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## PHOTOPOLYMERIZATION UV-THERMOSET MATERIALS

When it comes to the production of functional coatings for high-performance applications, photopolymerization is undoubtedly the method of choice. Considered as a green technology, the photopolymerization reactions are characterized by a solvent-free, low-temperature and rapid through cure process.[1] Since the polymerizations can be induced through free-radical, cationic mechanisms or both simultaneously, a large range of reactive functions is thereby available. SPECIFIC POLYMERS sells various monomers and polymers bearing photopolymerization moieties in addition to specific additional functionalities which offer the opportunity to give targeted properties to your materials (hydrophilicity, hydrophobicity, oleophobicity, optical, anticorrosive, fireproofing, ...).

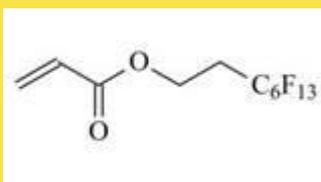
[1] Tehfe, M.; Louradour, F.; Lalevée, J.; Fouassier, J.-P. *Applied Sciences* 2013, 3, 490.

## RADICAL PHOTOPOLYMERIZATION

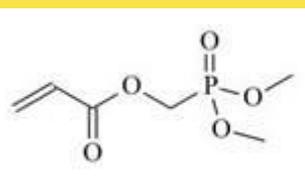
### UV-CURABLE ACRYLATES & METHACRYLATES

Photoinduced radical polymerization of monomers, oligomers or polymers bearing acrylate or methacrylate moieties leads to highly crosslinked polymeric networks. Acrylate monomers are the most reactive and corresponding crosslinking reaction is very fast. Methacrylate monomers are less reactive but efficiently copolymerized when they are combined with acrylate monomers.

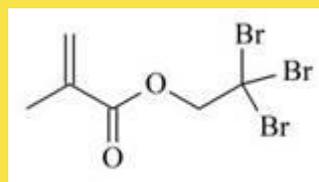
#### • Monofunctional Building-Blocks



**SP-49-007**  
Tridecafluorooctyl Acrylate



**SP-41-010**  
AAPC1-Me

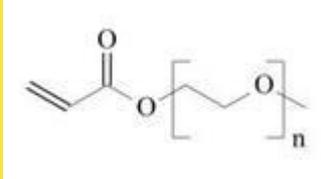


**SP-49-012**  
Tribromoethyl methacrylate

Hydro/Oleophobicity

Metal Adhesion

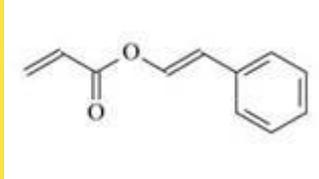
Dental Restorative Materials



**SP-43-3-005**

**PEG Acrylate**

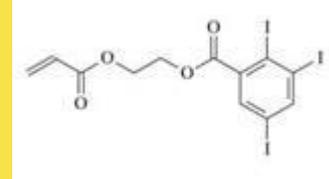
*Hydrophilicity*



**SP-43-0-016**

**Cinnamyl Methacrylate**

*Self-Healing ; Shape memory*

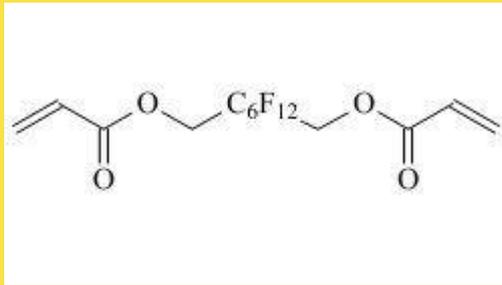


**SP-49-022**

**AOETIB**

*Magnetic Resonance Imaging*

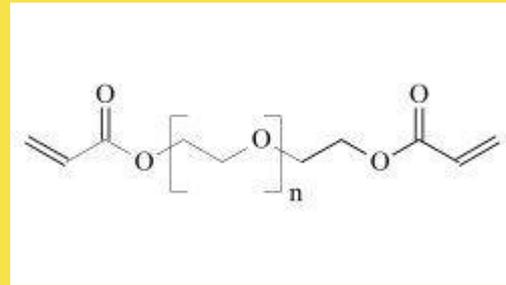
## • Bifunctional Building-Blocks



**SP-60-0-002**

**Dodecafluorooctane Bis-Acrylate**

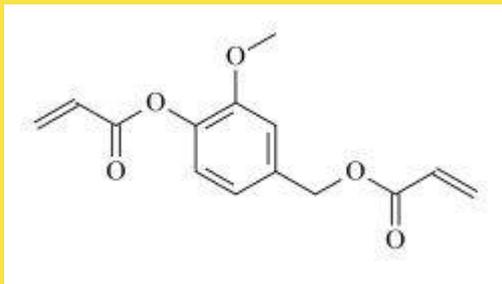
*Hydro/Oleophobicity*



**SP-1P-7-001**

**PEG Bis-Acrylate**

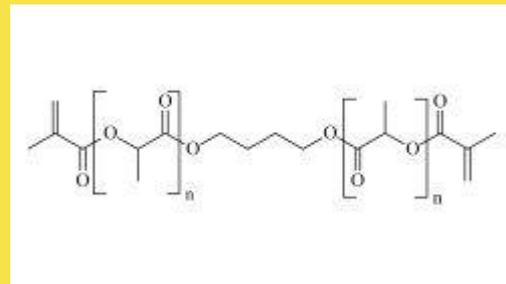
*Hydrophilicity*



**SP-68-029**

**Vanillin Bis-Acrylate**

*Green Chemistry*



**SP-2P-7-004**

**PLA(D,L) Bis-Methacrylate**

*Biomedical*

Molecular weight and functionality of selected building-blocks allow adjusting the mechanical properties of corresponding materials by mastering the crosslinking density. Surface or bulk physico-chemical properties are directly linked to the functionality of the selected monomers or co-monomers.

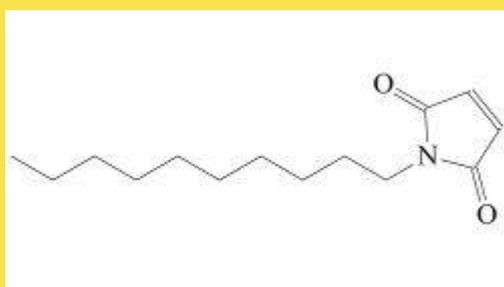
## MALEIMIDES - PHOTOINITIATOR FREE POLYMERIZATION

Maleimides are very interesting chemical functions in high performance applications since they provide excellent thermal stability to the resulting materials and can also be used in self-healing systems.[2] Thanks to the high electrophilic character of the carbon double bond, they can be polymerized according to a free-radical mechanism that can be induced under UV irradiation. Besides, these compounds present the significant advantage to also act as photo-initiator.[3] Maleimides are known to copolymerize, without photo-initiator, with donor monomers such as vinyl ethers, leading to alternated copolymers or thermoset matrices in case of bismaleimide and difunctionalized comonomers.[4] These systems are very attractive because of the very fast rate of polymerization and the low sensitivity to oxygen.

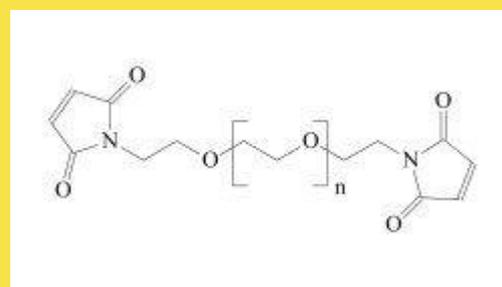
[2] Liu, Y. L.; Chuo, T. W. *Polym Chem-Uk* 2013, 4, 2194.

[3] Dolci, E.; Froidevaux, V.; Joly-Duhamel, C.; Auvergne, R.; Boutevin, B.; Caillol, S. *Polym Rev* 2016, 56, 512.

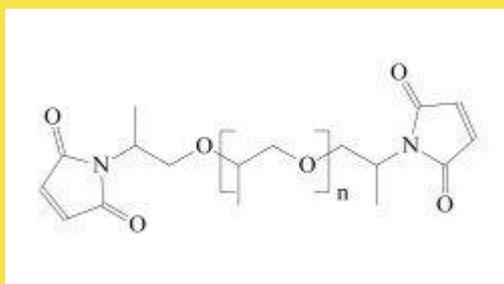
[4] Jonsson, S.; Sundell, P. E.; Hultgren, J.; Sheng, D.; Hoyle, C. E. *Prog Org Coat* 1996, 27, 107.



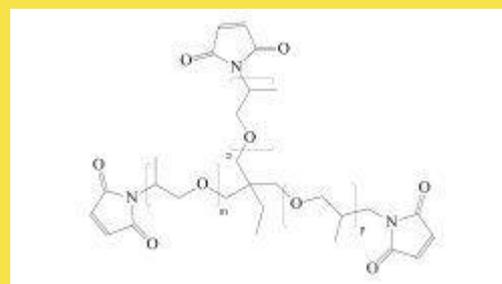
**SP-3-9-002**  
C10 Maleimide



**SP-1P-9-008**  
PEG Bis-Maleimide



**SP-1P-9-014**  
PPG Bis-Maleimide



**SP-1P-9-018**  
PPG Tris-Maleimide

## THIOL-POLYENE RESINS

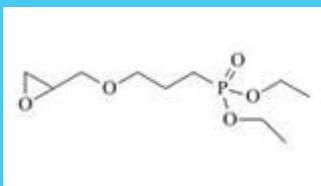
Stable and uniform crosslinked networks can be obtained from the light-induced "click-reaction" between a tetrafunctional thiol and a diene (alkene, vinyl-ether, maleimide, styrene, unsaturated ester). These thiol-ene systems are insensitive to oxygen and conduct to materials with low shrinkage stress. These systems can also be associated to acrylate, leading to ternary networks with various chemical structures.[5]

[5] Hoyle, C. E.; Lee, T. Y.; Roper, T. *J Polym Sci Pol Chem* 2004, 42, 5301.

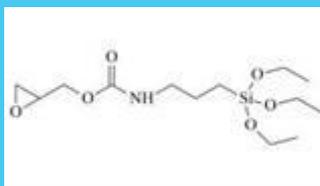
# CATIONIC PHOTOPOLYMERIZATION

## UV-CURABLE EPOXIES

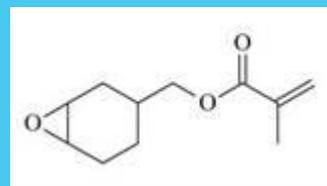
Epoxy functional building-blocks can photopolymerize under UV in the presence of protonic acid produced by photolysis of an onium salt. The cationic photopolymerization is a ring opening polymerization of oxonium ions leading to polyethers chains. The use of multifunctional epoxy building-blocks allow the synthesis of crosslinked materials. The polymerization rate of epoxy is lower than that of acrylate in radical photopolymerization.



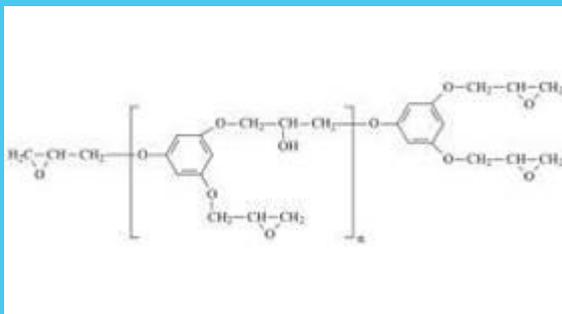
**SP-3-15-005**  
Epoxy C3  
Diethylphosphonate



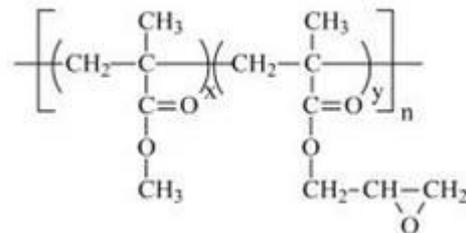
**SP-3-25-001**  
Epoxy Propyl Urethane  
Triethoxysilane



**SP-45-002**  
Epoxycyclohexyl methyl  
methacrylate



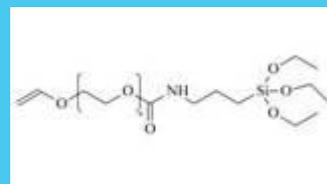
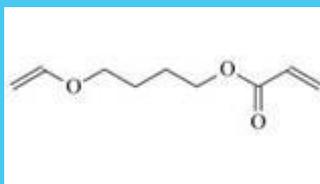
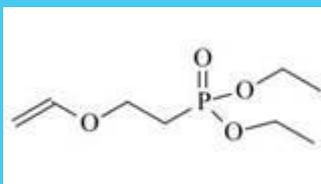
**SP-9S-5-003**  
Phloroglucinol Triglycidyl Ether



**SP-4P-5-002**  
Poly(MMA-*stat*-MAGLY)

## UV-CURABLE VINYL ETHERS

Vinyl ether building-blocks can also be polymerized by UV-cationic photopolymerization. In presence of sulfonium salts, the photopolymerization of vinyl ether monomers occurs with a kinetic rate similar to acrylate radical photopolymerization's.



**SP-61-007**

Ethyl Diethylphosphonate  
Vinyl Ether

**SP-46-008**

4-Vinyloxybutyl acrylate

**SP-1P-72-001**

PEG Vinyl Triethoxysilane

## HYBRID MATERIALS

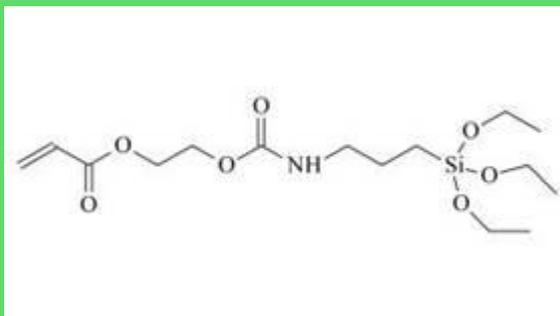
More recently, photopolymerisation has been applied to the preparation of hybrid materials which are the answers to most of the current technological challenges. It was demonstrated for instance that generation of functional nanoparticles into UV-cured resin[6] or the synthesis of sol-gel hybrid films[7] could be achieved in a one-step process. These promising results opened fascinating opportunities for photopolymerisation in the tailor-made materials field.

In this area of application, the sol-gel process has known a tremendous expansion these last decades. The high versatility provided by the tunability of the colloidal state as well as the mild synthetic conditions of this synthetic route were highly attractive for the material's field. It enabled in particular the incorporation of organic components into inorganic network. So far, sol-gel materials were thermally cured but **recent studies highlighted the ability to prepare them upon UV light thanks to the generation of acids during the photoinitiator photolysis.**[7] This major breakthrough happens to be particularly interesting for the development of hybrid films exhibiting good stiffness resistance according to a high throughput process.[8]

[6] Nazar, R.; Ronchetti, S.; Roppolo, I.; Sangermano, M.; Bongiovanni, R. M. *Macromol Mater Eng* 2015, 300, 226.

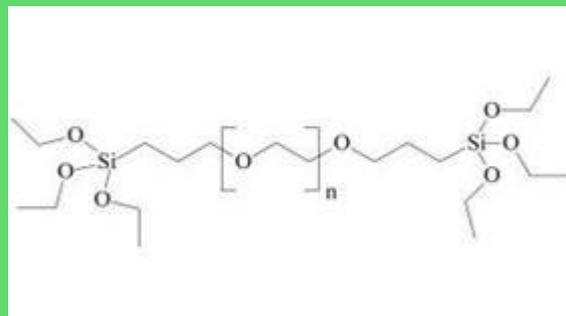
[7] Belon, C.; Chemtob, A.; Croutxe-Barghorn, C.; Rigolet, S.; Le Houerou, V.; Gauthier, C. *J Polym Sci Pol Chem* 2010, 48, 4150.

[8] Belon, C.; Schmitt, M.; Bistac, S.; Croutxe-Barghorn, C.; Chemtob, A. *Applied Surface Science* 2011, 257, 6618.



**SP-42-0-001**

Acrylate Urethane Triethoxysilane



**SP-1P-2-006**

PEG Bis-Triethoxysilane

## Looking for UV reactive Functional Building-Blocks ? SPECIFIC POLYMERS offer CUSTOM SYNTHESIS programs

- SPECIFIC POLYMERS can produce **from grams to hundred grams** depending on the targeted molecule.
- All products are delivered with a **synthesis report** including experimental details and analyses.
- Report on the project progress by **regular phone meeting**
- **Feasibility evaluation** can be proposed depending of customer wishes (targeted structures, quantities)

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