

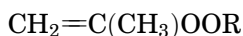
## METHACRYLIC ESTER POLYMERS

### 1. Introduction

Historically speaking, methacrylic ester polymers and acrylic ester polymers developed concomitantly. In 1933, acrylates were copolymerized with ethyl methacrylate; this work led to the commercialization of ethyl methacrylate monomer. The homopolymerization of methyl methacrylate [80-62-6] to form poly(methyl methacrylate) [9011-14-7] (PMMA) found a special market in safety glass which consisted of two glass plates separated by a thin layer of poly(methyl methacrylate) (see LAMINATED MATERIALS, GLASS). Cast sheets of PMMA were brought to market in the 1930s by the Rohm and Haas Co. and E. I. duPont de Nemours & Co., Inc., in the United States as well as by Rohm and Haas A-G and Imperial Chemicals Industries, Ltd., in Europe. These cast sheets were used as structural materials; the shatter resistance, light weight, high transparency, and moldability recommended the use of PMMA for windows and military aircraft canopies. Methacrylates entered the injection and compression molding arenas in 1938. Finally, during the 1930s, methyl methacrylate found a great deal of use as a comonomer in the production of acrylic polymers by emulsion and solution polymerization (1,2).

### 2. Physical Properties

Methacrylic ester monomers are a versatile group of monomers whose chemical properties are primarily determined by the nature of the R side chain group in the structure:



Polymer physical and chemical properties also depend upon the R group, the molecular weight, and the tacticity of the polymer.

Methacrylic monomers differ from acrylics (see ACRYLIC ESTER POLYMERS) in that they have a methyl group in the  $\alpha$  position of the vinyl group; this methyl group lends stability, hardness, and stiffness to the polymers formed from methacrylic ester monomers. Methacrylics will readily polymerize with other methacrylic and acrylic monomers. This ability to form copolymers among these two already diverse groups allows the industrial chemist to create polymers with an incredible breadth of properties ranging from tacky adhesives to hard powders and rigid sheets. Although more costly than many other commonly employed industrial monomers, methacrylics have found a great deal of industrial usage because of their unique balance of performance properties as well as their ease of use. Methacrylic ester monomers can be copolymerized readily with either methacrylic or acrylic ester monomers to form an even greater variety of acrylic copolymers. These polymers find applications that range from extremely tacky adhesives to hard powders and sheets.

Table 1. Physical Properties of Methacrylate Homopolymers

Polymer	CAS Registry number	$T_g$ , °C <sup>a</sup>	Density <sup>b</sup> at 20°C, g/cm <sup>3</sup>	Solubility parameter, <sup>b,c</sup> (J/cm <sup>3</sup> ) <sup>1/2</sup>	Refractive index $n_D$ <sup>20d</sup>
poly(methyl methacrylate)	[9011-14-7]	105	1.190	18.6	1.490
poly(ethyl methacrylate)	[9003-42-3]	65	1.119	18.3	1.485
poly( <i>n</i> -propyl methacrylate)	[25609-74-9]	35	1.085	18.0	1.484
poly(isopropyl methacrylate)	[26655-94-7]	81	1.033		1.552
poly( <i>n</i> -butyl methacrylate)	[9003-63-8]	20	1.055	17.8	1.483
poly( <i>sec</i> -butyl methacrylate)	[29356-88-5]	60	1.052		1.480
poly(isobutyl methacrylate)	[9011-15-8]	53	1.045	16.8	1.477
poly( <i>t</i> -butyl methacrylate)	[25213-39-2]	107	1.022	17.0	1.4638
poly( <i>n</i> -hexyl methacrylate)	[25087-17-6]	−5	1.007 <sup>25</sup>	17.6	1.4813
poly(2-ethylbutyl methacrylate)	[25087-19-8]	11	1.040		
poly( <i>n</i> -octyl methacrylate)	[25087-18-7]	−20	0.971 <sup>25</sup>	17.2	
poly(2-ethylhexyl methacrylate)	[25719-51-1]	−10			
poly( <i>n</i> -decyl methacrylate)	[29320-53-4]	−60			
poly(lauryl methacrylate)	[25719-52-2]	−65	0.929	16.8	1.474
poly(tetradecyl methacrylate)	[30525-99-6]	−72			1.47463
poly(hexadecyl methacrylate)	[25986-80-5]				1.47503
poly(octadecyl methacrylate)	[25639-21-8]	−100		16.0	
poly(stearyl methacrylate)	[9086-85-5]			16.0	
poly(cyclohexyl methacrylate)	[25768-50-7]	104	1.100		1.50645
poly(isobornyl methacrylate)	[28854-39-9]	170(110)	1.06	16.6	1.5000
poly(phenyl methacrylate)	[25189-01-9]	110	1.21		1.571
poly(benzyl methacrylate)	[25085-83-1]	54	1.179	20.3	1.5680
poly(ethylthioethyl methacrylate)	[27273-87-0]	−20			1.5300
poly(3,3,5-trimethylcyclohexyl methacrylate)	[75673-26-6]	79			1.485

<sup>a</sup>Refs. 4–12.<sup>b</sup>Refs. 5, 12, and 13.<sup>c</sup>To convert (J/cm<sup>3</sup>)<sup>1/2</sup> to (cal/cm<sup>3</sup>)<sup>1/2</sup>, divide by 2.05.<sup>d</sup>Refs. 5, 10, 12, and 13.

**2.1. Glass Transition Temperature ( $T_g$ ).** Although often cited as a single value, the glass transition often takes place over a broad range of temperatures. The glass transition is manifested in a polymeric material as an embrittlement when moving across the range from high to low temperatures. Other properties, such as chemical reactivity, mechanical and dielectric relaxation, viscous flow, load bearing capacity, hardness, tack, heat capacity, refractive index, thermal expansivity, creep and diffusion, register large changes after traversing the glass transition range.

Methacrylic ester polymers display the same change from hard, brittle, glass-like materials below the  $T_g$  value to relatively soft, flexible, rubbery materials above the  $T_g$ . Movement to even higher temperatures can result in a change to a flowable, tacky material. Table 1 contains basic physical data (density, solubility parameters, and refractive index values) for the most common methacrylic ester polymers.

The glass transition can be measured by a variety of techniques. The most commonly accepted methods currently are differential scanning calorimetry (dsc) (3,4) and dynamic mechanical analysis (dma) (5,6). Other methods employed in the past have included the approximation methods of Vicat softening temperature and brittle point measurement. More accurate numbers were also determined by methods which rely on the changes manifested in the physical properties of the polymer, such as dilatometry (volume) and refractive index measurements. The  $T_g$  values for a large variety of polymers are found in References 7, 8, 14, and 15.

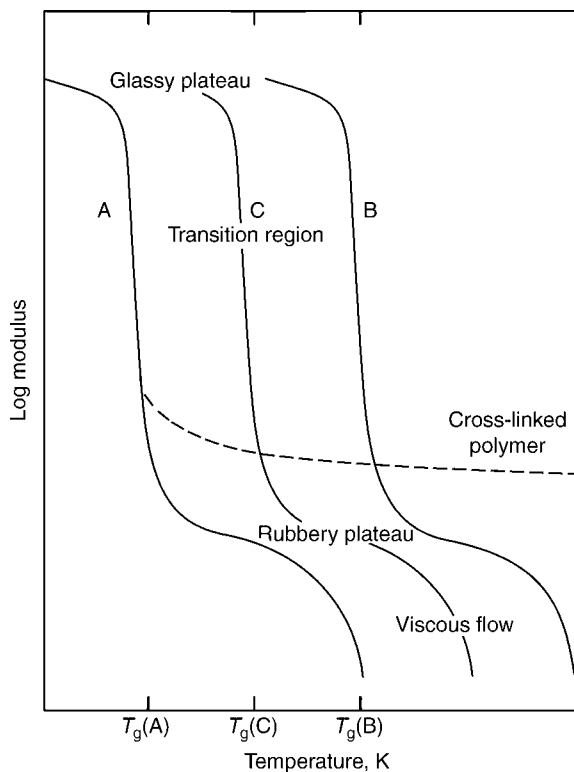
The tacticity of the polymer backbone can significantly influence the glass transition temperature of a given type of polymer. In general,  $T_g$  values decrease in the order syndiotactic > atactic > isotactic. Free radical polymerization (which constitutes the vast majority of industrial acrylic polymer production) generates mainly atactic polymers due to the symmetric nature of the radical species. Table 2 contains the  $T_g$  values for a variety of methacrylic ester polymers with different tacticity types.

A wide range of glass-transition temperatures can be accessed by copolymerizing methacrylic and acrylic ester monomers (Fig. 1). Values for the glass transition temperature can be calculated from the overall composition of the polymer as well as the individual  $T_g$  values for the homopolymers of the

**Table 2. Glass-Transition Temperatures of Atactic, Syndiotactic, and Isotactic Polymethacrylate Esters, °C<sup>a</sup>**

Methacrylate	Atactic	Syndiotactic	Isotactic
methyl	105	105	38
ethyl	65	66	12
<i>n</i> -propyl	35		
isopropyl	84	85	27
<i>n</i> -butyl	20		-24
isobutyl	53		8
<i>sec</i> -butyl	60		
<i>t</i> -butyl	118	114	7
cyclohexyl	104		110

<sup>a</sup> Refs. 13 and 14.



**Fig. 1.** Modulus-temperature curve of amorphous and cross-linked methacrylic polymers where A is a softer polymer, B, a harder polymer, and C, a 1:1 copolymer of A and B.

constituent monomers (17). Soft (low  $T_g$ ) components can be used as internal plasticizers or softeners which are permanently bound to the polymer backbone.

Modulus-temperature curves of the type shown in Figure 1 are useful for analyzing the degree of rigidity within a polymer. Not only can one observe the differences in hardness of a polymer, but crosslinking can also be measured through the proper use of the modulus-temperature curves (18). Crosslinking is generally used to increase the physical toughness and decrease the solubility of a polymer.

**2.2. Molecular Weight.** The properties of methacrylic ester polymers (and most other types of polymers for that matter) improve as molecular weight increases. Beyond a certain level (100,000–200,000 for methacrylic ester polymers) this improvement in polymer properties reaches a plateau. One example of a property that follows this trend is the glass transition temperature which can be described by the equation:

$$T_g = T_{gi} - k/M_n$$

where  $T_{gi}$  is the glass transition temperature for a polymer of infinite molecular weight and  $M_n$  is the number average molecular weight. Typical values of  $k$  fall in the range of  $2 \times 10^5$  (11) for methacrylic polymers. Reference 19 summarizes the effect of molecular weight on polymer properties.

Table 3. Comparison of Mechanical Properties of Polyacrylate and Methyl Methacrylate<sup>a</sup>

Ester	Tensile strength, MPa <sup>b</sup>		Elongation at break, %	
	Polymethacrylate	Polyacrylate	Polymethacrylate	Polyacrylate
methyl	62	6.9	4	750
ethyl	34	0.2	7	1800
butyl	6.9	0.02	230	2000

<sup>a</sup> Refs. 18 and 19.<sup>b</sup> To convert MPa to psi, multiply by 145.

**2.3. Mechanical Properties Related to Polymer Structure.** Although the contributions of the side chains influence polymer properties in similar fashion for both methacrylic and acrylic compositions, methacrylates exhibit higher  $T_g$  values than their acrylic counterparts (same side chain) because the  $\alpha$  hydrogen on the polymer backbone restricts the rotational motion of the backbone. This stiffening of the backbone is manifested as higher tensile strength and lower elongation for the methacrylic analogs to the acrylic polymers given the same side chain (see Table 3).

The smallest side chain monomer in the alkyl methacrylate series, methyl methacrylate polymerizes to form a hard material ( $T_g = 105^\circ\text{C}$ ) which can be cut into shapes. If the material is heated above its glass transition temperature, the p(MMA) can be bent or molded to fit any form desired. Upon cooling, the material retains the molded shape upon cooling; in this manner, fighter plane canopies, among other objects were made out of p(MMA) during World War II. This highly useful “flexible plastic glass” was sold by the Rohm and Haas Company under the trade name Plexiglas for several decades.

As the side chain length is increased for the methacrylate monomers, the  $T_g$  decreases rapidly for the series of C1–C12. *n*-Butyl methacrylate [97-88-1] homopolymer, for example, has a  $T_g$  value of  $20^\circ\text{C}$  and is far softer than p(MMA); lauryl methacrylate [142-90-5] continues the progression to softer, more rubbery materials ( $T_g = -65^\circ\text{C}$ ). After a certain length of chain is passed, the van der Waals attractive forces among the chains reach a level high enough that crystallization of the side chains takes place and the  $T_g$  moves to higher values. Octadecyl methacrylate [32360-05-7] polymerizes to form a hard polymer with a  $T_g$  of  $36^\circ\text{C}$ .

Another factor in the determination of how rigid a polymer backbone will be is the steric bulk of the side chain. Branching within the side chain will restrict the freedom of movement for the backbone in similar fashion as the  $\alpha$  hydrogen of the methacrylate monomers. As cited above, *n*-butyl methacrylate homopolymer has a  $T_g$  value of  $20^\circ\text{C}$ ; poly(*t*-butyl methacrylate), on the other hand, has a  $T_g$  of  $107^\circ\text{C}$ . The effect is proportional to the overall size of the side chain as well; the longer and more branched the chain, the more movement will be restricted and  $T_g$  will be elevated.

**2.4. Optical Properties.** Poly(methyl methacrylate) is essentially transparent in the 400–700 nm visible light range (23); this clarity along with the ease of machining described above, contribute to this material’s popularity as a substitute for glass. The polymer gradually becomes less transparent as the wavelength range is increased until the material is opaque beyond 2800 nm. Additives are commonly incorporated in poly(methyl methacrylate) cast sheets

Table 4. **Electrical Properties of 6.35-mm Thick Poly(methyl methacrylate) Sheet<sup>a</sup>**

Property	Typical values	ASTM method
dielectric strength short-term test, V/ $\mu\text{m}^b$	>16.9–20.9	D149
dielectric constant, V/ mm <sup>c</sup>		D150
at 60 Hz	142–154	
1,000 Hz	130–134	
power factor, V/cm <sup>d</sup>		D150
at 60 Hz	20–24	
1,000 Hz	16–20	
1,000,000 Hz	8–12	
loss factor, V/cm <sup>d</sup>		D150
at 60 Hz	75–87	
1,000 Hz	51–59	
1,000,000 Hz	24–31	
arc resistance	No tracking	D495
volume resistivity, $\Omega \cdot \text{cm}$	$1 \times 10^{14} - 6 \times 10^{17}$	D257
surface resistivity, $\Omega/\text{square}$	$1 \times 10^{17} - 2 \times 10^{18}$	D257

<sup>a</sup> Ref. 22.<sup>b</sup> To convert V/ $\mu\text{m}$  to V/mil, multiply by 25.4.<sup>c</sup> To convert V/mm to V/mil, divide by 39.4.<sup>d</sup> To convert V/cm to V/mil, divide by 394.

to block the transmission of UV rays in the wavelength range 290–350 nm. Poly(methyl methacrylate) allows radio and television broadcast waves to transfer through the material while blocking alpha and beta radiations (24).

Poly(methyl methacrylate) is capable of serving as a waveguide for visible light. When light is shone through the edge of poly(methyl methacrylate), the light emerges through the opposite edge of the material with virtually no loss of intensity; the primary reason for this property is that when visible light reaches the air/polymer interface at an angle of 42.2° or greater, it reflects back into the polymer intact. This useful optical property in combination with the mechanical properties described above has resulted in the p(MMA)'s use in fiberoptics, automotive taillights, camera lenses, remote lighting, reducers, magnifiers, and prisms (25).

**2.5. Electrical Properties.** Poly(methyl methacrylate) has an extremely high surface resistivity which, combined with the weather-resistance of the material, leads to the use of p(MMA) in high voltage applications. Some of these basic electrical properties (24) are listed in Table 4.

### 3. Chemical Properties

The chemical resistance properties of methacrylic ester polymers are even higher than those of the acrylic esters. Methacrylic esters undergo a lower degree of

Table 5. **Relative Outdoor Stability of Poly(methyl methacrylate)<sup>a</sup>**

Material	Light transmittance		Haze	
	Initial, %	After exposure, <sup>b</sup> %	Initial, %	After exposure, <sup>b</sup> %
poly(methyl methacrylate)	92	92	1	2
polycarbonate	85	82	3	19
cellulose acetate butyrate	89	68	3	70

<sup>a</sup> Ref. 25.<sup>b</sup> Three-yr outdoor.

hydrolysis in either acidic or alkaline media than acrylics. Both acrylics and methacrylics easily outperform vinyl acetate-containing polymers which are well known to be susceptible to hydrolysis of the side chain ester. There are marked differences in the chemical resistance properties of different forms of p(MMA). The syndiotactic (alternating) form of p(MMA) is the most chemically inert. The rate of hydrolysis for syndiotactic p(MMA) is lower than that of isotactic; radical polymerizations generate large portions of syndiotactic p(MMA) and benefit in terms of stability.

In terms of solubility resistance (22), p(MMA) is generally not harmed by inorganic solutions, mineral oils, animal oils, low concentrations of alcohols, paraffins, olefins, amines, alkyl monohalides, and aliphatic hydrocarbons and higher esters (>10 carbon atoms). Chemical species which will degrade p(MMA) include lower esters (ethyl acetate, isopropyl acetate), aromatic hydrocarbons (benzene, toluene, xylene, phenols), cresol, carbolic acid, aryl halides (chlorobenzene, bromobenzene), aliphatic acids (butyric acid, acetic acid), alkyl polyhalides (ethylene dichloride, methylene chloride), high concentrations of alcohols (methanol, ethanol, 2-propanol), and high concentrations of alkalies and oxidizing agents.

The chemical and photochemical resistance properties of p(MMA) are compared to two other transparent plastic materials in Table 5 (27). In terms of thermal stability, methacrylates will depolymerize (28) at a greater than 95% level when exposed to temperatures above 300°C.

#### 4. Methacrylate Monomers

**4.1. Properties.** Table 1 of METHACRYLIC ACID AND DERIVATIVES lists many of the basic properties of methacrylic acid monomers. Tables 6 and 7 contain many of the additional physical and thermodynamic properties for commercially important monomers (29–32).

**4.2. Manufacture of Monomers.** The commercial processes for manufacturing these monomers are contained in METHACRYLIC ACID AND DERIVATIVES (33).

**4.3. Handling, Health, and Safety of Methacrylic Monomers.** Mild steel is the material of choice for transporting and storing methacrylic ester monomers which are shipped by way of rail cars or tanker trucks. Stainless steel (Types 304 and 316) are used for transport and storage of acidic monomers.

Methacrylic monomers are relatively nontoxic based upon oral, dermal, and inhalation exposure test data for rats and rabbits (30,34,35). However, these

Table 6. Physical Properties of Commercially Available Methacrylate Monomers  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOR}^c$

Compound	Mol wt	Mp, °C	Bp, °C	Refractive index, $n_D^{25}$	Density $d_4^{25}$ , g/cm <sup>3</sup>	Flash point, °C <sup>b</sup>		Typical inhibitor, ppm <sup>c</sup>
						COC	TOC	
methacrylic acid	86.09	14	159–163 <sup>d</sup>	1.4288	1.015	77		100 MEHQ
methyl methacrylate	100.11	–48	100–101 <sup>d</sup>	1.4120	0.939		13	10 MEHQ
ethyl methacrylate	114.14		118–119 <sup>d</sup>	1.4116	0.909	35	21	15 MEHQ
<i>n</i> -butyl methacrylate	142.19		163.5–170.5 <sup>d</sup>	1.4220	0.889	66		10 MEHQ
isobutyl methacrylate	142.19		155 <sup>d</sup>	1.4172	0.882		49	10 MEHQ
isodecyl methacrylate	226		120 <sup>e,f</sup>	1.4410	0.878	121		10 HQ + MEHQ
lauryl methacrylate	262	–22	272–343 <sup>d</sup>	1.444	0.868	132		100 HQ
stearyl methacrylate	332	15	310–370 <sup>d</sup>	1.4502	0.864	>149		100 HQ
2-hydroxyethyl methacrylate	130.14	–12	95 <sup>g</sup>	1.4505	1.064	108		1200 MEHQ
2-hydroxypropyl methacrylate	144.17	<–70	96 <sup>g</sup>	1.4456	1.027	121		1200 MEHQ
2-dimethylaminoethyl methacrylate	157.20	ca –30	68.5 <sup>g</sup>	1.4376	0.933		74	200 MEHQ
2- <i>t</i> -butylaminoethyl methacrylate	185.25	>–70	93 <sup>g</sup>	1.4400	0.914	11		1000 MEHQ
glycidyl methacrylate	142.1		75 <sup>g</sup>	1.4482	0.073		84	25 MEHQ
ethylene glycol dimethacrylate	198.2		96–98 <sup>h</sup>	1.4520	1.048	113		60 MEHQ
1,3-butylene dimethacrylate	226		110 <sup>i</sup>	1.4502	1.011	124		200 MEHQ
trimethylolpropane trimethacrylate	338	–14	155 <sup>a</sup>	1.471	1.06	>149		90 HQ

<sup>a</sup>Refs. 27–30.

<sup>b</sup>COC = Cleveland open cup; TOC = Tagliabue open cup.

<sup>c</sup>MEHQ = monomethylether of hydroquinone; HQ = hydroquinone.

<sup>d</sup>At 101 kPa (1 atm).

<sup>e</sup>At 0.4 kPa/f.

<sup>f</sup>To convert kPa to mm Hg, multiply by 7.5.

<sup>g</sup>At 1.3 kPa/f.

<sup>h</sup>At 0.53 kPa/f.

<sup>i</sup>At 0.13 kPa/f.



Table 7. Thermodynamic Properties of Methacrylates<sup>a</sup>

Methacrylate	Heat of vaporization, kJ/g <sup>b</sup>	Heat capacity, J/(g · K) <sup>b</sup>	Heat of polymerization, kJ/mol <sup>b</sup>
methacrylic acid		2.1–2.3	56.5
methyl methacrylate	0.36	1.9	57.7
ethyl methacrylate	0.35	1.9	57.7
<i>n</i> -butyl methacrylate		1.9	56.5
2-hydroxyethyl methacrylate			49.8
2-hydroxypropyl methacrylate			50.6
2-dimethylaminoethyl methacrylate	0.31		

<sup>a</sup> Ref. 29.<sup>b</sup> To convert J to cal, divide by 4.184.

monomers can be skin sensitizers and are mildly to severely irritating after eye or skin contact. Liver and kidney damage can result from repeated near-lethal exposures. Overall toxicity is generally inversely proportional to the length of the side chain ester group (see METHACRYLIC ACID AND DERIVATIVES).

## 5. Manufacture and Processing

**5.1. Radical Polymerization.** The majority of commercial methacrylic ester polymers are produced by free-radical initiators. Peroxides and azo compounds function as typical initiators for this type of polymerization. Other possible routes for producing methacrylic polymers with radicals include photoinitiation and radiation-induced polymerization. Both gamma ray and electron beam radiation have been employed in the production of methacrylic ester polymers (36–38). At constant temperature, there is a first order dependence of the polymerization rate on monomer concentration and a one-half order dependence upon initiator concentration. Rate data for the polymerization of various methacrylic monomers using the azo compound 2,2'-azobisisobutyronitrile (AIBN) [78-67-1] are shown in Table 8.

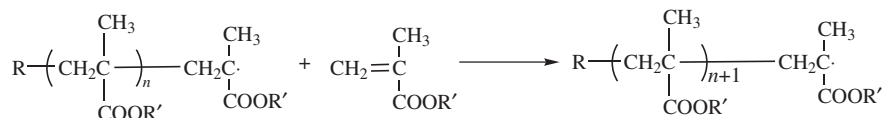
Table 8. Polymerization Data for Methacrylic Ester Monomers<sup>a</sup>

Methacrylates	$k_{sp}$ , <sup>b</sup> 44.1°C	Heat of polymerization, kJ/mol <sup>c</sup>	Shrinkage, vol%
methyl	27 <sup>d</sup>	57.7	21.0
ethyl	25 <sup>e</sup>	57.7	18.2
butyl	41 <sup>d</sup>	59.4	14.9

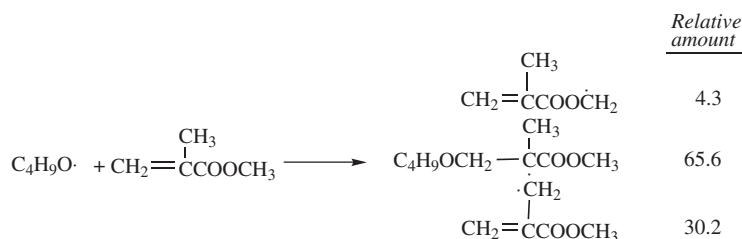
<sup>a</sup> Ref. 34.<sup>b</sup> The units of  $k_{sp}$  are L<sup>1/2</sup>/mol<sup>1/2</sup> · h<sup>-1</sup>. Initial rate of polymerization is calculated from  $k_{sp}$  and the concentration of AIBN using the following equation: initial rate of polymerization in %/h =  $k_{sp}$ /AIBN.<sup>c</sup> To convert kJ to kcal, divide by 4.184.<sup>d</sup> In bulk.<sup>e</sup> 2.5 M solution in benzene.

The polymerization of methacrylic monomers is highly exothermic and involves an increase in the density of the forming polymeric material. Both effects must be accounted for in industrial processes. The degree of shrinkage upon conversion from monomer to polymer decreases as the side chain length increases, but on a molar basis, the shrinkage level is relatively constant (40).

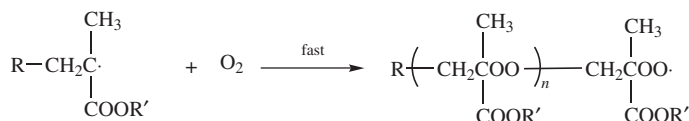
The propagation mechanism for the free-radical polymerization of methacrylic monomers involves the head-to-tail chain addition of monomer units to grow the polymer chain. Chain termination can occur by either radical combination or disproportionation (41).



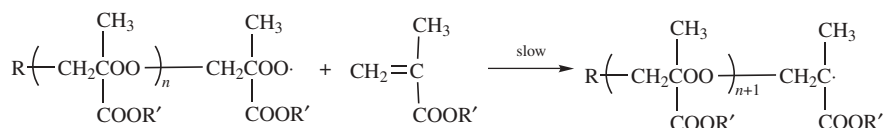
In the case of free-radical polymerizations initiated by oxygen-based radicals (eg *t*-butoxy radical), hydrogen abstraction from both the polymer backbone and the  $\alpha$ -methyl side chain also occurs (42–45).



As in many free-radical processes, oxygen will form an adduct with the active radical end of a polymer and slow the rate of polymerization. An alternating polymer consisting of methyl methacrylate and dioxygen units can be formed through this inhibition mechanism. For this reason, a positive flow of nitrogen is typically used in industrial processes. Extra care must be taken to exclude oxygen when running polymerizations at lower temperatures where oxygen solubility in water is higher.



The addition of the  $\text{O}_2$  unit is very rapid, but due to this relative stability of this adduct, the overall rate of polymerization slows down markedly. Termination levels increase as more  $\text{O}_2$  adducts are formed.



In addition to the decrease in overall polymerization rate, there are decreases in kinetic chain length and molecular weight distribution observed when these polymerizations are run in the presence of oxygen (46).

Copolymerization affords a great deal of leverage in tuning the final properties of methacrylic polymers. Methacrylic ester monomer copolymerize smoothly with acrylic monomers; this ease of copolymerization allows one to create copolymer materials with widely varying properties by using the soft, flexible acrylics with hard, brittle methacrylics. One can control properties further by controlling molecular architecture such that alternating polymer chains with methacrylate-rich and acrylate-rich segments are formed. Finally, specialty monomers can be used in small amounts to specifically target certain properties (eg, film adhesion to certain substrates) or to allow for further reactions such as crosslinking. Some of the more common specialty functional monomers are displayed in Table 9.

**Bulk Polymerization.** Bulk polymerization is used primarily for the production of cast sheets of poly(methyl methacrylate). During the course of these polymerizations, an auto-acceleration known as the Trommsdorf or Gel Effect is observed at approximately 20–50% conversion. This phenomenon is attributable to an increase in viscosity as monomer is converted to polymer within the

Table 9. **Common Functional Monomers for Copolymerization with Acrylic and Methacrylic Esters**

Functionality	Monomer	Structure
carboxyl	methacrylic acid	$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{COOH}$
	acrylic acid	$\text{CH}_2=\text{CHCOOH}$
	itaconic acid	$\text{CH}_2=\underset{\text{CH}_2\text{COOH}}{\text{C}}-\text{COOH}$
amino	2- <i>t</i> -butylaminoethyl methacrylate	$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{COO}(\text{CH}_2)_2\text{NHC}(\text{CH}_3)_3$
	2-dimethylaminoethyl methacrylate	$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{COO}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$
hydroxyl	2-hydroxyethyl methacrylate	$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{COOCH}_2\text{CH}_2\text{OH}$
	2-hydroxyethyl acrylate	$\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{OH}$
<i>N</i> -hydroxymethyl	<i>N</i> -hydroxymethyl acrylamide	$\text{CH}_2=\text{CHCONHCH}_2\text{OH}$
	<i>N</i> -hydroxymethyl methacrylamide	$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{CONHCH}_2\text{OH}$
oxirane	glycidyl methacrylate	$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{COOCH}_2\text{CH}(\text{O})\text{CH}_2$
multifunctional	1,4-butylene dimethacrylate	$(\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{COOCH}_2\text{CH}_2)_2$

reactor. Once the viscosity reaches the critical point, termination begins to slow down below the rate of propagation. Therefore, the overall rate of polymerization increases and an increase in the rate of heat generated from the reactor is observed. Because termination is slowing, the molecular weight of material generated after the Gel Effect point has been reached is higher than material generated earlier in the process; molecular weight in this case is limited only by the diffusion of monomer to the growing radical chain end (47).

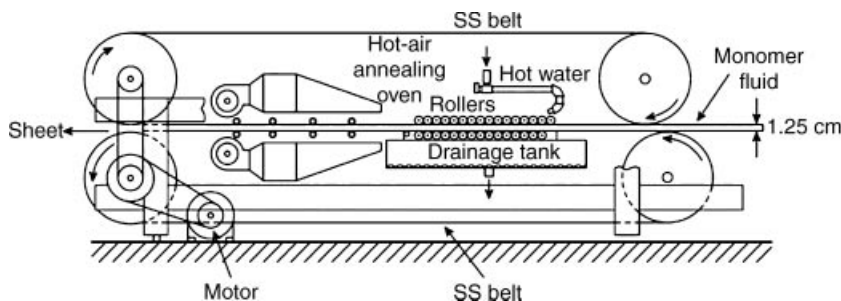
Three main types of bulk polymerization are practiced commercially: batch cell casting, continuous casting, and continuous bulk. Batch cell casting is used to produce roughly half of the poly(methyl methacrylate) generated globally with the continuous casting and continuous bulk methods splitting the remainder of production equally. Sheets are produced with widths of approximately one meter and lengths of several meters; thicknesses range from 0.16 to 15 cm.

*Sheet Production.* p(MMA) sheets are produced with all three methods of bulk polymerization. Due to its inherent ease of operation, batch cell dominates this area (48–52). In this method, each sheet is formed in a mold composed of two plate glass sheets separated by a flexible spacer; a flexible spacer with springs attached is needed so that the plates can be brought closer together during the course of the polymerization to account for the increase in density as monomer is being converted to polymer. The mold is filled from one open corner with monomer (or monomer/polymer syrup), initiator, and other additives; the mold is then closed to begin the curing process. Curing itself is accomplished through the use of a carefully controlled temperature ramp to ensure complete cure and to minimize any possibility of losing control of the polymerization exotherm. The curing process takes anywhere from 10 hours for thin sheets to several days for the thickest materials. Once formed, the polymer sheets are cooled separated from their reusable glass holders. The finished sheet is then annealed at 140–150°C over the course of several hours to reduce stress within the sheets and guarantee completeness of cure.

Monomer–polymer syrups are used to: 1) aid in the shrinkage issues encountered in the formation of p(MMA) sheets, 2) shorten the polymerization induction period, and 3) lower the temperature necessary for initiation. These syrups contain roughly 20% polymeric material along with the monomer and can be made either by dissolving 20% finished p(MMA) in monomer or partially polymerizing a batch of p(MMA) to the 20% level. Batch cell casting can also be used for the production of p(MMA) rods and tubes.

Continuous production of p(MMA) is accomplished using a method developed in 1968 (53). This method (Figure 2) utilizes a polymer/monomer syrup which is delivered to a curing and annealing apparatus between two parallel stainless steel belts that are held at an angle to maintain the desired spacing between the belts. A gasket seals the reacting zone of the setup while it moves down the line at approximately 1 m/min. The reaction conditions for this type of reactor are ~70°C for ~45 min and ~10 min annealing time at ~110°C. Masking tape is used to protect the sheets when they have cooled.

Poly(methyl methacrylate) is thermoplastic and can be formed into practically any shape when heated (54,55). Continuous production is employed when thin sheets are desired or highly filled materials (e.g. synthetic marble) are being formed.



**Fig. 2.** Continuous process for manufacturing poly(methyl methacrylate) plastic sheet.

**Molding Powder.** Poly(methyl methacrylate) is used extensively in injection and extrusion molding of plastics (56). The p(MMA) can take many forms from 0.3 cm pellets to fine beads and granulated powders. The molding powders are formed by extrusion of either bulk polymerized methyl methacrylate or from a polymer–monomer syrup which is heat treated to remove the unreacted MMA. The p(MMA) emerges as a narrow rod which is chopped into the appropriately sized powder.

**Synthetic Marble.** Highly filled monomer or monomer–polymer syrup mixtures are used to form synthetic marble materials. A single belt approach can be employed in the formation of synthetic marble with only one smooth side (57,58). Aluminum oxide, calcium carbonate, titanium dioxide, etc. are used at loading levels of ~60%; the specific materials of choice are determined according to the translucence, chemical resistance, and water resistance properties desired (59,60).

**Solution Polymerization.** Solution polymerization is a commercially significant means of manufacturing methacrylic polymers for the coatings, adhesives and laminates markets. Soluble peroxides, peroxyphthalates, and azo initiators are used to initiate the polymerization in an organic solvent. Polymers with molecular weights in the range of 2,000–200,000 are made by this process. Higher molecular weights generate viscosities which are very difficult to process and are typically made by other processes (61,62).

The solubility properties of solution polymers depend upon the length of the ester side chain. Polymers with less than four carbons are soluble in aromatic hydrocarbons and only sparingly soluble in aliphatic hydrocarbons. Those polymers which are made from higher alcohols are soluble in aliphatic hydrocarbons. Solvent not only plays a role in solubilizing the polymer but also as a chain transfer agent which helps control the viscosity of the solution polymer by keeping the molecular weight low. Chain transfer constants ( $C_s$ ) for methyl methacrylate in common solvents are given in Table 10.

Initiator choice is another important consideration for solution polymerizations; the rate of thermolysis, cost, and initiator solubility in the diluent solvent are considerations in the choice of reaction solvent. Use levels range from a few hundredths of a percent to several percent by weight on the monomer used in the synthesis. The molecular weight of the polymer produced is inversely proportional to the level of initiator employed in the synthesis. Another consideration in the choice of initiator is the tendency of hydroperoxides to abstract hydrogens

Table 10. Chain-Transfer Constants for Methyl Methacrylate

Type	$C_s \times 10^5$ at 80°C	$C_s$ at 60°C
<i>Solvents</i> <sup>a</sup>		
benzene	0.8	
toluene	5.3	
chlorobenzene	2.1	
2-propanol	19.1	
isobutyl alcohol	2.3	
3-pentanone	17.3	
chloroform	11.3	
carbon tetrachloride	24.2	
<i>Chain-transfer agent</i> <sup>b</sup>		
carbon tetrabromide		0.27
butanethiol		0.66
<i>t</i> -butyl mercaptan		0.18
thiophenol		2.7
ethyl mercaptoacetate		0.63

<sup>a</sup> Refs. 58 and 59.<sup>b</sup> Ref. 60.

from the polymer backbone and side chains. *Tert*-amylhydroperoxide and di-*tert*-amylperoxide generate *tert*-amylloxy radicals which undergo beta scission to generate ethyl radicals and one equivalent of acetone. The carbon-based ethyl radicals have lower energy than their oxygen based sources (63). In addition to solvent and initiator selection, molecular weight can be controlled through the use of chain transfer agents and manipulation of the monomer concentration and reaction temperature (64).

Stainless steel is the material of choice for reactors used in solution polymerization. Nickel and glass can also be employed provided that the reactor is constructed to withstand pressures of 446 kPa (65 psi). Because of the wide range of viscosities encountered in solution polymerization, a variety of stirring impellers are employed. For lower viscosities (<1000 cP) an anchor-type agitator is used; higher viscosities necessitate the use of a ribbon-type impeller which sweeps virtually the entire volume of the reactor and, therefore, prevents polymer from remaining near the edges of the reactor.

Temperature control is of utmost importance in solution polymerizations due to the large quantity of heat liberated during the course of the polymerization. All industrial-scale reactors include cooling jackets and rupture disks in order to control the temperature and conditions within the reactor. In order to maintain efficient cooling of a solution polymer batch, it is imperative to maintain control over the viscosity of the batch. Another method for controlling reactor temperature is through the gradual addition of monomers to the batch; total cycle times for these batches generally fall in the range of 8–24 hours (65). As a final precaution a chemical inhibitor is stored in the reactor area in order to quickly shut down the polymerization in the event that temperature control is compromised.

A typical reactor charge sheet for the solution polymerization of a terpolymer containing 27.5% 2-ethylhexyl acrylate, 41.3% methyl methacrylate, and 31.2% hydroxyethyl methacrylate is shown below:

<i>Reactor charge</i>	<i>Parts, wt%</i>
xylene	28.4
ethoxyethanol	14.1
<i>Monomer charge</i>	
2-ethylhexyl methacrylate	15.5
methyl methacrylate	23.3
hydroxyethyl methacrylate	17.6
<i>Initiator charge</i>	
<i>t</i> -butyl perbenzoate	1.1

For this polymerization, a reactor temperature of  $\sim 140^{\circ}\text{C}$  is maintained for roughly three hours while the monomer mixture is fed into the reactor. Following the completion of the monomer addition, the batch is held at  $140^{\circ}\text{C}$  to finish the batch. The final product consists of a 58% solids clear, viscous polymer which is cooled and packaged for delivery to the customer (66).

Stainless steel is used for the shipping and ground transport of methacrylic resins. Depending on the size of a particular order, these resins can be delivered in drums, tank trucks, or rail cars; water is rigorously excluded to prevent rusting and discoloration of the solution polymer. Because of the temperature dependence of the viscosity of these polymers, all transport containers are maintained at a specific temperature in order to permit effective transfer of the material once it has been delivered (67). Again, steel is the material of choice for the construction of transfer valves and pipes.

**Emulsion Polymerization.** Methacrylic ester latex polymers and copolymers are employed in the architectural coatings, paper, textile, floor polish, and leather industries. Methacrylic esters are most typically copolymerized with acrylates such as ethyl acrylate and butyl acrylate. These products are opaque, milky-white dispersions which can be formed at 30–60 wt% solids levels. One of the principal advantages to the use of emulsion polymerization versus solution is that the viscosity of the material is independent of molecular weight (68,69). Extremely high molecular weights ( $>1,000,000$ ) can be obtained without any viscosity penalty being incurred. Particle sizes for these polymer latexes typically fall in the range of 0.1–1  $\mu\text{m}$ . The polymerizations themselves take place very rapidly with the latex water continuous phase providing a tremendous amount of heat capacity to the batch so that temperature control becomes more facile than in solution polymerization. The use of water also allows the polymer producer to eliminate the expensive and hazardous solvents often employed in solution polymerization.

Surfactants are employed to stabilize the emulsion polymer particles; anionic, cationic, and steric stabilizers are all used for the production of latexes depending on whether one wants a negative, positive or neutral potential surface on the formed polymer particle. The specific anionic options available for use are alkyl sulfates, alkyl sulfosuccinates, and alkylarene sulfonates and phosphates. Standard nonionic surfactants include alkyl or aryl polyoxyethylenes. In recent years, alkyl phenol ethoxylates have fallen into disfavor because of their reported problems with bioaccumulation in aquatic life. This still somewhat controversial environmentally-driven issue has necessitated the use of alternative surfactants which have a lower impact on the environment. Typically, the aryl ring is eliminated to solve this problem.

Initiation for emulsion polymerizations occurs in the aqueous continuum; therefore, water soluble initiators such as ammonium or sodium persulfate are used. This oxidizing initiator can be cleaved either thermally or via redox reaction to generate sulfate radicals which function as the initiating species for these polymerizations. One of the advantages in using the redox approach for initiation is the temperature-independence of the rate for this reaction. Emulsion polymerizations can be run in the 25–60°C range versus 75–90°C for thermally initiated runs. In order to run a redox-initiated polymerization, a reductant is needed to directly or indirectly (through the use of a multivalent metal promoter) reduce the oxidant. Although there are many choices, common reductants include isoascorbic acid [89-65-6], sodium sulfoxylate formaldehyde [6035-47-8], and sodium hydrogensulfite [7631-90-5].

Reactors for the emulsion polymerization of methacrylic esters are made of stainless steel and are jacketed for temperature control; these reactors are built to withstand pressures of 446 kPa (65 psi) and contain emergency stacks with rupture disks in case of excess pressure buildup within the reactor. Agitation is a critical issue for emulsion polymerization. Variable speed drive shafts are used along with stainless steel agitators to mix the batch. Baffles on the reactor walls are also common features of industrial emulsion polymerization reactors. Temperature control is maintained through the use of steam and cold water circulation with the jacket of the reactor. Feed lines for the monomer emulsion, initiators, and reductants are placed at the top of the kettle. Figure 3 contains a schematic for a typical industrial emulsion polymerization reactor.

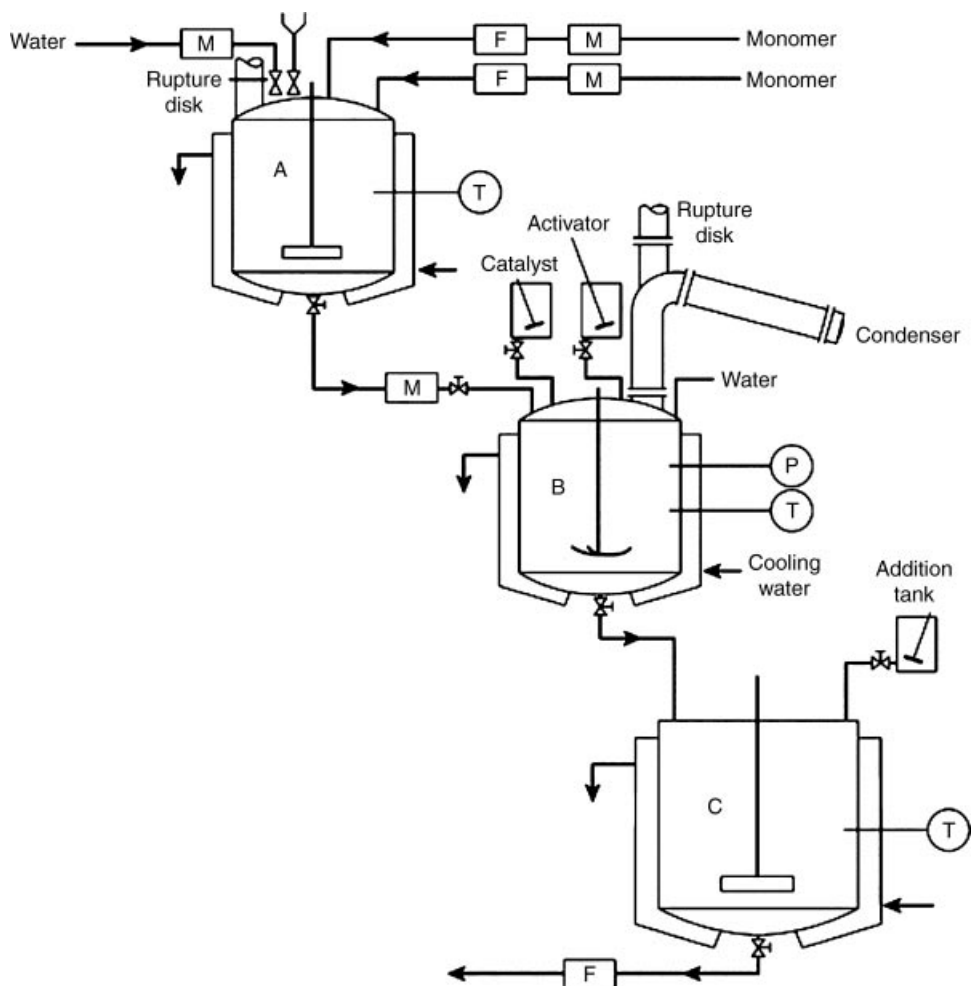
Monomer emulsion preparation takes place in stainless steel tanks which are equipped with their own pressure gauges, temperature indicators, and rupture disks. Due to the high (>70%) monomer content in a typical emulsion, close attention must be paid to the emulsion to ensure that it does not autoinitiate and produce an uncontrolled exotherm. Once safely formed, monomer emulsions can be added to the main reactor chamber either all at once or via gradual addition. Gradual addition is more commonly employed so that a high degree of temperature control is maintained.

Following the polymerization, the polymer latex is transferred to a drumming tank which serves as a temporary storage vessel from which the polymer is packaged for delivery to the customer. Drumming tanks are additionally used to adjust the pH, solids content, and other final properties of the latex. For this purpose, drumming tanks are equipped with their own agitation systems. Following filtration, the latex is transferred from the drumming tank into a storage vessel either for immediate delivery or for temporary storage on-site.

A typical recipe for an emulsion polymerization process is contained in the table below (70,71):

<i>Monomer emulsion charge</i>	<i>Parts</i>
deionized water	13.65
sodium lauryl sulfate	0.11
methyl methacrylate	22.50
butyl acrylate	22.05
methacrylic acid	0.45





**Fig. 3.** Emulsion polymerization plant: A, emulsion feed tank; B, polymerization reactor; C, drumming tank; F, filter; M, meter; P, pressure gauge; and T, temperature indication.

This process generates a 50% methyl methacrylate, 49% butyl acrylate, 1% methacrylic acid terpolymer at 45% solids. The monomer emulsion is first formed by adding the ingredients in the order listed while agitating the monomer emulsion container. The reactor charge (30.90 parts deionized water and 0.11 parts sodium lauryl sulfate) are added and heated to 85°C. The initiator (0.23 parts ammonium persulfate) is then charged prior to the beginning of the monomer emulsion feed. The emulsion is fed over 2.5 hours, and a reactor temperature of 85°C is maintained during the monomer emulsion feed and subsequent polymerization. Upon completion of the emulsion feed, the reactor temperature is raised to 95°C for 1/2 hour to complete the polymerization both in terms of monomer conversion and persulfate decomposition. The polymer latex is then cooled to room temperature, filtered, and packaged.

Latex polymers and copolymers of methacrylic esters are shipped in drums, tank trucks, and rail cars constructed of stainless-steel or resin-coated steel and are insulated to prevent freezing of the latex. Storage tanks are, likewise, insulated and in some cases heated to prevent freezing of the latex material. Sedimentation, skinning (surface film), gritting (solids formation within latex), gumming (deposition on walls), and sponging (aerogel formation) are all concerns in the stabilization of methacrylic polymer dispersions. Other issues in the storage and handling of latexes include pH drift, evaporation, temperature fluctuation, shear and turbulence, and foaming (see FOAMS). Bactericides are commonly used to preserve polymer latexes from microbial attack (65).

**Suspension Polymerization.** In order to form polymer dispersions with particle sizes  $>1$  mm, suspension polymerization is used. The beads generated via this method of polymerization find their main usage in ion-exchange resins and molding powders. Molding powder compositions range from 100% methyl methacrylate to 20% acrylate copolymer for increased flexibility and improved processing properties. Amino or acid functional monomers are additional options in copolymer suspension polymerizations for ion-exchange; di- or tri-functional monomers are included in order to controllably crosslink the polymer beads.

The initial step in a suspension polymerization involves the suspension of 0.1–5 mm monomer droplets in water. The droplets are stabilized against ripening by the inclusion of a protective colloid or suspension agent. Unlike emulsion polymerization, an oil soluble initiator is used for suspension polymerizations. The initiator enters the monomer droplet and is thermally dissociated to produce radicals and initiate polymer chain growth. Water again served as a dispersion medium and a heat sink within these polymerizations. Particle sizes generated using this method are in the 0.1–5 mm range and are controlled through the suspension agent as well as the agitation rate. The polymer beads are isolated and washed via filtration or centrifugation.

Suspension agents commonly used include cellulose derivatives, polyacrylate salts, starch, poly(vinyl alcohol), gelatin, talc, clay, and clay derivatives (65,72). The primary role of these agents is the preserve a specific monomer droplet size and prevent the ripening (enlargement through coalescence) of the monomer droplets. Glycerol, glycols, polyglycols, and inorganic salts are also used to enhance suspension polymer properties (65). Finally, lubricants such as lauryl or cetyl alcohol and stearic acid and crosslinkers such as di- and trivinylbenzene, diallylesters of dibasic acids, and glycol dimethacrylates are common components of suspension processes.

Polymerization takes place within the monomer droplets and, therefore, follows a course consistent with the behavior of a bulk polymerization (65,73). Ideally, there are no transfer processes taking place between the aqueous continuum and the monomer droplets during these polymerizations. Initiators such as azo and peroxy compounds are chosen such that they are highly soluble in the monomer phase and highly insoluble in the aqueous phase; molecular weight distributions are determined in large part by the amount of initiator charged to a particular polymerization (65).

Reactor equipment is very similar to that used in emulsion polymerizations as depicted in Figure 3. The agitation and safety hardware are virtually identical as are the materials of construction. In a typical polymerization the water,

suspension agents, monomer mixture, initiator and other additives are charged to the reactor kettle in this order. The reaction mixture is then heated under careful agitation to the desired initiation temperature. Large rises in temperature and/or pressures are often encountered in suspension polymerizations; reaction times are quite rapid for this type of polymerization. Once finished, the slurry is cooled and filtered or centrifuged to isolate the polymer beads. The beads are then washed with copious amounts of water and dried either on aluminum trays in an oven maintained at 80–120°C or in a stainless steel rotary vacuum drier (65) (see DRYING).

A standard suspension polymerization process for the production of poly(methyl methacrylate) beads begins with the charging of 24.64 parts of methyl methacrylate and 0.25 parts of benzoyl peroxide to a 30°C solution containing 0.42 parts disodium phosphate, 0.02 parts monosodium phosphate, and 0.74 parts of Cyanomer A-370 (polyacrylamide resin) in 79.93 parts of deionized water. The reaction mixture is brought to 75°C and held there for three hours. After cooling, the beads are isolated by filtration, washed with water, and dried (74).

**Nonaqueous Dispersion Polymerization.** A nonaqueous dispersion polymer (NAD) can be formed by first dissolving a methacrylic monomer in organic solvent and polymerizing to form an insoluble polymer in the presence of an amphipathic graft or block copolymer. The block or graft copolymer serves as a stabilizing agent and allows the insoluble methacrylic polymer to form a stable colloidal particle. Particle sizes for these samples range from 0.1 to 1.0  $\mu\text{m}$  with outliers in the range of 15  $\mu\text{m}$  possible (75–77). These polymers are often used in the coatings industry as substitutes for aqueous emulsion polymers. The advantages of NADs over emulsion polymers include low heat of evaporation and drying which is independent of the prevailing humidity level; disadvantages include toxicity of organic solvents, odor, cost, and flammability. Table 11 displays some examples of commercially significant NADs.

**Graft Polymerization.** The construction of graft polymers involves the attachment of side branches of one composition to a main chain of a separate composition. One method of preparation depends upon the creation of radical sites along the main chain so that branches of the second composition can be

Table 11. **Examples of Methacrylic Nonaqueous Dispersion Polymers**

Polymer	Diluent	Dispersant	Reference
poly(methyl methacrylate)	aliphatic hydrocarbon	hydroxystearic acid–acrylic graft copolymer	70
poly(methyl methacrylate)	aliphatic hydrocarbon	drying oil-modified polyester	72
poly(methyl methacrylate)	hexane	isobutylene-co-isoprene graft copolymer	73
poly(methyl methacrylate)	methanol	ethylene glycol–methyl methacrylate graft copolymer	74
poly(octyl methacrylate)	methanol	ethylene glycol–octyl methacrylate graft copolymer	70
poly(methacrylic acid)	chloroform–ethanol	methacrylate functional polyester	70

grown out from monomer to create the grafted portions (80–82). Graft polymers may take the form of solution polymers, bulk polymers, or dispersions. MBS and MABS are the most commercially significant graft polymers. Grafting methods used have included chemical (83,84), photochemical (85), radiation (85,86), and mastication (87). Methyl methacrylate has been grafted onto such diverse polymer backbones as cellulose (88), poly(vinyl alcohol) (89), polyester (90), polyethylene (91), poly(styrene) (92), poly(vinyl chloride) (93), and other alkyl methacrylates (94).

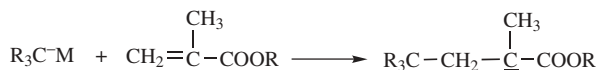
The preparation of MABS first involves the dissolution or dispersion of polybutadiene in a methyl methacrylate/acrylonitrile mixture which can either serve as the continuous phase in bulk polymerization or take the form of monomer droplets in suspension polymerization. The refractive indices of the two phases formed are matched such that the final material is tough, transparent, highly impact-resistant, and able to be melted and formed into diverse shapes.

MBS polymers are prepared via an emulsion polymerization process which consists of the formation of methyl methacrylate and styrene grafts on an already-formed styrene-butadiene backbone. The final product is used as an impact modifier in poly(vinyl chloride) materials.

**5.2. Ionic Polymerization.** Cationic polymerization is not an option in the formation of methacrylic ester polymers. Methacrylic monomers can, in fact, be used as solvents or cosolvents in the formation of polymer by a cationic mechanism (95,96).

Anionic polymerization, on the other hand, is frequently used to form methacrylic ester polymers. Initiation is accomplished in organic solvents via organometallic initiating species. Polymers of exceptionally narrow molecular weight distributions are possible by using anionic polymerization; molecular architecture can be finely controlled as well. Polymers with high degrees of crystallinity are also obtainable through the careful control of reaction conditions. The method has not yet achieved large scale commercial success because of the high costs involved in the formation of these polymers. Stereoregular poly(methyl methacrylate) (97,98) and poly(*n*-butyl methacrylate) have been prepared through the use of anionic polymerization. Polar solvents are used to form syndiotactic polymers and nonpolar solvents are employed in the formation of isotactic anionic polymers; solvent choice can, therefore, be used to form polymers with entirely different physical properties. The anionic polymerization of methacrylic esters has been covered extensively in the literature (100–103).

Michael additions are thought to be responsible for initiation in anionic polymerization:



Chain growth occurs through the head-to-tail addition of monomer units:



Although it is possible to polymerize both methacrylic and acrylic esters by anionic polymerization (104), copolymers of these two classes are not observed.

Group transfer polymerization (GTP), first reported by DuPont in 1983 (105), allows the production of methacrylic esters with controlled architectures. This technique uses a silyl ketene acetal initiator to produce block polymers, comb-graft polymers, star polymers, and functional polymers (105,106).

**5.3. Living Polymerization.** One of the most exciting areas currently in the radical polymerization of methacrylic ester monomers is the field of living polymerization. Living polymers are defined by Szwarc in ref. 107 as: "polymers that retain their ability to propagate for a long time and grow to a desired maximum size while their degree of termination or chain transfer is still negligible." Due to these properties, exceptional control can be exercised over the topology (ie, linear, comb), composition (ie, block, graft), and functional form (ie, telechelic, macromonomer) of these polymers (108).

Atom transfer radical polymerization (ATRP) and nitroxide-mediated (109–111) polymerization both show promise in terms of the ability to fine-tune polymer architecture using living radical methods. ATRP has been successfully used in the polymerization of methyl methacrylate using copper (112), ruthenium/aluminum alkoxide (113), iron (114), and nickel (115) catalyst systems.

## 6. Analytical Test Methods and Specifications

**6.1. Plastic Sheet.** Clear and colored transparent, clear and colored translucent, and colored semi-opaque poly(methyl methacrylate) sheets are manufactured commercially. Properties such as ultraviolet resistance, mar resistance, crazing resistance, impact resistance, and flame resistance can be improved through the use of additives. Some of the physical properties of poly(methyl methacrylates) are displayed in Table 12.

**6.2. Solution Polymers.** The main properties of interest for solution polymers are their composition, solids content, solvent type, viscosity, molecular weight, and glass-transition temperature. Composition information can be obtained through refractive index measurements, spectroscopic techniques, and pyrolytic gas-liquid chromatography. Solids content is measured by volatilizing the diluent solvent and measuring the percentage decrease in sample mass. Solution viscosities can be measured via Brookfield viscometer; intrinsic viscosity can be used to obtain estimates of solution polymer molecular weights (117).

**6.3. Emulsion Polymers.** Methacrylic ester latex properties for characterization include composition, solids content, particle-size distribution, viscosity, pH, glass-transition temperature ( $T_g$ ), and minimum film-forming temperature (MFFT). Composition information is obtained through NMR spectroscopy, pyrolytic gas-chromatography, and refractive index measurement. Gravimetric methods are used to measure solids content; particle size distribution information is obtained through light scattering methods, microscopy or capillary hydrodynamic flow (CHDF) techniques. Photon correlation spectroscopy is also used to measure particle size distributions (118). Viscosity measurements are made

Table 12. Typical Properties of Commercial Poly(methyl methacrylate) Sheet<sup>a</sup>

Property	Value	ASTM test method
specific gravity	1.19	D792 66
refractive index	1.49	D542 50 (1965)
tensile strength		D638 64T
maximum, MPa <sup>b</sup>	72.4	
rupture, MPa <sup>b</sup>	72.4	
elongation, max, %	4.9	
elongation, rupture, %	4.9	
modulus of elasticity, MPa <sup>b</sup>	3103	
flexural strength		D790 66
maximum, MPa <sup>b</sup>	110.3	
rupture, MPa <sup>b</sup>	110.3	
deflection, max, cm	1.52	
deflection, rupture, cm	1.52	
modulus of elasticity, MPa <sup>b</sup>	3103	
compressive strength		D695 68T
maximum, MPa <sup>b</sup>	124.1	
modulus of elasticity, MPa <sup>b</sup>	3103	
compressive deformation under load <sup>c</sup>		D621 64
14 MPa <sup>b</sup> at 50°C, 24 h, %	0.2	
28 MPa <sup>b</sup> at 50°C, 24 h, %	0.5 <sup>e</sup>	
shear strength, MPa <sup>b</sup>	62.1	D732 46 (1961)
impact strength		
charpy unnotched, J/cm <sup>2d</sup>	2.94	D255 56 (1961)
Rockwell hardness	M-93 <sup>e</sup>	
hot forming temperature, °C	144–182	
heat distortion temperature		D648 56 (1961)
2°C/min, 1.8 MPa, <sup>b</sup> °C	96 <sup>e</sup>	
2°C/min, 0.46 MPa, <sup>b</sup> °C	107 <sup>e</sup>	
maximum recommended continuous service temperature, °C	82–94	
coefficient of thermal expansion, cm/cm/°C × 10 <sup>-5</sup>		
-40°C	5.0 × 10 <sup>-5</sup>	
-18°C	5.6 × 10 <sup>-5</sup>	
5°C	6.5 × 10 <sup>-5</sup>	
27°C	7.6 × 10 <sup>-5</sup>	
38°C	8.3 × 10 <sup>-5</sup>	
coefficient of thermal conductivity, kW/(m · K)	0.00344	
specific heat, 25°C, kJ/(kg · °C) <sup>f</sup>	0.452	

<sup>a</sup> Ref. 102.<sup>b</sup> To convert MPa to psi, multiply by 145.<sup>c</sup> Conditioned 48 h at 50°C.<sup>d</sup> To convert J/cm<sup>2</sup> to lbf/in., divide by 0.0175.<sup>e</sup> Values change with thickness; the reported value is for 0.635 cm.<sup>f</sup> To convert kJ to kcal, divide by 4.184.

using Brookfield or similar viscometers. Finally, glass-transition measurements can be made either by dynamic mechanical analysis (DMA) or differential scanning calorimetry (DSC).

Emulsion polymers typically have a series of stability tests run on them before they are approved for sale commercially (119). These tests include

freeze–thaw, mechanical shear, and thermal stability. The settling tendencies of a latex are assessed as are the formulation stability with regard to other dispersions, salts, surfactants, and pigments.

**6.4. Suspension Polymers.** Suspension polymers of methacrylic esters are characterized by their composition and particle size distribution. Because of their large particle sizes, these materials are typically passed through sizing screens which separate the various fractions according to polymer bead diameter. Materials destined for the molding powders market are subjected to melt-flow studies under the conditions of use that they will encounter for their specific application. Ion-exchange beads are, likewise, studied with regard to their ion-exchange capacity, density (wet and apparent), solvent swelling, moisture holding capacity, porosity, and salt-splitting characteristics (120).

## 7. Health and Safety Aspects

Provided that there are no toxic additives or high levels of residual monomers, methacrylic ester polymers are classified as nontoxic. These materials find use in dental fillings, dentures (see DENTAL APPLICATIONS), contact lenses, medicine dispensers, and food packaging. However, some acrylic and methacrylic dispersions can be skin or eye irritants due to the surfactants used in stabilization.

Due to the toxicity of the monomers involved in forming methacrylic ester polymers, extra precautions are taken to avoid any release of monomer into the surrounding area. Most industrial polymerization reactors are run with closed kettles to prevent monomer vapor from escaping into the surrounding air.

One of the hazards uniquely associated with the production of methacrylic powders and sheets is explosion of polymer dust. These materials are flammable and must be treated with care to avoid static discharges which can serve as ignition sources. Poly(methyl methacrylate) is widely used in buildings under codes which limit the fire hazards associated with this material. Solution polymers of methacrylic esters are considered flammable while latex emulsion polymers are nonflammable due to the aqueous continuous phase.

## 8. Uses

The primary market for methacrylate resins in the US is in the glazing and skylights area. These resins also find significant usage in consumer products, transportation signs, lighting fixtures, plumbing (spas, tubs, showers, sinks, etc), panels, and siding (121,122).

**8.1. Glazing.** Methacrylic ester polymers are well-suited for use as glazing, lighting, or decorative materials because of their unique balance of light transmittance, light weight, dimensional stability, and formability as well as their weather, impact, and bullet resistance. Some of the specific applications for these materials include windows for aircraft fuselages (123), banks, police cars, hockey rinks, storm doors, bath and shower doors, and showcases. The ability to manufacture either colored or clear versions of methacrylate sheets recommends their use in decorative window mosaics, side glazing, color

coordinated structures, and in sunscreens (124,125). Both sheets and molding pellets have been used for lighting, solar control, and in signs (126–130).

**8.2. Medicine.** For years, dentures, dental fillings, and denture bases have been made using methacrylic ester polymers (131,132) (see DENTAL MATERIALS). These polymers can also be used to prevent tooth decay in natural teeth by serving as a barrier which can be coated over the surface of the tooth. The dimensional behavior of these bone-cement composites has been reported (133) as has the structure of the cold-cured acrylic resin (134). Both hard and soft contact lenses have been made using polymethacrylates (135,136). Hydrogels (qv) comprising poly(2-hydroxyethyl methacrylate) are used in soft contact lenses (137,138).

**8.3. Optics.** Polymethacrylates are naturally good choices for the fiber-optics market because of their optical clarity and low thermal resistance (139). Fresnel and eyeglass lenses have been made using polymethacrylates (140–142).

**8.4. Oil Additives.** Long-chain polymethacrylates increase the viscosity of oil as temperature increases and are therefore used as additives to improve the performance of lubricating oils and hydraulic fluids in internal combustion engines (143). Through the careful control of polymer molecular weight and composition, oils of constant performance over broad temperature ranges are made possible (144). Polymethacrylates can be used to improve the viscosity index, sludge dispersancy, and antioxidant properties of an oil (145) (see ANTIOXIDANTS). Through the grafting of polyethylene and polypropylene onto long-chain polymethacrylates, multipurpose lubricants having viscosity index, pour point depression properties, and detergent dispersing capabilities are possible (146).

**8.5. Other.** Synthetic marble fixtures and bathtubs are made using methacrylic ester polymers (147,148). Opaque and clear methacrylate sheets have been used as structural components in the manufacture of recreational vehicles (149). These materials are additionally used for electrical insulation. Thermoplastic methacrylate resins are used in lacquer coatings for plastics, in printing inks, as heat seal lacquers for packaging, as screen printing media for decorative porcelain, in traffic paints, and for the protection of buildings from acid rain and weathering (150). Other copolymer used are discussed in the article ACRYLIC ESTER POLYMERS.

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