product with an unprecedented proportion of hydroxyl-bearing components.

**Table 3** shows the characteristics of the ultra-high hydroxyl value pentaerythritol acrylate (ultra-high hydroxyl value PETA, ARONIX MT-3548) that we have launched.

Its compatibility with water (**Photo 1**) and the water contact angle of the cured coating film are superior to those of PETA obtained by existing manufacturing methods, and it is expected to be applied to antifog coatings and resist materials.

**Table 3: Comparison between ARONIX MT-3548 and existing PETA**

	Ultra-high hydroxyl value PETA ARONIX MT-3548	PETA from existing process ARONIX M-305
Viscosity (25°C, approximate value) (mPa·s)	600	600
Product composition (approximate values) Mono/di/tri/tetraacrylate	5/30/50/15	0/0/55/45
Hydroxyl value (approximate value) (mgKOH/g)	280	120
Compatibility with water <sup>a)</sup>	> 15	< 5
Water contact angle <sup>b)</sup> (°)	54	64

- a) Amount of water (g) that causes turbidity (layer separation) when water is added to 100 g of product  
 b) Formulation: Monomer/Irgacure 184 (manufactured by BASF) = 100 parts/3 parts  
 Substrate: adhesion-modified PET (TOYOBO COSMOSHINE A4300, thickness: 100 μm)  
 Coating: In air, film thickness 5 μm  
 Light source: High-pressure mercury lamp, irradiance 500 mW/cm<sup>2</sup>, dose 800 mJ/cm<sup>2</sup> (UV-A)

**Photo 1: Compatibility evaluation with water**



100 g product/5 g water

100 g product/15 g water

### 2.3 High purity DPHA (ARONIX MT-3549)

Synthesis of multifunctional acrylates such as dipentaerythritol hexaacrylate (DPHA) is often carried out by dehydration esterification reactions using acidic catalysts such as sulfuric acid.

However, while acidic catalysts such as sulfuric acid have excellent catalytic activity, they also easily induce side reactions such as Michael addition (**Fig. 3**). Because Michael adducts are difficult to separate during purification, they remain in the product and contribute to its high molecular weight and high viscosity.

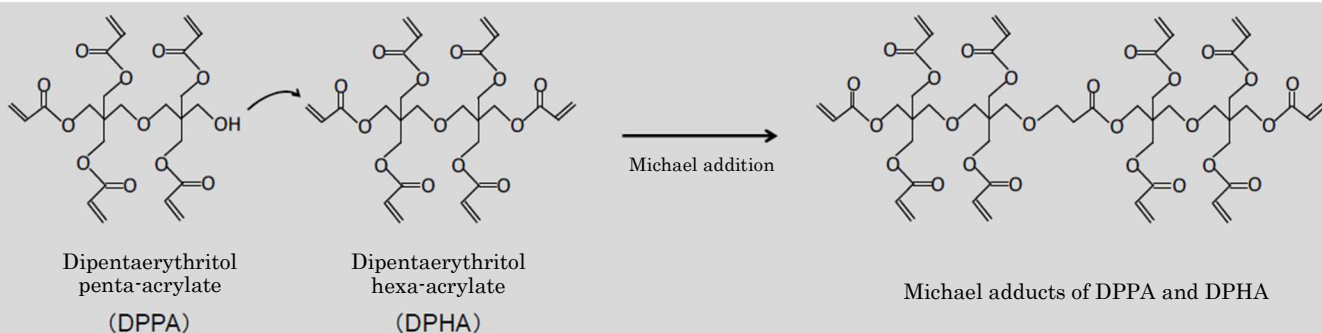
It is also known that trace amounts of impurities derived from acidic catalysts remain in the product, causing quality degradation over time and metal corrosion<sup>3)</sup>. This tendency is especially prominent when alcohols with a large number of hydroxyl groups are used as raw materials.

In our ongoing pursuit of higher quality multifunctional acrylates, we have developed new manufacturing methods that do not rely on acidic catalysts such as sulfuric acid. Using our proprietary transesterification technology, we have achieved both lower viscosity and higher purity in DPHA.

**Table 4: Comparison between ARONIX MT-3549 and existing DPHA**

	High-purity DPHA ARONIX MT-3549	Existing manufacturing method DPHA (using sulfuric acid)
Viscosity (25°C, approximate value) (mPa·s)	3,000	7,000
Color tone (approximate value) APHA	50	30
Curability <sup>a) b)</sup> Number of passes to tack-free state	1 pass	1 pass
Pencil hardness <sup>a) c)</sup> (750gf)	3H	3H
Universal hardness <sup>a) d)</sup> (N/mm <sup>2</sup> )	400	390
Scratch resistance <sup>a) c) e)</sup> Steel wool #0000	No scratch	No scratch

- a) Formulation: Monomer/Irgacure 184 (manufactured by BASF) = 100 parts/5 parts  
 b) Substrate: adhesion-modified PET (TOYOBO COSMOSHINE A4300, thickness: 100 μm)  
 Coating: In air, film thickness 5 μm  
 Light source: High-pressure mercury lamp, irradiance 460 mW/cm<sup>2</sup>, dose 100 mJ/cm<sup>2</sup> (UV-A)  
 c) Substrate: adhesion-modified PET (TOYOBO COSMOSHINE A4300, thickness: 100 μm)  
 Coating: In air, film thickness 5 μm  
 Light source: High-pressure mercury lamp, irradiance 530 mW/cm<sup>2</sup>, dose 800 mJ/cm<sup>2</sup> (UV-A)  
 d) Substrate: Glass  
 Coating: In air, 20 μm film thickness  
 Light source: High-pressure mercury lamp, irradiance 530 mW/cm<sup>2</sup>, dose 800 mJ/cm<sup>2</sup> (UV-A)  
 e) 500 gf/cm<sup>2</sup>, 100 cycles



**Figure 3: Michael addition reaction of DPPA and DPHA**

**Table 4** shows the physical properties of high-purity dipentaerythritol hexaacrylate (high-purity DPFA, product name: ARONIX MT-3549) that we have launched. MT-3549 has significantly lower viscosity than DPFA obtained by the existing manufacturing method using sulfuric acid.

Furthermore, changes over time and metal corrosiveness are improved for MT-3549, since it does not contain impurities derived from acidic catalysts (**Tables 5 and 6, Photo 2**).

Owing to its excellent long-term stability and metal corrosion resistance, MT-3549 is expected to improve durability in automotive applications and to suppress migration in resist applications.

### 3. Conclusion

Engineers in the field of developing curable resins for paints, inks, adhesives, pattern formers, etc. are responsible for optimizing and maximizing product performance by blending multiple resin components. In doing so, they seek resin materials with unprecedented levels of performance, allowing them to broaden their formulation design space and develop new functions.

The multifunctional acrylates obtained by our transesterification method introduced in this article have unprecedented levels of performance in terms of coating film hardness, viscosity, hydroxyl value, compatibility, and purity, and we are confident that they will contribute to the further development of curable resins.

**Table 5: Comparison between ARONIX MT-3549 and existing DPFA**

(change in acrylic acid concentration over time <sup>a)</sup>)

		High-purity DPFA ARONIX MT-3549	Existing manufacturing method DPFA (using sulfuric acid)
Acrylic acid (wtppm)	Before test	5	109
	70°C- After 2 weeks <sup>a)</sup>	8	2,540

a) 50 g of monomer was placed in a 100 cc resin container and stored in an oven at 70°C for 2 weeks. Acrylic acid concentrations before and after leaving in the oven were measured by liquid chromatography.

### Reference

- 1) Y. Sanai, "Optimal Adjustment, Design, and Evaluation of Functional Hard Coating and Its Future Prospects," AndTech Corporation (2007), pp. 43-54.
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- 3) K. Hayashi and J. Kamei, Hitachi Chemical Technical Report, **46** (2006).

**Table 6: Comparison between ARONIX MT-3549 and existing DPFA**

(evaluation of metal corrosiveness <sup>a)</sup>)

		High-purity DPFA ARONIX MT-3549	Existing manufacturing method DPFA (using sulfuric acid)
Aluminum (wtppb)	Before test	< 30	< 30
	70°C- After 2 weeks <sup>a)</sup>	< 30	34
Iron (wtppb)	Before test	< 30	< 30
	70°C- After 2 weeks <sup>a)</sup>	< 30	220
Copper (wtppb)	Before test	< 30	< 30
	70°C- After 2 weeks <sup>a)</sup>	44	49,000

a) 50 g of monomer was placed in a 100 cc resin container with a metal test piece (aluminum, iron, or copper) immersed in it, and stored in an oven at 70°C for 2 weeks. The test piece was then removed and the concentration of metal leached into the monomer solution was measured by ICP mass spectrometry.

**Photo 2: Evaluation of metal corrosiveness**

