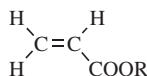# ACRYLIC ESTER POLYMERS

1. Introduction

The usage of acrylic esters as building blocks for polymers of industrial importance began in earnest with the experimentation of Otto Rohm (1). The first recorded preparation of the basic building block for acrylic ester polymers, acrylic acid, took place in 1843; this synthesis relied on the air oxidation of acrolein (2,3). The first acrylic acid derivatives to be made were methyl acrylate and ethyl acrylate. Although these two monomers were synthesized in 1873, their utility in the polymer area was not discovered until 1880 when Kahlbaum polymerized methyl acrylate and tested its thermal stability. To his surprise, the polymerized methyl acrylate did not depolymerize at temperatures up to 320°C (4). Despite this finding of incredibly high thermal stability, the industrial production of acrylic ester polymers did not take place for almost another 50 years.

The commercial discovery of acrylic ester polymers took place while Otto Rohm was conducting his doctoral research in 1901. Rohm obtained a U.S. patent in 1912 covering the vulcanization of acrylates with sulfur (5). Commercial production of acrylic ester polymers by the Rohm and Haas Co. of Darmstadt, Germany, commenced in 1927 (6).

2. Physical Properties

The structure of the acrylic ester monomers is represented by the following:

$$\underset{H}{\overset{H}{\diagdown}}C=C\overset{H}{\underset{COOR}{\diagup}}$$

The R ester group dominates the properties of the polymers formed. This R side-chain group conveys such a wide range of properties that acrylic ester polymers are used in applications varying from paints to adhesives and concrete modifiers and thickeners. The glass-transition range for a polymer describes

the temperature range below which segmental pinning takes place and the polymer takes on a stiff, rigid, inflexible nature. This range can vary widely among the acrylic ester polymers from $-54°C$ for butyl acrylate $(R = C_4H_9)$ to $103°C$ for acrylic acid $(R = H)$. Film properties are dramatically influenced by this changing of the polymer flexibility.

When copolymerized, the actylic ester monomers typically randomly incorporate themselves into the polymer chains according to the percentage concentration of each monomer in the reactor initial charge. Alternatively, acrylic ester monomers can be copolymerized with styrene, methacrylic ester monomers, acrylonitrile, and vinyl acetate to produce commercially significant polymers.

Acrylic ester monomers are typically synthesized from the combination of acrylic acid and an alcohol. The properties of the polymers they form are dominated by the nature of the ester side chain as well as the molecular weight of the product. Acrylic ester polymers are similar to others in that they show an improvement in properties as a function of molecular weight until a certain threshold beyond which no further improvement is observed. This threshold is reached at a molecular weight value of 100,000−200,000 for acrylic polymers.

2.1. Glass-Transition Temperature.   The glass-transition temperature (T_g) (qv) describes the approximate temperature below which segmental rigidity (ie, loss of rotational and translational motion) sets in. Although a single value is often cited, in reality a polymer film undergoes the transition over a range of temperatures. The reason for this range of temperatures for the glass transition is that segmental mobility is a function of both the experimental method used [dynamic mechanical analysis (dma) vs differential scanning calorimetry (dac)] as well as the experimental conditions. Factors such as hydroplasticization in varying degrees of humidity can skew T_g results. Most polymers experience an increase in the specific volume, coefficient of expansion, compressibility, specific heat, and refractive index. The T_g is typically measured as the midpoint of the range over which the discontinuity of these properties takes place. Care should be taken when analyzing T_g data, however, as some experimenters cite the onset of the discontinuity as the T_g value.

The rigidity upon cooling below T_g is manifested as an embrittlement of the polymer to the point where films are glass-like and incapable of handling significant mechanical stress without cracking. If, on the other hand, one raises the temperature to which a film is exposed above the glass-transition range, the polymer film becomes stretchable, soft, and elastic. For amorphous acrylic polymers, many physical properties show dramatic changes after passing through the glass-transition temperature range. Among these physical properties are diffusion chemical reactivity, mechanical and dielectric relaxation, viscous flow, load-bearing capacity, hardness, tack, heat capacity, refractive index, thermal expansivity, creep, and crystallization.

The most common thermal analyses used to determine the glass-transition temperature are dma and dsc. More information on these techniques and how to interpret the results are contained in References 7−9. The T_g values for the most Common homopolymers of acrylic esters are listed in Table 1.

The most common way of tailoring acrylic ester polymer properties is to copolymerize two or more monomers. In this fashion, the balance of hard (high T_g) and soft (low T_g) monomers used to make up the overall composition will

Table 1. **Physical Properties of Acrylic Polymers**

Polymer	Monomer molecular formula	CAS registry number	T_g, °C[a]	Density, g/cm^3[b]	Refractive index, n_D
methyl acrylate	$C_4H_6O_2$	[9003-21-8]	6	1.22	1.479
ethyl acrylate	$C_5H_8O_2$	[9003-32-1]	−24	1.12	1.464
propyl acrylate	$C_6H_{10}O_2$	[24979-82-6]	−45		
isopropyl acrylate	$C_6H_{10}O_2$	[26124-32-3]	−3	1.08	
n-butyl acrylate	$C_7H_{12}O_2$	[9003-49-0]	−50	1.08	1.474
sec-butyl acrylate	$C_7H_{12}O_2$	[30347-35-4]	−20		
isobutyl acrylate	$C_7H_{12}O_2$	[26335-74-0]	−43		
tert-butyl acrylate	$C_7H_{12}O_2$	[25232-27-3]	43		
hexyl acrylate	$C_9H_{16}O_2$	[27103-47-5]	−57		
heptyl acrylate	$C_{10}H_{18}O_2$	[29500-72-9]	−60		
2-heptyl acrylate	$C_{10}H_{18}O_2$	[61634-83-1]	−38		
2-ethylhexyl acrylate	$C_{11}H_{20}O_2$	[9003-77-4]	−65		
2-ethylbutyl acrylate	$C_9H_{16}O_2$	[39979-32-3]	−50		
dodecyl acrylate	$C_{15}H_{28}O_2$	[26246-92-4]	−30		
hexadecyl acrylate	$C_{19}H_{36}O_2$	[25986-78-1]	35		
2-ethoxyethyl acrylate	$C_7H_{12}O_3$	[26677-77-0]	−50		
isobornyl acrylate	$C_{13}H_{20}O_2$	[30323-87-6]	94		
cyclohexyl acrylate	$C_9H_{14}O_2$	[27458-65-7]	16		

[a] Refs. 7 and 10.
[b] Ref. 11

determine the overall hardness and softness of the polymer film. An estimate of the T_g, and therefore the film hardness, can be calculated using the Fox equation (eq. (1)) (12):

$$1/T_g = \Sigma W(i)/T_g(i) \qquad (1)$$

The factor W in this equation refers to the weight, or percent composition, of a given monomer with a given T_g value for the homopolymer.

As can be seen in Table 1, the most common acrylic ester polymers have low T_g values and, therefore, soften films in which they are copolymerized with other vinylic monomers. This effect results in an internal plasticization of the polymer. That is, the plasticization effect from acrylic esters, unlike plasticizer additives which are not covalently bound, will not be removed via volatilization or extraction.

Nondestructive techniques such as torsional modulus analysis can provide a great deal of information on the mechanical properties of viscoelastic materials (8,13–25). For this type of analysis, a higher modulus value is measured for those polymers which are stiffer, harder, or have a higher degree of cross-linking. The regions of elastic behavior are shown in Figure 1 with curve A representing a soft polymer and curve B a harder polymer. A copolymir with a composition
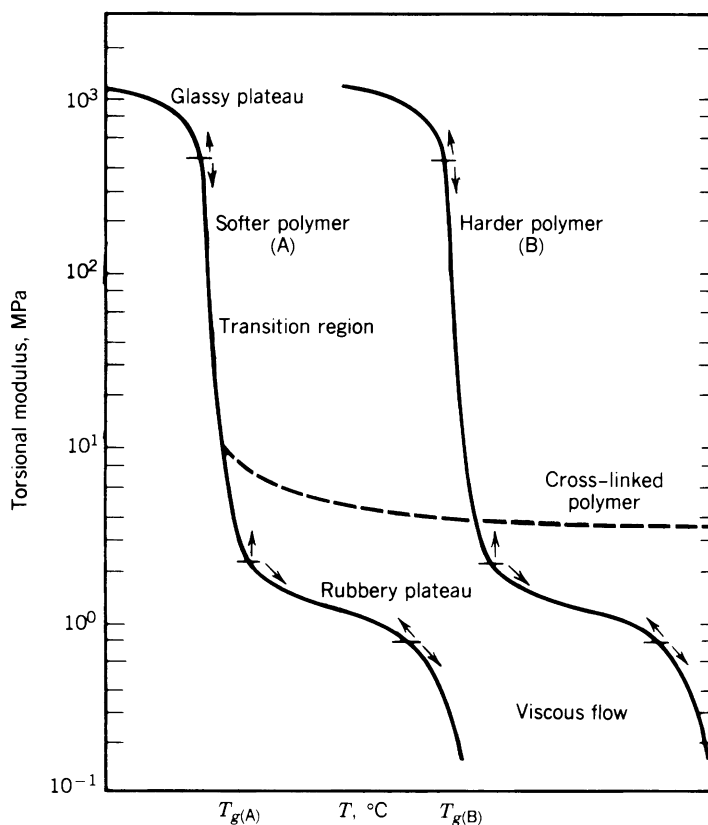
Fig. 1. Modulus-temperature curve of amorphous and cross-linked acrylic polymers. To convert MPa to kg/cm^2, multiply by 10.

between these two homopolymers would fall between the two depicted curves, with the relative distance from each curve determined by the similarity of the copolymer composition to one homopolymer or the other (26–28).

Acrylic ester polymers are susceptible to the covalent bonding of two or more polymer chains to form a cross-link (11,29–38). The above-described thermal analysis techniques are capable of distinguishing not only T_g but also varying degrees of cross-linking between polymers. A higher degree of cross-linking results in an elevation and extension of the rubbery plateau region. After a certain level of cross-linking is obtained, the segmental mobility of the polymer chains is impeded (23,25,28). This loss of mobility is measured as an increase in the T_g of the polymer. Further details on cross-linking within and between polymer chains can be found in References 11 and 29–38.

2.2. Molecular Weight. The properties of acrylic 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 acrylic ester polymers) this improvement in polymer properties reaches a plateau. The glass-transition

temperature 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 2×10^5 (39). Reference 40 summarizes the effect of molecular weight on polymer properties.

2.3. Mechanical and Thermal Properties. The mechanical and thermal properties of a polymer are strongly dependent on the nature of the ester side-chain groups of its composite monomers. With H as a side chain, poly(acrylic acid) is a brittle material at room temperature, which is capable of absorbing large quantities of water. The first member of the acrylic ester family, poly (methyl acrylate), is a tough, rubbery, tack-free material at room temperature. The next higher chain length material, poly(ethyl acrylate), is softer, more rubbery, and more extensible. Poly(butyl acrylate) has considerable tack at room temperature and is capable of serving as an adhesive material. Information on these homopolymers is summarized in Table 2 (41). Softness of these polymers increases with increasing chain length until one reaches poly(n-nonyl acrylate). Beginning with this chain length, the side chains start to crystallize, which leads to a stiffening of the polymer. This stiffening translates into an embrittlement of the polymer (42); poly(n-hexadecyl acrylate), for example, is a hard, waxy material at room temperature.

Acrylic ester polymers are quite resilient to extreme conditions. This resilience gives finished products the durability that has earned acrylic polymers their reputation for value over time. In contrast to polymers of methacrylic esters, acrylic esters are stable when heated to high temperatures. Poly(methyl acrylate) can withstand exposure to 292–399°C in vacuo without generating significant quantities of monomer (43,44). Acrylic ester polymers are also resistant to oxidation. Hydroperoxides can be formed from polymer radicals and oxygen under forcing conditions (45–47), but by and large this is a minor concern.

2.4. Solublilty. Like most other properties, the side chain of acrylic ester polymers determines their solubility in organic solvents. Shorter side-chain polymers are relatively polar and will dissolve in polar solvents such as ether alcohols, ketones, and esters. With longer side-chain polymers, the solubility of a polymer shifts to the more hydrophobic solvents such as aromatic or aliphatic hydrocarbons. If a polymer is soluble in a given solvent, typically it is soluble in all proportions. Film formation occurs with the evaporation of the solvent, increase in solution viscosity, and the entanglement of the polymer chains.

Table 2. **Mechanical Properties of Acrylic Polymers**

Polyacrylate	Elongation, %	Tensile strength, kPa[a]
methyl	750	6895
ethyl	1800	228
butyl	2000	21

[a] To convert kPa to psi, multiply by 0.145.

Table 3. **Solubility Parameters of Acrylic Homopolymers Calculated by Small's Method**[a]

Polymer	$(\text{J/cm}^3)^{1/2}$ [b]
methyl acrylate	4.7
ethyl acrylate	4.5
n-butyl acrylate	4.3

[a] Refs. 23 and 53.
[b] To convert $(\text{J/cm}^3)^{1/2}$ to $(\text{cal/cm}^3)^{1/2}$, divide by 2.05.

Phase separation and precipitation are not usually observed for solution polymers.

Solubility is determined by the free energy equation (the Flory-Huggins equation) governing the mutual miscibility of polymers (eq. (2):

$$\Delta G_{\text{Mix}} = kT \ (N_1 \ln \nu_1 + N_2 \ln \nu_2 + \chi_1 N_1 \nu_2) \qquad (2)$$

where k is the Boltzmann's constant, T the temperature, N_1 the number of solvent molecules, N_2 the number of polymer molecules, ν_1 the volume fraction of the solvent, ν_2 the volume fraction of the polymer, and χ_1 the Flory-Huggins interaction parameter.

With this equation, polymer dissolution takes place when the free energy of mixing is negative. A polymer in solution always has a much higher entropy level than undissolved polymer since it is free to move to a far greater extent. This means the change in entropy term will always have a large positive value. Therefore, the factor which determines whether or not a polymer will dissolve in a particular solvent is the heat term. If the difference in the solubility parameters for two substances is small, dissolution will occur since the heat of mixing will be small and the entropy difference will be large (this translates into a negative overall energy of mixing). A polymer will dissolve in a particular solvent if the solubility parameters and the polarities for the polymer and the solvent are comparable (38,48–53). Some relevant solubility parameters are given in Table 3.

Polymer solution viscosity is a function of the polymer molecular weight, concentration in solvent, temperature, polymer composition, and solvent composition (9,54–56).

3. Chemical Properties

Acrylic polymers and copolymers are highly resistant to hydrolysis. This property differentiates acrylic polymers from poly(vinyl acetate) and vinyl acetate copolymers. When exposed to highly extremely acidic or alkaline environments, acrylic ester polymers can hydrolyze to poly(acrylic acid) and the corresponding alcohol. Resistance to hydrolysis decreases in the order butyl acrylate > ethyl ethyl acrylate > methyl acrylate. Although it is the least hydrolytically stable, methyl acrylate is still far more resistant to hydrolysis than vinyl acetate (57,58).

Ultraviolet radiation is the other main stress encountered by polymers in the coatings arena. One hundred percent acrylic polymers are highly resistant
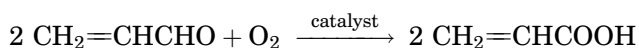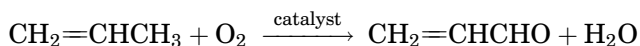
to photodegradation because they are transparent to the vast majority of the solar spectrum (59). When uv-absorbing monomers, such as styrene, are incorporated into the polymer backbone, the uv-resistance of the resulting polymer decreases dramatically and a more rapid deterioration in polymer/coating properties is observed. On the other hand, a noncovalently bound uv absorber, such as hydroxybenzophenone further improves the uv stability of 100% acrylic polymers (59).

Higher energy radiation such as from gamma ray or electron beam sources results in the scission of both main and side chains (60). The ratio of backbone to side-chain scission is determined by the nature of the side chain (61,62).

4. Acrylic Ester Monomers

A wide variety of properties are encountered in the acrylic monomers area. This range of properties is made accessible by the variability of the side chain for acrylic monomers. Some of the key physical properties of the most commercially important monomers are included in Table 4. A more complete listing of both monomers and their properties is found in the article ACRYLIC ACID AND DERIVATIVES.

The two most common methods for production of acrylic ester monomers are (1) the semicatalytic Reppe process which utilizes a highly toxic nickel carbonyl catalyst and (2) the propylene oxidation process which primarily employs molybdenum catalyst. Because of its decreased cost and increased level of safety, the propylene oxidation process accounts for most of the acrylic ester production currently. In this process, acrolein is formed by the catalytic oxidation of propylene vapor at high temperature in the presence of steam. The acrolein intermediate is then oxidized to acrylic acid [79-10-7].

$$CH_2\!\!=\!\!CHCH_3 + O_2 \xrightarrow{\text{catalyst}} CH_2\!\!=\!\!CHCHO + H_2O$$

$$2\ CH_2\!\!=\!\!CHCHO + O_2 \xrightarrow{\text{catalyst}} 2\ CH_2\!\!=\!\!CHCOOH$$

Once the acrylic acid has been formed, the various acrylic ester monomers are synthesized by esterification of acrylic acid with the appropriate alcohol (63–66).

These monomers are then prevented from highly exothermic and hazardous autopolymerization processes during shipping and storage by the addition of a chemical inhibitor. The most common inhibitors currently used are hydroquinone, the methyl ether of hydroquinone (MEHQ) [150-76-5], and the newest member of the inhibitor family, 4-hydroxy TEMPO. 4-Hydroxy TEMPO, unlike the quinone inhibitors, does not require the presence of oxygen in order to be effective. Chemical inhibitors are only added at the <100 ppm level and are not typically removed prior to their commercial use. Finally, copper and its alloys can also function as inhibitors and should, therefore, be avoided when constructing a reactor for purposes of producing acrylic ester (co)polymers (67). With no inhibitor added, the monomers must be stored at temperatures below 10°C for

Table 4. Physical Properties of Acrylic Monomers

Acrylate	CAS registry number	Molecular weight	Bp, °C[a]	d^{25}, g/cm^3	Flash point, °C[b]	Water solubility, g/100 g H$_2$O	Heat of evaporation, J/g[c]	Specific heat, J/g·K[c]
methyl	[96-33-3]	86	79–81	0.950	10	5	385	2.01
ethyl	[140-88-5]	100	99–100	0.917	10	1.5	347	1.97
n-butyl	[141-32-2]	128	144–149	0.894	39	0.2	192	1.92
isobutyl	[106-63-8]	128	61–63[d]	0.884	42	0.2	297	1.92
t-butyl	[1663-39-4]	128	120	0.879	19	0.2		
2-ethylhexyl	[103-11-7]	184	214–220	0.880	90[e]	0.01	255	1.92

[a] At 101.3 kPa unless otherwise noted.
[b] Tag open cup unless otherwise noted.
[c] To convert J to cal, divide by 4.184.
[d] At 6.7 kPa = 50 mm Hg.
[e] Cleveland open cup.

Table 5. **Toxicities of Acrylic Monomers**

Monomer	Acute oral LD$_{50}$ (rats), mg/kg	Acute Percutaneous LD$_{50}$ (rabbits), mg/kg	Inhalation	
			LC$_{50}$ (rats), mg/L	TLV, ppm
methyl acrylate	300	1235	3.8	10
ethyl acrylate	760	1800	7.4	25
butyl acrylate	3730	3000	5.3	

no longer than a few weeks. Failure to exercise these precautions can result in violent, uncontrolled, and potentially deadly polymerizations.

Common acrylic ester monomers are combustible liquids. Commercial acrylic monomers are shipped with DOT (Department of Transportation) red labels in bulk quantities, tank cars, or tank trucks. Mild steel is the usual material of choice for the construction of bulk storage facilities for acrylic monomers; moisture is excluded to avoid rusting of the storage tanks and contamination of the monomers.

A variety of methods are available for determining the purity of monomers by the measurement of their saponification equivalent and bromine number, specific gravity, refractive index, and color (68–70). Minor components are determined by iodimetry or colorimetry for hydroquinone or MEHQ, Karl-Fisher method for water content, and turbidimetry for measuring trace levels of polymer. Gas-liquid chromatography is useful in both the general measurement of monomer purity as well as the identification of minor species within a monomer solution.

Although toxicities for acrylic ester monomers range from slight to moderate, they can be handled safely and without difficulty by trained, personnel, provided that the proper safety instructions are followed (67,71). Table 5 contains animal toxicity data for common acrylic ester monomers under acute toxicity conditions.

Because of their higher vapor pressures, liquid methyl and ethyl acrylate are the two most potentially harmful acrylic ester monomers. Threshold limit values (TLV) for long-term low level exposures to these monomers in industrial situations have been established by OSHA (Table 5). Local regulations and classifications sometimes apply, however, to these monomers. Ethyl acrylate, for example, has been labeled a known carcinogen by the State of California (71).

5. Polymerization

5.1. Radical Polymerization. Free-radical initiators such as azo compounds, peroxides, or hydroperoxides are commonly used to initiate the polymerization of acrylic ester monomers. Photochemical (72–74) and radiation-initiated (75) polymerization are also possible. At constant temperature, the initial rate of polymerization is first order in monomer and one-half order in initiator. Rate data for the homopolymerization of several common acrylic ester monomers initiated by 2,2′-azobisisobutryonitrile (AIBN) [78-67-1] have been determined

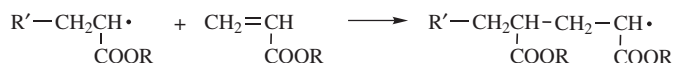Table 6. **Polymerization Data for Acrylic Ester Monomers in Solution**[a]

Acrylate	Concentration, solvent	k_{sp}, L/mol·h[b]	Heat, kJ/mol[c]	Shrinkage, vol%
methyl	3 M, methyl propionate	250	78.7	24.8
ethyl	3 M, benzene	313	77.8	20.6
butyl	1.5 M, toluene	324	77.4	15.7

[a] Ref. 76.
[b] At 44.1°C.
[c] To convert kJ to kcal, divide by 4.184.

and are contained in Table 6. Also included in this table are heats of polymerization and volume shrinkage data (76).
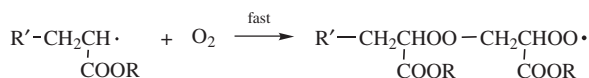
The polymerization of both acrylic and methacrylic ester monomers is accompanied by the release of a large quantity of heat as well as a substantial decrease in sample volume. Commercial processes must account for both these phenomena. Excess heat must be removed from industrial reactors by the use of high surface area heat exchangers. As for the shrinkage issue, the percent shrinkage encountered upon polymerization of the monomer is, in general, inversely proportional to the length of the monomer side chain. Mole for mole, the shrinkage amount is relatively constant (77).

The free-radical polymerization of acrylic monomers takes place through the classical stepwise chain-growth mechanism, which is described as the head-to-tail addition of individual monomer units through attack df the monomer double bond and formation of a single bond between the newly incorporated monomer units.

$$R'-CH_2CH\cdot \quad + \quad CH_2{=}CH \quad \longrightarrow \quad R'-CH_2CH{-}CH_2{-}CH\cdot$$
$$\quad\quad | \quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad | \quad\quad\quad\quad |$$
$$\quad COOR \quad\quad\quad COOR \quad\quad\quad\quad\quad COOR \quad\quad COOR$$
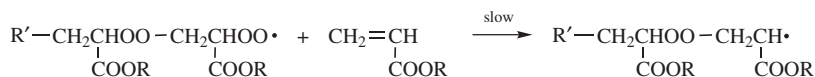
This stepwise growth continues until either termination or chain transfer of the radical chain end takes place. Termination can occur by combination or disproportionation, depending on the conditions of the polymerization (78,79).

The addition step typically takes place as a head-to-tail process although head-to-head addition has been observed as well (80). Oxygen has a strong inhibitory effect on the rate of polymerization of acrylic ester polymers. Oxygen is, therefore, excluded from commercial reactors primarily through the use of positive nitrogen flow. The nature of the oxygen inhibition is known: an alternating copolymer can be formed between oxygen and acrylic ester monomers (81,82).

$$R'-CH_2CH\cdot \quad + \quad O_2 \quad \xrightarrow{\text{fast}} \quad R'-CH_2CHOO-CH_2CHOO\cdot$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad |$$
$$\quad COOR \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad COOR \quad\quad COOR$$

The oxygen chain end is relatively unreactive when compared to the acrylic chain end and reduces the overall rate of polymerization. Additionally, the peroxy radical undergoes a faster rate of termination than the standard

acrylic-based radical:

$$R'-CH_2CHOO-CH_2CHOO\cdot \ + \ CH_2=CH \ \xrightarrow{\text{slow}} \ R'-CH_2CHOO-CH_2CH\cdot$$
$$\begin{array}{ccccc} & & & & \\ COOR & COOR & & COOR & COOR \end{array}$$

One will observe a drop in overall reaction rate, a change in polymer composition and properties, as well as a decrease in polymer molecular weight if oxygen is not excluded from a reactor when polymerizing acrylic ester monomers (83).

The wide variety of acrylic ester monomers dictates that a wide variety of homopolymers with radically different properties are accessible. An even wider variety of polymers can be formed through the copolymerization of two or more acrylic ester monomers (84,85).

Acrylic ester monomers are, in general, readily copolymerized with other acrylic and vinylic monomers. Table 7 presents data for the free-radical copolymerization of a variety of monomers 1:1 with acrylic ester monomers. These numbers are calculated through the use of reactivity ratios:

$$r_1 = k_{11}/k_{12}$$
$$r_2 = k_{22}/k_{21}$$

For a binary copolymer, the smaller reactivity ratio is divided by the larger r value and multiplied by 100. Values greater than 25 indicate that copolymerization proceeds smoothly; low values for the ease of copolymerization can be helped through the adjustment of comonomer composition as well as the monomer addition method (86).

A growing chain with monomer 1 as the chain-end radical has a rate constant for self-addition of k_{11}; the rate for addition of monomer 2 is k_{12}. The self-addition rate for a terminal monomer 2 radical is given as k_{22}; the rate for addition of monomer 1 is k_{21}. The reactivity ratios can also be calculated from the Price-Alfrey measures (87) of resonance stabilization (Q) and polarity (e) which are shown for common acrylic esters in Table 8. NMR can also be used to determine the composition distribution characteristics of acrylic copolymers (88,89).

Table 7. **Relative Ease of Copolymer Formation for 1:1 Ratios of Acrylic and Other Monomers, $\frac{r\text{(smaller)}}{r\text{(larger)}} \times 100$**

		Monomer 1		
Monomer 2	CAS registry number	Methyl acrylate	Ethyl acrylate	Butyl acrylate
acrylonitrile	[107-13-1]	53	46	74
butadiene	[106-99-0]	66	4.7	8.1
methyl methacrylate	[80-62-6]	50.3	30.6	14.6
styrene	[100-42-5]	21	16	26
vinyl chloride	[75-01-4]	2.7	2.1	1.6
vinylidene chloride	[75-35-4]	100	52	55
vinyl acetate	[108-05-4]	1.1	0.7	0.6

Table 8. **Q and e Values for Acrylic Monomers**[a]

Monomer	Q	e
methyl acrylate	0.44	+0.60
ethyl acrylate	0.41	+0.46
butyl acrylate	0.30	+0.74
isobutyl acrylate	0.41	+0.34
2-ethylhexyl acrylate	0.14	+0.90

[a] Ref. 88.

In addition to the standard side-chain variation discussed above, special functionality can be added to acrylic ester monomers by use of the appropriate functional alcohol. Through the use of small levels of functional monomers, one can allow an acrylic ester polymer to react with metalions, cross-linkers, or other types of resins. Table 9 contains information on some of the more common functional monomers.

Table 9. **Functional Monomers for Copolymerization with Acrylic Monomers**

Monomer	Structure	CAS registry number	Molecular formula
Carboxyl			
methacrylic acid	$CH_2{=}CCOOH$ with CH_3	[79-41-4]	$C_4H_6O_2$
acrylic acid	$CH_2{=}CHCOOH$	[79-10-7]	$C_3H_4O_2$
itaconic acid	CH_2COOH / $CH_2{=}CCOOH$	[97-65-4]	$C_5H_6O_4$
Amino			
t-butylaminoethyl methacrylate	CH_3 / $CH_2{=}CCOO(CH_2)_2NHC(CH_3)_3$	[24171-27-5]	$C_{10}H_{19}NO_2$
dimethylaminoethyl methacrylate	CH_3 / $CH_2{=}CCOO(CH_2)_2N(CH_3)_2$	[2867-47-2]	$C_8H_{15}NO_2$
Hydroxyl			
2-hydroxyethyl methacrylate	CH_3 / $CH_2{=}CCOOCH_2CH_2OH$	[868-77-9]	$C_6H_{10}O_3$
2-hydroxyethyl acrylate	$CH_2{=}CHCOOCH_2CH_2OH$	[818-61-1]	$C_5H_8O_3$
N-Hydroxymethyl			
N-hydroxymethyl acrylamide	$CH_2{=}CHCONHCH_2OH$	[924-42-5]	$C_4H_7NO_2$
N-hydroxymethyl methacrylamide	CH_3 / $CH_2{=}CCONHCH_2OH$	[923-02-04]	$C_5H_9NO_2$
Oxirane			
glycidyl methacrylate	CH_3 / $CH_2{=}CCOOCH_2CH{-}CH_2$ with O	[106-91-2]	$C_7H_{10}O_3$
Multifunctional			
1,4-butylene dimethacrylate	CH_3 / $(CH_2{=}CCOOCH_2)_2$	[2082-81-7]	$C_{12}H_{18}O_4$

5.2. Bulk Polymerization. Bulk polymerizations of acrylic ester monomers are characterized by the rapid formation of an insoluble network of polymers at low conversion with a concomitant rapid increase in reaction viscosity (90,91). These properties are thought to come from the chain transfer of the active radical via hydrogen abstraction from the polymer backbone. When two of these backbone radical sites propagate toward one another and terminate, a cross-link is formed (91).

5.3. Solution Polymerization. Of far greater commercial value than that of simple bulk polymerizations, solution polymerizations employ a co-solvent to aid in minimizing reaction viscosity as well as controlling polymer molecular weight and architecture. Lower polyacrylates are, in general, soluble in aromatic hydrocarbons, esters, ketones, and chlorohydrocarbons. Solubilities in aliphatic hydrocarbons, ethers, and alcohols are somewhat lower. As one moves to longer alcohol side-chain lengths, acrylics become insoluble in oxygenated organic solvents and soluble in aliphatic and aromatic hydrocarbons and chlorohydrocarbons. Solvent choices for acrylic solution polymerizations are made on the basis of cost, toxicity, flammability, volatility, and chain-transfer activity. The chain-transfer constants (C_s) for a variety of solvents in the solution polymerization of poly(ethyl acrylate) are shown in Table 10.

Initiators serve the dual role of beginning the polymerization of an individual chain as well as controlling the molecular weight distribution of a polymer sample. Initiators are chosen based on their solubility, thermal stability (rate of decomposition), and the end use for the polymer. Additionally, initiators can be used to control polymer architecture by cross-linking control; this property also allows initiators to serve a role in the regulation of molecular weight distribution. Levels of usage vary from hundredths of a percent to several percent by weight on the polymer formed. The types of initiators most commonly employed in solution polymerizations are organic peroxides, hydroperoxides, and azo compounds.

Molecular weight control can also be achieved through the use of a chain-transfer agent. The most commonly used species in this class are chlorinated aliphatic compounds and thiols (94). The chain-transfer constants (C_s at 60°C) for some of these compounds in the formation of poly(methyl acrylate) are as follows (87): carbon tetrabromide, 0.41: ethanethiol, 1.57; and butanethiol, 1.69.

Because of the volatile nature of the monomers used and high temperatures often employed, solution polymerizations are typically performed in reactors

Table 10. **Chain-Transfer Constants to Common Solvents for Poly(ethyl acrylate)**[a]

Solvent	$C_s \times 10^5$
benzene	5.2
toluene	26.0
isopropyl alcohol	260
isobutyl alcohol	46.5
chloroform	14.9
carbon tetrachloride	15.5

[a] Refs. 79, 92, and 93.

which can withstand pressures of at least 446 kPa (65 psi). Standard materials of construction include stainless steel (which may be glass-lined) or nickel. Anchor-type agitators are used for solution polymerizations with viscosities up to 1.0 Pa·s (1000 cP), but when viscosity levels move above this range, a slow ribbon-type agitator is used to sweep material away from the reactor walls. Improper agitation can result in the severe fouling of a reactor. Most industrial reactors are jacketed for steam heating and/or water cooling of a batch and contain a rupture disk to relieve pressure buildup. Additionally, there are numerous inlets in a typical industrial reactor as well as a thermocouple for monitoring temperatute. A valve is placed in the bottom of the reactor to release polymerized material to storage containers.

Cooling within a reactor is typically provided by a reflux condenser. Since polymerization is a highly exothermic process, temperature control is a safety concern as well as a product integrity issue. Temperature control is primarily obtained through the gradual addition of monomers into the reactor by gravity from storage containers close to the reactor. In this manner, the rate of monomer addition and reaction can be matched to the cooling capacity of the teactor so that temperatures remain relatively constant throughout the polymerization. If these measures fail to control the temperature of a particular batch, a chemical inhibitor, such as a hydroquinone, can be added to retard the rate of polymerization.

Oxygen can serve as an inhibitor of polymerization. Reactors typically maintain a blanket of nitrogen over the entire reactor kettle. In polymerizations with temperatures below reflux, nitrogen is used to purge the reaction solution; a nitrogen blanket is then placed over the reactor prior to the addition of the initiator. Total cycle times for solution polymerizations run in the range of 24 h (95).

A typical solution polymerization recipe is shown below:

Composition	Parts
Reactor charge	
Ethyl acetate	61.4
Benzoyl peroxide	0.1
Monomer charge	
Ethyl acrylate	36.5
Acrylic acid	2.0

This copolymer has an overall composition of 94.8% ethyl acrylate/5.2% acrylic acid with the monomer charged at a level of 39 wt% in a solution of ethyl acetate. Initially, the solvent and initiator, benzoyl peroxide in this case, are added to the reactor and heated to reflux (80°C). Forty percent of the monomer mixture is added to the reactor in one charge. Then, four equal aliquots of monomer are added 24,50, 79, and 110 min after the initial charge. Reflux is maintained within the reactor overnight to ensure complete reaction; the product is then cooled and packaged the next morning (96).

Storage and handling equipment are typically made from steel. In order to prevent corrosion and the transfer of rust to product, moisture is typically

excluded from solution polymer handling and storage systems (97). Because of the temperature-sensitive nature of the viscosity of solution polymers, the temperature of the storage tanks and tranfer lines is regulated either through prudent location of these facilities or through the use of insulation, heating, and cooling equipment.

5.4. Emulsion Polymerization. Emulsion polymerization is the most industrially important method of polymerizing acrylic ester monomers (98,99). The principal ingredients within this type of polymerization are water, monomer, surfactant, and water-soluble initiator. Products generated by emulsion polymerization find usage as coatings or binders in paints, paper, adhesives, textile, floor care, and leather goods markets. Because of their film-forming properties at room temperature, most commercial acrylic ester Polymers are copolymers of ethyl acrylate and butyl acrylate with methyl methacrylate.

Lower acrylates are capable of polymerizing in water in the presence of an emulsifier and a water-soluble initiator. The polymeric product is typically a milky-white dispersion of polymer in water at a polymer solids content of $30-60\%$. Particle sizes for these latices fall in the range of $0.1-1.0$ μm. Because of the compartmentalized nature of the process (99), high molecular weights are obtained with most emulsion polymerizations without the resulting viscosity build encountered with solution polymerizations. Additionally, the use of water as a dispersion medium provides attractive safety, environmental, and heat removal benefits when compared to other methods of polymerizing acrylic ester monomers. The emulsion polymerization of the higher (relatively water insoluble) acrylates can even be accomplished now through the use of a patented method for catalytically transferring monomer from droplets to the growing polymer particles (100).

The types of surfactants used in an emulsion polymerization span the entire range of anionic, cationic, and nonionic species. The most commonly used soaps are alkyl sulfates such as sodium lauryl sulfate, alkylaryl sulfates such as sodium dodecyl benzene sulfonate, and alkyl or aryl polyoxyethylene nonionic surfactants (87,101−104). Product stability and particle size control are the driving forces which determine the types of surfactants employed; mixtures of nonionic and anionic surfactants are commonly used to achieve these goals (105−108).

Water-soluble peroxides, such as sodium or ammonium persulfate, are commonly used in the industrial arena. The thermal dissociation of this initiator (109) results in the formation of sulfate radicals which initiate polymer chains in the aqueous phase. It is possible to use other oxidants, such as hydrogen peroxide [7722-84-1] or persulfates in the presence of reducing agents and/or polyvalent metal ions (87). In this manner, a redox initiator system is formed which allows the experimenter to initiate polymer chains over a much broader range of temperatures $(25-90°C)$ than simple thermal initiation $(75-90°C)$ (110). The primary disadvantage of this initiation method is that greater level of salt impurities are introduced to the reactor which could, perhaps, adversely influence final polymer properties such as stability.

Emulsion polymerization batches on the industrial scale are typically run in either stainless steel or glass-lined steel reactors which can safely handle internal pressures of 446 kPa (65 psi). Agitation within the reactors is controlled by

use of a variable speed stirring shaft coupled at times with a baffling system within the reactor to improve mixing. Care must be taken to avoid excessive mixing forces being placed on the latex as coagulum will form under extreme conditions. Temperature control of batches is maintained through the use of either steam or cold waterjacketing. Multiple feed lines are necessary to provide for the addition of multiple streams of reactants such as initiators, monomer emulsions, inhibitors if necessary, and cooling water. Monitoring equipment for batches typically consists of thermocouples, manometers, sightglasses, as well as an emergency stack with a rupture disk in case of pressure buildup within the reactor. A typical industrial emulsion polymerization plant is shown in Figure 2.

There are numerous examples of typical industrial emulsion polymerization recipes available in the open literature (111,112). A process for the synthesis of a polymer with a 50% methyl methacrylate, 49% butyl acrylate, and 1% methacrylic acid terpolymer at a solids content of 45% is described below:

Charge	Parts
Monomer emulsion charge	
Deionized water	13.65
Sodium lauryl sulfate	0.11
Methyl methacrylate	22.50
Butyl acrylate	22.05
Methacrylic acid	0.45
Initiator charge	
Ammonium persulfate	0.23
Reactor charge	
Deionized water	30.90
Sodium lauryl sulfate	0.11

The monomer emulsion is first formed in a separate agitation tank by combination of the water, soap, and monomer with a proper level of mixing. Care must be taken to avoid excessive levels of agitation in the monomer emulsion tank to avoid incorporating air into the emulsion. The reactor water is heated under a nitrogen blanket to a temperature of at least 75°C prior to the addition of the initiator. Following the addition of the initiator, the monomer emulsion is fed into the reactor over the course of approximately 2.5 h. Temperature control is maintained during this time through both control of the monomer feed rate as well as use of the reactor jacket heating/cooling system. After the monomer emulsion feed is completed, the temperature is held above 75°C for at least 30 min to reduce the level of residual standing monomer within the system. The product is then cooled, filtered, and packaged.

Once packaged, the storage of acrylic latices is a nontrivial matter; problems commonly encountered with these polymer colloids include skinning (surface film formation), sedimentation, grit formation within the latex, formation of coagulum on storage container walls, and sponging (aerogel formation). Exposure of the material to extremes in temperature is avoided through prudent location of these facilities or the use of insulation, heating, and cooling equipment.
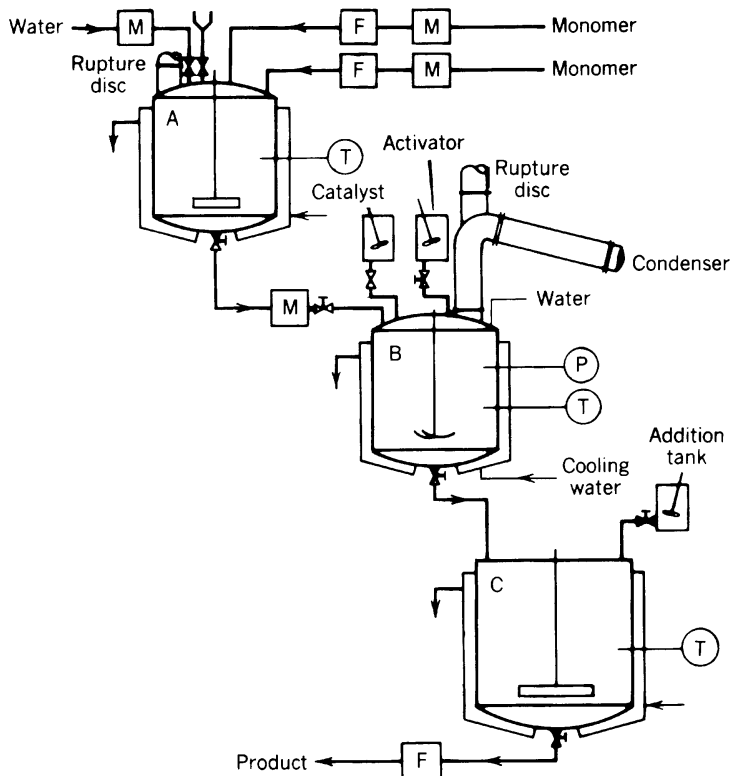
Fig. 2.   Emulsion polymerization plant. A, Emulsion feed tank; B, polymerization reac-
tor; C, drumming tank; F, filter; M, meter; P, pressure gauge; T, temperature indication.

Acrylic emulsion polymers, like many other types of polymers, are subject to bac-
terial attack. Proper adjustment of pH, addition of bactericides, and good house-
keeping practices (95) can alleviate the problems associated with bacterial
growth. Some advances in the industrial application of emulsion polymerization
have been described in the open literature (113).

    5.5. Suspension Polymerization. Suspension polymers of acrylic
esters are industrially used as molding powders and ion-exchange resins. In
this type of polymerization, monomers are dispersed as 0.1- to 5-mm droplets
in water and are stabilized by protective colloids or suspending agents. In
contrast to emulsion polymerization, initiation is accomplished by means of a
monomer-soluble agent and occurs within the suspended monomer droplet.
Water serves the same dual purpose as in emulsion (heat removal and polymer
dispersion). The particle size of the final material is controlled through the
control of agitation levels as well as the nature and level of the suspending
agent. Once formed, the 0.1- to 5-mni polymer beads can be isolated through
centrifugation or filtration.

    The most commonly used suspending agents are cellulose derivatives, poly-
acrylate salts, starch, poly(vinyl alcohol), gelatin, talc, and clay derivatives (95).

The important function these agents must serve is to prevent the coalescence of monomer droplets during the course of the polymerization (114). Thickeners can also be added to improve suspension quality (95). Other additives such as lauryl alcohol, stearyl acid or cetyl alcohol lubricants and di- or trivinyl benzene, diallyl esters of dibasic acids, and glycol dimethacrylates cross-linkers are used to improve bead uniformity and bead performance properties.

Unlike emulsion polymerization, the initiators employed in suspension polymerization must not be water-soluble; organic peroxides and azo species are most commonly used. In similar fashion to bulk polymerization, the level of initiator used directly influences the molecular weight of the product (95,115,116). Developments in the method of suspension polymerization have been reviewed in the open literature (117,118).

5.6. Graft Copolymerization.   Polymer chains can be attached to a pre-existing polymer backbone of a similar or completely different composition to form what is termed a graft copolymer. Acrylic branches can be added to either synthetic (119,120) or natural (121–124) backbones. Attachment of graft polymer branches to preformed backbones is accomplished by chemical (125–127), photochemical (128,129), radiation (130), and mechanical (131) means. The presence of distinct compositions in this branched geometry often conveys properties which cannot otherwise be attained (132,133).

5.7. Living Polymerization.   One of the most exciting areas currently in the radical polymerization of acrylic ester monomers is the field of living polymerization. Living polymers are defined in Reference 134 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." Because of 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 (135).

Atom-transfer radical polymerization (ATRP) and nitroxide-mediated (136–138) 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 acrylate (139,140) as well as functional acrylates containing alcohol (141), epoxide (142), and vinyl groups (143) on the side chain. The main drawbacks to the ATRP method of creating acrylic ester homo- and copolymers are the relatively long reaction times and the high levels of metal-containing initiator required.

5.8. Radiation-Induced Polymerization.   Coatings can be formed through the application of high energy radiation to either monomer or oligomer mixture. Ultraviolet curing is the most widely practiced method of radiation-based initiation (144–150); this method finds its main industrial applications in the areas of coatings, printing ink, and photoresists for computer chip manufacturing. The main disadvantage of the method is that uv radiation is incapable of penetrating highly pigmented systems.

To form a film via this method, a mixture of pigment, monomer, polymer, photoinitiator, and inhibitor are applied to a substrate and polymerized by controlled exposure to uv radiation. Polymers used as co-curing agents often have unsaturated methacrylate functionalities attached; higher order acrylates are often used as the solvent in photocure mixtures.

In order to avoid the problems associated with more highly pigmented systems, electron beam curing is employed (151). This high energy form of radiation is capable of penetrating through the entire coating regardless of the coating's pigment loading level.

5.9. Anionic Polymerization. The anionic polymerization of acrylic ester monomers, is accomplished by use of organometallic initiators in organic solvents. The main advantage to the use of anionic polymerization as opposed to other methods is its ability to generate stereoregular or block copolymers. Some examples of this type of polymerization include the anionic formation of poyl(*t*-butyl acrylate) (152–155), poly(isopropyl acrylate) (156), and poly(isobutyl acrylate) (157,158). Solvent conditions primarily determine tacticity of the resulting polymer product with nonpolar solvents generating isotactic product and polar solvents resulting in the formation of syndiotactic polymers. The strikingly different physical properties and mechanistic discussions on the formation of these two different types of polymer have been described in the polymer literature (159–162).

The initiation step for anionic polymerizations takes place via a Michael reaction:

$$R_3C^-M^+ + CH_2{=}CHCOOR \rightarrow R_3C{-\!\!\!-}CH_2{-\!\!\!-}\bar{C}H{-\!\!\!-}COOR$$
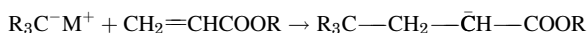
A subsequent polymer growth occurs by head-to-tail addition of monomer to the growing polymer chain.

$$R_3C{-}CH_2{-}\bar{C}H{-}COOR \;+\; CH_2{=}CHCOOR \;\longrightarrow\; R_3C{-}CH_2{-}\underset{\underset{\displaystyle COOR}{|}}{CH}{-}CH_2{-}\underset{\underset{\displaystyle COOR}{|}}{\bar{C}H}$$

Because of cost constraints and toxicity issues involved with the organometallic initiators, anionic polymerization is of limited commercial significance. Both the living methods described above as well as DuPont's group-transfer polymerization method (163–167) are seen as alternative ways to achieve the same level of control over polymer architecture as that of anionic polymerization. All these methods offer the promise of narrow and controllable molecular weight distributions as well as the ability to form block copolymers through the sequential addition of monomers. Additionally, all the methods suffer from slow overall reaction rates and the difficulty of removing the specialty initiators after polymer formation has taken place.

6. Analytical Methods and Specifications

6.1. Emulsion Polymers. Current analytical methods allow for complete characterization of all crucial aspects of an acrylic latex (87). The main properties of interest are an acrylic latex's composition, percent solids content, viscosity, pH, particle size distribution (168,169), glass-transition temperature, minimum film-forming temperature (170), and surfactant type. In addition to these basic properties, the stability of a latex with respect to mechanical

shear, freeze-thaw cycles, and sedimentation on standing for long periods of time are of interest in commercial products.

6.2. Solution Polymers. A solution polymer's composition, solids content, viscosity, molecular weight distribution, glass-transition temperature, and solvent are of interest. Standard methods allow for all of these properties to be readily determined (171,172).

7. Health and Safety Factors

Acrylic polymers are categorized as nontoxic and have been approved for the handling and packaging by the FDA. The main concerns with acrylic polymers deal with the levels of residual monomers and the presence of nonacrylic additives (primarily surfactants) which contribute to the overall toxicity of a material. As a result, some acrylic latex dispersions can be mild skin or eye irritants.

During the manufacture of an acrylic polymer, precautions are taken to maintain temperature control (173). In addition to these measures, polymerizations are run under conditions wherein the reactor are closed to the outside environment to prevent the release of monomer vapor into the local environment. As for final product properties, acrylic latices are classified as nonflammable substances and solution polymers are classified as flammable mixtures.

8. Uses

Because of their wide property range, clarity, and resistance to degradation by environmental forces, acrylic polymers are used in an astounding variety of applications that span the range from very soft adhesive materials to rigid non-film-forming products.

8.1. Coatings. Acrylic ester latex polymers are used widely as high quality paint binders because of their excellent durability, toughness, optical clarity, uv stability, and color retention. These properties allow acrylics to find use as binder vehicles in all types of paints (76): interior and exterior; flats, semigloss, and gloss; as well as primers to topcoats. Although all-acrylic compositions are most favored in exterior applications because of their excellent durability (174), other types of copolymers such as vinyl-acrylics and styrene-acrylics benefit in terms of performance properties from the acrylic portion of the composition; methods of manufacturing acrylic-based paints have been described previously in the literature (175). Acrylic emulsion polymers even find use in the protection of structural steel (176) (see COATING PROCESSES).

The industrial finishing area sees both acrylic emulsions as well as solution polymers utilized in a wide variety of applications including factory finished wood (177,178), metal furniture and containers (179), and can and coil coatings (180). In order to harden acrylic polymers for this type of demanding application, the polymers are often cross-linked with melamines, epoxies, and isocyanates. The coatings are applied via spraying, roll dipping, or curtain coating. Radiation curing using uv radiation or electron beam radiation (181–186), powder coating (187–190), electrode deposition of latices (191–193), and the use of higher solids

level emulsion (194) represent newer methods for applying acrylic coatings to form industrial finishes. Excellent reviews on the use of water-based emulsions (195,196) and solution acrylics (197−199) can be found in the open literature (see COATINGS).

Hydrophobically modified acrylics are finding extensive usage as thickening agents in the paints marketplace as well as the area of industrial finishes (200). Flow and leveling improvements are observed when changing a formulation over from hydroxyethylcellulose to acrylic-based thickeners. Unlike cellulosic thickeners, the modified acrylics act through an associative thickening mechanism; they stabilize the dispersed polymer phase rather than thickening the aqueous phase of a polymer latex. Two main types of modified acrylics are of commercial value: HASE (hydrophobically modified alkali-soluble emulsions) and HEUR (hydrophobically modified ethylene oxide urethane block copolymers). These acrylics compete with hydrophobically modified hydroxyethylcellulose in the marketplace (201−203).

8.2. Textiles.   Because of their durability, soft feel, and resistance to discoloration, acrylic emulsion polymers find a variety of uses in the textiles area including binders for fiberfill and nonwoven fabrics, textile bonding or laminating, flocking, backcoating and pigment printing applications. *N*-Methylolacrylamide is often used as a self-cross-linker in acrylic textile binders to improve washing and dry cleaning durability as well as overall binder strength (204).

Polyester (205−208), glass (209), and rayon (210) nonwoven and fiberfill mats have been manufactured using acrylic binders to hold the mats together. In this process, the acrylic emulsions are applied to a loose web or mat and are then heated to form a film at the fiber crossover points which maintains the structural integrity of the mat. The final products generated using this technology include quilting, clothing, disposable diapers, towels, filters, and roofing (see NONWOVEN FABRICS).

Acrylic polymers find use in applications that take advantage of their exceptional resistance to environmental assaults such as uv radiation, ozone, heat, water, dry cleaning, and aging (211). Acrylics are often used as the backing material for automotive and furniture upholstery to improve the dimensional handling properties, prevent pattern distortion, prevent unraveling, and minimize seam slippage. Strike-through problems are averted through the use of foamed or frothed acrylic coatings, which also yield a softer fabric and save on energy costs (212). Crushed acrylic latex foam are employed as backing materials for draperies. The foam protects the drapery from sun damage, mechanically stabilizes the fabric, improves drape, and gives a softer hand than conventional backing materials (213). Acrylics are also used as carpet-backings and to bond fabric-to-fabric, fabric-to-foam, and fabric-to-nonwoven materials (214).

The flocking process begins with the bonding of cut fibers to an adhesive-coated fabric to obtain a decorative and functional material (215). Acrylics can provide the softness and durability that are sought in flocked textiles; they also serve as binders for pigments in the printing of flocked fabrics (35,216,217).

The feel, soil release properties, and permanent-press behavior of a fabric can be finely tuned using acrylic as finishing polymers. Copolymers of acrylics with acrylic or methacrylic acid can be used as thickeners for textile coating formulation.

8.3. Adhesives.   Acrylic emulsion polymers are used in a wide variety of adhesives. Pressure-sensitive Adhesives, which typically have T_g values less than 20°C, are the main type of acrylic adhesive. Acrylic polymers and copolymers find use as PSAs in tapes, decals, and labels. Along with their aforementioned superior chemical resistance properties, acrylics possess an excellent balance of tack, peel, and shear properties which is crucial in the adhesives market (218,219). Other types of adhesives that employ acrylics include construction formulations and film-to-film laminates.

8.4. Paper.   Because of their excellent cost-performance balance, acrylic-vinyl acetate copolymer emulsion binders have been used as pigment binders for coated paper and boards. These binders provide higher brightness, opacity, coating solids, and improved adhesion versus styrene-butadiene copolymers (220,221). Acrylics also find usage as paper saturants with properties that compare favorably to natural rubber, butadiene-acrylonitrile, and butadiene-styrene (222). Finally, acrylic emulsion polymers are utilized in starch-latex-pigmented coatings (223) as well as size-press (224) and beater addition (225) applications.

8.5. Other Applications.   The leather finishing area is a traditional stronghold of acrylic emulsion polymers (226). Acrylics are used throughout the entire process of pigskin leather production; the use of acrylics lends uniformity, break improvement, better durability, and surface resistance while preserving the natural appearance of the pigskin (227).

Acrylics have been used to impart impact strength and better substrate adhesion to cement (228). The ceramics industry uses both acrylic solution and emulsion polymers as temporary binders, deflocculants, and additives in ceramics bodies and glazes (229) (see CERAMICS).

Acrylics are used in the manufacture of aqueous and solvent-based caulks and sealants (230,231). Elastomeric acrylics are used in mastics to prevent uv radiation and chemical damage to the underlying polyurethane foam. Acrylics also impart hailstone resistance as well as flexibility over a broad temperature range (232). The manufacturing process for poly(vinyl chloride) uses acrylics as processing aids and plate-out scavengers in calendered and blown films. Acrylics allow for the manufacture of thick, smooth calendered vinyl sheets through modification of the melt viscosity of the vinyl sheet polymer (233). In the agricultural area, thin layers of acrylic emulsions have been applied to citrus leaves and fruit to control "Greasy Spot," a disease which causes leaf-spotting and eventually leaf loss (234). Acrylics have found a great deal of use in the floor polish area; a guide to formulating these coatings has been published (235).

Acrylic polymers have been used as alternatives to nitrile rubbers in some hydraulic and gasket applications because of their excellent heat-resistance properties (236,237). Ethylene-acrylate copolymers have been used as transmission seals, vibration dampeners, dust boots, and steering and suspension seals (238).

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