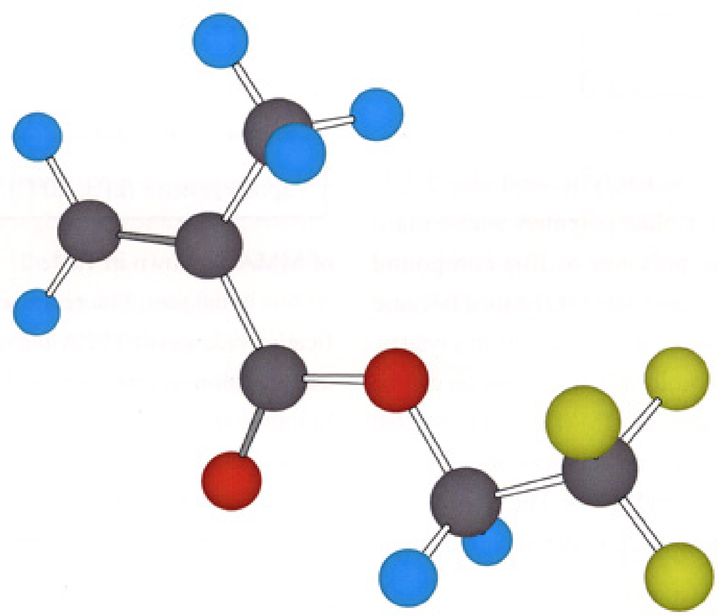
F L U O R E S T E R

2,2,2-TRIFLUOROETHYL METHACRYLATE

CAS. Reg. No. 352-87-4



TOSOH

TOSOH F-TECH, INC.

Introduction

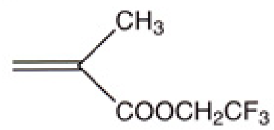
Fluorester is a new trade name assigned to TOSOH F-TECH, INC. the chemical name is 2,2,2-Trifluoroethyl methacrylate. In this technical bulletin, the properties, manufacturing method and applications will be discussed. Here is the specification of Fluorester (Table 1) .

Table 1. Specification

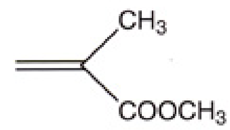
	Specification	Method
Appearance	Clear Liquid	Visual Observation
Color	<20	APHA
Purity	>99.0%	GC(FID) area%
Water	<0.05%	Karl Fischer's Method
Free Acid as Methacrylic acid	<0.1%	Acidmetry

What is Fluorester?

Fluorester is an ester of methacrylic acid and 2,2,2-trifluoroethanol (TFEA). Unlike polymers whose main chain contains fluorine, the polymer of this compound has excellent water repellency and stain resistance because it contains fluorine in its side chain. Like ordinary methacrylates, Fluorester is a transparent and colorless liquid which can be polymerized. Like methylmethacrylate (MMA), it can be used readily as a constituent of solvent-type thermoplastic, thermosetting and emulsion type paints, and others. The physical and chemical properties of Fluorester are compared with of those of MMA as shown in Table 2.



2,2,2-Trifluoroethyl Methacrylate (Fluorester)



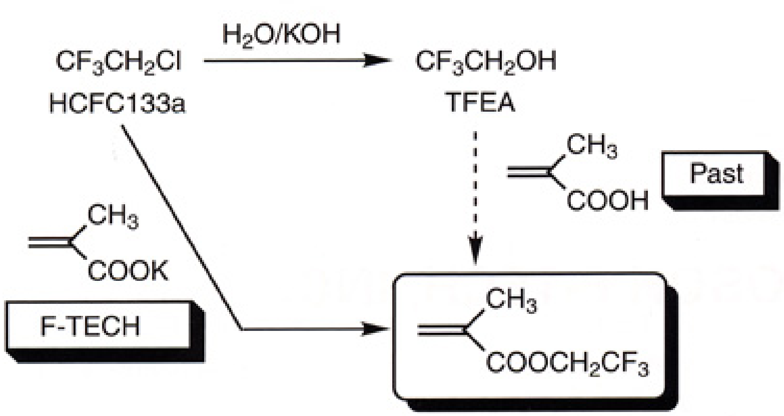
Methyl Methacrylate (MMA)

Table 2. Physical and Chemical Properties

	Fluoresrer	MMA
Molecular Weight	168.12	100.12
Boiling Point (℃)	107	101
Specific Garvity (g/cm^3, 20℃)	1.181	0.94
Refractive Index (nD^{25})	1.359	1.412
Flash Point (℃) closed cup	24.5	13
Viscosity (mPa.s, 20℃)	0.65	0.58
Solubility (wt%, 20℃)		
water in monomer	0:18	1.0
monomer in water	0.04	1.7
Vapor Pressure (kPa, 20℃)	2.2	3.7

In the past, Fluorester was manufactured by the esterification reaction of TFEA and methacrylic acid. However, this esterification reaction required a large amount of acid catalyst because the nucleophilic property of TFEA was weak. Additionally, the conversion rate of TFEA was not sufficient.

Tosoh F-Tech has succeeded in developing a technology capable of hydrolyzing 1-chloro-2,2,2-trifluoroethane (HCFC-133a) in γ-butyrolactone. As a result, the company became the world largest producer of TFEA. Based on TFEA manufacturing technology, the company is developing a large-scale production technology in which Fluorester can be manufactured directly from HCFC-133a and potassium methacrylate. Thus, it became possible for Tosoh F-Tech to supply this compound at lower costs by using its existing facilities and establishing an effective production system capable of coping with the changing demand.



Fluorester

Process of Fluorester

Characteristics of Fluorester polymer

Like MMA, Fluorester easily polymerizes by radical polymerization, as well as bulk, solution or emulsion polymerization. In the bulk or solution polymerization, organic peroxide like benzoyl peroxide and azo-type free-radical initiator like azobisisobutyronitrile are used while in the emulsion polymerization a water-soluble initiator such as potassium persulfate or ammonium persulfate is used.

Fluorester has the Q and e values as shown Table 3 and is able to copolymerize with ordinary vinyl monomers such as acrylic ester, styrene, acrylonitrile and vinyl acetate, and other fluorine-containing acrylic ester.

Table 3. Q and e value of Fluorester

Monomer	Q	e
$CH_2=C(CH_3)COOCH_2CF_3$	1.13	0.98
$CH_2=C(CH_3)COOCH_3$	0.74	0.40
$CH_2=CHCOOCH_2CF_3$	0.97	1.13
$CH_2=CHCOOCH_3$	0.42	0.60

The homopolymer of Fluorester is a transparent and amorphous polymer which has a glass-transition temperature of 82°C (Tg). Compared with MMA, its Tg is lower. However, it maintains a sufficiently high hardness and is considered to be suitable for paints and coating. (Table 4)

The atomic radius of fluorine atom is small for its atomic weight thus fluorine atom is a very compact atom. Due to the strong mutual attraction between electrons and nucleus, the polarization of fluorine atom is small and its electronegativity is the highest among all the elements. Meanwhile, the distance of its C-F bond is short and the bonding energy is higher than that of other bonds. As a result, the polarizability of the C-F bond becomes smaller, lowering the refractive index and dielectric constant of fluorine compounds. For this reason, the refractive index of the homopolymer of Fluorester is lower compared with that of MMA polymer. (Table 5)

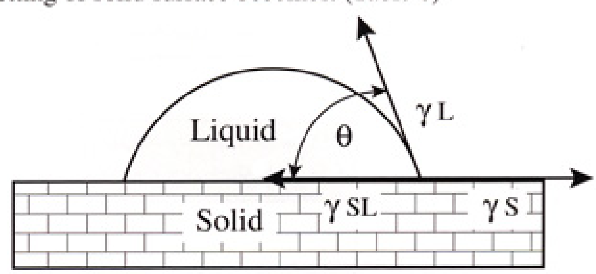
Table 4. Glass Transition Point (Tg) and Mechanical Strength of Homopolymer

Homopolymer	Tg (°C)	Breaking Point (kgf/cm^2)	Elongation (%)	Hardness (Vickers)	Hardness (Rockwell)
Fluorester	82	283	6.3	10.7	47
MMA	123	630	7.1	20.5	90

Table 5. Refractive Index

Homopolymer	Refractive Index (nD)
Fluorester	1.415
MMA	1.490

A smaller polarizability value means that the inter-molecular force is lower. This leads to the decrease in the cohesive energy between molecules and lowers the surface free energy (a force to draw the molecules existing on the surface into the inside) of polymer, thereby making the polymer less wettable and adhesive. Fluorester homopolymer has much better water repellency than MMA polymer. The critical surface tension (γc) indicates the degree of wetting difficulty on a solid surface. The smaller this value, the harder the wetting of solid surface becomes. (Table 6)



$$\gamma S = \gamma SL + \gamma L\cos\theta$$

Critical Surface Tension $\gamma c = \gamma L\ (\cos\theta = 1)$

Table 6. Critical Surface Tension of Homopolymer

Homopolymer	γc (dyn/cm)	Fluorine Content (wt%)
MMA	38	0
Fluorester	19	34
Tetrafluoroethylene	18.5	76

In fluoropolymer, its γc is determined by the structure of its side chain. In the polymer of TFE (Teflon) which has fluorine in its main chain, the weight ratio of fluorine atoms in its molecular weight is as high as 76 percent but its γc is only 18.5 dyn/cm. In general, because copolymers of fluoro olefin and hydrocarbon hydrocarbon olefin which are used for fluoro paints contain fluorine only in their main chain and hydrocarbon vinyl monomer is used for their copolymerization to increase their compatibility, the content of fluorine decreases further which leads to a larger c value. By contrast, in the case of Fluorester homopolymer in which fluorine is introduced in its side chain, its γc value is 19.0 dyn/cm or near that of Teflon although the weight ratio of its fluorine in its molecular weight is only 34 percent. The characteristics such as non-cohesiveness and water and oil repellency which are often the main purpose in the introduction of fluorine into paint become stronger with the decrease in the γc value.

Because of the high affinity of the oxygen atom to the fluorine atom, fluoropolymers enhance oxygen permeability. The use of Fluorester in contact lens fabrication is an example.

The electron-withdrawing properties of Fluorester polymers suggest their use in photocopy toners as an electrical charge control agent.

Toxicological Information

Table 7. Toxicity of Fluorester

Acute Toxicity	
oral	LD_{50}=285mg/kg (male) LD_{50}=429mg/kg (female)
Sensitization	
skin contact eye contact	no irritant (rabbit) minimally irritating (rabbit)
Specific effects	
mutagenicity	negative

Shipping Information

Fluorester is supplied in the following packing :

Steel drums containing 200kg net.

Steel drums containing 20kg net.

Fluorester Applications

More than 600 literature references have been published since 1982. According to reports, Fluorester polymers are or can be utilized for the fabrication of contact lenses, photocopy toners, optical fibers, paints and other coatings, photoresist materials, adhesives, medical instruments.

It is reported that Fluorester based polymers exhibit certain specific properties, including but not limited to water repellency, oxygen permeability, and low refractive index. The superior compatibility of Fluorester with other monomers is expected to broaden its use in newer applications such as resin modification, adhesion products, and in uses yet to be discovered.

Table 8. Fluorester Literature References since 1982

Applications	Number of Literature
Contact lenses	157
Toners	130
Optical fiber	127
Paints	82
Photoresists	28
Medical	13
Adhesive	4
Cosmetics	1
Others	91

Conclusion

Tosoh F-Tech has succeeded in mass-producing trifluoroethyl methacrylate (its trade name: Fluorester) and realized to supply it at low cost. As has been described so far, this compound is a monomer which is easy to handle like MMA while having various characteristics unique to fluoro monomers. However, as its price was too high, its commercial use for coating as one of their components has been slow though there have been many reports on the usefulness of its application to paints. Tosoh F-Tech intends to cooperate with users regarding the development of more applications for Fluorester while expecting that the research work on Fluorester as monomer used for paints will gradually progress and more applications are to be found for the compound.

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