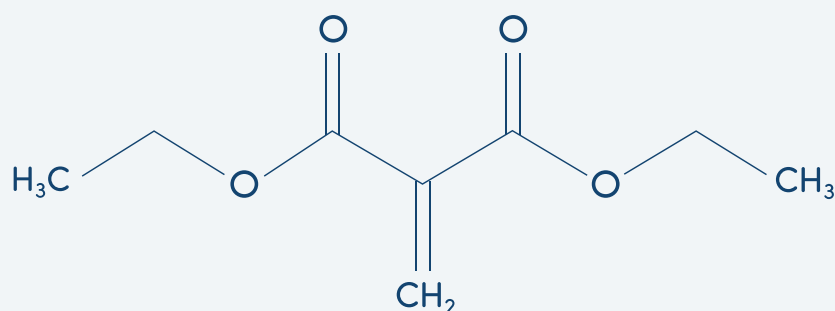


Chemilian™ M1000 XP

Chemilian™ M1000 XP is Diethyl Methylene Malonate (DEMM), CAS# 3377-20-6

Diethyl methylene malonate (DEMM) is a monofunctional methylene malonate monomer having low viscosity that can cure anionically in the presence of weak bases and free radically when it is exposed to a source of free radicals. The symmetric structure results in polymers with high degree of crystallinity. The double bond is significantly more electron withdrawing than those found in acrylates, which makes it susceptible to nucleophilic attack that can promote rapid anionic polymerization and Michael addition with hydroxyls at elevated temperatures, and thiols and amine groups at room temperature.



MONOMER FEATURES

- Low viscosity
- Optically clear
- Compatibility with other methylene malonate monomers and many acrylate monomers and oligomers
- Low- and room-temperature reactivity
- Can be polymerized free radically by UV and heat
- Can be used as an intermediate for synthesis of other methylene malonate functional compounds through transesterification and Michael addition

HOMOPOLYMER PROPERTIES

- Can be readily crystallized
- Rigid
- Optically clear when amorphous

SUGGESTED APPLICATIONS

- Reactive diluent in radically curing systems
- Intermediate in the synthesis of other methylene malonate derivatives
- Random and block copolymerization with other methylene malonates in solution or emulsion

MONOMER PROPERTIES

PROPERTY	VALUE
Purity, %	> 98
Appearance	Clear Liquid
Anionic Inhibitor, ppm	< 30
Radical Inhibitor, ppm	< 10,000
Density at 20°C, g/cc	1.05
Flash Point (Closed Cup), °C	92
Formula Weight, g/mol	172
Viscosity at 25°C, mPa·s	< 10*

*Modeled values

The observed polymer properties will depend on the method of polymerization and components of the formulation.

THERMAL PROPERTIES OF DEMM HOMOPOLYMER

POLY (DEMM)	BULK POLYMER	SOLUTION POLYMER
T_g^* , °C	23	37
T_m^* , °C	164	171
T_d^{**} , °C	234	236
Storage Modulus at 25°C ^{***} , MPa	1890	Not Measured

*Measured by modulated DSC **Measured by TGA ***Measured by DMA

THERMAL CHARACTERIZATION METHODS

- **MDSC:** Ramp rate 1°C/min, modulation amplitude $\pm 1.06^\circ\text{C}$, modulation Period 60s, sample size 4mg. Glass transition temperature (T_g) measured by the midpoint method.
- **TGA:** Ramp rate 5°C/min. Decomposition temperature (T_d) measured as the onset point (the intersection of the zero mass loss and the maximum rate of mass loss tangent lines).
- **DMA:** Ramp rate 5°C/min, frequency 1 Hz, 0.1 % oscillatory strain, tension clamp.

SAMPLE PREPARATION METHODS

Solution Polymerization in Tetrahydrofuran (THF)

- 1 g of DEMM was mixed with 9 g tetrahydrofuran (THF) in a 30 ml HDPE bottle and agitated with a magnetic stir bar. Under rapid mixing, a solution of 1 wt % tetramethyl guanidine (TMG) in THF was added to the solution at a ratio of 1 mol TMG to 1000 mol monomer to initiate polymerization. The polymerization reaction was allowed for 1 hour at ambient temperature. After 1 hour, a molar excess of trifluoroacetic acid (TFA) was added to the solution to terminate anionic polymerization. The molar ratio of TFA to TMG was 2:1. The solution polymer was then precipitated by adding it dropwise to a 300 mL bath of cold methanol under agitation. The polymer was filtered, dried under vacuum for 4 hours at ambient temperature and characterized using TGA and DSC for thermal properties.
- M_n and M_w for the poly(DEMM) obtained by solution polymerization were 98,000 and 351,000, respectively.

Bulk Film Polymerization using Triethylamine (TEA)

- Monomer films were prepared on glass slides. Prior to casting, glass slides were cleaned, passivated with dilute MSA solution and treated with a PDMS coating to facilitate film removal for testing. 0.99 g DEMM was mixed with 0.01 g of initiator solution [10 wt % TEA in Bis(2-ethylhexyl) adipate (BEHA)], centrifuged to eliminate bubbles and cast between two glass slides with 500 micron spacers. Films were cured at ambient temperature for 24 hours. The cured films were peeled off the substrate and characterized using MDSC, TGA and DMA for thermal properties.
- M_n and M_w for the poly (DEMM) obtained by bulk polymerization were 204,000 and 1,670,000, respectively.

STORAGE & HANDLING GUIDE

All methylene malonate based materials must be stored in a cool, dark place away from possible alkaline contamination sources. Refrigeration is recommended when material will not be used for extended periods of time. Presence of alkaline materials, direct sunlight, ignition sources can result in uncontrolled exothermic polymerization. Keep away from glass containers and longer term storage in olefinic containers is recommended. Do not store in an oxygen-free environment as polymerization may occur under these conditions.

Read the SDS sheet for each material before using it. Always use proper ventilation when using Chemilian™ products. Store material away from alkaline substances and in a cool, dark place. Always wear proper PPE when handling Chemilian™ products. Plastic pipettes are recommended for aliquots, and double dipping of the pipette is not recommended as it may have contacted a basic, initiating species and initiate undesired polymerization in the storage container. Consult your SIRRUS representative if you have further questions.



18/06/20