

# HYBRID MONOMERS

## 2-(2-VINYLOXY ETHOXY)ETHYL (METH)ACRYLATE

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### ABSTRACT

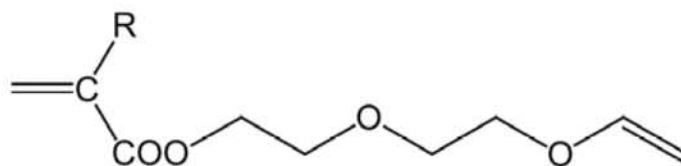
We have been developing the product of Hybrid monomers (2-(2-Vinyloxyethoxy)ethyl acrylate (VEEA) and 2-(2-Vinyloxyethoxy)ethyl methacrylate (VEEM)) which have different kinds of polymerizable groups such as (meth)acryloyl group and vinyl ether group combined in one molecule. These monomers are colorless liquid with low viscosity and low toxicological properties. The characteristic properties of VEEA and VEEM are an ability of viscosity reduction and rapid UV curing. Only small amount of UV radical initiator is necessary to cure without using UV cationic initiator. On the other hand, the mixture of acrylates and vinyl ethers was not cured only by radical initiator. The curing reaction takes place only by radical initiator especially in our hybrid monomers that have (meth)acryloyl group and vinyl ether group in one molecule.

### 1. INTRODUCTION

The radiation curing systems have been developed commercially in many applications such as coatings, adhesives, photoresists and printing inks. Compared with thermal curing processes, UV/EB curing technology provides outstanding advantages in terms of economics, ecology and product quality.

Conventional UV/EB curable monomers are classified in radical curable monomers such as (meth)acrylates, vinyl compounds and in cationic curable monomers such as vinyl ether, epoxy and cycloaliphatic compounds. However, radical curable monomers have disadvantages such as (1) Inhibition of polymerization by oxygen, (2) The large volume shrinkage during the curing process, (3) Strong odor and severe skin irritation, (4) Poor adhesivity to metals. While cationic curable monomers have disadvantages such as (1) Inhibition of polymerization by H<sub>2</sub>O or bases, (2) Proceeding of dark reaction, (3) High prices of monomers and initiators, (4) Limitation of commercially available monomers. <sup>1)</sup>

To overcome these disadvantages of both systems, we focused on designing monomers that have radical polymerizable group and cationic polymerizable group in one molecule. In this paper, we introduce our developing products of hybrid monomers (2-(2-Vinyloxyethoxy)ethyl acrylate (VEEA) and 2-(2-Vinyloxyethoxy)ethyl methacrylate (VEEM)) which have different kinds of polymerizable groups such as (meth)acryloyl group and vinyloxy group installed in one molecule as shown in Figure 1.



R = H: VEEA, R = CH<sub>3</sub>: VEEM

FIGURE 1. Structure of VEEA and of VEEM.

## 2. PROPERTIES

The principal properties of VEEA and VEEM are shown in Table 1. These monomers are colorless liquid with low viscosity and low odor. The toxicological information of VEEA and VEEM are shown in Table 2.

TABLE 1. The Principal Properties of VEEA and VEEM.

	VEEA	VEEM
CAS No.	86273-46-3	76392-22-8
Chemical formula	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>4</sub>
Molecule weight	186.20	200.23
Appearance	Colorless liquid	Colorless liquid
Density <sup>a)</sup>	1.04 g/ml (15 °C)	1.03 g/ml (15 °C)
Viscosity <sup>a)</sup>	3.65 mPa·s (25 °C)	3.19 mPa·s (25 °C)
Boiling point <sup>a)</sup>	115-116 °C/13.3 hPa	122-123 °C/13.3 hPa
Flash Point <sup>b)</sup>	122 °C	129 °C
Solubility in water <sup>a)</sup>	13 g/L (30 °C)	2.2 g/L (30 °C)

a) Data generated by NIPPON SHOKUBAI CO., LTD.

b) Data generated by external institute at a request of NIPPON SHOKUBAI CO., LTD.

TABLE 2. Toxicological Information of VEEA and VEEM.

	VEEA	VEEM
Primary Irritation Index <sup>b)</sup>	P.I.I. = 2.00	P.I.I. = 1.17
Eye Irritation <sup>b)</sup>	Not irritation	Minimally irritation
Acute toxicity LD <sub>50</sub> (Oral-Rat) <sup>b)</sup>	Male: 2026 mg/kg Female: 1790 mg/kg	Male: >5000 mg/kg Female: >5000 mg/kg
Mutagenic effects <sup>b)</sup>	Negative in AEMS test	Negative in AEMS test
Biodegradability <sup>b)</sup>	82 % (BOD)	89 % (BOD)

b) Data generated by external institute at a request of NIPPON SHOKUBAI CO., LTD.

### 3. PERFORMANCE FOR UV CURABLE REACTIVE DILUENTS

The hybrid monomer, VEEA and VEEM, have an ability of viscosity reduction. In Figure 2, the viscosity of composition containing VEEA is shown compared with N-Vinyl pyrrolidone (NVP), Acryloylmorpholine (ACMO) and Diethyleneglycol diacrylate (DEGDA). It is found that VEEA showed comparable performance to NVP, regardless of higher molecular weight than that of NVP.

The hybrid monomer, VEEA and VEEM, showed high performances in radiation curable formulations. In Table 3, UV curing performance of VEEA is shown. We used DEGDA and Diethyleneglycol divinylether (DEGDV) to compare with our hybrid monomers.

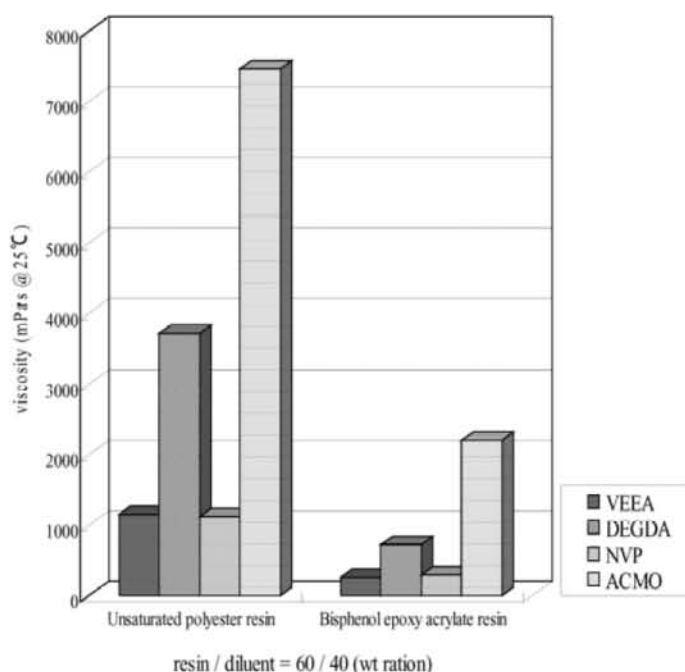


FIGURE 2. Dilution Performances.

The hybrid monomer, VEEA, showed high UV curing performance with only a little UV radical initiator. In addition, vinyl ether group of VEEA is polymerized by UV radical initiator without using UV cationic initiator. These results contradict with common knowledge. The mixture of DEGDA and DEGDV containing acryloyl group and vinyl ether group with equal molar ratio is not cured only by UV radical initiator. These experiments showed that the mixture of acrylates and vinyl ethers was not cured only by radical initiator. The curing reaction only by UV radical initiator was occurred specifically in our hybrid monomers that have (meth)acryloyl group and vinyl ether group in one molecule. We confirmed that the curing reaction was also occurred with UV cationic initiator and UV radical initiator.

TABLE 3. UV Curing Performance of VEEA.

Run No.		1	2	3
VEEA		100	-	-
DEGDA		-	100	53.53
DEGDV		-	-	46.47
Irgacure907		1	1	1
UV curing performance (1)	0.1 J/cm <sup>2</sup>	-	-	--
	0.2 J/cm <sup>2</sup>	-	-	--
	0.3 J/cm <sup>2</sup>	++	+	--
	0.4 J/cm <sup>2</sup>	++	+	--
	0.5 J/cm <sup>2</sup>	++	+	--
UV curing performance (2)	once	++	-	--
	twice	++	-	--
	3 times	++	-	--
	4 times	++	-	--
	5 times	++	-	--

UV curing performance (1): UV radiation device: PM25C-100 (Ushio Inc.) with 250 W ultrahigh-pressure mercury vapor lamp,

Thickness: 300 μm, Surface tackiness: evaluated by finger touch (++ = loss of tack, -- = not cured)

UV curing performance (2): UV radiation device: UB031-5BM (EYEGRAPHICS Co., Ltd.) with 80 W high-pressure mercury vapor lamp,

Thickness: 30 μm, Line speed: 14 m/min, Distance between lamp and substance: 10 cm,

Radiation energy of one time: 125 mJ/cm<sup>2</sup>, Surface tackiness: evaluated by finger touch (++ is loss of tack, -- is not cured)

TABLE 4. UV Curing Performance of VEEA as Reactive Diluent (1).

Run No.		4	5	6	7
Unsaturated polyester resin		60	60	-	-
Bisphenolic epoxy resin		-	-	60	60
VEEA		40	-	40	-
DEGDA		-	40	-	40
Irgacure907		1	1	1	1
Viscosity (25 °C)		1102 mPa·s	2670 mPa·s	295 mPa·s	855 mPa·s
UV curing performance (1)	0.1 J/cm <sup>2</sup>	--	--	-	-
	0.2 J/cm <sup>2</sup>	-	-	-	-
	0.5 J/cm <sup>2</sup>	-	-	-	-
	0.7 J/cm <sup>2</sup>	+	-	-	-
	1.0 J/cm <sup>2</sup>	+	-	-	-
	1.5 J/cm <sup>2</sup>	+	+	-	-
	2.0 J/cm <sup>2</sup>	++	+	+	-

UV curing performance (1): UV radiation device: PM25C-100 (Ushio Inc.) with 250 W ultrahigh-pressure mercury vapor lamp,

Thickness: 300 μm, Surface tackiness: evaluated by finger touch (++ = loss of tack, -- = not cured)

In Table 4, UV curing performance of VEEA used as reactive diluent for unsaturated polyester resin and for bisphenolic epoxyacrylate resin is shown. For both oligomers, VEEA showed high dilution performance. It also showed excellent UV curing performance as reactive diluent for unsaturated polyester resin and for bisphenolic epoxyacrylate resin.

In Table 5, UV curing performance of VEEA and of VEEM used as reactive diluent for unsaturated polyester resin are shown. We used a conveyer system of UV radiation device for this experiment. Although methacrylates have poor UV curing performance, VEEM showed better performance than that of DEGDA. Moreover, VEEA and VEEM showed rapid curing performances in thin film despite the inhibition of polymerization by oxygen.

TABLE 5. UV Curing Performance of VEEA and of VEEM as Reactive Diluent (2).

Run No.		8	9	10
Unsaturated polyester resin		60	60	60
VEEA		40	-	-
VEEM		-	40	-
DEGDA		-	-	40
Darocure1173		1	1	1
UV curing performance (3)	30 $\mu$ m	once	twice	5 times
	10 $\mu$ m	once	3 times	>10 times
Acetone resistance (100 times)		++	++	--

UV curing performance (3): UV radiation device: UB031-5BM (EYEGRAPHICS Co., Ltd.) with 80 W high-pressure mercury vapor lamp,

Thickness: 30  $\mu$ m, Line speed: 14 m/min, Distance between lamp and substance: 10 cm,

Radiation energy of one time: 125 mJ/cm<sup>2</sup>, Surface tackiness: evaluated by number of radiation times until loss of tackiness

Acetone resistance: evaluated after 10 times cured (++ = no change in gloss, -- = complete loss of gloss)

As shown above, we evaluated an ability of viscosity reduction and rapid curing performances of VEEA and of VEEM for various applications.<sup>2), 3)</sup>

#### 4. OTHER USAGE

The hybrid monomer, VEEA and VEEM, have capability to polymerize radically and cationically respectively under the controlled conditions. As shown in Figure 3, these monomers can be used not only for UV/EB curable reactive diluent but also for UV/EB curable oligomers.<sup>4), 5)</sup>

Moreover, various kinds of acetal compounds are derived from VEEA and VEEM by additional reaction. These acetal compounds are easily decomposed by heating or addition of acid.<sup>6) - 9)</sup>

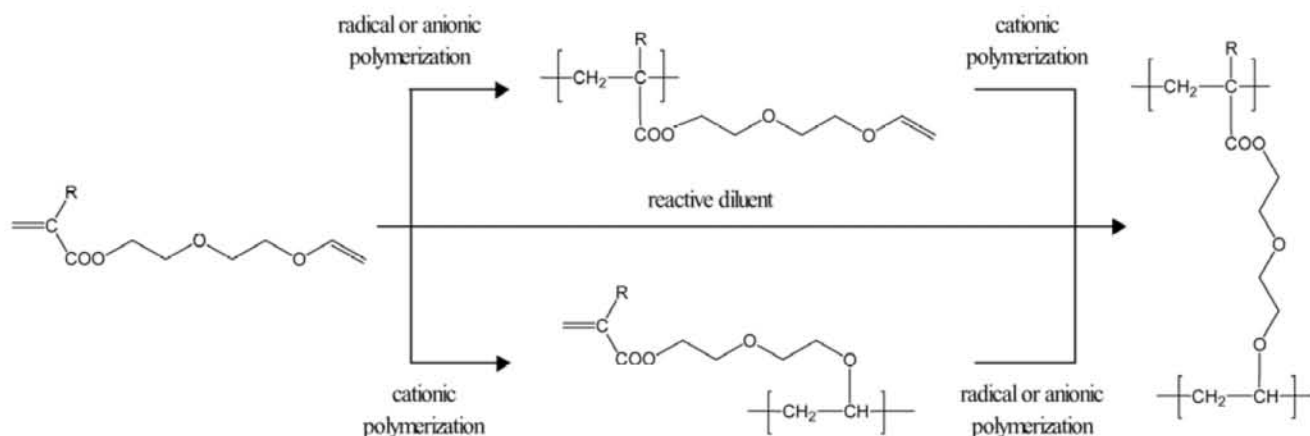


FIGURE 3. Polymerization Scheme of Hybrid Monomers.

## 5. CONCLUSION

The hybrid monomer, VEEA and VEEM, have distinguished properties comparing with conventional radical curable monomers and conventional cationic curable monomers. Especially, VEEA and VEEM show high dilution performances and rapid UV curing performances. These characteristics are shown not only in VEEA of acrylate type but also in VEEM of methacrylate type.

In addition, VEEA and VEEM can be used for functional polymers that have pendants of vinyl ether or pendants of (meth)acrylate. These chemicals also can be used various derivatives.

## 6. REFERENCES

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