METHACRYLIC ACID AND DERIVATIVES

1. Introduction

Methacrylic acid (MAA), 2-methylpropenoic acid, was first prepared in 1865 via the hydrolysis of ethyl methacrylate, which was in turn obtained by dehydrating ethyl α-hydroxyisobutyrate (1). The initial recognition of the potential importance of acrylic and methacrylic monomers, including the commercial value of resulting polymers, can be traced to the doctoral thesis of Otto Röhm at the University of Tübingen in 1901 (2). Röhm described the preparation of clear, colorless, rubbery materials that he thought could be of practical utility. Röhm was granted patent coverage for applications of acrylic polymers in 1914 (3). Although research for preparing acrylate and methacrylate monomers progressed, it was not until the 1920s that significant effort was spent on developing commercial processes for the monomers and their derived polymers. The first commercial productions of acrylate and methacrylate monomers occurred in the 1930s and were based on ethylene cyanohydrin and acetone cyanohydrin, respectively (4,5). Methyl methacrylate (MMA) and MAA made from acetone cyanohydrin still forms the basis for the majority of contemporary commercial methacrylate production.

2. Physical Properties

Selected physical properties for various methacrylate monomers are presented in Tables 1–4, where more detailed data for the more commercially

Table 1. **Properties of Methacrylic Esters, $CH_2{=}C(CH_3)COOR$**

R substituent	CAS Registry number	bp, °C (at kPa^a)	Refractive index, n_D^T	Specific gravity^b
Alkyl methacrylates				
methyl	[80-62-6]	100 (101)	1.412025	0.939_4
ethyl	[97-63-2]	119 (101)	1.411625	0.909_4
propyl	[2210-28-8]	141 (101)	1.418320	0.902_4^c
isopropyl	[4655-34-9]	125 (101)	1.433425	0.885_4^c
n-butyl	[97-88-1]	162–163 (101)	1.422025	0.889_4
isobutyl	[97-86-9]	155 (101)	1.4197^{20}	0.882_4
sec-butyl	[2998-18-7]	72–73 (6.7)	1.4195^{25}	
tert-butyl	[585-07-9]	52 (4.7)	1.4120^{25}	
n-hexyl	[142-09-6]	204–210 (101)	1.4310^{20}	0.894_4
n-octyl	[2157-01-9]	114 (1.9)	1.4373^{20}	
isooctyl	[28675-80-1]	68 (0.087)	1.4386^{20}	
2-ethylhexyl	[688-84-6]	47 (0.013)	1.4380_{20}	
n-decyl	[3179-47-3]	99–100 (0.17)	1.4425	
dodecyl	[142-90-5]		1.444	0.868^d
tetradecyl	[2549-53-3]	147–154 (0.093)	1.4480^{20}	
octadecyl	[32360-05-7]		1.4502^{25}	
Unsaturated alkyl methacrylates				
vinyl	[4245-37-8]	63 (16.4)		
allyl	[96-05-9]	32 (1.3)	1.4328^{25}	
oleyl	[13533-08-9]	165–170 (0.0027)	1.4607^{20}	
2-propynyl	[13861-22-8]	47–49 (1.5)	1.4483^{20}	
Cycloalkyl methacrylates				
cyclohexyl	[101-43-9]	44 (0.040)	1.4583^{20}	
1-methylcyclohexyl	[76392-14-8]	94–98 (1.3)	1.4588^{25}	
3-vinylcyclohexyl	[76392-15-9]	63–70 (0.013)	1.4692^{25}	
3,3,5-trimethylcyclohexyl	[75673-26-6]	51–52 (0.013)	1.4548^{20}	
bornyl	[4647-84-1]	68–70 (0.040)	1.4739^{25}	
isobornyl	[7534-94-31]	112–117 (0.33)	1.4748^{25}	0.980_4
cyclopenta-2,4-dienyl	[76741-96-31]	115 (0.093)	1.4990^{25}	
dicyclopentenyl	[51178-59-7]	137 (1.7)		
dicyclopentenyloxyethyl	[68586-19-6]	350–360		
Aryl methacrylates				
phenyl	[2177-70-0]	58–61 (0.13)	1.5184^{20}	
benzyl	[2495-37-6]	119–121 (0.1–0.2)	1.5095^{25}	
nonylphenyl	[76391-98-5]	120–127 (0.0040)	1.5020^{25}	
2-phenoxyethyl	[10595-06-9]	130–132 (1.0)		
Hydroxyalkyl methacrylates				
2-hydroxyethyl	[868-77-9]	87 (0.67)	1.4505^{25}	1.064_4
2-hydroxypropyl	[923-26-2]	87 (0.67)	1.4456^{25}	1.028
3-hydroxypropyl	[2761-09-3]	67–69 (0.013)	1.4496^{25}	
2-hydroxybutyl	[13159-51-8]	77–79 (0.26)		

Table 1. (*Continued*)

R substituent	CAS Registry number	bp, °C (at kPa[a])	Refractive index, n_D^T	Specific gravity[b]
4-hydroxybutyl	[997-46-6]	80–85 (0.013)		
5-hydroxypentyl	[61016-96-4]	85–90 (0.004)		
6-hydroxyhexyl	[13092-57-4]			
3,4-dihydroxybutyl	[62180-57-8]	110–111 (0.033)		
2,3-dihydroxypropyl	[5919-74-4]			
Methacrylates of ether alcohols				
methoxymethyl	[20363-82-0]	54 (2.0)	1.4233^{20}	
ethoxymethyl	[76392-16-0]	87–88 (7.3)	1.4216^{20}	
allyloxymethyl	[49978-33-8]	80–82 (2.7)	1.4422^{20}	
2-ethoxyethoxymethyl	[76392-17-1]	113–114 (2.3)	1.4302^{20}	
benzyloxymethyl	[76392-18-2]	136–137 (0.67)	1.5067^{20}	
cyclohexyloxymethyl	[76392-19-3]	91–92 (0.27)	1.4599^{20}	
1-ethoxyethyl	[51920-52-6]	64–65 (2.7)	1.4182^{25}	
2-ethoxyethyl	[2370-63-0]	85 (2.5)		
2-butoxyethyl	[13532-94-0]	104 (2.0)	1.4304^{25}	
1-methyl-(2-vinyloxy)ethyl	[76392-20-6]	50 (0.13)	1.4400^{20}	
methoxymethoxyethyl	[76392-21-7]	68–70 (0.27)	1.4310^{25}	
methoxyethoxyethyl	[45103-58-0]	67–75 (0.13)	1.4397^{20}	
vinyloxyethoxyethyl	[76392-22-8]	80–82 (0.13)	1.4515^{20}	
1-butoxypropyl	[76392-23-9]	51–53 (0.13)	1.4309^{20}	
1-ethoxybutyl	[76392-24-0]	85–88 (3.1)	1.4223^{20}	
tetrahydrofurfuryl	[2455-24-5]	59–62 (0.080)	1.4552^{20}	
furfuryl	[3454-28-2]	62–63 (0.40)	1.4770^{25}	
Heterocyclic methacrylates				
glycidyl	[106-91-2]	75 (1.3)	1.4482^{25}	1.073
2,3-epoxybutyl	[68212-07-7]	45–50 (0.033)	1.4422^{25}	
3,4-epoxybutyl	[55750-22-6]	55–56 (0.11)	1.4472^{25}	
2,3-epoxycyclohexyl	[76392-25-1]	70–73 (0.040)	1.4671^{25}	
10,11-epoxyundecyl	[23679-96-1]	115–119 (0.0027)	1.4553^{25}	
2-(1-aziridinyl)ethyl	[6498-81-3]	190		
thioglycidyl	[3139-91-1]	59 (0.18)		
3-thietanyl	[21806-33-7]	81–83 (1.3)		
Amino- and amidoalkyl methacrylates				
2-dimethylaminoethyl	[2867-47-2]	97.5 (5.3)	1.4396^{20}	0.933
2-diethylaminoethyl	[105-16-8]	49 (0.040)	1.4442^{20}	
2-*tert*-butylaminoethyl		97 (1.6)	1.4400^{25}	0.914
2-*tert*-octylaminoethyl	[14206-24-7]	138–139 (1.6–1.7)	1.4345^{25}	0.933
2-dibutylaminoethyl	[2397-75-3]	110 (0.13)	1.4474^{20}	
3-diethylaminopropyl	[17577-32-1]	105 (0.20)	1.4770^{20}	
3-dimethylaminopropyl	[20602-77-1]	88 (2.13)	1.4418^{20}	
4-dimethylaminobutyl	[60238-41-2]	72 (0.26)	1.4417	
7-amino-3,4-dimethyloctyl	[76392-26-2]	115–120 (1.10)	1.4570^{25}	0.922

Table 1. (*Continued*)

R substituent	CAS Registry number	bp, °C (at kPa^a)	Refractive index, n_D^T	Specific gravity^b
N-methylformamidoethyl	[25264-39-5]	121–123 (0.16)	1.4693^{25}	
2-ureidoethyl	[4206-97-7]	74–76 (0.40)		
2-piperidinylethyl	[19416-48-9]	78 (0.04)	1.4682	
3-morpholinylpropyl	[20602-96-4]	100 (0.13)	1.4704	
Glycol dimethacrylates				
methylene	[4245-38-9]	54–57 (0.024)	1.4520^{20}	
ethylene glycol	[97-90-5]	96–98 (0.53)	1.4520^{25}	
1,2-propanediol	[7559-82-2]	68–72 (0.13)	1.4450	
1,3-butanediol	[1189-08-8]	78–79 (0.053)	1.4523^{20}	
1,4-butanediol	[2082-81-7]	88 (0.027)	1.4872^{20}	
2,5-dimethyl-1,6-hexanediol	[76392-00-2]	125–127 (0.13)	1.4567^{20}	
1,10-decanediol	[6701-13-9]	170–178 (0.27)	1.4577^{25}	
diethylene glycol	[2358-84-1]	120–125 (0.27)	1.4550^{25}	
triethylene glycol	[109-16-0]	155 (0.13)	1.4604^{20}	
tetraethylene glycol	[109-17-1]	>200 (0.13)		
neopentyl glycol	[1985-51-9]	112 (0.21)		
1,6-hexanediol	[6606-59-3]	110 (2.6)		
1,12-dodecandiol	[72829-09-5]			
4,4′-isopropylidenediphenol	[3253-39-2]	70 (mp)		
Polyfunctional methacrylates				
trimethylolpropane trimethacrylate	[3290-92-4]	155 (0.13)	1.471	1.06
tris(2-methacryloxyethyl)-amine	[13884-43-0]	155–165 (0.0067)	1.4768^{25}	
pentaerythritol tetrameth-acrylate	[3253-41-6]			
Carbonyl-containing methacrylates				
R = carboxy- methyl	[76391-99-6]	108–111 (0.033)		
R = 2-carboxy ethyl	[13318-10-0]	104–106 (0.013)	1.4546^{25}	
R = acetonyl	[44901-95-3]	40 (0.067)	1.4437^{20}	
R = oxazolidinyl ethyl	[46235-93-2]	83–87 (0.067)	1.4688^{25}	
N-(2-methacryloyloxyethyl)-2-pyrrolidinone	[946-25-8]	115–128 (0.067)	1.4872^{20}	
N-(3-methacryloyloxyethyl)-2-pyrrolidinone	[76747-97-4]	127 (0.073)	1.4860^{20}	
N-(methacryloyloxy)-formamide	[76392-27-3]	127 (0.13)	1.4782^{20}	
Other nitrogen-containing methacrylates				
2-methacryloyloxyethyl-methylcyanamide	[76392-28-4]			

Table 1. (*Continued*)

R substituent	CAS Registry number	bp, °C (at kPa[a])	Refractive index, n_D^T	Specific gravity[b]
methacryloyloxyethyl-trimethylammonium chloride	[5039-78-1]			
N-(methacryloyloxyethyl)-diisobutylketimine		93–97 (0.027)	1.4543^{25}	
cyanomethyl methacrylate	[7726-87-6]	79,80 (1.3)	1.4381^{25}	
2-cyanoethyl methacrylate	[4513-53-5]	72 (0.067)	1.4459^{20}	
Methacrylates of halogenated alcohols				
chloromethyl	[27550-73-8]	54–56 (3.1)	1.4434^{25}	
1,3-dichloro-2-propyl	[44978-88-3]	58–60 (0.027)	1.4670^{25}	
4-bromophenyl	[36889-09-5]	80–85 (0.013)		
2-bromoethyl	[4513-56-8]	65 (0.67)	1.4750^{20}	
2,3-dibromopropyl	[3066-70-4]	70–76 (0.0040)	1.5132^{25}	
2-iodoethyl	[35531-61-4]	112–119 (4.0)		
1,1-dihydroperfluoroethyl	[352-87-4]	100 (13)		
1*H*,1*H*,5*H*-octafluoropentyl	[355-93-1]	179		
1*H*,1*H*,7*H*-dodecafluoro-heptyl	[2261-93-1]	107 (3.0)		
hexafluoroisopropyl	[3063-94-3]	50 (18.6)		
Sulfur-containing methacrylates				
methyl thiolmethacrylate	[52496-39-6]	57 (4.01)		
butyl thiolmethacrylate	[54667-21-9]	57 (0.27)	1.4828^{20}	
ethylsulfonylethyl methacrylate	[25289-10-5]	120–132 (0.020)		
ethylsulfinylethyl methacrylate	[3007-24-7]	116–119 (0.013)	1.4902^{25}	
thiocyanatomethyl methacrylate	[76392-29-5]	59 (0.020)	1.489925	
methylsulfinylmethyl methacrylate	[76392-30-8]	110–112 (0.04–0.06)	1.4963^{25}	
4-thiocyanatobutyl methacrylate	[76392-31-9]	102 (0.015)	1.4861^{25}	
bis(methacryloyloxyethyl)-sulfide	[35411-32-6]	115–125 (0.067)	1.4894^{25}	
2-dodecylthioethyl methacrylate	[14216-26-3]	155–160 (0.020)	1.4731^{25}	
Phosphorus-, boron-, and silicon-containing methacrylates				
2-(ethylenephosphito)propyl methacrylate	[76392-32-0]	73–80 (0.0027)	1.4635^{25}	

Table 1. (*Continued*)

R substituent	CAS Registry number	bp, °C (at kPa[a])	Refractive index, n_D^T	Specific gravity[b]
diethyl methacryloylphosphonate	[76392-33-1]	125–165 (0.027)	1.4668^{25}	
dimethylphosphinomethyl methacrylate	[41392-09-1]	80–85 (0.0053)	1.4347^{25}	
dimethylphosphonoethyl methacrylate	[22432-83-3]	78–84 (0.0093)	1.4426^{25}	
dipropyl methacryloyl phosphate	[76392-34-2]	75–76 (1.6)	1.4411^{20}	
diethyl methacryloyl phosphite	[3729-12-2]	64 (0.19)	1.4438^{25}	
2-methacryloyloxyethyl diethyl phosphite	[817-44-7]	83 (0.13)	1.4483^{20}	
diethylphosphatoethyl methacrylate	[814-35-7]	115–124 (0.067)	1.4340^{25}	
2-(dimethylphosphato)-propyl methacrylate	[76392-35-3]	85–90 (0.0027)	1.4359^{25}	
2-(dibutylphosphono)-ethyl methacrylate	[3729-11-1]	130–140 (0.0027)	1.4390^{25}	
2,3-butylene methacryloyl-oxyethyl borate	[76392-36-4]	88–94 (0.0027)	1.4451^{25}	
methyldiethoxymethacryl-oyloxyethoxysilane	[76392-37-5]	75–82 (0.0027)	1.4216^{25}	

[a] To convert kPa to mm Hg, multiply by 7.50.

[b] At 25°C, unless otherwise noted.

[c] At 20°C.

[d] Lauryl methacrylate, a mixture with myristyl methacrylate.

available methacrylic acid derivatives are summarized in Tables 3 and 4. Vapor–liquid equilibrium (VLE) data have been published for the methacrylic acid–water system (6). A minimum boiling azeotrope at 6 mol% MAA has been observed. Azeotrope data for MMA are given in Table 5. VLE data are available for methanol–MMA and methanol–MAA pairs (6,7), and also for MMA, MAA, methyl α-hydroxyisobutyrate, methanol, and water, which are the critical components obtained in the commercially important acetone cyanohydrin route to methyl methacrylate (8). The solubility of MMA in water at 25°C is 1.5%, while MAA is completely soluble. Water solubility of higher alkyl methacrylates ranges from slight to insoluble. Some functionalized esters exhibit moderate–excellent solubility in water and/or hydrolyze (eg, 2-dimethylaminoethyl methacrylate is miscible; 2-hydroxypropyl methacrylate has a 13% solubility in water at 25°C). Data on solubility in the ternary system MMA–methanol–water and the quaternary system MMA–MAA–methanol–water have been pub- lished (9–11). Methacrylic acid and its common esters are soluble

Table 2. **Properties of Amides of MAA**

Compound	CAS Registry number	bp, °C (at kPa[a])	mp, °C	Refractive index, n_D
N-methylmethacrylamide	[3887-02-3]	88 (0.47)		1.4740^{20}
N-ethylmethacrylamide	[7370-88-9]	79–82 (0.13)		
N-isopropylmethacrylamide	[13749-61-6]	112 (15.3)	90–91	
N-butylmethacrylamide	[28384-61-4]	113 (0.8)		
N-*tert*-butylmethacrylamide	[6554-73-0]		57.5	
N-cyclohexylmethacrylamide	[2918-67-4]		111	
N-phenylmethacrylamide	[1611-83-2]		84–85	
N-1-naphthylmethacrylamide	[22447-06-9]		114–115	
N-anisylmethacrylamide	[7274-71-7]		89–90	
N-anilinylmethacrylamide	[1611-83-2]		87	
N-morpholinylmethacrylamide	[5117-13-5]		125	
N-ethoxymethylmethacrylamide	[3644-09-5]	100 (0.67)		
N-butoxymethylmethacrylamide	[5153-77-5]	110–112 (0.27)		
N-hydroxymethyl-methacrylamide	[923-02-4]		53.5–54	
N-(2-hydroxyethyl)-methacrylamide	[5238-56-2]	147–157 (0.15)		1.5002^{25}
1-methacryloylamido-2-methyl-2-pentanol	[74987-95-4]	100–104 (0.013)	74–76	
4-methacryloylamido-4-methyl-2-pentanol	[23878-87-1]	114–119 (0.053)		1.4732^{25}
N-(methoxymethyl)-methacrylamide	[3644-12-0]	78–82 (0.03–0.05)		1.4707^{25}
N-(dimethylaminoethyl)-methacrylamide	[13081-44-2]	85–92 (0.1–0.4)		1.4744^{20}
N-(3-dimethylaminopropyl)-methacrylamide	[5205-93-6]	92 (0.0053)		1.4789^{20}
N-acetylmethacrylamide	[44810-87-9]	76 (0.16)		1.4835^{25}
N-methacryloylmaleamic acid	[76392-01-3]		192–193	
methacryloylamidoacetonitrile	[65993-30-8]	114–118 (0.053)	32–34	
N-(2-cyanoethyl)-methacrylamide	[24854-94-2]		46–48	
1-methacryloylurea	[20602-83-9]		138	
N-phenyl-*N*-phenylethylmethacrylamide	[76392-02-4]		63–64	

Table 2. (*Continued*)

Compound	CAS Registry number	bp, °C (at kPa[a])	mp, °C	Refractive index, n_D
N-(3-dibutylamino-propyl)-methacrylamide	[76392-03-5]	125 (0.017)		1.4731^{20}
N,N-dimethylmethacrylamide	[6976-91-6]	68 (0.80)		1.4600^{20}
N,N-diethylmethacrylamide	[5441-99-6]	71–72 (0.33)		
N-(2-cyanoethyl)-*N*-methyl-methacrylamide	[76392-04-6]	113–116 (0.15)		1.4755^{25}
N,N-bis(2-diethylaminoethyl)-meth-acrylamide	[76392-05-7]	122 (0.053)		1.4702^{20}
N-methyl-*N*-phenyl-methacrylamide	[2918-73-2]	88–96 (0.27)	50	
N,N′-methylenebis-methacrylamide	[2359-15-1]		163–164	
N,N′-ethylenebis-methacrylamide	[6117-25-5]		170 (dec)	
N-(diethylphosphono)-methacrylamide	[76392-06-8]	105–110 (0.0067)		1.4412^{25}
N-*tert*-butyl-*N*-(diethyl-phosphono)-meth-acrylamide	[76392-07-9]	80–85 (0.020)		1.4296^{25}

[a] To convert kPa to mm Hg, multiply by 7.50.

Table 3. **Selected Properties of Methacrylates**

Compound	Molecular weight	mp, °C	Viscosity, mPa(= cP)	Flash point, °C	Autoignition temperature, °C
methyl methacrylate[a]	100.11	−48	0.53	9[b]	435
ethylmeth-acrylate[a]	114.14	−17	0.92	16[c]	393
butyl methacrylate[a]	142.19	−50	0.92	49[d]	294
lauryl methacrylatee	262	−22		110	277
2-dimethyl-aminoethyl-methacrylate[f]	157.2	−30	1.1	75	
2-hydroxyethyl-methacrylate[g]	130.14	−12			66
2-hydroxypropyl methacrylate[g]	144.17	−89		7.1	98
glycidyl meth-acrylate	142.1	<−60		5	76

[a] Heat of polymerization = 57.5 kJ/mol (13.7 kcal/mol).

[b] Lower explosion limit (LEL) = 2.1%; upper explosion limit (UEL) = 12.5%.

[c] LEL = 1.8%; UEL to saturation.

[d] LEL = 2.0%; UEL = 8%.

[e] Made from a mixture of higher alcohols, predominantly C-12.

[f] $pK_a = 8.4$.

[g] Heat of polymerization = ~50 kJ/mol (12 kcal/mol).

Table 4. **Properties of MAA and Nonester Derivatives**

Compound	CAS Registry number	Molecular weight	mp °C	bp °C[a]	Refractive index	Specific gravity	Viscosity mPa(=cP)	Solubility in water at 25°C	Flash point, °C
methacrylic acid[b]	[79-41-4]	86.09	14	162	1.4288	1.015	1.3	miscible	67[c]
methacrylic anhydride	[760-93-0]	154.17		87[d]	1.453	1.035	3	reacts	84
methacrolein	[78-85-3]	70.09	−81	69	1.416	0.847		miscible	−15
methacrylonitrile	[126-98-7]	67.09	−35.8	90.92	1.4	0.8	0.39	2.6%	12
methacryloyl chloride	[920-46-7]	104.54		95.96	1.442	1.07		reacts	2

[a] At 101.3 kPa = 1 atm, unless otherwise indicated.

[b] $pK_a = 4.66$; heat of polymerization = 66.1 kJ/mol (15.8 kcal/mol).

[c] Autoignition temperature = 400°C.

[d] At 1.7 kPa = 13 mm Hg.

Table 5. **Azeotropic Mixtures with MMA**[a]

Component	Pressure, kPa[b]	bp, °C	MMA,%
water	101	83	86
	27	49	88.4
methanol	101	64.2	15.5
ethanol	27	34.5	18

[a] Ref. 12.

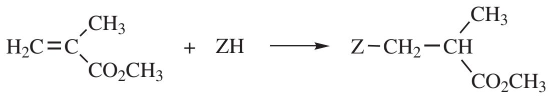
[b] To convert kPa to mm Hg, multiply by 7.50.

in most organic solvents. A summary of spectral data on methacrylates is available (12).

3. Reactions

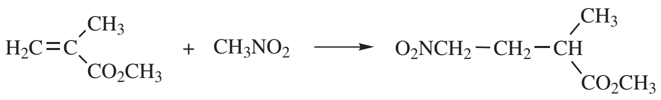
Methacrylic acid and its ester derivatives are α,β-unsaturated carbonyl compounds and exhibit the reactivity typical of this class of compounds, (eg, Michael and Michael-type conjugate addition reactions and a variety of cycloaddition, and related, reactions). Although less reactive than the corresponding acrylates due to the electron-donating effect and the steric hindrance of the α-methyl group, methacrylates readily undergo a wide variety of reactions and are valuable intermediates in many synthetic procedures.

3.1. Nucleophilic and Electrophilic Addition Reactions. Many nucleophiles undergo 1,4-conjugate addition to the methacrylate double bond, leading to β-substituted α-methyl propionates. Examples include addition of hydrogen cyanide, hydrogen halides, hydrogen sulfide, mercaptans, alkyl amines, alcohols, phosphines, dialkyl phosphites, and active methylene compounds (eg, nitroalkanes, esters, nitriles, ketones, and compounds possessing more than one of these functional groups) (13–16).



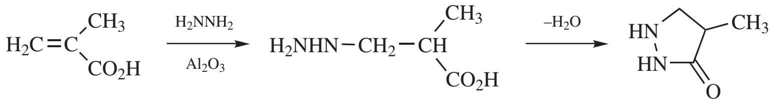
$$H_2C{=}C(CH_3)CO_2CH_3 + ZH \longrightarrow Z{-}CH_2{-}CH(CH_3)CO_2CH_3$$

Z = CN, RO, RS, R_2N, RHN, $(RO)_2PO$, X, etc;
R = Alkyl, Aryl, H;
X = Halogen

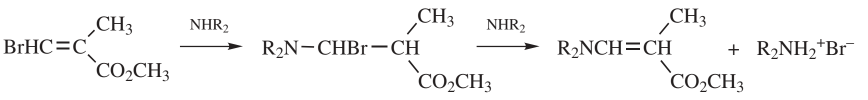


$$H_2C{=}C(CH_3)CO_2CH_3 + CH_3NO_2 \longrightarrow O_2NCH_2{-}CH_2{-}CH(CH_3)CO_2CH_3$$

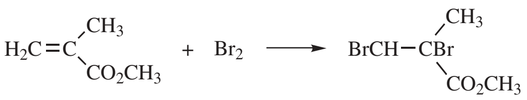
Multifunctional nucleophiles may undergo initial 1,4-conjugate addition, followed by reaction at the carbonyl moiety to give heterocyclic products (17–19).

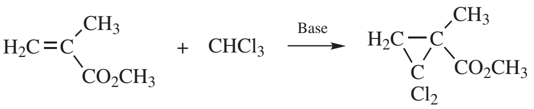


1,4-Conjugate addition to a β-halogen substituted methacrylate ultimately results in an addition–elimination reaction, regenerating an α,β-unsaturated product (20–22).



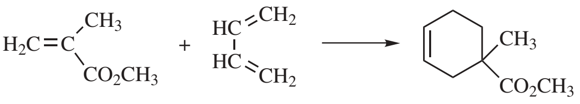
Electrophilic addition to the double bond is also possible and occurs with halogens and dihalocarbenes (23,24), the latter resulting in a cyclopropyl product.

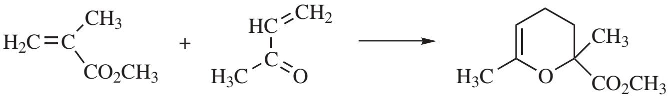


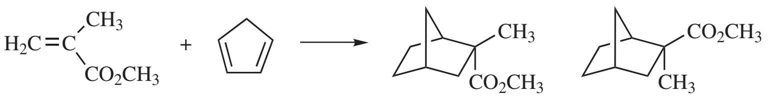


3.2. Cycloaddition Reactions.

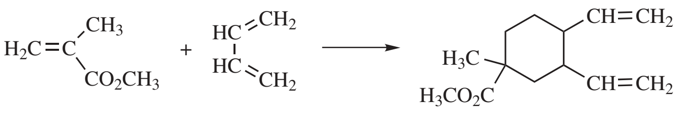
The methacrylate double bond undergoes a variety of cycloaddition reactions. In particular, methacrylates have been widely employed as dienophiles in Diels-Alder reactions (13,16,25–38).



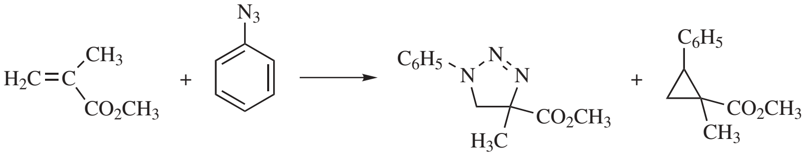


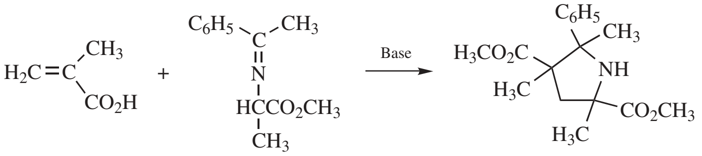


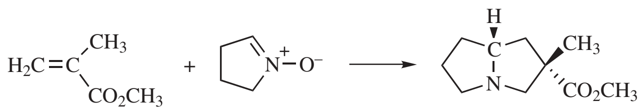
Reaction with 1,3-butadiene can also give cyclic cooligomerization, which is catalyzed by nickel complexes in the presence of phosphites and triethylaluminum (39–40).



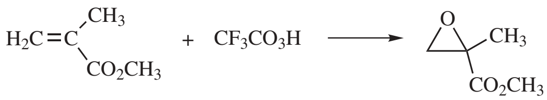
Nitrogen-containing heterocycles are accessible from 1,3-dipolar cycloaddition reactions of azides, imines, and nitrile oxides with methacrylates (41–46).

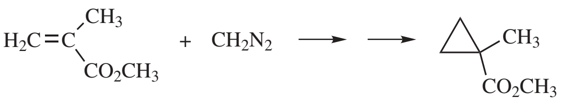


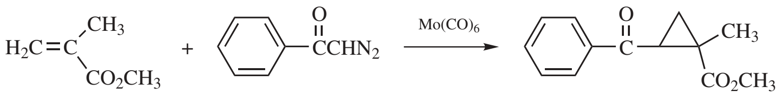




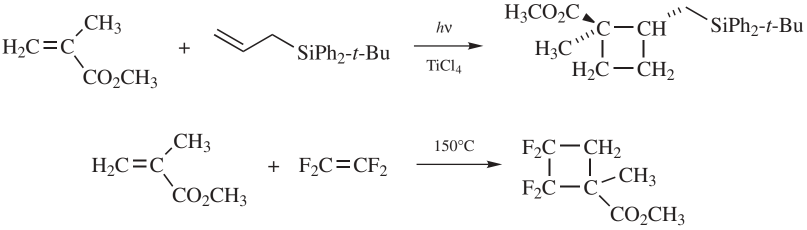
The methacrylate double bond also undergoes epoxidation reactions employing peroxides and cyclopropanation reactions with diazo reactants (47–51)



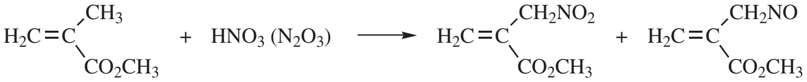




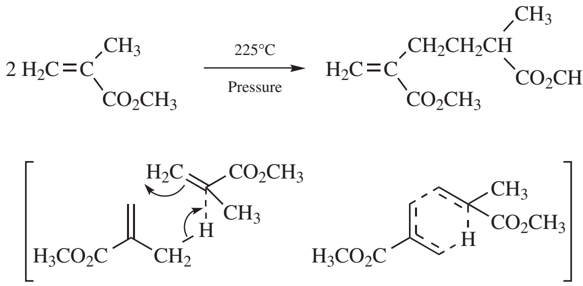
Methacrylates undergo [2 + 2] cyclization reactions with olefins that are promoted either photolytichemically or via $TiCl_4$ assistance (52–54). However, catalysts are not required in reactions with tetrafluoroethylenes (55).



3.3. α-Methyl Reactions. The reaction of methyl methacrylate with nitric acid containing various concentrations of dinitrogen trioxide results in the substitution of an allylic hydrogen with nitro or nitroso groups (56).



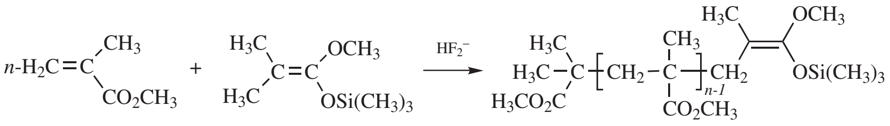
Methacrylates undergo dimerization reactions under high temperature and pressure, giving an α-methylene-δ-methyladipic acid derivative. This reaction is commonly referred to as the "ene-reaction" as discovered by Diels and Alder just before they found the "diene reaction" in about 1928. A transient cyclic complex is invoked as an intermediate which involves the allylic methyl C−H bond (57–59).



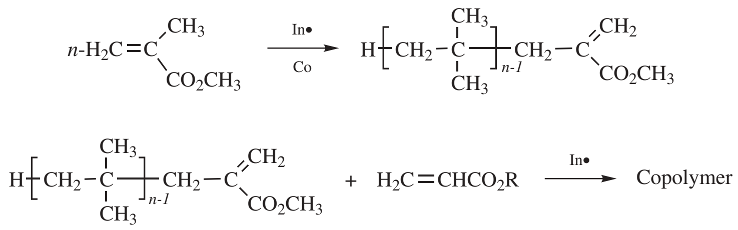
4. Polymerization

The majority of commercial applications of methacrylic acid and its esters arise from their facile free-radical polymerization reactions (see INITIATORS, FREE-RADICAL; METHACRYLIC POLYMERS; ACRYLIC ESTER POLYMERS; COPOLYMERS; and POLYMERS). These may include solution, suspension, emulsion, and bulk polymerizations. Anionic polymerizations of methacrylates have also been extensively studied; however, commercial use has been hampered by the need for anaerobic and anhydrous conditions and by the presence of unwanted side reactions of the propagating anion at the ester carbonyl. The back-biting of the carbonyl by the growing polymer leads to chain termination and catalyst inactivation with the release of alkoxide as the cyclic ketone is formed (60–66).

Advances have been made in methacrylate polymerization concerning the chain transfer step. Group-transfer polymerization allows for the synthesis of block copolymers that are not available from ordinary free-radical polymerization. In a prototypical group-transfer polymerization, the fluoride-ion-catalyzed reaction of a methacrylate (or acrylate) in the presence of a silyl ketene acetal gives a high molecular weight polymer (67–72).



In a recent development, a transition-metal (especially cobalt) -catalyzed chain-transfer polymerization of methacrylates, in combination with free-radical initiation, leads to terminally unsaturated, low molecular weight polymers. These macromonomer products may then undergo copolymerization with nonsterically hindered monomers, such as acrylates and styrenics, resulting in highly branched polymer structures (73–77).



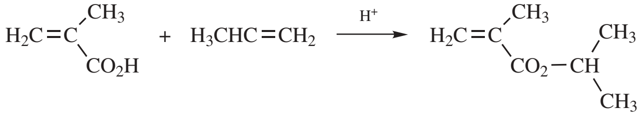
Methacrylic acid, methyl methacrylate, and simple alkyl methacrylates (see Section 5) are commonly used building blocks of commercial polymers. Free radical polymers containing methacrylate backbones are more rigid (ie, have a higher glass transition temperature) than the corresponding acrylate polymers. Copolymerization of the appropriate acrylates and methacrylates allows for an extensive range of polymer properties. Further product differentiation may be achieved by adding small amounts (1–10%) of monomers containing specific reactive functional groups that modify or enhance polymer properties or serve to allow subsequent reactions of the polymer, such as crosslinking or grafting. The preparation and use of functional monomers have been reviewed (78).

5. Higher Alkyl and Functional Methacrylates

Most large scale industrial methacrylate processes are designed to produce methyl methacrylate or methacrylic acid. In some instances, simple alkyl alcohols (eg, ethanol, propanol, and butanol) may be substituted for methanol to yield the higher alkyl methacrylates. In practice, however, these higher alkyl methacrylates are usually prepared from methacrylic acid by direct esterification or from transesterification of methyl methacrylate with the desired alcohol.

Direct esterification of methacrylic acid with alcohols typically requires strong acid catalysts, such as sulfuric acid, sulfonic acids, or phosphoric acid. Heterogeneous resin catalysts containing strong acid functionality have been used in order to facilitate catalyst removal from the product and to reduce process waste, by eliminating the necessity of neutralization and separation steps (79–81). More recently, heterogeneous metal oxide catalysts have been recognized for similar improvements to the direct esterification of (meth) acrylic acid (82,83) and to the transesterification of methyl methacrylate (84).

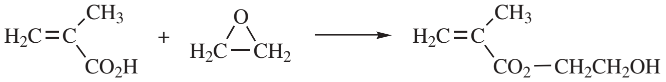
In a typical direct esterification, a mixture of water and methacrylic acid is taken overhead to shift the equilibrium toward the desired ester. The use of an appropriate solvent to remove water azeotropically allows operation at more moderate temperatures. Direct esterification reactions with alcohols of lower boiling point than water often require special processing techniques. Heterogeneously catalyzed vapor-phase reactions (85) or the use of drying agents such as molecular sieves have been used to give acceptable conversion. Secondary alcohols react more slowly than primary alcohols, and acid-catalyzed esterification of tertiary alcohols often fails as a result of elimination reactions leading to olefin. However, acid catalyzed reaction of olefins with methacrylic acid may be used to prepare branched alkyl esters (86,87).



$$H_2C{=}C(CH_3)CO_2H + H_3CHC{=}CH_2 \xrightarrow{H^+} H_2C{=}C(CH_3)CO_2{-}CH(CH_3)_2$$

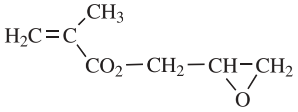
Transesterification of methyl methacrylate with the appropriate alcohol is often the preferred route for preparing higher alkyl and functional methacrylates. The reaction is driven to completion by the use of excess methyl methacrylate and by the removal of the methyl methacrylate–methanol azeotrope. Catalysts employed for transesterification include conventional acids and bases, where more recent work has shown lithium hydroxide and magnesium methoxide to be effective (88). In addition, transition-metal compounds exhibit good activity for transesterification and include complexes such as dialkyltin oxides (88), titanium(IV) alkoxides (89), zirconium acetoacetate (90), and ferric sulfate (84). The use of the transition-metal catalysts allows reaction under nearly neutral conditions and is therefore more tolerant of sensitive functionality in the ester alcohol moiety. In addition, transition-metal catalysts often exhibit higher selectivities than acidic catalysts, particularly with respect to by-product ether formation.

5.1. Functional Monomers. Hydroxy functional methacrylates are accessible by the reaction of MAA and ethylene oxide or propylene oxide in the presence of chromium (91), iron (92), or ion-exchange resin catalysts (93).

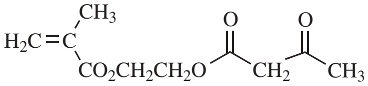


Hydroxy functional methacrylates are used in automotive coatings, dental resins, contact lenses and a variety of additional applications (94).

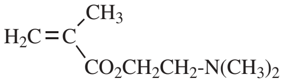
Reactive groups can be introduced into the polymer backbone by the choice of an appropriate functional monomer. Commercially available examples of such monomers include the following:



glycidyl methacrylate

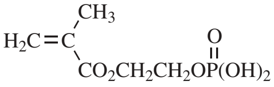


acetoacetoxyethyl methacrylate



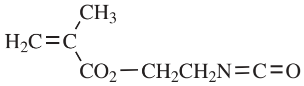
$H_2C{=}C(CH_3)CO_2CH_2CH_2\text{-}N(CH_3)_2$

dimethylaminoethyl methacrylate



$H_2C{=}C(CH_3)CO_2CH_2CH_2OP(O)(OH)_2$

phosphoethyl methacrylate



$H_2C{=}C(CH_3)CO_2{-}CH_2CH_2N{=}C{=}O$

isocyanatoethyl methacrylate

Shown are glycidyl methacrylate to introduce epoxide functionality, acetoacetoxyethyl methacrylate to introduce active methylene groups, dimethylaminoethyl methacrylate to introduce amine functionality, phosphoethyl methacrylate for strong acid functionality, and isocyanatoethyl methacrylate to introduce isocyanate functionality, which may then react with a wide variety of nucleophiles. Organometallic methacrylate monomers containing tin, silicon, germanium, lead, and titanium have become available in at least laboratory research quantities (95).

6. Manufacturing and Processing

The present, and proposed, manufacturing routes for MMA and MAA continue to be based on natural gas or crude oil as the ultimate feedstock. It is convenient to further categorize these various manufacturing routes according to the specific hydrocarbon raw materials. Specifically, Figures 1–3 outline general routes based on propylene (C-3), ethylene (C-2), and isobutane/isobutylene (C-4). Methanol is a common raw material for all processes to MMA. The commercial viability of a process is determined by the aggregate of raw material cost and utilization (ie, process yield), operating costs with particular attention to energy-related charges, waste disposal costs, environmental impact, and plant capital investment.

Until 1982, almost all methyl methacrylate produced worldwide was derived from the acetone cyanohydrin (C-3) process. Producers' desire to develop

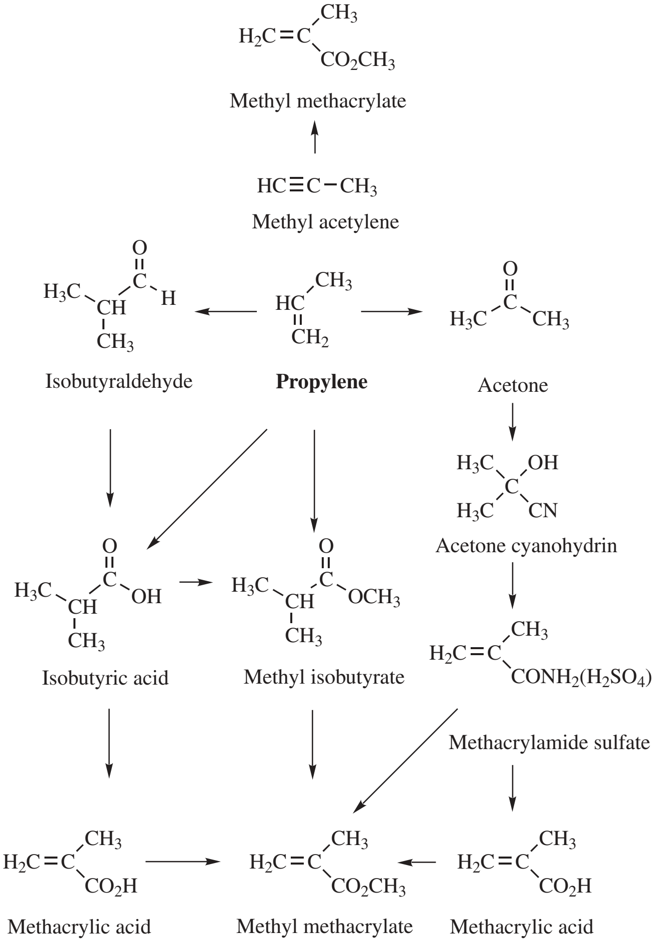


Fig. 1. C-3 routes to MMA/MAA.

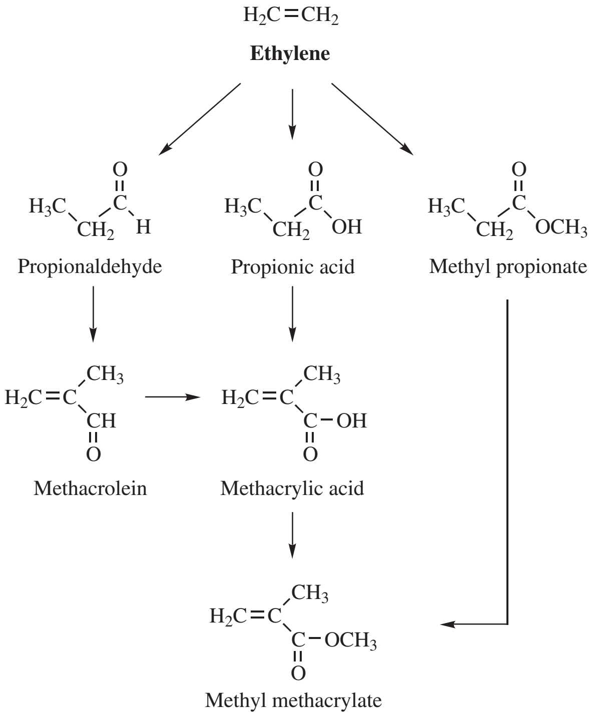


Fig. 2. C-2 routes to MMA/MAA.

alternative processes arises from the high costs for waste handling (ACH process makes 1.5 tons of ammonium bisulfate for every ton of MMA), the costs and corrosive nature of sulfuric acid and the anticipated tight supply for HCN as acrylonitrile producers improve their process selectivity to decrease the level of this by-product. In 1982, Nippon Shokubai Kagaku Kogyo Co. introduced an isobutylene-based (C-4) process, which was quickly followed by Mitsubishi Rayon Co. in 1983 (96). Japan Methacrylic Monomer Co., a joint venture of Nippon Shokubai and Sumitomo Chemical Co., introduced a C-4 based plant in 1984 (97). More recently, Asahi completed construction in late 1998 and Thai MMA, a joint venture of Mitsubishi Rayon and their interests, started in 1999 plants employing direct oxidation of isobutylene (98). In addition, several companies (including Asahi, Mitsubishi Rayon, Mitsui Toatsu, and Nihon Methacrylic) are exploring isobutane oxidation (99).

In 1990, BASF began operation of an ethylene-based (C-2) plant in Germany, where favorable economics due to syngas availability at this site aided commercialization. Although not presently a producer of MMA, Eastman has been working to improve the C-2 route further. The route is based on a condensation of formaldehyde and propionic acid. Optimization work includes catalyst regeneration, product purification, and employing alternative raw materials (98). Like BASF, Eastman is well integrated into C-2 technology due to substantial coal-derived syngas at Kingsport, Tennessee, where there already exists world-scale methanol and formaldehyde plants.

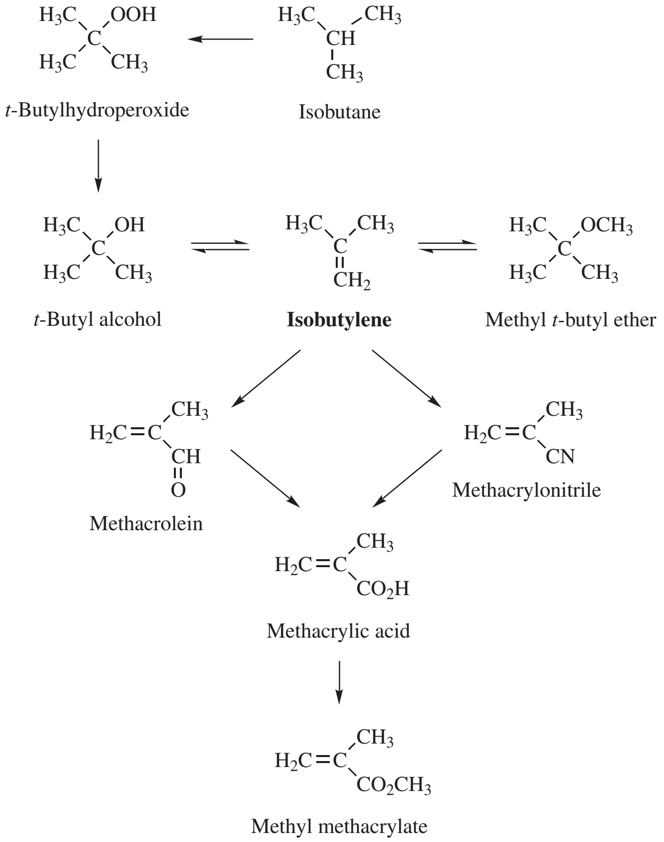


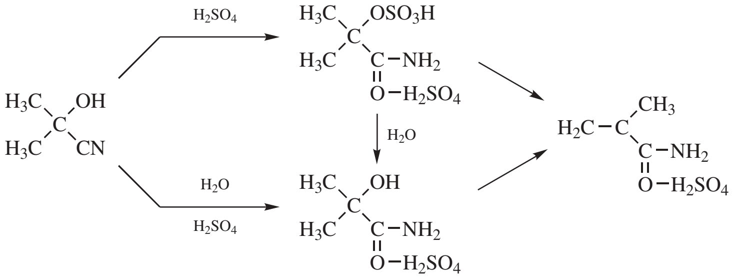
Fig. 3. C-4 routes to MMA/MAA.

Mitsubishi Gas Chemical (MGC) has developed and patented a modified acetone cyanohydrin-based (C-3) route that does not use sulfuric acid, which presents the opportunity for reduced waste costs. In place of the ammonium bisulfate coproduct in conventional ACH technology, formamide is produced and then dehydrated to regenerate HCN in the MGC process. Mitsubishi Gas Chemical has been operating a commercial plant based on this chemistry since 1997. Production costs are competitive with processes discussed above, and capital costs appear more favorable (98).

Another C-3 based route is the carbonylation of methyl acetylene. This process continues to be refined since the earliest reports in the late 1960s. Very high yields and selectivities have been reported by Shell using Pd complexes as catalysts (100). More recently, Ineos Acrylics, formerly a part of ICI, purchased rights to Shell's technology (100). Like the Eastman example above, Ineos Acrylics (now Lucite) benefits from integration of basic feedstocks. In particular, methyl acetylene is a coproduct of steam cracking, where a challenge remains in separating the methyl acetylene from propadiene coproduct.

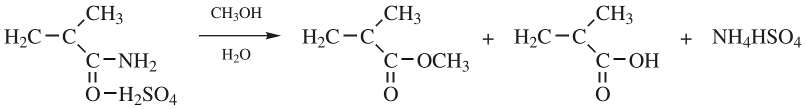
There continue to be significant improvements in processing steps and catalysts, which result in improved yields for key transformations in many of the routes discussed here. Therefore, it is likely that the commercial dominance of the acetone cyanohydrin process will continue to erode over time as these processes become more attractive and as the primary producers attempt to take advantage of their diversified raw material feedstocks.

6.1. C-3 Routes. *MMA from Acetone Cyanohydrin (ACH).* The ACH process has been practiced commercially since 1937 and is based on technology patented by ICI in 1934 (5). It involves the reaction of acetone cyanohydrin with sulfuric acid to ultimately give MMA via the intermediate methacrylamide sulfate [29194-31-8]. Acetone cyanohydrin [75-86-5] is prepared via the base-catalyzed reaction of acetone and hydrogen cyanide. In the ACH-MMA process, acetone cyanohydrin is added to an excess of sulfuric acid (1.4–1.8 mol/mol ACH), which acts as both reactant and solvent. The reaction between ACH and sulfuric acid produces α-sulfatoisobutyramide, which then undergoes an elimination reaction under the heated process conditions to give methacrylamide sulfate.



Kinetics and mechanistic work studying both the ACH conversion to α-substituted isobutyramides and their subsequent elimination reactions have appeared (101). Anhydrous conditions are maintained through this stage to minimize formation of α-hydroxy-isobutyramide sulfate. This by-product requires longer residence times and/or higher temperatures for conversion to methacrylamide sulfate, a condition that should be avoided due to yield loss from further decomposition reactions. Inhibitors are introduced at specific points in the process to prevent polymerization of the various unsaturated intermediates and products. If insufficient sulfuric acid is present, the reaction mixture becomes viscous and heat transfer is poor, resulting in decomposition of acetone cyanohydrin to acetone sulfonates, formamide, and carbon monoxide. The initial reaction is typically carried out at 80–100°C followed by brief thermal cracking (ie, elimination reactions) at 120–160°C to convert the α-hydroxyisobutyramide sulfate to methacrylamide sulfate. Total reaction time for this stage of the process is ~1 h. Hydroxy material that does not undergo cracking may then either decompose to acetone or convert to methyl α-hydroxyisobutyrate, an unwanted impurity present in the MMA product, during the esterification stages. In general, for this stage ACH conversion is typically 100% with a selectivity ~90–95% to methacrylamide sulfate. Recent work at Rohm and Haas and elsewhere shows that control of residence time during the cracking step can improve selectivity to methacrylamide sulfate by several percent (102).

In the next stage, sulfuric acid serves as catalyst in a combined hydrolysis/esterification of the methacrylamide sulfate to a mixture of MMA and MAA.



Ammonium bisulfate is formed as a coproduct at equimolar amounts to the amount of methacrylate formed. The conversion of methacrylamide sulfate to MMA can be carried out using a variety of procedures to aid recovery of crude MMA and for separation of methanol and MAA for recycling. In one scheme, the methacrylamide sulfate is reacted with aqueous methanol in a continuous reactor(s) at temperatures of 100–150°C and pressures of ~710 kPa (7 atm). Residence times are under 1 h. Some of the by-products from this stage include dimethyl ether, methyl α-hydroxy-isobutyrate, α-hydroxyisobutyric acid, methyl β-methoxy-isobutyrate, and methyl formate. The reactor effluent phase separates under pressure, and the lower layer is steam stripped to recover methacrylic acid for recycling to the hydrolysis-esterification stage. The waste ammonium acid–sulfate from the steam-stripping step can be treated with ammonia for conversion to fertilizer-grade ammonium sulfate, or burned in an acid recovery plant to regenerate sulfuric acid. The sulfur dioxide from combustion of the acid residue is oxidized to sulfur trioxide, which is then converted to sulfuric acid using conventional technology. The upper layer from the reactor effluent passes through a flash distillation column to remove low boiling components such as dimethyl ether and acetone. Often these components are recovered for fuel value or further purified for use elsewhere in the process. The bottoms from this column are then treated with aqueous ammonia to separate and recover MAA and methanol for recycling to the hydrolysis-esterification stage. The washed crude methyl methacrylate is dehydrated and purified in downstream distillation columns to provide product methyl methacrylate in >99% purity. A schematic of the overall process is given in Figure 4. The overall yield for MMA based on acetone cyanohydrin is ~90%. Most of the world supply for MMA is still produced by this process.

Recent work by Rohm and Haas workers has shown that the by-product methyl α-hydroxyisobutyrate in the bottoms from the MMA distillative purification step may be recycled back to the esterification reaction for further conversion. Alternatively, this stream may be passed over vapor phase catalysts to convert directly to methacrylate product (103).

Methacrylic acid is manufactured by hydrolysis of the methacrylamide sulfate stream using facilities and conditions similar to those used in the esterification step described above. The reactor effluent is separated into two phases. The upper organic layer is distilled to provide high purity MAA. The lower waste-acid layer is first steam stripped to recover a dilute methacrylic acid stream

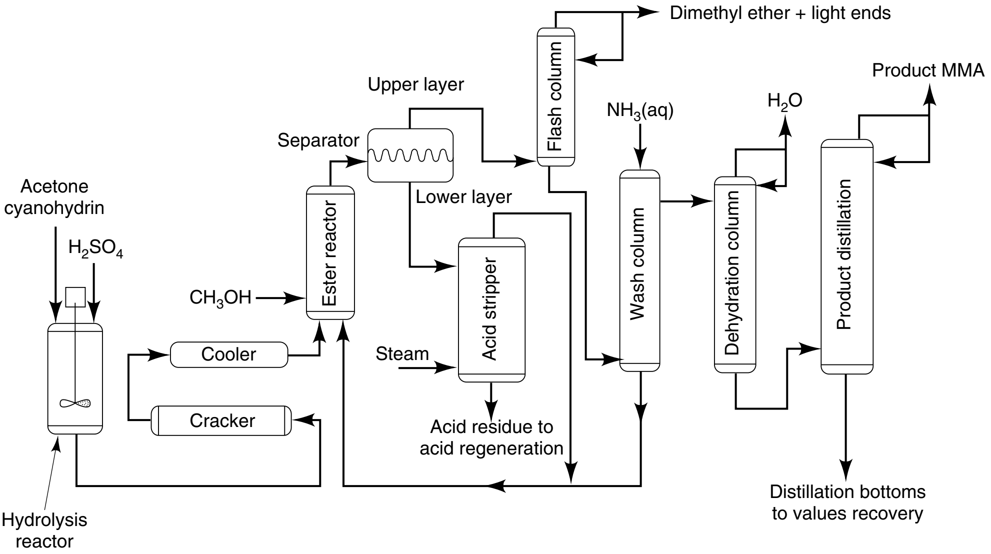
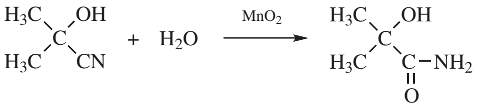


Fig. 4. MMA from acetone cyanohydrin via methacrylamide sulfate.

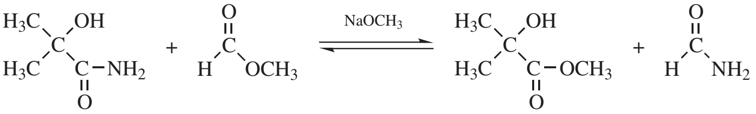
overhead for recycling to the process. The bottoms stream, which is composed mostly of ammonium bisulfate, sulfuric acid and water, is then sent to a sulfuric acid recovery plant. Again, overall yield of the MAA on acetone cyanohydrin is near 90%.

Mitsubishi Gas Chemical Company Process. The commercial MMA process based on reaction of acetone cyanohydrin with sulfuric acid suffers from the large quantities of ammonium bisulfate coproduced. Since ammonium sulfate [7783-20-2] has low value as fertilizer, regeneration back to sulfuric acid is necessary for viable manufacturing. Recently, Mitsubishi Gas Chemical (MGC) developed and patented a novel ACH process that does not employ sulfuric acid and attains an overall yield to MMA from acetone of ~84% (104). In addition to the absence of acid residue, further benefits include minimizing corrosion and the recovery and recycle of hydrogen cyanide. MGC began operating this process in 1997 at a 41,000 metric-ton/year plant at Niigata, Japan.

The first step of the MGC process hydrolyzes ACH to α-hydroxyisobutyramide in the liquid phase using a fixed bed of a modified MnO_2 catalyst (105,106). This reaction is carried out in acetone at temperatures near 60°C. Conversion of ACH exceeds 97% with selectivity to α-hydroxyisobutyramide near 98%.



The key step in the MGC process is the conversion of α-hydroxyisobutyramide to methyl α-hydroxy isobutyrate using methyl formate as the source for the methoxy group. Methyl formate is also made commercially by MGC via vapor-phase dehydrogenation of methanol (107). The liquid-phase ester–amide interchange reaction usually runs several hours <100°C under a pressure of carbon monoxide to minimize formamide decomposition (108). Effective catalysts for this step include alkali metal alkoxides (106) and strongly basic anion exchange resins (109). Conversion of the α-hydroxyisobutyramide is typically near 65% with selectivity to methyl α-hydroxyisobutyrate and formamide in excess of 99%.

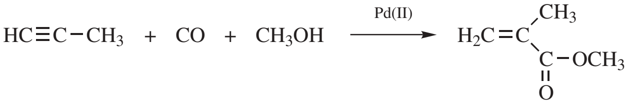


Unreacted α-hydroxyisobutyramide and methyl formate are separated from the product effluent in downstream separations stages and recycled back to the methylating reactor. It is this step that is responsible for the elimination of the waste acid stream (ie, sulfuric acid, ammonium sulfates) characteristic of the conventional H_2SO_4–ACH process. Employing methyl formate, in place of methanol, as an amide/ester interchange agent results in formamide as the coproduct instead of ammonium sulfate. Formamide can then be dehydrated to recover HCN for recycle to ACH production (106,110). Note that methyl formate may also be made in situ from methanol and carbon monoxide at high pressure (∼40 atm). Employing these conditions along with an anion exchange resin catalyst for the interchange reaction has been reported to give increased conversion of 85% while maintaining excellent selectivity to methyl α-hydroxyisobutyrate (>98%) and to formamide (∼97%) (109).

The methyl α-hydroxyisobutyrate is then dehydrated to MMA in two stages. First, the methyl α-hydroxyisobutyrate is vaporized and passed over a modified zeolite catalyst at ∼240°C. A second reactor, containing phosphoric acid catalyst, is operated at ∼150°C to promote esterification of methacrylic acid (MAA), which is also formed in the first stage (111). Methanol is cofed during these stages to improve selectivity. Conversion of methyl α-hydroxyisobutyrate is >99%, with selectivity to MMA near 96%. The reactor effluent is extracted with water to remove methanol, yielding crude MMA. The crude MMA is then further dried and distilled, providing for a purified product.

Other methacrylate products may be obtained with minor modifications to the above processing steps. Methacrylic acid is produced by first hydrolyzing the methyl α-hydroxyisobutyrate to α-hydroxyisobutyric acid employing an ion-exchange resin catalyst. The α-hydroxyisobutyric acid is then dehydrated in the liquid phase to MAA, with a conversion of 97% and selectivity near 99% (106). In another modification, instead of undergoing amide–ester interchange with methyl formate, the α-hydroxyisobutyamide intermediate may be first dehydrated in the gas phase over appropriate catalysts to give methacrylamide. This may then either be isolated or subjected to the amide–ester interchange with methyl formate, giving MMA and formamide. Conversion for this later step is 94%, with a selectivity to methyl methacrylate of 91% (112).

MMA from Propyne. Advances in transition-metal catalyzed carbonylation by Shell researchers have led to the development of a single-step process for producing MMA from propyne [74-99-7] (methylacetylene), carbon monoxide, and methanol (113–117).



$$HC\equiv C-CH_3 + CO + CH_3OH \xrightarrow{Pd(II)} H_2C=C(CH_3)-C(=O)-OCH_3$$

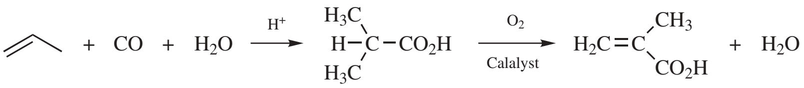
Novel palladium catalysts exhibit marked improvements in both yields and selectivities compared to nickel carbonyl catalysts utilized in earlier commercial carbonylation processes (118,119). The palladium catalysts are also expected to be less hazardous (ie, less toxic). The carbonylation process operates under mild temperatures (45–110°C) and elevated pressures (2–6 MPa = 20–60 atm), and can be carried out in MMA or in an inert solvent such as *N*-methylpyrrolidinone. Selectivities are claimed in excess of 99%, thereby requiring minimal purification to obtain high quality MMA product. The principal by-product is methyl crotonate. Recently, Daicel Chemical Industries has patented similar chemistry employing platinum-based catalysts (120).

An important feature for the palladium catalyst is a phosphine ligand environment, preferably possessing an imino group such as 2-(diphenylphosphino) pyridine (121). In addition, it is important to include a strong acid with a relatively non-coordinating anion, such as alkylsulfonates (eg, methanesulfonic acid), as part of the catalyst package. Second-generation catalyst systems include a tertiary amine or an imino nitrogen to prolong catalyst life. The amine/imine provides increased resistance of the metal catalyst to poisoning by propadiene, commonly found in the same C-3 streams from which propyne is obtained (118,122). Recently, ICI workers also reported on Pd(0) complexes with bidentate phosphine ligands as effective catalysts for this reaction (123).

A limitation of this technology is the relative unavailability of commercial-scale quantities of propyne. Propyne and propadiene are present, along with much higher levels of propylene and propane, in C-3 streams from ethylene plants. Quantities of propyne appear insufficient for MMA plants in excess of 45,000 ton/year, causing a reliance on propyne supplied from several ethylene plants. Advances in technology or changes in cracker operation could lead to intentionally higher percentages of propyne in C-3 streams, thus easing the demand for adequate supply in MMA production. Recovery of propyne from C-3 streams requires extractive distillation in a polar organic solvent. Propyne and propadiene can be concentrated in the bottoms stream, while propane and propylene are removed overhead (124). Although propadiene is a poison for the palladium-based system, it can be maintained at low levels (<0.4%) via isomerizing to propyne over potassium carbonate (125).

ICI acquired Shell's technology for the propyne-based route to MMA in 1997 (126). This may strategically work in ICI's manufacturing capability as they presently benefit from the integration of syngas, methanol, and methyl acetylene, a coproduct of their ethylene cracking. In 1999, Ineos Acrylics (formerly a part of ICI) purchased exclusive rights to this technology from ICI (127).

Propylene-Based Routes to MMA. Strong acid-catalyzed carbonylation and hydrolysis of propylene [115-07-1] to isobutyric acid (Koch reaction) (128) followed by oxidative dehydration to methacrylic acid has been extensively studied since the 1960s. Increased yields of methacrylic acid from isobutyric acid is critical to the development of an attractive process.



$$\text{CH}_2{=}\text{CHCH}_3 + CO + H_2O \xrightarrow{H^+} (H_3C)_2\text{CH}{-}CO_2H \xrightarrow[\text{Calalyst}]{O_2} H_2C{=}C(CH_3)CO_2H + H_2O$$

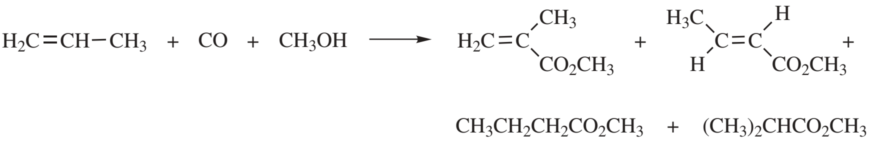
In early work, propylene was reacted with CO in aqueous hydrofluoric acid to give high yields of isobutyric acid (129,130). More recent work improved on handling anhydrous hydrogen fluoride by carefully passing through an isobutyryl fluoride intermediate (131–133). However, commercializing these processes continues to be hampered either by the high corrosivity or toxicity of working with large volumes of hydrogen fluoride (HF). Elf Aquitane, via Norsolor acquisition, was granted an exclusive European license for propylene–hydrogen fluoride technology developed by Ashland Oil (134). Further improvements have since been reported. Isobutyric acid is prepared in ~90% yield via the liquid-phase reaction of propylene, carbon monoxide, and water in sulfuric acid with a metal phthalocyanine cocatalyst (135). In addition, Röhm patented a process for the production of isobutyric acid in 98% yield via the isomerization of isopropyl formate in the presence of carbon monoxide and hydrofluoric acid (136). Furthermore, isobutyric acid may also be obtained via the oxidation of isobutyraldehyde, which is available from the hydroformylation of propylene. The hydroformylation reaction also gives *n*-butyraldehyde, which must be separated from the iso-isomer prior to the oxidation step.

The oxidative dehydrogenation of isobutyric acid [79-31-2] to methacrylic acid has been extensively studied employing fixed bed reactors packed with heterogeneous catalysts developed by various companies. Although many catalysts have been examined, this reaction is generally carried out over iron–phosphorus (137) or molybdenum–phosphorus (136–141) catalyst systems. Conversions in excess of 95% with selectivity to methacrylic acid of 75–85% are attainable, resulting in single-pass yields near 80%. Operating temperatures for the iron–phosphorus catalysts are near 400°C, while the molybdenum-based catalysts exhibit comparable activity at 300°C. The use of cesium-, copper-, and vanadium-doped catalysts are reported to be beneficial (142), as is the use of cesium in conjunction with quinoline (143). Also, an attrition-resistant iron phosphorus catalyst possessing low levels of alkali or alkaline earth metal and zeolite has been claimed (144). Although not quite as selective, oxidative dehydrogenation of isobutyraldehyde to methacrolein followed by oxidation to methacrylic acid has been observed (145).

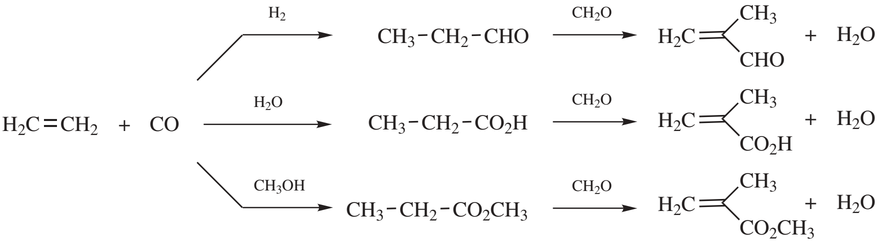
The separation of methacrylic acid from unreacted isobutyric acid is difficult via distillation due to their similar boiling points (162°C for MAA vs 155°C for IBA). Instead, the crude reaction mixture is esterified, and the resulting methyl methacrylate (101°C) and methyl isobutyrate (92°C) can be more readily separated.

An alternative, economically viable route to methyl methacrylate involves a similar two-step process where propylene, carbon monoxide, and methanol react in the liquid phase to make methyl isobutyrate, which is then oxydehydrogenated in the vapor phase to yield MMA (146). The first stage of this process uses a complex of boron trifluoride with methanol. Catalysts for the second stage dehydrogenation reaction are similar to the those employed for the oxidative dehydrogenation of isobutyric acid discussed earlier, including molybdenum–vanadium (147), tungsten–molybdenum (148), and phospho–molybdic acid with additives (149).

Alkoxycarbonylation of propylene is another potential C-3 route but has not resulted in acceptable selectivity to MAA or to MMA. In addition to the desired methacrylate, crotonate and saturated by-products are formed (150). However, this could be a viable process for methacrylates if greater selectivity could be attained.



6.2. C-2 Routes. *MMA from Ethylene.* Methyl methacrylate and methacrylic acid can be produced from ethylene [74-85-1] as a feedstock via propanal, propionic acid, or methyl propionate as intermediates.



Propanal is accessible through hydroformylation of ethylene over cobalt or rhodium catalysts (151). The propanal may then undergo liquid-phase reaction with formaldehyde in the presence of a secondary amine and, optionally, a carboxylic acid. This step presumably proceeds via a Mannich base intermediate that cracks to yield methacrolein (152). Alternatively, a gas-phase reaction between propanal and formaldehyde catalyzed by molecular sieves may be employed to produce methacrolein (153). The methacrolein is then oxidized to MAA over catalysts, as discussed in C-4 routes to MMA. BASF operates a plant at Ludwigshafen, Germany, with a capacity of 36,000 tons of MMA based on propanal, which is available at this site (154).

Propionic acid may be prepared by the liquid-phase hydrocarbonylation of ethylene over nickel or molybdenum carbonyl catalysts (155,156). Ruthenium and palladium catalysts may also be employed, as described below for methyl propionate. Alternatively, ethylene and formic acid may be reacted over an iridium catalyst to form the propionic acid (157). Catalyst systems can sometimes involve mixtures of transition-metal complexes (158) or other additives (156). In addition, propanal may be oxidized to give propionic acid (see Oxo process). Condensation of propionic acid with formaldehyde over supported cesium catalyst gives methacrylic acid with conversions of 30–40% and selectivities of 80–98% (158,160). Catalyst lifetime can be extended by adding low levels (several ppm) of cesium to the feed stream (161). Details for various cesium-containing catalyst systems have been recently summarized (162). In further catalyst development, Eastman reported MAA selectivities reaching 99% using a fixed-bed Nb–Si catalyst for the gas phase reaction of formaldehyde with propionic acid, where propionic acid conversion was ~15% (156). Optimization work by the Federal Energy Technology Research Center on their own Nb–Si catalyst has resulted in reactivation to 100% activity over multiple regeneration cycles (163).

A single-step synthesis for the preparation of methyl propionate has been claimed, which occurs via a rhodium-catalyzed reaction of ethylene and carbon monoxide in the presence of methanol (164). More recently, improved yields have been obtained employing a ruthenium acetylacetonate catalyst (165) or a palladium phosphine catalyst (166). The palladium catalyzed system has been refined to give very high selectivities (>99.9%) and catalyst turnover frequencies (>50,000) by including bidentate phosphine ligands (167). The reaction of methyl propionate with formaldehyde in the gas phase proceeds with good selectivity to MMA and MAA (~90–95%), but conversion for this reaction is still relatively modest (~30%). A variety of catalysts have been patented for this reaction, including V–Sb on silica–alumina (168), a mixture of P–Zr, Al, boron oxide (169), supported Fe–P (170), and alkali metal-containing silica modified with mixtures of Mg/B/Al/Zr/Hf (171). Note that methylal (dimethoxymethane) or methanol may be employed in place of formaldehyde, which often results in improved yields (172). Dimethyl ether has also been examined as a formaldehyde precursor (163).

The propanal route exhibits the highest conversions (99%) and selectivities (>98%) to MMA and MAA at this time. This route suffers only from the added expense for the additional step required to oxidize an aldehyde to the corresponding carboxylic acid (ie, methacrolein to methacrylic acid). Although selectivity >95% is possible from propionic acid or methyl propionate, these routes suffer from low conversion (15–40%). As a result, these processes do not appear economically viable due to the need for large recycle streams, which incur added production costs. However, as catalyst development moves forward (163) and because some companies can take advantage of integration with syngas/methanol/formaldehyde plants on a single site, competitive C-2 routes to MMA may be accessible in the near future (99). In this regard, Ineos Acrylics expects to complete a pilot plant by mid-2001 to demonstrate its ethylene-based MMA process (173).

6.3. C-4 Routes. *MMA from Isobutylene.* Isobutylene [115-11-7] or *tert*-butyl alcohol can be converted to MAA in a two-stage, gas-phase oxidation process via methacrolein as an intermediate. Either of these raw materials may be used interchangeably since *tert*-butyl alcohol [75-65-0] readily dehydrates to isobutylene under the reaction conditions in the initial stage. Variants of the C-4 oxidation process have been commercialized by several companies in Asia, including joint ventures (see Table 6). In addition, isobutylene oxidation research remains active within many firms (174).

The first-stage catalysts for the oxidation to methacrolein are based on complex mixed-metal oxides of molybdenum, bismuth, and iron, often with the addition of cobalt, nickel, antimony, tungsten, and alkali metals. Process optimization continues to be centered on incremental improvements in catalyst yield and lifetime. Typically, a dilute stream, 5–10% isobutylene (or *tert*-butyl alcohol) in steam (10%) and air, is passed over a catalyst at 300–420°C. Conversion is often nearly quantitative, with selectivities to methacrolein ranging from 85% to >95% (175–179). Often there is accompanying selectivity to methacrylic acid of an additional 2–5%. A patent to Mitsui Toatsu Chemicals reports selectivity to methacrolein of better than 97% at conversions >98% for a yield of methacrolein of nearly 96% (180).

The second-stage oxidation of methacrolein to methacrylic acid is most often performed over a phosphomolybdic acid-based catalyst, usually with copper, vanadium, and a heavy alkali metal additive. Arsenic and antimony are other common dopants. Conversions of methacrolein are in the 85–95% range, with selectivities to methacrylic acid of 85–95%. Although numerous catalyst improvements have been reported since the 1980s (181–184), the highest claimed yield of MAA (86%) is still that described in a 1981 patent to Air Products (185).

In typical processes, the MAA product is isolated as a 20–40% aqueous solution by cooling the gaseous effluent from the second-stage oxidation and feeding this to an absorber. The MAA may then be concentrated by extraction into an organic solvent such as butyl acetate, toluene, or dibutyl ketone. Azeotropic dehydration and solvent recovery, followed by fractional distillation, provides pure product. Water, solvent, and low boiling by-products are removed in a first-stage column. The column bottoms are then fed to a second column where MAA is taken overhead. Esterification to MMA or other esters is easily achieved employing acid catalysis.

Table 6. **World Production Capacity of MMA**[a]

Producer	Capacity, 10^3 t	Process[b]
	North America	
Rohm and Haas	372	ACH
Lucite (formerly Ineos and ICI)	290	ACH
CYRO	125	ACH
total	*787*	
	Europe	
Ineos	220	ACH
Rohm/DeGussa [Robin]	200	ACH
Elf Atochem	158	ACH
BASF	40	C-2[c]
Repsol Quimica	30	ACH
total	*648*	
	Japan	
Mitsubishi Gas	50	ACH
Mitsubishi Rayon	215	ACH/C-4
Asahi Chemical	90	ACH/C-4
Japan Methacryl Monomer (Nippon Shokubai/Sumitomo jv)	80	C-4
Kuraray	60	ACH
Kyodo Monomer	50	C-4
other [NSCL (15); MITSUI (16)]	31	ACH/C-4
total	*576*	
	Asia	
Formosa Plastics (Taiwan)	154	ACH
Koahsiung Monomer (Taiwan)	85	ACH
LG Chemical (Nippon Shokubai/Sumitomo/Lucky jv; Korea)	50	C-4
NSCL/Sumitomo jv (Singapore)	50	C-4
Mitsubishi Rayon (Thailand)	55	C-4
Mitsui Chemical (Korea)	50	C-4
Thai MMA (Thailand)	70	
other (China)	50	
total	*564*	
	Latin America	
Fenoquimica (Mexico)	16	ACH
Quimica Metacril (Brazil)	13	ACH
total	*29*	
2000 worldwide capacity	*2,604*[d]	

[a] References include articles from past few years in trade journals, including: *Chemical Week, Chemical Week Newswire, Chemical Marketing Reporter, European Chemical News, Japan Chemical Daily, Japan Chemical Weekly.*

[b] ACH = acetone cyanohydrin; C-4 = *tert*-butyl alcohol and/or isobutylene; C-2 = ethylene.

[c] Via propionaldehyde.

[d] Includes 45,000 tons from other countries not specifically mentioned.

Several variations of the above practice have emerged. In a Sumitomo-Nippon Shokubai process, the effluent from the first-stage reactor containing methacrolein and low levels of methacrylic acid is fed directly to the second-stage oxidation without isolation or purification. In this process, overall yields are maximized by optimizing selectivity to methacrolein plus methacrylic acid in the first stage (186,187). In another variation, Asahi Chemical has reported the oxidative esterification of methacrolein directly to methyl methacrylate in 80% yield without isolation of the intermediate MAA (188,189). Work continues on identifying improved catalysts for the oxidative esterification reaction (190). Asahi and Mitsubishi Rayon recently completed construction of new commercial plants based on direct oxidation of isobutylene to MMA (98).

With the advent of using methyl *tert*-butyl ether (MTBE) as an oxygenated gasoline additive, there has been considerable emphasis on the synthesis of isobutylene or *tert*-butyl alcohol, which can be used as feedstocks for MTBE production. Isobutylene is a primary by-product in the C-4 stream from ethylene plants. After butadiene has been extracted, the isobutylene may be separated from the linear saturated and unsaturated butenes, or the separation may be facilitated by conversion of the isobutylene to *tert*-butyl alcohol. In addition, *n*-butane may be readily isomerized to isobutane, which can then be dehydrogenated to isobutylene. *Tert*-Butyl alcohol is also available as a by-product in the manufacture of styrene or in the manufacture of propylene oxide. Isobutane may also be oxidized to give *tert*-butyl hydroperoxide, which, upon reaction with propylene, yields propylene oxide and *tert*-butyl alcohol (191). The use of isobutylene or *tert*-butyl alcohol as a feedstock for MTBE production creates an economic disincentive for their use as a raw material for MAA and MMA production, because MTBE is the product with the higher value. However, reports have suggested potential environmental problems with MTBE as a fuel additive (192).

Isobutane Route. A proposed process for preparing methacrylic acid from isobutane and oxygen as the only reactants involves a multistep route (193). The reaction steps include oxidation of isobutane to form *tert*-butyl hydroperoxide and *tert*-butyl alcohol; reaction of the *tert*-butyl hydroperoxide with methacrolein to give methacrylic acid and *tert*-butyl alcohol; dehydration of *tert*-butyl alcohol to isobutylene; and oxidation of isobutylene to methacrolein. Although the stated yields for each step appear satisfactory, the overall yield is probably too low to be economical due to the large number of reaction steps. Other processes based on isobutane include initial dehydrogenation to isobutylene and, more importantly, oxidation of isobutane directly to methacrylate products. Although significant research effort is progressing for isobutane oxidation (99,194), improved yields for all these steps are needed for commercial success.

Methacrylonitrile Process. Ammoxidation of isobutylene can produce methacrylonitrile, which may then be converted to MMA and MAA. The ammoxidation involves passing a mixture of isobutylene, ammonia, and air over a complex mixed-metal oxide catalyst at elevated temperatures. Yields of 70–80% methacrylonitrile can be attained with catalysts that include mixtures of molybdenum, bismuth, iron, and antimony, in addition to a noble metal (195–197). The methacrylonitrile may then be hydrolyzed to methacrylamide by treatment with one equivalent of sulfuric acid. The methacrylamide can be either esterified to MMA or hydrolyzed to MAA under conditions similar to those used in the ACH process. The relatively modest yields obtained from the ammoxidation reaction combined with the generation of a significant waste acid stream from the later steps makes this overall process less desirable than the ACH or C-4 oxidation routes.

Monomer Recovery from Polymer. Poly(methyl methacrylate), when heated in excess of 300°C, depolymerizes to yield the monomer (198). Yields depend on both chemical and physical properties for the scrap or off-grade polymer used as a raw material, including how the feed is prepared. However, if a relatively clean feedstock of poly-MMA waste is employed, yields >96% are attainable (198,199). In collaboration with Mitsubishi Rayon, ICI was targeting commercialization of just such a recovery of ~10 million lb/year MMA in the United Kingdom.

7. Economic Aspects

Domestic production of methyl methacrylate from 1971 to 2000 showed a 5.7% annualized growth rate; however, growth in the 1990s has slowed to ~2.5% (200):

Year	Production, 10^3 t
1971	210
1977	338
1981	490
1990	536
1995	683
2000	787

Worldwide production capacity for year 2000 is shown in Table 6. Economic conditions in the late 1980s and early 1990s led to global overcapacity of methyl methacrylate, which caused many plants to operate at less than optimum levels. Worldwide growth over the next few years from year 2000 is expected to be 3–3.5% (200).

Historical list prices for bulk quantities of selected methacrylates are outlined in Table 7 (201). The price trends reflect the combined effects of improved manufacturing capability and the market price of crude oil, the basic raw material to which these monomers are ultimately tied.

8. Uses

Methacrylic acid and its esters are used in a wide variety of polymers with a broad spectrum of applications. Poly(methacrylic acid) or its neutralized salts

Table 7. **Prices for Methacrylates, \$/kg**[a]

Year	MMA	EMA	n-BMA	i-BMA	Lauryl	MAA
1955	0.81	1.14	1.21		1.43	
1960	0.64	1.10	1.21		1.43	0.88
1965	0.46	0.95	0.70	0.84	1.43	0.66
1970	0.42	0.95	0.64	0.84	1.43	0.66
1975	0.66	1.25	1.05	1.01	2.31	0.88
1980	1.10	1.94	1.41	1.52	2.42	1.43
1985	1.18	2.33	1.94	1.91	3.78	1.72
1990	1.56	2.71	1.95	2.20	4.48	2.18
1995	1.72	4.74	2.12	2.36	4.78	2.136
2000	1.43	4.74	2.12	2.36	4.78	2.42

[a] Ref. 201.

serve as the basis for detergent builders and rheology modifiers. Methacrylic esters, the most important of which is methyl methacrylate, provide for hard, tough polymers in contrast to the softer acrylates. Copolymerization of methacrylic esters with acrylates allows for the preparation of hard but flexible polymers, which are important for paints, polishes, and many other coatings. Methacrylate polymers are especially noted for their clarity, color compatibility, weatherability, and ultraviolet light stability, which allows for use in both indoor and outdoor applications. The principal end uses of methacrylates are in acrylic sheet and molding resins which find commercial application in signs, displays, glazing compounds, lighting fixtures, building panels, automotive components, plumbing fixtures, and appliances. They are also used as impact modifiers in poly(vinyl chloride) (PVC) siding, film, sheet, and plastic bottle manufacture (200,202). The methacrylate market segments include acrylic sheet (32%), molding products (20%), coatings (23%), impact modifiers (10%), and other (15%). The relative size of these different segments has remained nearly unchanged since the late 1960s.

9. Storage and Handling

Polymerizations of methacrylic acid and its derivatives are very exothermic (MAA, 66.1 kJ/mol; MMA, 57.5 kJ/mol = 13.7 kcal/mol). Therefore, potential for the rapid evolution of heat with concomitant generation of pressure presents an explosion hazard if these materials are stored in closed or poorly vented containers. Methacrylic acid polymer is insoluble in the monomer, which can result in plugging of transfer lines and vent systems. Polymers of the lower alkyl esters are usually soluble in the parent monomer and may be detected by an increase in solution viscosity. Alternatively, dilution with a nonsolvent for the polymer, such as methanol, results in the formation of a haze and can be used as a diagnostic tool for determining presence of polymer.

To prolong usable shelf-life, commercially available methacrylic monomers are typically inhibited with the methyl ether of hydroquinone [95-71-6] (MEHQ). Other inhibitors commonly employed include alkylphenols and hydroquinone. Once inhibited, methacrylates may be handled as flammable materials. Methacrylic acid is typically inhibited with 100–250 ppm MEHQ, where at the higher inhibitor level the MAA is stable for over two years at 38°C. Stability decreases rapidly with increasing storage temperature. Recommended storage temperatures are 18–40°C and preferrably 20–25°C. Some loss in purity of methacrylates is to be expected upon extended storage (eg, see discussions below). The lower alkyl esters of methacrylic acid are more stable than methacrylic acid itself, and 25 ppm or less of MEHQ is often sufficient to achieve the desired shelf life. Aminomethacrylates and polyfunctional methacrylates are less stable and require higher levels of inhibitors; they possess more limited storage life. Also, in general, to avoid photoinitiation of polymerization, all methacrylates should be stored with minimal exposure to light.

It is important to note that dissolved oxygen is required for phenolic inhibitors such as MEHQ to function efficiently as inhibitors (203). Therefore, methacrylate monomers should never be handled or stored under an oxygen-free atmosphere. Methacrylic acid vapor in air at room temperature does not form a flammable mixture, so air or gas mixtures containing 5–21% oxygen may be employed. Because oxygen is consumed as part of the MEHQ radical trapping mechanism, periodic venting is necessary to replenish the oxygen.

Many unwanted polymerization events of methacrylic monomers occur because of overheating, leading to inhibitor and/or oxygen depletion, which in turn causes inhibitor deactivation. Care should be taken to avoid stagnant areas in transfer lines or pump heads where polymerization may begin and which may then act to seed polymerization of the bulk material. Because poly(MAA) is insoluble in the monomer, the appearance of haze in the monomer provides the earliest indicator of instability. The onset of uncontrolled polymerization, accompanied by heat evolution, may ensue a short time after the first appearance of haze.

Unwanted polymerization events may also result from contamination of the monomer, often via corrosion of the storage vessel. This can introduce metal ions, which can act to initiate polymerization. The preferred material of construction for equipment that comes in contact with methacrylic acid is, besides glass, 316 L stainless steel. The use of 316-L stainless also avoids the formation of rust (ie, iron contamination), which can promote radical formation from the peroxide contaminants that form over time upon storage.

The relatively high freezing point of methacrylic acid (15°C) presents special problems. Because the inhibitor tends to partition into the liquid phase upon freezing, thawing frozen monomer can create localized pools of uninhibited material which are susceptible to polymerization. Care should be taken to limit thawing temperatures to <40°C and to ensure good mixing of the thawed monomer. No material should be withdrawn from a partially frozen container, as it may possess little inhibitor or, conversely, it may possess the bulk of the inhibitor necessary for stabilizing the remainder of the container.

For most polymer applications the removal of inhibitors from the monomer is unnecessary. Since the inhibitors used for storing MAA and its esters

Table 8. **Acute Toxicity of Methacrylate Monomers**

Compound	Acute oral LD_{50}, g/kg (rat)	Inhalation toxicity, LC_{50} (rat) (ppm/4 h)	Dermal LD_{50}, g/kg (rabbit)	Irritation data	Sensitization data
methyl methacrylate	>5	7094	>5	slightly-moderately irritating to skin/eyes	possible skin sensitizer
ethyl methacrylate	>5	8300	>5	slighly-moderately irritating to skin/eyes	possible skin sensitizer
butyl methacrylate	>2	4910	>2	slightly-moderately irritating to skin slightly irritating to eyes	possible skin sensitizer
lauryl methacrylate	>5	[a]	>3	slightly irritating to skin/eyes	possible skin sensitizer
methacrylic acid	1.06		0.5	corrosive to skin/eyes	possible skin sensitizer
glycidyl methacrylate	0.6	45	0.5	severely irritating to skin/moderately irritating to eyes	possible skin sensitizer
hydroxypropyl methacrylate	>5	[a]	>5	moderately irritating to skin/ severely irritating to eyes	possible skin sensitizer
hydroxyethyl methacrylate	>5	[a]	>3	slightly-moderately irritating to skin/severely irritating to eyes	possible skin sensitizer
dimethylaminoethylmethacrylate	1.5–3	96	>3	moderately irritating to skin/ eyes	possible skin sensitizer

[a] Saturated air for 1 h; not lethal.

require oxygen to be effective, purging oxygen either by applying a nitrogen sparge or a vacuum will deactivate the inhibitors enough so that added initiators may be used for controlled polymerization. Should it be required, the phenolic inhibitors can be removed by an alkaline wash or by treatment with a suitable ion-exchange resin. Uninhibited MMA is sufficiently stable to be shipped under carefully controlled temperature and time restrictions. In general, however, uninhibited monomers should always be monitored carefully and used promptly.

10. Health and Safety Factors

The toxicity of methacrylates has been studied extensively and new data are constantly generated. Acute toxicity testing by oral, dermal, and inhalation routes shows methacrylic esters are only slightly toxic after single exposures to rats and rabbits (Table 8).

Methacrylate monomers are slightly to severely irritating to skin and eyes and are potential skin sensitizers. That is, after initial exposure, sensitive individuals may experience severe allergic skin reactions (rashes and swelling) upon subsequent exposures to even small amounts of the same or different monomers. Repeated exposure to the methacrylates results in little systemic toxicity. Nasal tissue is the primary target organ in inhalation studies, with irritation and inflammatory changes occurring at the site of contact. Repeated exposure of animals to near-lethal concentrations results in liver and kidney damage (204,205).

In general, toxicity of the methacrylate esters decreases with increasing molecular weight due to diminished rate at which higher molecular weight materials are absorbed into the body. Nevertheless, MMA serves as a toxicological representative of other methacrylate esters. The chronic toxicity of MMA is well documented. Several lifetime exposure studies by a variety of routes (oral capsule, drinking water, inhalation) in rodents have shown it to be noncarcinogenic. Methyl methacrylate is also nonteratogenic (does not produce birth defects) after inhalation; however, headaches, vomiting, and drowsiness are symptomatic of overexposure to vapors (206).

All methacrylate esters are hydrolyzed to methacrylic acid in the process of conversion to CO_2 before excretion. Methacrylic acid is corrosive. Mucous membranes of the eyes, nose, and throat are particularly sensitive, and prolonged exposure can lead to nasal or eye tissue damage. The pungent odor and irritant nature of the methacrylate monomers serves as a warning property and tends to keep exposures low in the workplace.

The methacrylates are slightly to essentially nontoxic to fish and other aquatic species. Hydrolysis data support rapid breakdown under alkaline conditions, and studies show that MMA is ultimately biodegradable in sewage sludge effluents. This information indicates that methacrylates are not considered to be a significant environmental hazard.

Monomers with reactive functional groups (eg, amino or glycidyl) in the ester moiety exhibit a toxicological profile of the functional group and should be considered on an individual basis. In addition, manufacturing methods for the specific monomers should be evaluated for whether by-products, even at trace levels, may affect the overall biological response.

Appropriate protective clothing and equipment should be worn when handling methacrylates to minimize exposure to these materials, including their vapors. Chemically resistant clothes and gloves and splash-proof safety goggles are recommended. The working area should be adequately ventilated to limit vapors. If chemical exposure should occur, contaminated clothing should be removed and affected areas washed with copious amounts of water. Medical attention should be sought if symptoms appear. Further safety handling information for MMA and other methacrylates is available (207).

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ROBERT WILCZYNSKI
JAMIE JERRICK JULIETTE
Rohm and Haas Company