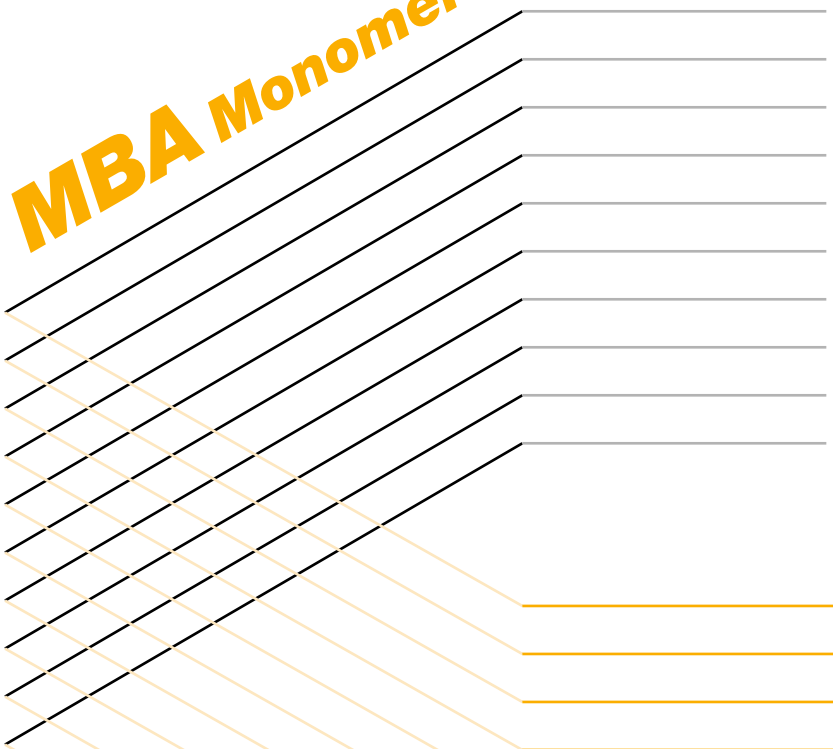
CYLINK®

MBA Monomer



CYTEC

CYLINK® **MBA** ***Monomer (N,N'-Methylene Bisacrylamide)***

INTRODUCTION

CYLINK® N,N'-methylene bisacrylamide (MBA) monomer is a highly effective and very versatile bifunctional monomer that can be copolymerized with acrylics, styrene-acrylics, vinyl-acrylics, vinyl acetate, EVA, etc. via emulsion, solution, suspension or bulk polymerization techniques. It undergoes reactions that are typical of vinyl and amide groups. Currently, it is used in many industries and products, such as exchange resins, thickeners, and coagulating and flocculating agents. It has been especially useful in the preparation of super-absorbent and non-woven products, such as sanitary products, filters and membranes, pharmaceutical hydrogels, and battery separators, for example. A list of representative applications for MBA begins on page 5. ■

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TYPICAL PROPERTIES

Appearance	Crystalline solid
Molecular weight (theoretical)	154.17
Active content	96.0% min
Moisture content	1.0% max
Water insolubles	0.5% max
Inorganic sulfate	2.5% max
Apparent density @ 30°C (86°F)	≈ 1.24 g/cc (10.35 lb/gal)

Solubility	***g/100 ml Solvent***	***Temperature °C***	***°F***
Water	2	10	50
Water	3	25	77
Water	6.5	50	122
Water	13	70	158
Water	42	90	194
Acetone	1.0	30	86
Benzene	<0.1	30	86
Butyl cellosolve	2.5	30	86
Chloroform	0.3	30	86
Dioxane	1.1	30	86
Ethanol	5.4	30	86
Ethyl acetate	0.4	30	86
Heptane	<0.02	30	86
Methanol	8.2	30	86

Stability
MBA is stable at ambient and higher temperatures but melts at 300°C (572°F). Pyrolysis-gas chromatography studies at 200°C (392°F) and 400°C (752°F) show that acrylamide is not released as MBA progressively decomposes. This method is capable of detecting 5-10 micrograms of acrylamide in a 1 gm sample (5-10 mg/liter). Chromatographic indications are that MBA decomposes at these temperatures forming water, carbon dioxide, and nitrogen.

CHEMICAL REACTIONS

The bifunctionl chemistry of MBA has been studied extensively and new uses are constantly being discovered. Some 531 references are included in this brochure, attesting to the intense industrial activity expended in exploring the potential for this monomer. This outstanding property of MBA enables it to form highly crosslinked polymers during copolymerization with various monomers, yet to have available amide groups for further reactions. These reactions, for example, may be with aldehydes for subsequent curing (crosslinking) by heat and/or acid generating catalysts[462].

Polymerization
MBA can be copolymerized or graft polymerized with a variety of monomers and polymer substrates in the presence of conventional vinyl polymerization catalysts such as: peroxides, persulfates and redox systems[171, 182, 415, 418] electron[11, 13, 306], and UV light and ionizing-type irradiators[4], and by photopolymerization[14-23.]

- ☐ MBA copolymerizes with a variety of other monomers in the presence of peroxide catalysts[24, 25] yielding crosslinked, insoluble resins. As an example, the amide may be dissolved in ethylene sulfonic acid, the mixture cooled and diluted with water, and potassium persulfate added as a catalyst. Gelation occurs almost instantly[243]; the dried gel has essentially no water solubility. Similar results have been obtained with other vinyl substituted sulfonic acids, with acrylic acid and with chloromaleic acid[243, 244].

- ☐ Hard resins[6, 36, 38, 178, 469] are synthesized when MBA reacts with alkyd resins and polyesters, such as those of the ethylene glycol-fumarate-sebacate type, at moderately high temperatures and in the presence of a peroxide catalyst.

- MBA also copolymerizes with vinyl sulfonic acids to produce water-insoluble cation exchange resins[243]. When ground and screened to a particle size of about 8-60 mesh, the resin prepared from acrylic acid and MBA has a good ratio between capacity, based on sodium bicarbonate as the exhausting solution, and the density of the resin. Variations in the proportions of the two initial monomers produce variations in the capacity-density ratio[64, 243].

- Anionic, cationic and amphoteric ion exchange resins may be prepared from MBA — refer to ion exchange resins in the Representative Applications section.

- Reaction of MBA with vinyl monomers[511, 514], cellulose[512], starch[513], and polyvinyl alcohols[471] takes place with addition and/or copolymerization at the double bond. Water insensitive polymers and films, thickeners of increased efficiency, fabrics having ion exchange properties, and textiles of increased dyeability are produced. Please see the reactivity ratios on page 4 to determine feed rate and copolymer parameters.

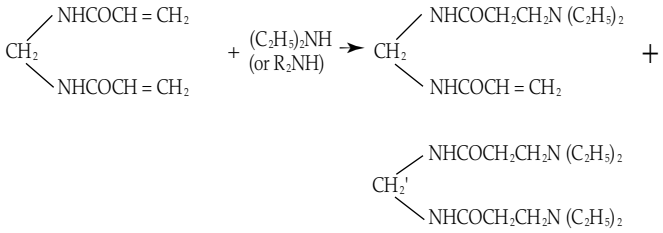
- Polyvinylpyrrolidone and polyamides have been crosslinked with MBA[517-520].

- The mechanism of crosslinking MBA with polyacrylates has also been explored[515].

Crosslinking and Grafting
Irradiation techniques can be used for producing graft polymers. For example, it has been reported in the literature that a polyoxymethylene can be reacted with 2%, 5% and 10% MBA by exposing films of such mixtures to electrons produced by a Van de Graf generator[4].

To impart antistatic properties, grafting of MBA onto textiles has also been explored[484, 485, 497].

Reactions through Vinyl Groups with Amines, Amino Acids, Sulfites and Hydroxy Compounds
MBA reacts wtih amines, amino acids, hydroxy compounds and sodium bisulfites, addition taking place at one or both double bonds[2, 27, 28, 493]:



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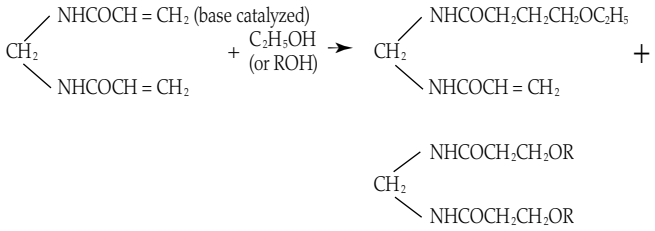
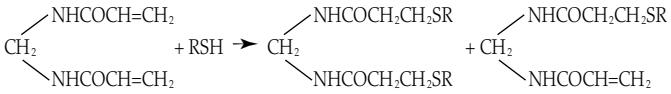


These reactions are not very selective, mixtures of mono- and di-substituted products are produced as well as some unreacted starting materials. Similar mono-substituted products are reported as polymerizing easily in the presence of peroxide catalyst[27, 28].

The kinetics of the base addition of alcohols to many vinyl compounds including MBA has been studied in some detail[516].

Michael Type Addition of Amines
MBA can be reacted by a Michael type addition, with collage "at the free amino groups of the side chain of the lysinyl residues, thus furnishing additional sites for graft polymerization of vinyl monomers"[510].

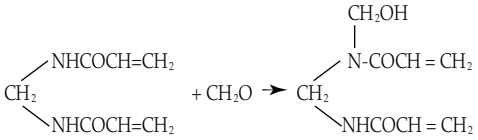
Reactions with Thiols, Thiol Acids, Mercaptans, and Dioximes
Mono- and di-functional thiols and thiol acids[29], mercaptans[30], H_2S[31] and dioximes[29] add to the double bond of MBA:



Reactions with Silanes and Dialkyl Phosphites and Dialky Phosphonates
Silanes[32] and dialkyl phosphites[33] also dialkyl phosphonates[34] can be added to the double bonds of MBA to form polymers or polymerizable compounds useful as flameproofing agents[469, 486, 487, 489, 496].

Diels-Alder Adducts
Polymeric Diels-Alder adducts can be prepared by reacting MBA with *p*-benzoquinone or *p*-phenylenebismaleimide[35, 521].

Reaction with Formaldehyde
MBA reacts with one mole of formaldehyde in basic solution to give a syrup[462]. The exact composition of the products is not known, but reaction probably occurs on one of the nitrogen atoms:



This methylol compound cures to a hard film when heated at 150°C (302°F). Reports indicate that MBA does not react with formaldehyde in acidic solutions[462].

REACTIVITY RATIOS
MBA with Other Common Vinyl Monomers

These reactivity ratios have been calculated using experimentally determined 'Q' and 'e' values. These can be used to predict approximate copolymer composition and determine co-feed ratios and rates (for semi-continuous, delayed co-feed).

MBA = monomer 1

	r1	*r2*	*Reactivity of monomers towards MBA*
MBA:Acrylic Acid	0.51	1.86	0.54
MBA:Acrylamide	0.80	1.21	0.83
MBA:Acrylonitrile	1.51	0.64	1.56
MBA:Butyl Acrylate	1.57	0.63	1.59
MBA:Ethylene	14.90	0.02	50.00
MBA:Ethyl Acrylate	0.65	0.83	1.20
MBA:2-Ethyl Hexyl Acrylate	0.98	0.70	1.43
MBA:Methyl Methacrylate	0.55	1.27	0.79
MBA:Styrene	0.12	0.32	3.13
MBA:Vinyl Acetate	8.40	0.03	33.33

TOXICITY

The single oral LD50s of MBA administered as a 5 percent aqueous solution to young male albino rats and male albino mice are 390 mg/kg and 380 mg/kg, respectively. Doses of 1.0 gm/kg of MBA moistened to form an aqueous paste do not produce any systemic toxicity when applied to the clipped skin of albino rabbits 6 days per week for 2 weeks. MBA is not irritating to rabbit eyes or skin.

The 4-hr. inhalation LC50 (rat) value is estimated to be greater than 2 mg/L. Oral doses of up to 200 mg/kg for 10 weeks produced no neurotoxicity.

MBA dust may be harmful if inhaled.

FDA REGULATIONS

Approved by the U.S. Food and Drug Administration — Food Additives Regulation 175.105 Adhesives — homopolymers or copolymers with other listed monomers.

REPRESENTATIVE APPLICATIONS FOR MBA

Super-Absorbing Sheets

MBA is widely used in this application to prepare hygroscopioc super-absorbing non-woven fabrics and sheets. Some examples of this application are:

- **Sanitary products** such as disposable baby diapers, sanitary napkins and adult incontinence garments. These are generally acrylate-based copolymers containing MBA, coated onto a polyester-based non-woven fabric.[5, 6, 7, 12, 20, 21, 25, 28, 31]
- Linked microgel particles for **adsorbents, filter and separation membranes.** These microgels can be supported on films, papers, fibers, non-woven fabrics, glass, metals and ceramics.[9]
- Temperature-sensitive, **anti-fogging, dew-preventing materials.** These are suitable for interior walls. They absorb moisture at low temperature/high relative humidity, and release moisture at high temperature/low relative humidity.[11, 12, 16, 18]
- **Blood purification** - MBA can be used to prepare non-woven fabric absorbents for extracorporeal circulation therapy, and blood plasma exchange therapy to separate stem cells from blood.[2, 3, 14, 17]
- **Oil dehydrating sheets, battery separators** - Generally in the form of a coating of MBA-sodium acrylate co-polymer on polyolefinic substrates.[1, 4, 8, 9, 15, 19, 20, 29]
- In the manufacture of **pharmaceutical hydrogel particles** used as reaction sites for catalyzing biological enzymatic reactions.[10]
- Water-absorbing composites for **waterproof cables.** These cables can be, for example, PVC, polyolefin, or optical fiber and can be used for overhead and underwater applications.[13, 22, 41]
- In **textile applications** - In a variety of applications including the following:[32-40]
  - Thickeners for use in printing pastes
  - Bondable interlinings for fabrics
  - Cross-linking nucleophilic dyes on wool
  - Sewing threads with improved bonding to water-tight sewn materials
  - Creaseproof cellulosic fibers for wash-and-wear applications
- In the preparation of siloxane primer compositions for bonding fluorosilicone rubbers to metals, plastics, olefinic fibers and non-woven fabrics.[42]

Other applications

- **Adhesives and laminates** - MBA is used in making polymers for laminating fiber glass, paper metals and plastics.[43, 45, 50, 51, 53]
- **Coagulating and flocculanting agents** - In the preparation of clarifying agents for all kinds of beverages and foods, and precipitants, flocculants and settling agents.[98-100]
- **Coatings** - MBA can be used in the following coating applications:
  - Anti-corrosive films on metals[60]
  - Wood coating[55]
  - Powder coatings[56]
  - Room temperature curable coatings[57-59]
  - Coatings for TV color tubes[54]

- ☐ **Ion Exchange Resins -**
  - ☐ Cation exchange resins[243, 244, 248, 251, 254]
  - ☐ Amphoteric exchange resins[247, 253]
  - ☐ Anion exchange resins[249, 252]
  - ☐ Exchange resins for biologically active materials[255]
  - ☐ Solvent gel ion exchange resins[250]
  - ☐ Ion exchange sheets & films[245, 402]
  - ☐ Pearly cation exchange resins[251]
- ☐ **Construction materials** - In polymers used for waterproofing concrete and masonry, increasing the compression strength and hardness of cement, and in manufacturing gels for stabilizing concrete [61-68]
- ☐ **Fiber forming compositions** - For fibers having improved properties, such as spinning, dimensional and thermal stability, decreased dirt absorption, better dyeability and decreased static build-up [69, 70-80, 96]
- ☐ **Foam products** - In polymers used in heat insulation and sound proofing [111]
- ☐ In cross-linked surfaces for **ice skating** rinks[101]
- ☐ **Paper treatment and paper products** - MBA is used in the following:
  - ☐ Paper sizes [102, 110, 95]
  - ☐ Wet and dry strength paper [97, 103, 104, 106, 108,109]
  - ☐ Electrically conductive paper [105, 107, 113]
  - ☐ Paper dewatering additive [112]
- ☐ **Photosensitive compositions and photographic products** -
  - ☐ Photosensitive printing plates [81, 90, 92-94, 118, 119, 123, 124]
  - ☐ Photographic picture transfer process [84, 91]
  - ☐ Polymeric resist images [117, 120-122]
  - ☐ Dye-sensitized photopolymers [88, 125]

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