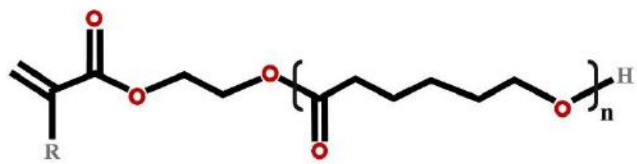
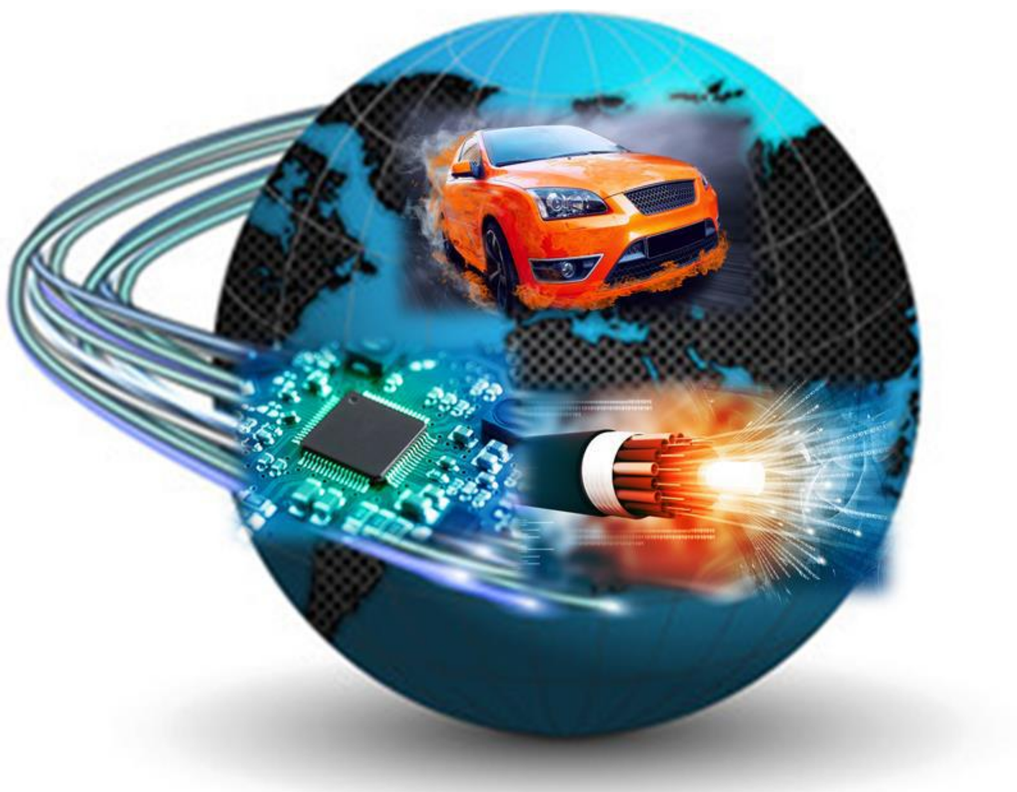
Caprolactone (Meth)acrylate Monomers-Hydroxy Functional



R = H , PLACCEL FA ; Acrylate derivative

R = CH_3 , PLACCEL FM ; Methacrylate derivative

n = 1, 2, 3, 4, 5, 10



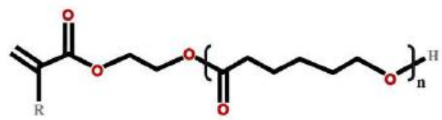
INTEGRITY

INNOVATION

VALUE

RESPECT

Our caprolactone-modified acrylate (FA-series) and methacrylate (FM-series) reactive monomers contain caprolactone chains with a primary hydroxyl end-functionality. These unique hydroxyl-terminated caprolactone-modified (meth)acrylic monomers (HCL(M)As) are incorporated in various acrylic resin systems where they can be subsequently crosslinked with isocyanate or melamine crosslinking agents. The primary hydroxyl moiety reacts particularly well with conventional melamine-formaldehyde crosslinking agents and multi-functional isocyanates to afford high performance coatings, adhesives and films. These caprolactone acrylate monomers are also used in the preparation of UV curable urethane acrylates and UV curable acrylate formulations where the wide range of viscosities of the oligomeric monomers provide good formulating latitude.



R - H, PLACCEL FA ; Acrylate derivative
R - CH_3, PLACCEL FM ; Methacrylate derivative
n - 1, 2, 3, 4, 5, 10

Attributes

By positioning the primary hydroxyl function away from the main chain in an acrylic copolymer, formulators can engineer these oligomeric caprolactone meth(acrylates) to achieve the following benefits, which also apply to UV cured urethane acrylates and acrylate formulations:

- Higher cure speeds with crosslinking agents, higher cure productivity & efficiencies
- Enhanced impact resistance, toughness, and flexibility in the crosslinked product
- Improved chemical resistance, especially to fuels, oils and solvents
- Increases in the mechanical properties and durability of the cured resins
- Balancing hardness and flexibility
- Improved abrasion & scratch resistance, adhesion, and better pigment wetting
- Weatherability improvements and non-yellowing

The HCL(M)A monomers are used in automotive, coil, plastic and elastomer protective coatings, cementitious coatings, powder coatings, adhesives, UV cure and graphic arts.

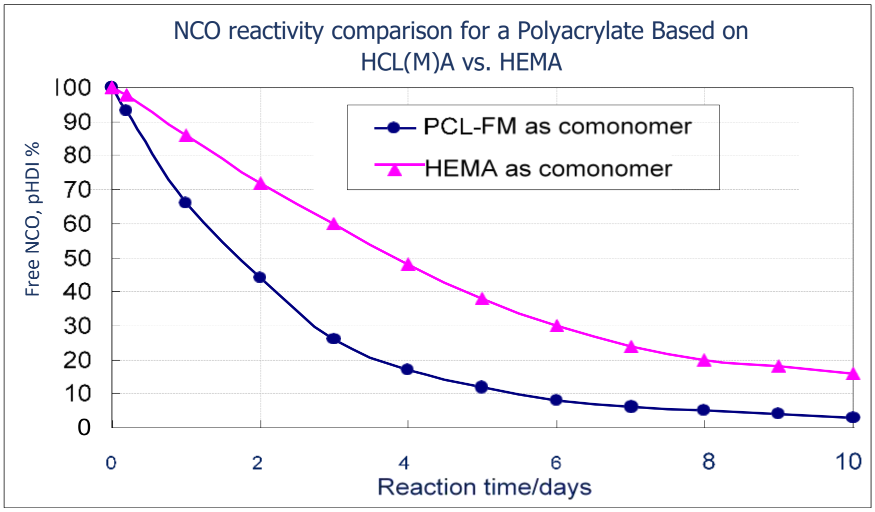
<u>Applications for Hydroxy Functional Caprolactone Acrylates</u>

- Water-borne & Solvent based Coatings
- Powder Coatings
- Adhesives & Sealants
- UV/EB Cured Systems
- Printing Inks
- 3D Printing

Acrylic Copolymer Application

Crosslinkable acrylic and styrenic copolymers using HCL(M)A monomers are used in architectural coatings, OEM product finishes, metal coil coatings, and special-purpose coatings. Protective coatings such as fabric and leather finishes, floor polishes, and wood & paper coatings are also based on these modified acrylate monomers. After copolymerization and film formation, crosslinking is achieved through the primary hydroxy with melamine or multifunctional isocyanate curing agents. Coating technologies include water-borne and solvent based systems, and powder coatings.

The higher reactivity of the hydroxyl function in HCL(M)A vs. that based on HEMA is shown in the figure below. The data is based on measuring the residual NCO content over ten days.



UV Cure Systems

The HCL(M)A monomers offer distinct advantages in UV/EB cured systems including their inherently low viscosities. A basic photopolymerizable formulation consists of a polymerizable vehicle (oligomeric acrylate binder) and a light sensitive compound such as benzophenone or benzoin, capable of initiating a free-radical polymerization through absorbed light energy.

The hydroxy-caprolactone (meth)acrylates can be used directly as UV curable binders or reacted with di-isocyanates in a ratio of 2:1 to produce urethane acrylates. Preferred isocyanates are the aliphatic IPDI and H_{12}MDI. Through the selection of the appropriate HCL(M)A monomer or associated urethane acrylate, coatings and printing inks can be achieved with superior strength, flexibility, durability, adhesion properties and processing characteristics.

The use of caprolactone acrylates has been growing in all aspects of the UV/EB cure market. The urethane acrylates are ideal for 3D printing. Other applications are in coatings, laminating and pressure sensitive adhesives, graphic arts, doming resins, and cure-in-place gasketing systems. An advantage inherent with the HCL(M)A monomers is their low viscosities (the caprolactone chains have low MWDs).

The table below compares the mechanical properties of cured urethane acrylates based on an HCL(M)A vs. systems based on HEA (Hydroxyethyl Acrylate). The system using FA2D exhibited a lower modulus value, but a significantly higher degree of compression repair as measured by Nanoindentation using a displacement at a maximum load value (Elionics Corp.).

Mechanical Properties of Urethane Acrylates

Properties	PCL 205U/IPDI/FA2D	PCL 205U/IPDI/HEA	1,6-HDO-AA/IPDI/HEA
Initial Viscosity of UA	1,900 cps, 75°C	6,200 cps, 75°C	4,900 cps, 75°C
Elongation at Break	79%	99%	106%
Film Modulus	9.8 MPa	77 MPa	21 MPa
Coating Hardness	21 N/mm^2	80 N/mm^2	14.3 N/mm^2
Coating Modulus	100 N/mm^2	6602 N/mm^2	150 N/mm^2
Degree of Restoration	80%	31%	58%

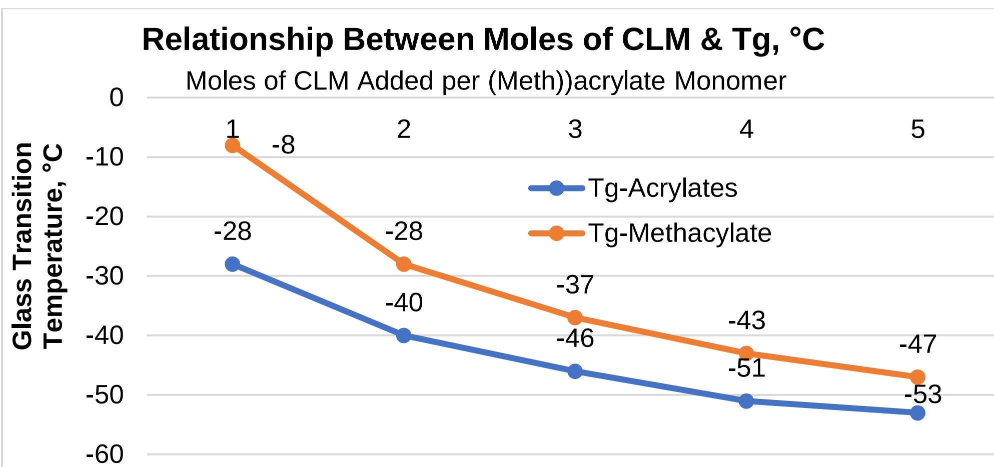
HCL(M)A Product Line

The table below lists the wide range of options available in the Placcel® caprolactone acrylate and methacrylate series produced by Daicel Corporation. Daicel is the only producer of the methacrylate (FM) series. The advantages of the Daicel product line include high purity, low color and odor, a very low level of residual catalyst, and a broad spectrum of Tg's and chain lengths. Levels of di(meth)acrylate in the caprolactone (meth)acrylate monomers are very low (<< 1%) and acrylic polyols prepared from these monomers do not show the presence of gels.

PLACCEL® CAPROLACTONE (METH) ACRYLIC MONOMERS						
Product	**MW**	**Appearance**	**OH Value, KOHmg/g**	**M.P., °C**	**Acid Value, KOHmg/g**	**Viscosity, mPa.s , @ 25 °C**
Placcel° FA Series - Acrylates						
FA 1	230	Liquid	244	-24	3.48	32
FA 2	344	Liquid	163	-12	2.50	78
FA 3	458	Liquid	122	12	1.75	125
FA 5	686	Wax	81.8	36	0.94	130/40°C
FA 10L	1258	Solution	31	Toluene	0.67	48
Placcel° FM Series - Methacrylates						
FM 1	244	Liquid	224.3	-60	3.41	30
FM 2	358	Liquid	154.5	-20	3.244	72
FM 3	473	Paste	116.2	4	1.95	130
FM 4	586	Paste	93.6	15	1.59	200
FM 5	701	Wax	78.2	21	1.36	121/40°C

The HCL(M)A monomers are supplied in 200 Kg. drums and 1 MT IBC totes.

The following figure shows the relationship between the Tg of the Placcel® acrylate (FA series) and methacrylate (FM series) monomers and the moles of caprolactone added per molecule. As the content of caprolactone units increase, the contribution Tg of the acrylic monomer decreases, with the acrylates exhibiting a lower Tg vs. their methacrylate counterpart.



Styrene-Acrylic Coating Properties

Caprolactone methacrylate modified styrene-acrylic resins were prepared in solution using the following recipe. 333 parts of butyl acetate, 333 parts of toluene and 10 parts of DTBP were charged to a reactor and the temperature elevated to 120°C. Then 400 parts of styrene, 100 parts of methyl methacrylate, 100 parts of butyl acrylate, 10 parts of methacrylic acid, 400 parts of FM-1 monomer and 10 parts of AIBN were added dropwise to the mixture over 4 hours. Thereafter, the reaction was continued for an additional 4 hours to obtain a transparent, gel free solution. The same recipe was used with FM-2 monomer and HEMA.

The above acrylic resins were blended with an HDI-biuret multi-functional isocyanate at a OH/NCO ratio of 1.0 and coated onto a steel plate. Contiguous films were obtained by drying and curing the blend compositions. Film performance designated as "●●●●●" indicates an excellent result. Those designed by a "●●●" indicates fair-good performance.

Coating Properties				
		FM-1	**FM-2**	**HEMA**
Blend	Acrylic Polyol	FM-1	FM-2	HEMA
	Curing Agent	HDI Biuret	HDI Biuret	HDI Biuret
Film Properties	Tg, °C	35	40	35
	Pencil Hardness	H	H	F
	Cross-cut Test	100/100	100/100	100/100
	Impact Resistance (500 g.1”)cm	≥50	≥50	≥50
	Water Resistance (50°C, 48 hr.)			
	Whitening	●●●●●	●●●●●	●●●
	Blister	●●●●●	●●●●●	●●●
	Cross-cut	100/100	100/100	100/100
	Alkali Resistance (5% NaOH, 25°C, 48 hr.	●●●●●	●●●●●	●●●●●
	Acid Resistance (5% HCl, 25°C, 48 hr.)	●●●●●	●●●●●	●●●●●
	Solvent Resistance (xylene rubbing, 100 X)	●●●●●	●●●●●	●●●
	Bending Test (2 mm)	●●●●●	●●●●●	●●●
	Stain Resistance (black ink, 48 hr.)	●●●●●	●●●●●	●●●
	Elongation, %	61	77	30

The films obtained using the caprolactone methacrylates exhibited superior chemical, stain and solvent resistance, flex strength, impact properties, elongations and low temperature binding performance versus the system based on HEMA.

Comb Polymer Structures

Comb-shaped polymers can be designed using acrylic and styrene monomers copolymerized with HCL(M)A monomers to create the requisite branches on a high-polymer backbone. The polycaprolactone side chains mainly affect the melt and solution rheological properties of polymers, such as the extensional viscosity, shear viscosity and the important polymer strain hardening behavior under extensional deformations. Application areas include foam and film where strain hardening and extensional viscosity behavior are of high importance. By optimization of these parameters, super-elastomeric properties can be achieved.

Conclusions

Daicel’s product line of hydroxy functional caprolactone (meth)acrylates expand the options for formulators to design specific attributes into an array of acrylic resins and UV curable urethane acrylates. By selecting the appropriate degree of caprolactone modification in the (meth)acrylic monomer, these monomers allow optimizations of the following properties within an acrylic polymer or urethane acrylate system.

The advantages associated with the Daicel line-up of HCL(M)A monomers include high purity, low color and odor, and very low residual catalyst levels. The content of diacrylate monomers is very low allowing gel-free acrylic polyols to be prepared using these monomers.

- Cure efficiency
- Durability
- Toughness
- Chemical Resistance
- Hardness-flexibility balance
- Adhesion
- Abrasion Resistance
- Weatherability

To explore how our range of caprolactone (meth)acrylic oligomer monomers can address your unique applications, partner with the expert teams at Daicel Chem Tech, Inc. Our teams, armed with a wealth of technical knowledge and expertise, can guide you to the best solutions for your applications. **Contact Daicel Chem Tech, Inc. to get started.**

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