Technical Information

VISIOMER® Amino Methacrylates

INTRODUCTION

Evonik offers a wide range of aminofunctional monomers:

THE "FREE BASES"
The free bases are methacrylate monomers with a tertiary amino group in the side chain VISIOMER® MADAME: 2-dimethylamino ethyl methacrylate and VISIOMER® DMAPMA: 3-dimethylamino propyl methacrylamide.

THE "QUATS"
Quaternary methacrylate monomers are referred to as quats. Their side chain holds the quaternary amino group which is produced from the free bases and a quaternizing agent like methyl chloride. They provide polymers with a cationic charge which usually makes them water soluble. Such polymers are referred to as cationic poly-electrolytes.

VISIOMER® TMAEMC: 2-trimethylammonium ethyl methacrylate chloride and VISIOMER® MAPTAC: 3-trimethylammonium propyl methacrylamide chloride.

ALKYLATED METHACRYLAMIDE
VISIOMER® NIPMAA (N-isopropyl methacrylamide) is an alkylated methacrylamide derivative that completes this product family.

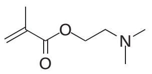
The versatility of these products results from the combination of a free-radically polymerizable double bond with an alkylated amino group.

All monomers listed here can be homopolymerized and copolymerized.

Details on the physical and chemical properties of these monomers are summarized at the end of this technical sheet.

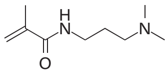
THE "FREE BASES"

VISIOMER® MADAME



CAS-No. 2867-47-2
2-dimethylamino ethyl methacrylate

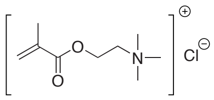
VISIOMER® DMAPMA



CAS-No. 5205-93-6
3-dimethylamino propyl methacrylamide

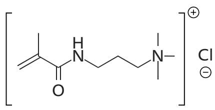
THE "QUATS"

VISIOMER® TMAEMC



75 % in water
CAS-No. 5039-78-1
2-trimethylammonium ethyl methacrylate chloride

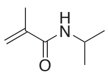
VISIOMER® MAPTAC



50 % in water
CAS-No. 51410-72-1
3-trimethylammonium propyl methacrylamide chloride

ALKYLATED METHACRYLAMIDE

VISIOMER® NIPMAA



CAS-No. 13749-61-6
N-isopropyl methacrylamide

BENEFIT: STABILITY

VISIOMER® NIPMAA, VISIOMER® DMAPMA and VISIOMER® MAPTAC are methacrylamides. They show an increased hydrolytic stability compared to methacrylic esters.

BENEFIT: ADHESION

The free amino group of our amino methacrylates provides increased adhesion to polar surfaces like metal, fibers or pigments.

CHEMICAL REACTIONS

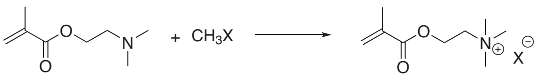
Amino methacrylates can undergo various chemical reactions due to their amino functionality. Possible reactions are illustrated by the example of MADAME. These reactions apply analogously to all other aminofunctional methacrylates mentioned here.

SALT FORMATION

Salt formation occurs with acids. The salts can be polymerized to water-soluble polymers. It is also possible to first polymerize the amino methacrylates and to form the salt afterwards with the help of acids.

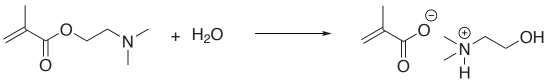
QUATERNIZATION

Quaternization occurs preferably with methyl chloride as the quaternizing agent. The polymers of these „quats" are normally water-soluble.



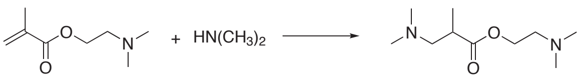
HYDROLYSIS

Aqueous solutions of MADAME hydrolyze autocatalytically, due to the basic character of the dimethylamino group. Neutralization with acids suppresses the hydrolysis. The amide DMAPMA is much more resistant to hydrolysis than the aforementioned ester.



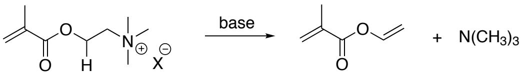
MICHAEL-ADDITION

Beta-substituted, saturated esters or amides are obtained by the addition of primary and secondary amines, for example, to the carbon-carbon double bond. Example: addition of dialkylamine to MADAME.



HOFMANN ELIMINATION

Quaternary ammonium salts can undergo Hofmann elimination under basic conditions. High pH-values and heat promote the release of the amine.



POLYMERIZATION

The most important property of the alkylaminofunctional methacrylates is their capability to undergo free radical polymerization or copolymerization. The „free bases" are usually polymerized in bulk, solution or emulsion, whereas the polymerization of the „quats" normally occurs in aqueous system, e.g. as a polymerization in solution or as an inverse emulsion polymerization. Useful initiator systems are peroxides or azo compounds, as well as, salts of peracids like APS. Using suitable UV-initiators, polymerization induced by UV-light is also possible.

A summary of copolymerization parameters for amino methacrylates is presented at the end of this technical sheet.

APPLICATION AREAS

FREE BASES

Processing aids for bead polymerization
Because of their polarity, aqueous solutions of homo- und copolymers of MADAME are used as dispersing systems in bead polymerization of vinyl monomers.

Paints, primers, coating systems
The adhesion of coating systems on metal surfaces can be noticeably improved by adding small quantities of MADAME as a co-monomer (< 5%) to thermoplastic acrylic resins. Therefore, it is also possible to produce corrosion-resistant paint systems by copolymerization with DMAPMA. Moreover, copolymers with amino-functional methacrylates are characterized by good dispersing action on pigments and fillers. Corrosion-resistant primers containing MADAME and DMAPMA are also used for car finishing.

Fibers, textiles
The application of poly-MADAME and its salts, together with suitable copolymers to cellulose fibers, improves the dyeability of the latter. For acrylonitrile fibers, the same effect is achieved by applying DMAPMA and other amino methacrylates. These can either be used directly as co-monomers in the production of these fibers or are subsequently grafted onto the fiber.

Retention agents and dewatering agents in papermaking
Polymers of acrylamide and amino methacrylates are suitable as retention agents in papermaking. Their efficiency is widely tunable via the molecular weight and the content of amino groups. In (weakly acidic) pulp suspensions, such polymers are present as cationic polyelectro-

lytes. Besides their role as retention agents, they ensure the rapid dewatering of the suspensions.

Cationic pigments (fillers) and starches
By incorporating copolymers of MADAME and methacrylic acid into fillers like alum earth, the filler surfaces can be made cationic. These alumina fillers can be used as reinforcing agents for rubber, as coating agents for paper and textiles, as antistatic additives in plastics and are used in the manufacturing process of lubricants, adhesives and synthetic fibers. Derivatised starches, on the other hand, serve as binders for pigments and fillers in paper coating compounds.

Chemicals for mineral oil production and processing
Copolymers containing NIPMAA can be used as kinetic hydrate inhibitors (KHI) in gas pipelines together with other additives like corrosion inhibitors. KHIs allow the transport of hydrate-forming fluids for a certain period of time, for a given pressure without hydrate formation and consequently avoid the risk of blocking a pipeline.

Ion exchange resins
Copolymers MADAME and DMAPMA are suitable for basic ion exchange resins crosslinked with divinylbenzene.

Fuels and lubricants
As a result of oxidation reactions, stored engine fuels often precipitate so-called „gums". Copolymers of VISIOMER® Terra C17.4-MA and MADAME with their antioxidant and dispersant properties prevent the formation of such deposits. The same applies to diesel oils and kerosene. The viscosity index of lube oils is improved by oil-soluble copolymers with amino methacrylates. Due to their amphiphilic structure, the latter also provide detergent and dispersant properties.

Cosmetic applications: haircare, skincare
Copolymers of DMAPMA or MADAME with N-vinyl pyrrolidone are used as styling polymers in haircare applications providing a volumizing or conditioning effect.

Thermoresponsive resins
Polymeric materials incorporating MADAME are known to be thermo- and pH-sensitive. These polymers can be used for a range of applications, e.g. drug delivery, bio separation, surface modification and tissue engineering.

QUATERNIZED MONOMERS (QUATS)

Flocculation aids for water and waste water treatment
Copolymerization of the quaternized monomers TMAEMC and MAPTAC with acrylamide, for example, leads to water soluble, high-polymeric salts. These products can be custom tailored by varying the amount of quats incorporated in the polymer.

Chemicals for mineral oil production and processing
Quats like TMAEMC and MAPTAC are used in high molecular weight cationic polymers. Applications of such polymers include cationic friction reducers for high salinity, high temperature reservoirs as well as production water treatment. They are suitable for separating the oil-in-water emulsion obtained in crude oil production and processing at the refinery.

Retention agents for papermaking
Copolymers of acrylamide and quaternized monomers — like the corresponding copolymers with amino methacrylates — act as retention and dewatering agents. Being „genuine" polyelectrolytes, they serve their purpose in the acid as well as neutral PH range.

Hair-care products
Cationic polyelectrolytes show good affinity to hair keratin and can be used for cationic adjustment by copolymerization of cationic monomers with hydrophobic, non ionic ones, leading to polyelectrolytes whose films are elastic and less hygroscopic.

Thickeners
Quats like TMAEMC and MAPTAC are used in high molecular weight cationic polymers. High molecular weights are an essential requirement for the use of cationic polyelectrolytes as thickening agents. Unlike flocculating aids, thickeners may also contain crosslinked polymers, which give the thickened product a different flow behavior.

Construction chemicals
Concrete additives such as superplasticizers are used for the production of high-performance concrete and to improve flow characteristics. Typically, they are statistical copolymers of VISIOMER® MPEG methacrylates and methacrylic acid. Quaternized monomers such as TMAEMC can be used to further optimize the performance of superplasticizers and subsequently the mechanical properties of the hardened concrete.

PHYSICAL AND CHEMICAL DATA

	FREE BASES			QUATS	
VISIOMER®	MADAME	DMAPMA	NIPMAA	TMAEMC (75% aq. solution)	MAPTAC (50% aq. solution)
Molecular weight	157.2	170.0	127.2	207.7	220.5
Density (20 °C)	0.97	0.94	1.04	1.1	1.06
Refractive index (20 °C)	1.440	1.478	n.d.	1.466	1.427
Boiling Point (1013 mbar)	182-192 °C	263 °C	209 °C	approx. 100 °C	100 °C
Vapour pressure	0.58 hPa (20 °C)	0.004 hPa (20 °C)	0.039 hPa (25 °C)	< 23 hPa (20 °C)	< 23 hPa (20 °C)
Heat of evaporation	49.4 kJ/mol	n.d.	n.d.	n.a.	n.a.
Melting point	-30 °C	< -60 °C	72-92 °C	-67 °C	< -22.5 °C
Viscosity	1.47 mm2/s (20 °C)	27.4 mPas (20 °C)	n.a.	20-50 mPas (23 °C)	20 mPas (20 °C)
Flash point	69 °C	129 °C	n.a.	n.a.	n.a.
Water solubility	miscible (25 °C)	miscible (20 °C)	30.5 g/l (20 °C)	miscible (20 °C)	miscible (20 °C)

COPOLYMERIZATION PARAMETERS

All listed copolymerization parameters are taken from literature. They depend on the type of polymerization and the chosen polymerization conditions.

MONOMER 1	MONOMER 2	r_1	r_2	SOLVENT	SOURCE
MADAME	MMA	0.85	0.86	Toluene	Polymer International (2009), 58(9), 1014-1022
MADAME	Methacrylic acid	0.35	0.67	Benzene	Makromolekulare Chemie (1984), 185(6), 1177-86
MADAME	Styrene	0.43	1.74	Toluene	Polymer International (2009), 58(9), 1014-1022
MADAME	tBuMA	0.97	1.26	$CDCl_3$	Journal of Polymer Science, Part A: Polymer Chemistry (2005), 43(19), 4666-4669
MADAME	HEMA	0.446	1.626	Bulk	Journal of Polymer Science, Part A: Polymer Chemistry (2003), 41(17), 2659-2666
MADAME	Vinyl acetate	18.91	0.03	Iso-propanol	Vysokomolekulyarnye Soedineniya, Seriya B: Kratkie Soobshcheniya (1984), 26(1), 23-5
MADAME	Acrylamide	1.68	1.26	Water	Journal of Polymer Science, Polymer Chemistry Edition (1986), 24(1), 29-36
DMAPMA	N-Vinyl pyrrolidone	5.67	0.37	Water	Polymer (2004), 45(25), 8311-8322
DMAPMA	N-Isopropyl acrylamide	0.6	0.6	Water	Polymer (2001), 42(15), 6329-6337
DMAPMA	Methacrylic acid	0.41	1.88	Water	Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya (1996), 39(4-5), 191-193
DMAPMA	Acrylamide	1.1	0.47	Water	Journal of Polymer Science, Polymer Chemistry Edition (1986), 24(1), 29-36
TMAEMC	Stearyl MA	0.83	0.25	Ethanol	Journal of Polymer Science, Part A: Polymer Chemistry (2009), 47(18), 4670-4684
TMAEMC	Hydroxy ethylacrylate	1.35	0.65	Water	Journal of Polymer Science, Part B: Polymer Physics (2006), 44(5), 845-853
TMAEMC	Acrylamide	1.4	0.23	Kerosene	Radiation Physics and Chemistry (1997), 50(3), 253-258
TMAEMC	Acrylamide	0.19	2.52	Water	Advances in Chemistry Series (1989), 223 (Polym. Aqueous Media), 175-92
TMAEMC	Acrylamide	1.77	0.32	Water	Gaofenzi Xuebao (2006), (8), 944-947
MAPTAC	Butyl acrylate	2.61	0.92	Ethanol	Journal of Polymer Science, Part A: Polymer Chemistry (2001), 39(7), 1031-1039
MAPTAC	Butyl acrylate	0.9	0.79	Methanol	Journal of Polymer Science, Part A: Polymer Chemistry (2001), 39(7), 1031-1039
MAPTAC	Acrylamide	1.13	0.57	Water	Journal of Polymer Science, Polymer Chemistry Edition (1986), 24(1), 29-36

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EUROPE, AFRICA, MIDEAST
EVONIK RESOURCE EFFICIENCY GMBH
Oil Additives
Kirschenallee,
64293 Darmstadt/Germany
Phone +49 6151 1809

AMERICAS
EVONIK OIL ADDITIVES USA INC.
723 Electronic Drive, Horsham,
Pennsylvania 19044-4050/USA
Phone +1 215 706 5800
TOLL-FREE: +1 888 876 4629

ASIA PACIFIC
EVONIK OIL ADDITIVES ASIA PACIFIC PTE LTD.
3 International Business Park 07-18
Nordic European Centre, Singapore 609927
Phone +65 6809 6571

visiomer@evonik.com
www.visiomer.com

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