ACRYLAMIDE POLYMERS

1. Introduction

The terminology used to describe acrylamide-containing polymers in the technical literature varies in its precision. In order to avoid confusion, throughout this article the term “poly(acrylamide)” will be reserved for the nonionic homopolymer of acrylamide, whereas the term “polyacrylamides” or “acrylamide polymers” will refer to acrylamide-containing polymers, including the homopolymer and copolymers. Specific nomenclature will be used for particular copolymers, for example, poly(acrylamide-co-sodium acrylate).

The diverse class of water-soluble and water-swellable polymers comprising polyacrylamides contains some of the most important synthetic polymeric materials used to improve the quality of life in our modern society. Acrylamide-containing polymers fall into three main categories: nonionic, anionic, and cationic. The projected annual sales growth rate of polyacrylamides between

1999 and 2002 is 4–7% (1). The multi-billion-dollar global market value of this class of materials makes it an economically important segment of the chemical industry.

Poly(acrylamide) is made by the free radical polymerization of acrylamide, which is derived from acrylonitrile by either catalytic hydrolysis or bioconversion. The unique chemistry of acrylamide, its favorable reactivity ratios with many comonomers, and the ability of poly(acrylamide) to be derivatized allows for a substantial variety of polymers to be tailor-made over a wide range of molecular weights (approximately 10^3–50×10^6 daltons), charge densities, and chemical functionalities.

The very large number of applications for acrylamide-containing polymers has been extensively reviewed (2–7). One major application area for polyacrylamides is in solid–liquid separations. The largest market segments therein are for use as flocculants and dewatering aids for municipal wastewater, thickening aids for industrial wastewater, secondary clarification and clarification of potable water, solids removal from biological broths, and animal feed recovery from waste. Because of major concern for the environment, the allowable suspended solids in most effluent streams are becoming more restricted by government regulations. New technologies for producing cationic polymers with a wide range of charge levels, novel structures, and very high molecular weights have addressed this need. These polymers have greatly improved the dewatering performances of centrifuges, screw presses, and belt presses used for such purposes. This has resulted in drier dewatered solids, which has translated into lower costs to either landfill or incinerate the solids.

The largest volume applications for polyacrylamides in paper mills are in on-machine wet-end processes. Paper retention aids and drainage aids are used to flocculate or bind fillers, fibers, and pigments. Glyoxalated cationic polyacrylamides are used as strengthening agents and promoters for paper sizing. Other papermaking applications include off-machine processes for recovering fiber from recycled paper waste and for deinking.

High-molecular-weight polyacrylamides have also traditionally been used in the minerals processing industry. Recent polymer technology developments, including-ultra-high-molecular-weight and novel anionic polyacrylamides, have yielded important materials. These products are used as flocculants in coal mining, the Bayer process for alumina recovery (red mud flocculants), precious metals recovery, and the solid–liquid separation of underflow streams in a variety of mining processes. Novel chemical modifications of low molecular weight polyacrylamides have resulted in materials that are used as modifiers in the selective separation of metal sulfides and magnetite and as depressants and flotation aids.

One large market segment for anionic polyacrylamides had traditionally been in enhanced oil recovery. However, low oil prices have resulted in a large decline in such applications. Since 1990, polymer flooding has virtually disappeared in the United States. However, during 1999 crude oil prices started to increase.

Other significant application areas for polyacrylamides include soil conditioning and erosion control, drag reduction, sugar processing, additives in cosmetics, and superabsorbents.

2. Physical Properties

2.1. Solid Polyacrylamides. Completely dry poly(acrylamide) is a brittle white solid. It is nontoxic, unlike the monomer. Dry polyacrylamides (including copolymers) are commercially available as nondusting powders and as spherical beads. These products can contain small amounts of additives that aid in both the stability and dissolution of the polymers in water. Commercially available acrylamide copolymer powders, which are typically dried under mild conditions, will usually contain about 5–15% water depending on their ionicity. The powders are hygroscopic, and generally become increasingly hygroscopic as the ionic character of the polymer increases. Cationic polymers are particularly hygroscopic.

Some physical properties of nonionic poly(acrylamide) are listed in Table 1. The tacticity and linearity of the polymer chain is claimed to be dependent on the polymerization temperature. Syndiotacticity is favored at low temperatures (8). Linear polymer chains are reportedly obtained below 50°C, but branching begins to occur as the temperature is increased above this level (9). A wide range of values of the glass transition temperature (T_g) of poly(acrylamide) have been published. This is because the measured value is highly sensitive to the presence of water, and also to the presence of nonacrylamide species along the polymer backbone. For example, small amounts of acrylate groups can arise from hydrolysis of the amide group during or after polymerization. This can dramatically change the T_g.

2.2. Solution Properties. The amide group (—$CONH_2$) in poly(acrylamide) provides for its solubility in water and in a few other polar solvents such as glycerol, ethylene glycol, and formamide. We can acquire a sense of poly(acrylamide)'s affinity for water by examining a few characteristic parameters. Theta (Θ) conditions for a polymer delineate a particular combination of solvent and temperature at which the polymer acts in an ideal manner (10), ie, the chains behave as random coils. The Θ temperature of poly(acrylamide) in water has been determined to be −8°C (11). Thus water at 25°C is a solvent of intermediate

Table 1. **Physical Properties of Solid Poly(acrylamide)**

Property	Value	Ref.
density	1.302 g/cm^3 (23°C)	250
glass-transition temperature (T_g)	195°C	251
critical surface tension (γ_c)	52.3 mN/m (20°C)	252
chain structure	mainly heterotactic linear or	253
	branched, some	25
	head-to-head addition	84, 254
crystallinity	amorphous (high molecular weight)	255
solvents	water, ethylene glycol, formamide	256
nonsolvents	ketones, hydrocarbons, ethers, alcohols	257
fractionation solvents	water–methanol	258
gases evolved on combustion in air	H_2, CO, CO_2, NH_3, nitrogen oxides	259

Table 2. **Physical Properties of Poly(acrylamide) in Solution**

Property	Value	Conditions	Ref.
steric hindrance parameter (σ)	2.72	water @ 30°C	260
characteristic ratio (C_∞)	14.8	water @ 30°C	260
persistence length (y)	15.2 Å	water @ 25°C	—[a]
partial specific volume (ν)	0.693 cm^3/g	water @ 20°C	261
theta temperature (Θ)	−8°C	water @ 25°C	11
theta conditions	0.40 v/v methanol/water	water @ 25°C	12
Flory χ parameter	0.48 ± 0.01	water @ 30°C	13
refractive index increment (dn/dc)	0.187 cm^3/g	$\lambda = 546.1$ nm	262
	0.185 cm^3/g	$\lambda = 632.8$ nm	

[a] Calculated from the values of K_0 (Mark-Houwink-Sakurada prefactor under Θ conditions) and Θ_0 (viscosity constant) found in Ref. 9, using the relationship: $y = \left(\frac{M_0}{2b}\right)\left(\frac{K_0}{\Theta_0}\right)^{2/3}$, where M_0 is the monomer molecular weight (71 g/mol), and b is the monomer length (2.5 Å).

quality for poly(acrylamide). Aqueous methanol (40 vol %), however, is a Θ solvent for poly(acrylamide) at 25°C (12). The Flory χ parameter, which is a measure of the relative affinity between the polymer segments with each other vs with the solvent, is 0.5 under Θ conditions. The Flory χ parameter of poly(acrylamide) has been determined to be 0.48 in water at 30°C (13). These and other properties of poly(acrylamide) in solution are collected in Table 2.

Poly(acrylamide) is soluble in liquid water at all concentrations, temperatures, and pH values. However, at high pH (> 10.5) the polymer will begin to hydrolyze on standing (14). Poly(acrylamide) is generally soluble in most salt solutions but can phase separate in some highly concentrated salt solutions, such as $(NH_4)_2SO_4$. Each amide group in poly(acrylamide) has roughly 2 strongly bound water molecules (15) associated with it, whereas the entire first hydration sheath contains a total of about 4–5 waters per monomer (16). This may be compared to poly(sodium acrylate), which has 4 strongly bound waters per repeat unit (17) and a total of 11 waters of hydration per repeat unit (18). Certain salts, however, can alter the hydrogen bonding between the primary amide groups and water in individual chains. For example, addition of potassium iodide [7681-11-0] to a poly(acrylamide) solution can increase the solution viscosity slightly (19). The inferred coil expansion involves a change in the hydration sheath of the polymer.

The amide group is capable of strong hydrogen bonding, which has effects on both the monomer and polymer properties. The relative rates of acrylamide polymerization in various organic solvents (20–22) are influenced by solvent–monomer interactions, which depend on the polarity and hydrogen bonding ability of acrylamide. Hydrogen bonding has been evidenced (with NMR) to occur mainly with the carbonyl oxygen in the acrylamide (23,24).

The hydrogen bonding ability of the amide group is also well worth considering when rationalizing the solution properties of polymers containing acrylamide. Two examples are presented here. The slow evolution of hydrogen-bonded aggregates (see the following) have been implicated in explaining the time dependence of the viscosities of poly(acrylamide) solutions in aqueous media (25,26). Second, it is well known that copolymers of acrylamide and sodium acrylate exhibit maximum values of the mean square radius (R_g), second virial coefficient (A_2), and intrinsic viscosity [η] at 60–70 mol % acrylate content (27). This can be rationalized from a consideration of intermolecular hydrogen bonding and electrostatic interactions.

Copolymers of acrylamide with ionic comonomers are also generally quite soluble in water. However, the solution properties of ionized copolymers of acrylamide are substantially different from those of the homopolymer. The incorporation of ionic comonomers leads to all of the traditional polyion effects such as chain expansion and viscosification at low ionic strength (polyelectrolyte effect), ionization-dependent dissociation constants, counterion condensation, ion exchange with charged surfaces, and specific binding of certain multi-valent ions. For example, anionic copolymers containing carboxylate groups will precipitate at certain multi-valent salt concentrations (28–30). Poly(sodium acrylate) can phase separate in the presence of divalent salts when there are about 0.8 equivalents of the divalent cations (31). The phase behavior of acrylamide–acrylic acid copolymers in mixtures of mono and divalent salts has been studied by François et al. (32). Trivalent cations (eg, Al^{3+} and Cr^{3+}) are even more efficient at precipitating polyions containing carboxylate groups (33). Under the right conditions, these physical cross-links can be used to form a reversible gel. This strategy has been employed in mobility control systems used in oil recovery (34).

The rate of dissolution of polyacrylamides can depend on the agitation conditions, dissolved salts, the material form of the polymer (eg, solid or emulsion), state of hydration, and the presence of other components. While salts only weakly affect the dissolution rate of poly(acrylamide), ionic copolymers tend to dissolve decidedly more slowly in salt solutions than in pure water. Increasing the mechanical energy input typically speeds up the dissolution process; however, mechanical degradation (chain scission) of very high-molecular-weight chains can occur. Flows with elongational components (eg, turbulent and porous media flows) are usually most egregious in this regard. The coil-to-stretched transition initiated at a critical elongation rate in these flows can be responsible for such phenomena as drag reduction (35) and apparent viscosity enhancement in porous media flow (36,37). However, chain scission can also occur at a second critical elongation rate. These critical elongation rates are functions of the degree of polymerization, the solvent quality, and the polymer concentration (38–42). Care is often taken to avoid mechanical degradation of the polymer during mixing [especially in impeller-type mixers (43), gear pumps, and orifice flow], filtration, and flow through a packed column (eg, in HPSEC analysis), all of which expose the polymer chains to some elongational flow kinematics.

Linear polyacrylamides in solution adopt nearly random coil configurations that are partially permeable (draining) to solvent. The coils are unassociated in dilute solution. The average shape of the isolated coils has been described as an ellipsoidal or bean-shaped structure (44). The individual chains are quite flexible, as is common with most vinyl polymers. This is indicated from several parameters shown in Table 2, such as the persistence length, steric hindrance parameter (σ), and characteristic ratio (C_∞). The persistence length of 15.2 Å for poly(acrylamide) in water is quite similar to the average intrinsic (bare) persistence length (~14 Å) of many vinyl polymers (45).

Table 3. **Suggested R_g–M_w Correlations for Polyacrylamides in Solution $R_G = K_r M_w^{a_r}$ (R_g in nm)**

Polymer	Solvent	Temp. (°C)	MW range (10^6 daltons)	$10^2 K_r$ (nm)	a_r	Ref.
poly(acrylamide)	water	25	0.83–13.4	0.725	0.64	11
poly(acrylamide)	0.1 *M* NaCl + 0.2% NaN_3	20	0.16–8.2	0.749	0.64	55
poly(Na acrylate$_{29}$–co-acrylamide$_{71}$)	0.1 *M* NaCl		0.96–6	2.50	0.60	30
poly(Na acrylate$_{20}$–co-acrylamide$_{80}$)	1 *M* NaCl pH 9	ambient	0.1–3.0	4.06	0.55	56
poly(acrylamide$_{70}$–co-AETAC$_{30}$)	1 *M* NaCl + biocide		0.5–2.7	3.30	0.54	58

One measure of the size of a polymer in solution is its mean square radius (R_g), sometimes referred to as its radius of gyration. The mean square radius scales with the weight-average molecular weight (M_w) to a fractional power (a_r) for a homologous series of polymers all within the same topology class (e.g., linear chains); $R_g = K_r M_w^{a_r}$. The K_r and a_r values depend on the polymer, solvent, and temperature. Suggested values derived from the literature for poly(acrylamide) and a few copolymers are listed in Table 3.

2.3. Solution Rheology.

Solutions of polyacrylamides tend to behave as pseudoplastic fluids in viscometric flows. Dilute solutions are Newtonian (viscosity is independent of shear rate) at low shear rates and transition to pseudoplastic, shear thinning behavior above a critical value of the shear rate. This critical shear rate decreases with the polymer molecular weight, polymer concentration, and the thermodynamic quality of the solvent. A second Newtonian plateau at high shear rates is not readily seen, probably due to mechanical degradation of the chains (25). Viscometric data for dilute and semidilute poly (acrylamide) solutions can often be fit to a Carreau model (46,47). It is wise to remember the cautions that were cited previously about mechanical degradation of the high-molecular-weight components of a polyacrylamide sample when analyzing rheological data.

The viscosities of fully dissolved, high-molecular-weight poly(acrylamide)s in aqueous solutions have often, but not always, been seen to change with time over the periods of days to weeks. Typically, the solution viscosity decreases with time. Extensive studies of this instability phenomenon have been made by Kulicke and co-workers (25,26). They concluded that the evolution of intramolecular hydrogen bonds and the resulting change in macromolecular conformation were responsible for the time dependence, and not any molecular weight degradation. The instability can be avoided completely when the polymers are dissolved in formamide, aqueous ethylene glycol, or 2% 2-propanol in water. Competing viewpoints do exist about the interpretation of this solution aging (48,49).

The intrinsic viscosity [η] of a polymer in solution is a measure of its molecular volume divided by its molecular weight. The [η] value can be empirically correlated to the viscosity-average molecular weight (M_η) via the Mark-Houwink-Sakurada relationship (50): $[\eta] = K_\eta M_\eta^{a_\eta}$. Poly(acrylamide) and ionic

Table 4. **Suggested Mark-Houwink-Sakurada Correlations for Polyacrylamides in Solution $[\eta] = K_\eta M_\eta a_\eta$ ($[\eta]$ in cm^3/g)**

Polymer	Solvent	Temp. (°C)	MW range (10^6 daltons)	$10^2 K_\eta$ (cm^3/g)	a_η	Ref.
poly(acrylamide)	water	25	0.038–9	1.00	0.76	263
poly(acrylamide)	0.5 *M* NaCl	25	0.5–5.5	0.719	0.77	264
poly(acrylamide)	1.0 *M* NaCl	25	1.1–14.6	2.57	0.67	265
poly(Na $acrylate_{20}$–co-$acrylamide_{80}$)	0.5 *M* NaCl pH 9	25	0.12–3.0	1.40	0.75	56[a]
poly(Na $acrylate_{20}$–co-$acrylamide_{80}$)	0.5 *M* NaCl pH 9	25	0.12–3.0	1.09	0.78	56[b]
poly(Na $acrylate_{30}$–co-$acrylamide_{70}$)	0.5 *M* NaCl	25	0.77–5.5	1.12	0.79	264
poly(Na $acrylate_{20}$–co-$acrylamide_{80}$)	1.0 *M* NaCl pH 9	25	0.12–3.0	1.41	0.74	56[a]
poly(Na $acrylate_{20}$–co-$acrylamide_{80}$)	1.0 *M* NaCl pH 9	25	0.12–3.0	1.31	0.76	56[b]
poly($acrylamide_{70}$–co-$AETAC_{30}$)	1.0 *M* NaCl + biocide	25	0.5–2.7	1.05	0.73	58

[a] Uncorrected for polydispersity.

[b] Corrected for polydispersity.

copolymers of acrylamide follow this empirical relationship, which is often used to estimate the polymer molecular weight. Table 4 lists suggested literature values of K_η and a_η for poly(acrylamide) and several copolymers in a variety of solvents.

At high concentrations of univalent ions (~ 1 molar) the solution properties of ionic copolymers of acrylamide tend to resemble those of the homopolymer, but they are not exactly the same. Considering the intrinsic viscosity data, the exponents a_η for anionic and cationic polyacrylamides in high salt concentrations tend to cluster between 0.7 and 0.8, which is similar to that for poly(acrylamide) (11, 25, 51–58). However, the prefactors (K_η) vary over a larger range, and this cannot be rationalized simply by considering only the degree of polymerization. This means that there are real differences in the short-range interactions along the chains, which depend on the copolymer composition.

The polymer concentration (c) dependence of the zero-shear-rate viscosity (η_0) for aqueous poly(acrylamide) solutions of various viscosity-average molecular weights does not seem to follow the entanglement model, wherein polymer chain interpenetration would dominate the viscometric behavior, and a master curve should result when η_0 is plotted against cM_η. Instead, the data can be better described using a suspension model, wherein $c[\eta]$ correlates the η_0 data on a master plot. Kulicke et al. (25) make a concise presentation of the relationship between η_0, M_η and c for poly(acrylamide) in water at 25°C.

Solutions of poly(acrylamide) that are well in excess of the overlap concentration can display viscoelastic properties. Viscoelasticity of these polymeric fluids can be observed in a variety of ways, including the presence of a normal stress and/or flow irregularities (eg, vortices) in steady-shear flow, stress overshoot during shear flow startup, a measurable storage modulus (G') in oscillatory flow, an apparent shear thickening in flows with an elongational component (eg, porous media flow), a measurable elongational viscosity, or the ability to pull a solution “fiber” (tubeless siphon effect). A simple means for qualitatively assessing the molecular weight of a linear poly(acrylamide) in solution is to see how long a thread one can pull out of a semidilute solution of the polymer using a rod.

3. Acrylamide Polymerization

Acrylamide [79-06-1] (2-propenamide, $C_{3J}H_5ON$) readily undergoes free-radical polymerization to high-molecular-weight poly(acrylamide) [9003-05-8]. The synthetic methods have been reviewed extensively (25). Free-radical initiation can be accomplished using organic peroxides, azo compounds, inorganic peroxides including persulfates, redox pairs, photoinduction, radiation-induction, electroinitiation, or ultrasonication. Several reasons account for the ultra-high-molecular-weights achievable. First, preparations of polyacrylamides are usually conducted in water, and the chain transfer constant to monomer and polymer appears to be zero in water (59). Second, the value of $k_p/k_t^{1/2}$, about 4.2, is unusually high (60) and is independent of the pH of the media. The rate of polymerization is proportional to the 1.2–1.5 power of the monomer concentration and to the square root of the initiator concentration (61–63). All this results in a high rate of propagation. Chain termination is primarily by disproportionation (64).

The large amount of heat (82.8 kJ/mol) that evolves during polymerization can result in a rapid temperature rise. One way in which this exotherm problem has been addressed in commercial high-solids and high-molecular-weight processes has been through the use of an adiabatic gel process in which the initiation temperature is 0°C. In another approach, controllable-rate redox polymerization of aqueous acrylamide-in-oil emulsions can be carried out at moderate temperatures of 40–60°C in order to accommodate the exotherm and to achieve very high molecular weights. At 70–100°C, a persulfate initiator can give a grafted or branched polymer (65). Additives greatly affect the rate and the kinetics of polymerization (66,67). These additives include metal ions, surfactants, chelating agents, and organic solvents. The high chain transfer constant of compounds such as 2-propanol, bisulfite ion, or persulfate ion to active polymer has been reported (68). Chain transfer agents have been used purposely to control molecular weight, minimize insoluble polymer, and control cross-linking and the degree of branching in commercial preparations.

4. Structural Modifications of Poly(acrylamide)

Poly(acrylamide) (PAM) is a relatively stable organic polymer. However, PAM can be degraded (eg, molecular weight decreases) under certain conditions. The amide functionality is acidic in nature and is capable of undergoing most of the chemical reactions of primary amides. Consequently, acrylamide polymers can be functionalized by post-polymerization chemical reactions. Examples illustrated in the following constitute the most-used chemical modifications. To obtain anionic derivatives, PAM can be hydrolyzed with caustic. Sulfomethylated PAM can be prepared by reacting PAM with formaldehyde and sodium bisulfite under acidic conditions. Reacting PAM with hydroxylamine under alkaline conditions can yield hydroxamated PAM. As an example of a cationic derivative, Mannich-base PAM can be obtained by reacting PAM with formaldehyde and dimethylamine to produce a cationic polymer with a charge that varies with pH. As an example of a nonionic derivative, PAM can be reacted with glyoxal to yield pendant aldehyde functionality. These structurally modified polyacrylamides are successful commercial products.

4.1. Degradation. Dry poly(acrylamide) is relatively stable. The onset of dry PAM decomposition occurs at 180°C (69). Inter- or intra-amide condensation (70) to an imide can occur in acidic media at high temperatures (140–160°C). At temperatures above 160°C, thermal degradation, imidization, nitrile formation, and dehydration take place. Polymer stability is very important in actual applications in order to maintain consistent and excellent performance. In most applications, polymer solutions are prepared and used at moderate temperatures; however, there are exceptions such as in the harsh reservoir conditions (high temperature and high salinity) found in some enhanced oil recovery operations. Impurities such as residual persulfate from batch manufacturing can degrade the polymer (71,72). A residual Fe^{2+} ETDA complex in the product can also enhance degradation at both ambient and elevated temperatures (73–75). Hydroxy radicals, which can form in the presence of oxygen (76,77), can attack the polymer backbone. In the absence of oxygen, anionic polyacrylamide solutions were stable at 90°C for 20 mo (78). Polyacrylamide in aqueous solution, in the presence of oxidizing agents such as $KMnO_4$, bromine, and $AgNO_3$, will degrade. The degraded polymer shows a reduced molecular weight, crosslinking and chain stiffening (79). Recently potassium peroxosulfate (80) was also reported to degrade hydrolyzed polyacrylamide. In the presence of ozone, very little degradation was found at low pH. However, random chain scission occurred at pH 10 (81). In the presence of sodium azide, a bactericide, a PAM in solution at room temperature showed no degradation for a long time (55). A combination of both pressure and elevated temperature can enhance polyacrylamide degradation. Polymer degradation can also occur under shear and elongational stresses (76,82). Backbone homolytic cleavage has been confirmed by a free radical trap technique. Under certain shear conditions one macroradical per 12 monomer units can be formed.

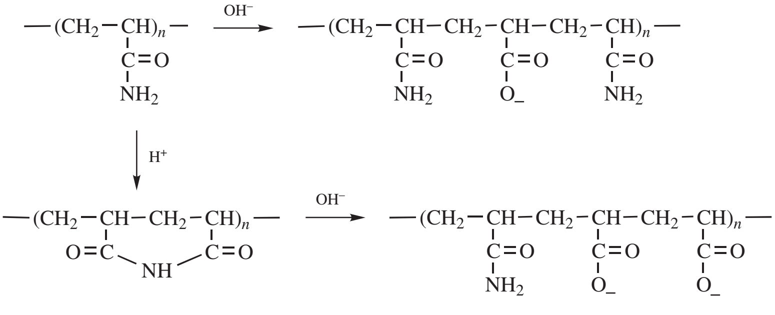
Numerous types of oxygen scavengers are used to inhibit and prevent oxidative degradation. These stabilizers have been reviewed (79) extensively. Effective compounds are thio compounds, hydroquinone, bisulfite, phenolic compounds, hydroxylamine, hydrazine, and others.

The biodegradability of PAM has not been definitively delineated in the literature (79). Recently, however, microorganisms (83), enterobacter agglomerans and azomonas macrocytogenes, were isolated from soil and the molecular weight of poly(acrylamide) in the presence of these microorganisms was found to undergo a 40-fold reduction as a result of chain degradation. The rate of biodegradation was equivalent to 20% of the carbon being consumed each day.

4.2. Hydrolyzed Polyacrylamide. Hydrolysis of poly(acrylamide) proceeds smoothly over a wide range of pH (see scheme below). Fundamental studies have been reviewed extensively (84–87). At alkaline pH, three reaction kinetics constants have been described, k_0, k_1 and k_2. The subscripts characterize the number of neighboring carboxylate groups next to the amide group being hydrolyzed. The rate constant k_0 is for no carboxylate neighbors, k_1 is for one carboxylate neighbor, and k_2 is for two carboxylate neighbors. Indirect evidence has shown that $k_0 > k_1 > k_2$. Under alkaline conditions, the rate of hydrolysis of poly(acrylamide) decreases with increasing conversion. The electrostatic repulsion from the increasing number of carboxylate groups in the backbone polymer opposes the approaching hydroxyl ion. Consequently, further hydrolysis will be severely retarded. Only about 80% of the amide groups (93) can be hydrolyzed by excess hydroxide ion even at elevated temperatures.

^{13}C-nmr studies (88–90) have shown that hydrolysis at high pH results in a nearly random distribution of carboxylate groups. In one industrial process, a polyacrylamide with about 30 mol % hydrolysis is prepared by heating an aqueous PAM solution containing excess sodium carbonate [497-19-8] (91). Polymerization of acrylamide in a water-in-oil emulsion in the presence of sodium hydroxide has also yielded a copolymer with about 30 mol % hydrolysis (92). A method of preparing a hydrolyzed PAM (93) with a viscosity-average molecular weight greater than 30×10^6 daltons was achieved in an inverse emulsion in the presence of caustic, ethoxylated fatty amine, and oil.

Hydrolysis of poly(acrylamide) proceeds slowly under acidic conditions. The undissociated carboxylic acid groups are protonated, neutral species under those conditions. The intramolecular catalysis by means of undissociated —COOH groups at low pH has been proposed as the main mechanism (75). An imide structure has been proposed to be an intermediate in the low-pH hydrolysis of poly(acrylamide), yielding short blocks of carboxyl groups distributed along the polymer chain (see scheme below). To date, there has been limited application of these block copolymer structures, and ones with high molecular weight have not been commercialized.

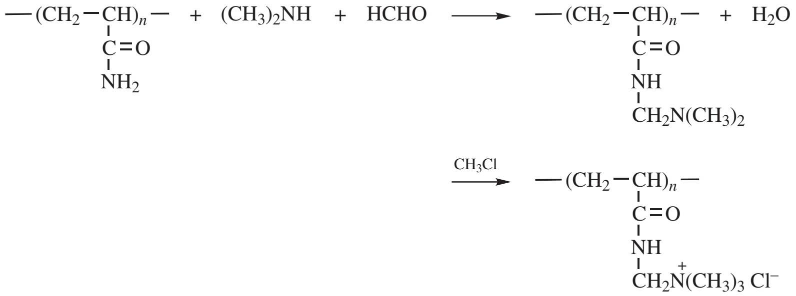


Under neutral conditions, the observed mechanism of hydrolysis cannot be explained by a simple superposition of the retardation kinetics at high pH and intramolecular catalysis at low pH (75).

4.3. Cationic Carbamoyl Polymers. Poly(acrylamide) reacts with formaldehyde, [50-00-0], CH_2O, and dimethylamine, [124-40-3], C_2H_7N, to produce aminomethylated polyacrylamide (see the following scheme). This reaction has been studied extensively (94–98). A wide range of substitution can be produced in solution or in water-in-oil emulsion. ^{13}C-nmr studies (98) have verified that the Mannich substitution reaction follows second-order kinetics. The formation of the formaldehyde-dimethylamine adduct is very rapid. The high rate of Mannich substitution at high pH indicates a fast base-catalyzed condensation mechanism. The Mannich reaction is reversible and pH dependent. At low pH, the rate of substitution is very slow.

Because of the simplicity of the process, the small capital investment for manufacturing equipment and the low raw materials costs, this group of cationic water-soluble polymers constitutes a substantial percentage of commercially important flocculants. Solution Mannich PAMs are prepared and sold only at 4–6% solids, limited by the large solution viscosities and propensity for cross-linking on standing. The addition of formaldehyde scavengers such as guinadine compounds and dicyandiamide [461-58-5] (99) have improved the shelf stability. Aminomethylation of PAM is a reversible reaction. The reverse reaction can be retarded if the pendant amine groups are protonated by addition of an acid. Mannich base products protonated with organic acids or mineral acids have been patented (100). Low-charge-density quaternized aminomethylated products are also sold at polymer solids less than 3% due to very high solution viscosities at higher polymer concentrations.

Several disadvantages of solution Mannich PAMs are the problem of handling high solution viscosities, the added expense of shipping low-solids formulations, and the limitations to applications with low-pH substrates due to the decrease in cationic charge with increasing pH. Quaternized aminomethylated products in water-in-oil emulsions with greater than 20% solids have been developed. The charges in both high- and low-charge products were nearly independent of pH (97, 101–103). Microemulsion formulations have been developed and now replace certain polymer macroemulsions. In one such case, poly(acrylamide) was functionalized in a microdroplet (~100 nm in diameter) that contained only a few poly(acrylamide) molecules (104). Products based on this technology have been commercially successful as high performance cationic organic flocculants for municipal and industrial wastewater applications (105,106).



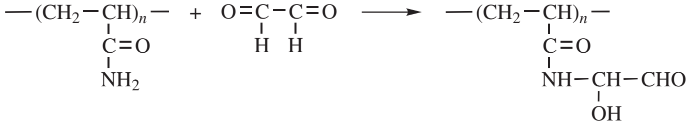
$$\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{NH_2}}}{-(\mathrm{CH_2-CH})_n-} + (\mathrm{CH_3})_2\mathrm{NH} + \mathrm{HCHO} \longrightarrow \underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{NH}\\ |\\ \mathrm{CH_2N(CH_3)_2}}}{-(\mathrm{CH_2-CH})_n-} + \mathrm{H_2O}$$

$$\xrightarrow{\mathrm{CH_3Cl}} \underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{NH}\\ |\\ \mathrm{CH_2\overset{+}{N}(CH_3)_3\,Cl^-}}}{-(\mathrm{CH_2-CH})_n-}$$

4.4. Sulfomethylation. The reaction of formaldehyde and sodium bisulfite [7631-90-5] with polyacrylamide under strongly alkaline conditions at low temperature to produce sulfomethylated polyacrylamides has been reported many times (107–109). A more recent publication (110) suggests, however, that the expected sulfomethyl substitution is not obtained under the previously described strongly alkaline conditions of pH 10–12. This nmr study indicates that hydrolysis of polyacrylamide occurs and the resulting ammonia reacts with the sodium bisulfite and formaldehyde to form sulfomethyl amines and hexamethylenetetramine [100-97-0]. A recent patent describes a high-pressure, high-temperature process at slightly acid pH for the preparation of sulfomethylated polyacrylamide (111).

$$\underset{\substack{|\\ C=O\\ |\\ NH_2}}{-(CH_2-CH)_n-} + NaHSO_3 + HCHO \longrightarrow \underset{\substack{|\\ C=O\\ |\\ NHCH_2SO_3^-\ Na^+}}{-(CH_2-CH)_n-} + H_2O$$

4.5. Reaction with Other Aldehydes. Poly(acrylamide) reacts with glyoxal [107-22-2], $C_2H_2O_2$, under mild alkaline conditions to yield a polymer with pendant aldehyde functionality.

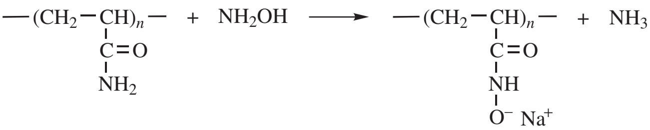


$$\underset{\substack{|\\ C=O\\ |\\ NH_2}}{-(CH_2-CH)_n-} + O=\underset{H}{C}-\underset{H}{C}=O \longrightarrow \underset{\substack{|\\ C=O\\ |\\ NH-\underset{OH}{CH}-CHO}}{-(CH_2-CH)_n-}$$

The rate of this reaction can be controlled by varying the pH and reaction temperature. Cross-linking is a competing reaction. The reaction rate increases rapidly with increasing pH and with increasing polymer concentration. In a typical commercial preparation a 10% aqueous solution of a low-molecular-weight polyacrylamide reacts with glyoxal at pH 8–9 at room temperature. As the reaction proceeds, solution viscosity increases slowly and then more rapidly as the level of functionalization and cross-linking increases. When the desired extent of reaction is achieved, before the gel point, the reaction is acidified to a pH below 6 to slow the reaction down to a negligible rate. These glyoxalated polyacrylamides are used as paper additives for improving wet strength (112).

A similar reaction occurs when poly(acrylamide) is mixed with glyoxylic acid [298-12-4], $C_2H_2O_3$, at pH about 8. This reaction produces a polymer with the CONHCH(OH)COOH functionality, which has found application in phosphate ore processing (113).

4.6. Transamidation. Poly(acrylamide) reacts with hydroxylamine [7803-49-8], H_2NOH, to form hydroxamated polyacrylamides with loss of ammonia (114).



$$\underset{\substack{|\\ C=O\\ |\\ NH_2}}{-(CH_2-CH)_n-} + NH_2OH \longrightarrow \underset{\substack{|\\ C=O\\ |\\ NH\\ |\\ O^-\ Na^+}}{-(CH_2-CH)_n-} + NH_3$$

This hydroxamation reaction occurs under alkaline conditions (115–117). Carboxyl groups can be produced due to hydrolysis of the amide (115,116). Acrylamide polymers can also be reacted with primary amines such as 2-aminoethanesulfonic acid (taurine) [107-35-7] at high temperature and acid pH to yield N—substituted copolymers containing sulfoethyl groups (118).

4.7. Hofmann Reaction. Polyacrylamide reacts with alkaline sodium hypochlorite [7681-52-9], NaOCl, or calcium hypochlorite [7778-54-3],

$Ca(OCl)_2$, to form a polymer with primary amine groups (119). Optimum conditions for the reaction include addition of a slight molar excess of sodium hypochlorite followed by addition of concentrated sodium hydroxide at low temperature (120). A two-stage addition of sodium hydroxide minimizes a side reaction between the pendant amine groups and isocyanate groups formed by the Hofmann rearrangement (121). Cross-linking sometimes occurs if the polymer concentration is high. High temperatures can result in chain scission. If long reaction times are used, NaOCl will cause chain scission and molecular weight decline. If very short reaction times are used at temperatures above 50°C, then polymers with high primary amine content can be obtained (122).

4.8. Reaction with Chlorine. Poly(acrylamide) reacts with chlorine under acid conditions or with NaOCl under mild alkaline conditions at low temperature to form reasonably stable *N*-chloropolyacrylamides. The polymers are water soluble and can provide good dry strength, wet strength, and wet web strength in paper (123).

5. Chemistry of Acrylamide Copolymers

5.1. Cationic Copolymers. The largest segment of the acrylamide polymer market has been dominated by cationic copolymers. The copolymers of acrylamide (AMD) and cationic quaternary ammonium monomers are manufactured by various commercial processes, which will be discussed in a later section. The most widely used of these cationic comonomers are cationic quaternary amino derivatives of (meth)acrylic acid esters or (meth)acrylamides, and diallydimethylammonium chloride.

The quaternary ammonium monomer contents in these copolymers are typically between 5 and 80 mol % for most applications. The composition actually employed depends on cost–performance relationships. Costs are largely dominated by the cationic monomer. Thus the cationic demand of the substrate for each application has to be optimized. Normally, low- to medium-charge copolymers are used for paper waste applications and medium- to high-charge copolymers are used for sludge dewatering. The molecular weights for flocculants are usually 5×10^6 daltons or greater. The higher-molecular-weight polymers often have the advantage of lower dosages in water treating and better fines capture in paper manufacture. Commercially important cationic comonomers, along with their reactivity ratios with acrylamide, are listed in Table 5.

Copolymers [69418-26-4] of acrylamide and AETAC (see Table 5, footnote abbreviation) are the most important flocculants because of a uniform sequence distribution of comonomers (124,125). Reactivity ratios obtained under very different free-radical copolymerization conditions can agree very well. For example, in one case, a free radical copolymerization was initiated using potassium persulfate (KPS) [7727-21-1] in aqueous solution at pH 6.1 (125), while in the other case the copolymerization was initiated using a TBHP/MBS redox pair in an inverse emulsion stabilized with sorbitan monooleate (SMO) at pH 3.5 (124). The surfactant in an inverse emulsion may alter the reactivity of both AMD and AETAC. For example, when SMO is utilized, in formulations made below the azeotropic monomer composition (ie, the copolymer composition is the same as the monomer

Table 5. **Acrylamide Monomer (M_1) Reactivity Ratios**

Comonomer M_2	CAS Registry Number	Molecular formula	r_1	r_2	Initiators[a]	Temp. (°C)	Ref.
Cationic Comonomer M[b]							
AETAC	[44992-01-0]	$C_8H_{16}NO_2Cl$	0.61	0.47	TBHP/MBS	40	124
AETAC	[44992-01-0]	$C_8H_{16}NO_2Cl$	0.61	0.47	KPS	40	125
METAC	[5039-78-1]	$C_9H_{18}NO_2Cl$	0.24	2.47	TBHP/MBS	40	124
METAC	[5039-78-1]	$C_9H_{18}NO_2Cl$	0.25	1.71	KPS	40	125
METAC	[5039-78-1]	$C_9H_{18}NO_2Cl$	0.57	1.11	KPS/NAS	26	127
DMAPAA	[3845-76-9]	$C_6H_{16}N_2O$	0.47	1.1	KPS	40	125
MAPTAC	[51410-72-1]	$C_{10}H_{21}N_2OCl$	0.57	1.13	KPS	40	125
DADMAC	[7398-69-8]	$C_8H_{16}NCl$	6.4–7.54	0.05–0.58	APS, ACV	20–60	125, 134, 140
Anionic Comonomer M[b]							
AA	[79-10-7]	$C_3H_4O_2$	0.25–0.95	0.3–0.95	KPS	30	139, 140
AA	[79-10-7]	$C_3H_4O_2$	0.89	0.92	AIBN	45	141
MAA	[79-41-4]	$C_4H_6O_2$	2.8–0.39	0.2–0.51	KPS	30	140
NaAMPS	[5165-97-9]	$C_6H_{12}O_4NSNa$	0.98	0.49	APS	30	142

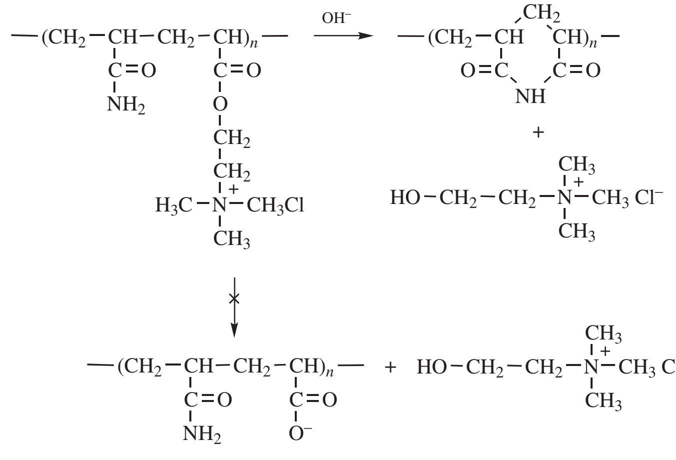
[a] TBHP: *tert*-Butylhydroperoxide, MBS: sodium meta-bisulfite, KPS: potassium persulfate, APS: ammonium persulfate, ACV: azocyanovaleric acid, NAS: sodium sulfite, AIBN: 2,2′-azobisisobutyronitrile.

[b] AETAC: Acryloyloxyethyltrimethylammonium chloride, $CH_2{=}CHCO_2(CH_2)_2N^+(CH_3)_3Cl^-$; METAC: methacryloyloxyethyltrimethylammonium chloride, $CH_2{=}CCH_3CO_2(CH_2)_2N^+(CH_3)_3Cl^-$; DMAPAA: dimethylaminopropylacrylamide, $CH_2{=}CHCONH(CH_2)_3N(CH_3)_2$; MAPTAC: methacrylamidopropylacrylamide, $CH_2{=}CCH_3CONH(CH_2)_3N^+(CH_3)_3Cl^-$; DADMAC: diallyldimethylammonium chloride, $(CH_2{=}CHCH_2)_2N^+(CH_3)_2Cl^-$; AA: acrylic acid, $CH_2{=}CHCO_2H$; MAA: methacrylic acid, $CH_2{=}\ CCH_3CO_2H$; NaAMPS: 2-acrylamido-2-methylpropanesulfonic acid, Na salt, $CH_2{=}CHCONH\ (CH_3)_2CH_2SO_3\text{-}Na^+$.

feed composition, at about 58 mol % AETAC), AETAC is consumed slightly faster than AMD. On the other hand, if a block copolymeric surfactant, poly(ethylene oxide-b-12-hydroxysteric acid) (HB246), is utilized (126), then AMD is the faster reacting monomer. The results suggest that in the interfacial region near the discrete aqueous droplets, the AMD concentration is greater in the HB246 case than in the SMO case.

During AMD/MAETAC copolymerizations, MAETAC [5039-78-1] reacts with its own monomer significantly faster than with AMD. Consequently, copolymers [35429-19-7] can have severe compositional drift and often poor performance. Ha et al. (127) have studied how the sequence distribution can be improved if copolymerizations of AMD and MAETAC are conducted in water-in-oil microemulsion recipes. $K_2S_2O_8$-Na_2SO_3 redox initiator, the composite surfactants sorbitan monooleate, and octylphenol ethoxylate were used. They found reactivity ratios for AMD/MAETAC values were $r_{\mathrm{AMD}} = 0.57$ and $r_{\mathrm{MAETAC}} = 1.11$ (see Table 5).

Quaternary aminoester copolymers are very susceptible to base hydrolysis and are stable under very acidic conditions (124). In both manufacturing and in applications of these products great care is needed to control the pH in order to prevent hydrolysis. These products should possess sufficient buffering acid to maintain very acidic conditions. The hydrolytic instability of ester copolymers is primarily attributed to a base-catalyzed ester cleavage reaction that forms cyclic imides between neighboring AMD and AETAC groups. The loss in cationic charge is not due to direct ester hydrolysis (128). The chemistry of the six-membered imide ring is shown below (124,129).



The effect of pH on hydrolytic stability of cationic ester–acrylamide copolymers has been long recognized (128). The decrease in viscosity and effectiveness, characteristic of this instability, do not take place in aqueous solutions at pH 2–5. Cationicity loss in AETAC and MAETAC copolymers depends on both pH and composition. For example, in a 43 mol % AETAC copolymer, at least 95% of the ester groups have at least one AMD neighbor. The effect of pH on cationicity loss in this copolymer was minimal at a pH of 2–3 at 90°C for 9 h. Above pH 3, ester loss increased dramatically. Prolonged heating (24 h) resulted in a greater degree of ester loss. It was found that the rate of isolated ester hydrolysis was first order in hydroxide concentration at 60°C at constant buffer pH of 5.5. If there were neighboring acrylamide groups in the chain, then there was a second-order dependence of ester disappearance on hydroxide concentration. This indicated that the imidization reaction was also first order in hydroxide ion concentration. The percentage of esters cleaved increased as the number of AETAC groups with neighboring AMD groups increased. Polymers with esters and no AMD neighbors such as the homopolymers of AETAC or MAETAC were found to have a low degree of hydrolysis. The rate of hydrolysis of AETAC and MAETAC copolymers were the same only when both had the same numbers of AMD neighbors.

Cationic copolymers derived from amide monomers, such as MAPTAC [51410-72-1] and APTAC [45021-77-0], are reasonably random and are hydrolytically stable. However, they are more expensive. The molecular weights of high-charge AMD/APTAC [75150-29-1] and AMD/MAPTAC [58627-30-8] copolymers typically do not reach the high molecular weights of AMD/AETAC copolymers because of impurities in the APTAC and MAPTAC. However, low-charge AMD/MAPTAC copolymers, containing ~3 mol % MAPTAC, are significant commercial products.

Diallydimethylammonium chloride (DADMAC) [7398-69-8] is the least expensive commercially available cationic monomer. This monomer has been successfully produced by reacting allyl chloride, dimethylamine, and sodium hydroxide in aqueous solution. (130,131). Monomer solutions with solids of 60–70% can be achieved and used directly for polymerization without further isolation and purification. DADMAC is a nonconjungated diene monomer that was found to homopolymerize to high-molecular-weight linear cationic polymer without cross-linking (130,132). Poly(diallydimethylammonium chloride) (PDADMAC) [26062-79-3] was the first synthetic organic flocculant approved for potable water clarification by the United State Public Health Service (133). The polymerization of DADMAC is known as kinetically favorable to give 98% of inter–intra cycloaddition and 2% pendant double bonds (134). The initiator radical attacks the terminal carbon on one allyl group, and the radical formed attacks the internal carbon on the other allyl group in the same molecule to form a five-membered pyrrodinium ring with a cis-to-trans ratio of 6:1 (135).

The rate law for DADMAC polymerization in an aqueous system, when persulfate is used, is not simple: $R_p = (S_2O_8{}^{2-})^{0.8}(\mathrm{DADMAC})^{2.9}$. A combination of complicated initiation reactions and dimeric DADMAC interactions can account for the unusually high exponent of the DADMAC concentration (136). High monomer concentrations (> 1.5 mol/L) used in commercial processes result in greater rates of polymerization and higher molecular weights. PDADMAC with low residual unreacted monomer can be manufactured in water using either persulfate addition or ammonium persulfate with sodium metabisulfite (137). Polymerization of DADMAC has also been studied in water-in-oil emulsion in a continuous stirred tank reactor (138). In that case, the oil-soluble initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN), and the surfactants sodium di-2-ethylhexylsulfosuccinate (AOT) and sorbitan monoleate (SMO) were used. The rate of polymerization was: $R_p = k\ (\mathrm{ADVN})^{0.4}(\mathrm{AOT})^{0.5}(\mathrm{SMO})^{-0.4}(\mathrm{DADMAC})^{3}$.

The negative order of SMO concentration was due to the fact that SMO is a radical scavenger. The influences of partitioning effects and ionic strength contributed to the third order in DADMAC concentration.

The molecular weight of PDADMAC is not as high as for acrylic polymers because of the large chain transfer constant of allylic radicals. However, a molecular weight of 5×10^5 daltons is sufficient for applications such as potable water clarification, color removal, and textile processing. These applications rely on the very high cationic charge of PDADMAC. This polymer is often used along with a high-molecular-weight anionic polyacrylamide in process-water clarification in paper deinking mills.

5.2. Anionic Copolymers.

Anionic acrylamide copolymers such as poly(acrylamide-co-sodium acrylate) [25085-02-3] poly(acrylamide-co-ammonium acrylate) [26100-47-0], poly(acrylamide-co-sodium-2-acrylamido-2-methylpropanesulfonate [38193-60-1] (AMD/NaAMPS), and poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid) [40623-73-2] (AMD/AMPS) have considerable practical importance. They can be prepared in solution, inverse emulsion (139,140), and inverse microemulsion (141). Comonomer reactivity ratios of AMD with acrylic acid or acrylic acid salts are given in Table 5. Reactivity ratios vary with pH. At high pH the reactivity ratio for AMD is higher, but at low pH the reactivity ratio of acrylic acid is higher. At a pH about 5 a random copolymer can be obtained. When AMD and sodium acrylate are copolymerized in a microemulsion at pH about 10, copolymer composition is independent of conversion and the reactivity ratios are equal. The copolymer chain composition conforms to Bernoullian statistics (141). These copolymers are used extensively as industrial flocculants for water treating, mining and paper manufacture, drag reduction agents, and in secondary and tertiary oil recovery. Reasons for their extensive use include their low cost and very high molecular weights. Their limitations include poor solubility at low pH and precipitation of the salt form in the presence of calcium ions.

Comonomer reactivity ratios for AMD and NaAMPS are given in Table 5 (142). AMD/AMPS copolymers and AMD/NaAMPS copolymers maintain their anionic charge at low pH and have a high tolerance to many divalent cations. They are used as flocculants for phosphate slimes, uranium leach residues, and coal refuse. There are also many oilfield applications.

6. Commercial Processes

There are numerous laboratory methods to prepare polyacrylamides. However, there are only a few viable commercial processes used to manufacture materials that meet the necessary performance standards. There are many requirements for commercial materials: very low to very high molecular weights, low insolubles content, low residual monomer content, fast dissolution rate, ease of handling, minimal dusting (for dry solids), product uniformity, long-term storage stability (to ensure performance consistency), high solids (to reduce shipping costs), and consistent performance characteristics. Several common commercial processes are summarized below.

6.1. Solution Polymerization. Commercial production of polyacrylamides by solution polymerization is conducted in aqueous solution, either adiabatically or isothermally. Process development is directed at molecular weight control, exotherm control, producing low levels of residual monomer, and control of the polymer solids to ensure that the final product is fluid and pumpable. A generic example of a solution polymerization follows.

An acrylamide monomer solution (2–30 wt % in water) is typically prepared, and deaerated by sparging it with an inert gas (eg, nitrogen) to reduce the oxygen content in solution. Stainless steel batch reactors or glass continuous stirred tank reactors are often used for solution polymerizations. A chelating agent is added to complex autopolymerization inhibitors such as copper or other metals if they are present. The polymerization is then initiated using one of several free-radical initiator systems (azo, peroxy, persulfate, redox, or combinations) at concentrations ranging from 0.001 to 10 wt % on monomer. The rate of polymerization depends on reaction conditions, but typically depends on the 1.2–1.6 order of monomer concentration and 0.5 order of initiator concentration. The heat evolved during polymerization (82.8 kJ/mol) can be removed by an external cooling system. For adiabatic processes, the temperature rise needs to be estimated and great care needs to be exercised to avoid exceeding the reflux temperature. Chain transfer agents and inorganic salts can be added to improve processing and to reduce insolubles. Monomer-to-polymer conversions of 99.5% are achievable in 4–6 h polymerization time. The products can have a molecular weight ranging from 1 thousand to 4 million. Polymer solids can be 2–30%. The process can be used in conjunction with thermal drying or precipitation methods in order to obtain products in either powder or granular form. Short residence times in drum drying have been used to avoid chain degradation and formation of insolubles. Precipitation in C_1–C_4 alcohols can be done to obtain nonsticky rubbery polymer gel that can be further extruded and then dried with hot air. The resulting granules can be milled and sieved to produce a uniform product. Care is taken to avoid very finely divided material that can cause dusting problems.

Some commercial low-molecular-weight polyacrylamides (LMPAM) are manufactured in solution and sold at 10–50% solids. For example, LMPAM containing DADMAC comonomer is made at 40% solids and can be reacted with glyoxal to produce a strengthening resin for paper. Furthermore, LMPAM hydrolyzed with sodium hydroxide to polyacrylate is manufactured at 30% solids and is used as an antiscalant. High-molecular-weight PAM is also prepared in solution at 2–6 wt % solids and is often further modified using, for example, the Mannich reaction.

6.2. Inverse Emulsion Process. A method of avoiding the high solution viscosities of high-molecular-weight water-soluble polymers comprises emulsifying the aqueous monomer solution in an oil containing surfactants, homogenizing the mixture to form a water-in-oil (inverse) emulsion, and then polymerizing the monomers in the emulsion. The resulting polymer latex can be inverted in water, releasing the polymer for use. A basic patent (143) illustrated this inverse emulsion process. Processes in which the inverse emulsion polymerization results in finely divided particles that are small enough to retard settling and can be sold without further modification have been developed

(144,145). Stability of the inverse emulsion to mechanical shear has recently been improved (146). Commercial production of inverse emulsion polymerization of AMD has been reviewed (147).

6.3. Polymerization on Moving Belts. Dry polyacrylamides are sometimes preferred, particularly when transportation distances are long. A variety of continuous processes has been developed for preparing dry polyacrylamides that consist of polymerizing aqueous acrylamide on a moving belt and drying the resulting polymer (148–150). In one such process (152) an aqueous solution of acrylamide and a photosensitizer is pumped onto a moving stainless steel belt, cooled on the underside by a water spray and covered on the upper side by a humid inert atmosphere. The belt passes under ultraviolet lamps that photoinitiate polymerization. The belt speed can be controlled so that the polymerization is complete when the polymer reaches the end of the belt. At the end of the belt the polymer gel that has formed can be sliced into small granules and dried in an oven. The dried polymer is then passed through a grinder to produce the desired particle size for handling and use.

Several recent patents describe improvements in the basic belt process. In one case a higher solids polymerization is achieved by cooling the starting monomer solution until some monomer crystallizes, and then introducing the resulting monomer slurry onto a belt. The latent heat of fusion of the monomer crystals absorbs some of the heat of polymerization, which otherwise limits the solids content of the polymerization (151). In another patent a concave belt that flattens near the end is described. This change is said to result in improved release of polymer from the belt (152).

6.4. Dry Bead Process. Dry polyacrylamides can also be prepared in the form of dry beads with bead sizes ranging from about 100 to 2000 μm (153,154). These beads are formed by azeotropically distilling water from inverse suspension polyacrylamides, collecting the beads by filtration, and further drying the beads in a fluid bed drier for short times. The resulting beads can be dissolved in water in a similar manner to other dry polyacrylamides. The size and shape of the beads prepared in the suspension polymerization process are a function of the types and amounts of surfactants and additives employed. Typically, 0.03–0.2 wt % (based on water plus polymer) of an oil-soluble polymeric surfactant is used to obtain the desired bead size. Greater amounts of surfactants lead to smaller beads (153). Certain water-soluble ionic organic compounds are said to be effective in improving the stability of the beads and providing a narrower bead size distribution when used in conjunction with the polymeric stabilizers (153). In the absence of the stabilizer, irregularly shaped, unstable particles can result. The choice of the stabilizer is considered to be dependent on the charge of the polyacrylamide being produced (153).

6.5. Microemulsion Polymerization. One inherent problem with water-in-oil emulsions of acrylamide-based polymers is the potential formation of unstable lattices both during production and in finished products. The coagulum that can form in the reactor can result in a time consuming cleanout (155). Technology has continuously improved reactor configuration, types of agitation, proper cooling (155), and a proper balance of aqueous, oil and emulsifier ratios (144,145). Microemulsion polymerization (156–166) can provide improvements to address these problems. Monomer microemulsions are thermodynamically stable systems comprising two liquids, insoluble in each other, and surfactant. They form spontaneously without homogenization. The resulting polymer microlattices are typically nonsettling, transparent, and about 100 nm in diameter. These systems can have high emulsifier levels: more than 8 wt %, which is about 4–5 times more than emulsifier levels in conventional inverse emulsions. Consequently, the cost of producing microemulsions becomes less attractive. However, further refinements to technology lead to the development of cost-effective microemulsified Mannich acrylamide polymers (167, 104–106). This technology was used to develop functionalized polyacrylamides (168). In one case, a PAM microlatex was reacted with formaldehyde and dimethylamine (Mannich reaction), and then quaternized with methyl chloride to yield a very highly charged cationic carbamoyl polymer (104–106, 169). These commercial products are widely used in many applications for solid–liquid separation. These products have been improved by treating them with buffer acid, a formaldehyde scavenger, and heat to produce a high-performance cationic polymer (170).

6.6. Environmentally Friendly Polyacrylamides. In recent years, commercial processes that use biodegradable oils to replace petroleum hydrocarbons have received a great deal of attention. Also, there has been a great deal of interest in polymerization in supercritical fluids. These future directions for the manufacture of polyacrylamides are summarized in the following.

6.7. Dispersion Polymerization. Water-in-oil emulsions contain at least 30% by weight of a petroleum-based hydrocarbon that is a valuable natural resource. By using such formulations, oils are consumed unnecessarily and can enter the world's waterways as a source of secondary pollution. An aqueous polymer dispersion is one environmentally responsible formulation that contains no oil or surfactant, and near-zero amounts of volatile organic compounds. Dispersion polymerization can be used to prepare cationic, anionic, and nonionic polyacrylamides.

6.8. Inverse Emulsions with Biodegradable Oils. Some examples of inverse emulsion polymerization processes employing biodegradable oils include materials with aqueous phase monomer mixtures, such as AMD and AETAC or AMD and MAETAC, dispersed in a biodegradable oil, such as bis-(2-ethylhexyl) adipate (171), containing a polymeric emulsifier that is a copolymer of dimethylaminoethylmethacrylate and mixtures of methacrylates. A buffering acid, such as a dicarboxylic acid, is used to stabilize cationic copolymers. Aliphatic dialkylethers are also used as biodegradable oils (172), in conjunction with SMO as an emulsifier, to produce high-molecular-weight cationic copolymers.

6.9. Inverse Emulsion Polymerization Acrylamide in Near-Critical and Supercritical Fluid Conditions. Supercritical fluids exhibit both liquid-like properties (eg, solubilizing power), and gaslike properties (eg, low viscosities). Aqueous AMD has been dispersed and even microemulsified in near-supercritical ethane–propane mixtures using nonionic surfactants such as ethoxylated alcohols (eg, Brij 30 and Brij 52). Emulsion polymerization of AMD was then conducted at 60°C for 5 h and 379 bar, at the near-supercritical condition of certain ethane–propane mixtures (173). 2,2′-azobis(isobutyronitrile) (AIBN) was used as the initiator. The resulting poly(acrylamide) had a low molecular weight, in the range of $(2.7–5.8) \times 10^5$ daltons. The ethane and propane can be easily recovered and recycled in a production plant.

Emulsion polymerization of AMD was also conducted at 60°C for 1 h and 345 bar in near-supercritical CO_2. AIBN was the initiator. An amide end-capped hexafluoropropylene oxide oligomer that has high solubility in the near-supercritical CO_2 was found to stabilize the dispersed particles (174–176). Only a few classes of polymers have good solubility in near-supercritical CO_2. The advantages of using carbon dioxide include very low viscosities during polymerization and ease of recovery.

7. Applications

Dewatering. Polyelectrolyte-assisted dewatering constitutes one of the most important application areas of polyacrylamides (3). Solid–liquid separations in aqueous media can be enhanced by the flocculation of small suspended particles into larger aggregates, which increases separation rates. Floc formation requires a destabilization and adherence of the smaller particles. This is usually accomplished by means of surface charge neutralization, charge-patch formation, and/or polymer bridging (177). Acrylamide-containing polymers make ideal candidates for such flocculants because of the large molecular weights achievable with them. High-molecular-weight cationic copolymers are typically employed in wastewater treatment. Solid–liquid separations in mining industries often benefit from the use of anionic copolymers, or in some cases dual polymer systems (cationic and anionic in sequence). Various dewatering processes in the papermaking industry regularly make use of cationic, anionic, or dual addition systems (178). Nonionic poly(acrylamide) finds less use in solid–liquid separations, save for some mining applications.

Mineral Processing. Both synthetic and natural hydrophilic polymers are used in the mineral processing industry as flocculants and flotation modifiers. Most synthetic polymers in use are polyacrylamides. Nonionic polymers are effective as flocculants for the insoluble gangue minerals in the acid leaching of copper and uranium (179,180), for thickening of iron ore slimes (181), and for thickening of gold flotation tailings (182). In some uranium leach operations, a cationic polymer with a relatively low charge density is used along with the nonionic polymer to improve supernatant clarity.

Anionic polyacrylamides are extensively used in the mining industry. They are used as flocculants for insoluble residues formed in cyanide leaching of gold (183). Acrylamide–acrylic acid copolymers are used for thickening copper, lead, and zinc concentrates in flotation of sulfide ores. These copolymers, containing from 50 to 100% carboxylate groups, are used to flocculate fine iron oxide particles in the manufacture of alumina from bauxite at high pH (184). Hydroxamated polyacrylamides, prepared by reaction of nonionic polyacrylamide or anionic polyacrylamide with hydroxylamine salts, are also effective in this Bayer process (185). Other uses for hydroxamated polyacrylamides include reduction of titanaceous and siliceous scale in Bayer alumina processes (186) and flocculation of titanium ore copper ore tailings in froth flotation processes (187). Copolymers [40623-73-2] of acrylamide and acrylamido-2-methylpropanesulfonic acid [15214-89-8] have been patented as phosphate slime dewatering aids (188).

Low-molecular-weight polyacrylamide derivatives with mineral specific functionalities have been developed as highly selective depressants for separation of valuable minerals from gangue minerals in froth flotation processes. These depressants have certain ecological advantages over natural depressants such as starches and guar gums. The depressants provide efficient mineral recovery without flocculation. They are often used along with hydrophobic mineral collectors (eg, sodium alkyl xanthates) and froth modifiers. Partially hydrolyzed polyacrylamides with molecular weights of 7,000–85,000 can be used in sylvanite (KCl) recovery (189). Polymers having the functionality —$CONHCH_2OH$ are efficient modifiers in hematite–silica separations (190). Polymers containing the —CONHCH(OH)COOH functionality provide excellent selectivity in separation of apatite from siliceous gangue in phosphate benefication. Valuable sulfide minerals containing copper and nickel can be separated effectively from gangue sulfide minerals such as pyrite in froth flotation processes when acrylamide–allylthiourea copolymers or acrylamide–allylthiourea–hydroxyethylmethacrylate terpolymers are added to depress the pyrite (191). Acrylamide copolymers can be used as iron ore pellet binders (192). When the ore slurry in water has a pH above 8, anionic polymers are effective. If the ore is acid washed to remove manganese, then a cationic polymer is effective.

Paper Manufacture. Polyacrylamides are used as wet-end additives to promote drainage of water from the cellulose web, to retain white pigments and clay fillers in the sheet, to promote sheet uniformity, and to provide dry tensile strength improvements (193). An important advance in papermaking technology has been the use of microparticle retention aids. Organic microparticles, prepared from acrylamide and anionic comonomers by microemulsion polymerization, provide good sheet formation characteristics and controlled drainage (194,195). Cationic polyacrylamides that have been reacted with glyoxal are used to promote wet strength (196). These wet strength resins have been used in paper towels. Recently, these glyoxalated polymers have been modified so that they can be used in toilet tissue. These polymers provide an initial high wet tensile strength with rapid tensile strength decay in water so that sewers may not become clogged (197,198). Anionic polyacrylamides have been used with alum to increase dry strength (199). Primary amide functionality promotes strong interfiber bonds between cellulose fibers. Sometimes paper mills use dry strength additives so that recycled fiber, groundwood, thermomechanical pulp, and other low cost fiber can be used to produce liner board and other paper grades which must meet ICC requirements for burst strength and crush strengths. Recently there has been an increasing demand for writing papers and copy paper that have good print characteristics. Print quality can be improved by use of surface sizes combined with acrylamide polymers. The acrylamide polymer gives the paper sheet better surface strength (200). Details on paper manufacture can be found in Reference 201. All additives used for manufacture of food-grade papers are subject to FDA regulations, and are listed in the *Code of Federal Regulations*, paragraphs 176.170, 176.180, 178.3400, and 178.3650 (1998).

Enhanced Oil Recovery. Polymer flooding is a potentially important use for anionic polyacrylamides having molecular weights greater than 5 million and carboxyl contents of about 30%. The ionic groups provide the proper viscosity and mobility ratio for efficient displacement. The anionic charge prevents excessive adsorption onto negatively charged pores in reservoir rock. Viscosity loss is observed in brines particularly when calcium ion is present. A primary advantage of anionic polyacrylamides is low cost (202). Profile modification is a process wherein flooding water is diverted from zones with high permeability to other zones of lower permeability containing oil. Polymeric hydrogels are used for this. Metals such as chromium and aluminum can be injected with anionic polyacrylamides to cross-link the polymers in more permeable reservoir zones prior to the water flood (203,204). The development of new more environmentally acceptable cross-linking systems has continued. A recent patent claims a composition consisting of hexamethylenetetramine [100-97-0] and 4-aminobenzoic acid [150-13-0] for this purpose (205).

Polyacrylamides are used in many other oilfield applications. These include cement additives for fluid loss control in well-cementing operations (206), viscosity control additives for drilling muds (207) and brines, and for fracturing fluids (208). Copolymers [40623-73-2] of acrylamide and acrylamidomethylpropanesulfonic acid do not degrade with the high concentrations of acids used in acid fracturing.

Hydrophobically Associating Polymers. Extensive research in the 1980s and 1990s focused on acrylamide copolymers containing small amounts of hydrophobic side chains. At zero or low shear rates, the apparent viscosity can be very large because of association of the hydrophobic groups between chains. In oil reservoir conditions, the polymers tolerate high salt concentrations while providing proper viscosifying properties (209). These associative thickeners are also used in coatings (210) and in oil spill cleanup (211). Reference 212 gives more information about associative polymers.

Hydrophobically associating acrylamide copolymers can be prepared by micellar polymerization. These copolymers have short blocks of hydrophobic groups randomly distributed in the backbone. A recent paper reviews the major advances in this area (213).

Superabsorbents. Water-swellable polymers are used extensively in consumer articles and for industrial applications. Most of these polymers are cross-linked acrylic copolymers of metal salts of acrylic acid and acrylamide or other monomers such as 2-acrylamido-2-methylpropanesulfonic acid. These hydrogel-forming systems can have high gel strength, as measured by the shear modulus (214). Sometimes, inorganic water-insoluble powder is blended with the polymer to increase gel strength (215). Patents describe processes for making cross-linked polyurethane foams that contain superabsorbent polymers (216,217). Recent patents describe grafted copolymers that are highly absorbent to aqueous electrolyte solutions (218).

8. Analytical Methods

Most of the traditional methods for polymer analysis (219) are applicable to polyacrylamides. We will only point out several special features regarding the use of some of these techniques for the analysis of polyacrylamides.

Oftentimes a preliminary step applied before many analytical methods is the isolation of the polymer. The isolation of polyacrylamides from the other components of the media in which they were prepared (eg, aqueous solution or inverse emulsion, with attendant surfactants and oil) is often readily accomplished by precipitation in short-chain alcohols or acetone. The individual solubilities of formulation components should be tested if there is any doubt. Experience shows that anionic copolymers are often best precipitated in the alcohols, and cationic copolymers in acetone (homopolyaminoesters are soluble in methanol). Since acrylamide is soluble in these organic solvents, it will also be separated from the polymer in this procedure.

Once the polymer is isolated, its chemical composition can be quantified using infrared or nmr spectroscopies (25,220). An nmr study can also give some information about chain architecture in the case of copolymers (221). Elemental analysis can be employed to confirm a composition. Ultraviolet spectroscopy is generally not used for compositional analysis per se; however, polymers containing acrylamide do absorb short-wavelength uv radiation, along with many other materials. A uv detector set around 215 nm is a common choice for measuring polymer concentration in the absence of interfering substances; many surfactants and some salts (eg, NO_3^-, SCN^-) are problematic in this regard. Differential refractometry is the logical alternative for concentration monitoring when uv-absorbing substances are present.

The extent of conversion during an acrylamide polymerization is most easily followed by determining the disappearance of the monomer. High-performance liquid chromatography (HPLC) is often found best for this purpose. An HPLC method in which poly(acrylamide) inverse emulsions can be used directly has been developed (222). In the case of copolymers, HPLC protocols that allow the simultaneous determination of all the unreacted monomers can be used to evaluate compositional drift as a function of conversion.

Global properties of the polymer chains (eg, molecular weight, coil dimensions, branching content) are most often evaluated using scattering, hydrodynamic, or viscometric techniques on dilute polymer solutions. The conventional methods appropriate for soluble polymeric materials typically apply equally well to polyacrylamides. In the case of high-molecular-weight polyacrylamides, the main difficulties in obtaining accurate information involve preparing a purified polymer solution that is in an equilibrium state, and passing it through the measurement device without substantially altering it in either process.

When using viscometric methods, experiment protocols can be designed to address any effects that instabilities may have on the viscosities of the polyacrylamide solutions, if not to alleviate the instabilities altogether. Mechanical degradation can also occur in high-molecular-weight polymers. This can happen during sample preparation (eg, mixing), purification (eg, filtration), or during the viscosity measurement itself (especially in elongational flows). In any case, one should estimate these handling effects for any set of protocols.

The presence of colloidal-size contamination (“dust”) in polymer solutions can possibly affect either static or dynamic light scattering experiments (223,224). Neutron scattering is less afflicted by this kind of contamination (225). For high-molecular-weight polyacrylamides whose coil dimensions are roughly in the same size range as the colloidal contaminants, and which have a natural propensity to adsorb onto suspended materials (after all, many of these polymers are flocculants), any problems of sample purification should not be ignored. If one is simply looking for a clean sample, it is possible to exhaustively filter a solution in a recycle loop (226). Clarification of dilute polymer solutions by centrifugation is another method that can minimize mechanical degradation of the polymers. Centrifuging dilute solutions of high-molecular-weight linear polyacrylamides from 4 to 8 h in excess of 15,000 × G is satisfactory in many instances. Good light scattering data can be acquired even in the case of a marginally clean polymer solution by attempting to "look through the dust." This is made easier by reducing the scattering volume, slowing (or stopping) the solution flow, and monitoring the scattering volume (either manually or with the aid of a computer algorithm) for periods that are free of point scatterers.

The effects of sample clarification must be gauged when trying to preserve and analyze the polymer in its original form. This includes situations when samples are passed through packed columns, as in HPSEC analysis. A uv absorbance study can be used to determine polymer loss if there are no interferences in the solution. A method that can monitor the molecular weight distribution (eg, HPSEC or dynamic light scattering), or one that is sensitive to the high-molecular-weight component (eg, elongational viscometry), can be used to assay for mechanical degradation.

The double extrapolation of light scattering data to zero polymer concentration and zero scattering angle yields an average property of the macromolecular ensemble: the weight-average molecular weight (M_w) from static light scattering and the z-average hydrodynamic radius ($\langle R_h \rangle_z$) from dynamic light scattering. In some cases, the details of the distribution of these quantities are also of interest. Dynamic light scattering data can be analyzed directly to give a distribution of the hydrodynamic size distribution of a sample. DiNapoli et al. (227) have demonstrated how to derive molecular weight distributions from dynamic light scattering data, but this involves knowing the correlation between the polymer diffusion coefficient and molecular weight, a relationship that is not always available.

Methods involving a physical separation of the components of the distribution, coupled with a method for measuring some feature of the macromolecules across this separated collection, find more use in determining molecular-weight (or size) distributions. Size exclusion chromatography (SEC) remains a popular way to separate macromolecular populations (228), including polyacrylamides (229). More recently, flow field flow fractionation (FFFF) (230) has been shown to have some advantages over SEC methods, especially for very high-molecular-weight polymers, including polyacrylamides. Since the fluid contact surface in FFFF is a membrane, as opposed to a packed bed of finely divided particles in SEC, there is less opportunity for altering the native distribution by means of polymer adsorption, retention, or mechanical degradation. High-molecular-weight cationic copolymers of acrylamide can be difficult to pass unaltered through commercial SEC columns. Ultracentrifugation (46,231,232) has also been used to separate the components of polyacrylamide samples for subsequent analysis, but this is currently a less popular method than either SEC or FFFF.

The early approaches to characterizing the molecular-weight distributions of samples separated using SEC or FFFF were based on retention time, requiring a correspondence to be made between the retention time and molecular weight. This was typically done by calibrating the separation device using fractionated (narrowly distributed) standards, which in some cases were only vaguely related chemically to the polymer of interest. More recently the use of in-line light scattering detectors for the purpose of directly determining M_w, R_g (static light scattering photometer), or R_h (dynamic light scattering photometer) for each "slice" of the separated distribution has been an alternative to these approaches (233). This has generally improved one's ability to characterize the details of the molecular-weight or size distributions for many acrylamide-containing polymers, for which standards consisting of narrow fractions are not readily available.

Titration methods are mostly applicable to ionic copolymers of acrylamide. Typically, potentiometric titrations are used for high salt concentrations, and conductometric titrations are used for low salt concentrations. This kind of information can be important since ionogenic groups with weak acid or base properties will have both dissociation-dependent and salt-dependent pK_as when they are in a polymer chain. In addition to titrating ionic acrylamide copolymers with low-molecular-weight titrants, their titration with other oppositely charged polyelectrolytes has proven useful (234). For example, poly(potassium vinylsulfonate) can be used to titrate cationic copolymers of acrylamide. This titration gives information about the available charge on the host macromolecule. Usually the macroion titrant is of lower molecular weight than the polymer of interest. In any case, the conditions of the polyelectrolyte–polyelectrolyte complexation reaction must allow for complete 1:1 complex formation. Care must be taken such that the kinetics of the complex formation does not influence the results. The end point can be detected in any one of several ways, including turbidometrically, or using a dye indicator. The color change of the dye at the end point can be determined visually or spectrophotometrically with an "optrode."

Detecting Polyacrylamides. In order to detect low concentrations of polyacrylamides as part of an analysis scheme (235), to optimize the use of, or to monitor the fate of these polymers in a variety of technological applications, an assay method for trace amounts of these polymers that remain in solution is usually needed. One approach, more appropriate for laboratory studies, has been to incorporate fluorescent groups in the polymer either by copolymerization or by post-polymerization derivatization. Acrylamide copolymers containing sodium fluorescein (236), various dyes [phenol red, or brilliant yellow (237)], *N*-2,4-dinitroaniline-acrylamide (238), or a pyrene-labeled monomer (239) have been described. Early methods based on chemical derivatizations describe coupling fluorescein isothiocyanate to amine groups on Hofmann-reacted poly(acrylamide) (240,241). Various other approaches have been developed to add fluorescein (242), dansyl (243), 9-xanthydrol (244), and other fluorescent groups to acrylamide-containing chains (245).

A completely different approach to detecting low levels of high-molecular-weight polyacrylamides in solution without recourse to prelabeling the polymers has been used in a number of instances. Methods based on the flocculation capacity of these polymers are surprisingly sensitive. Both the turbidity and the settling rate of a suspension can change measurably after exposure to even low concentrations (several ppm) of a flocculant. Lentz et al. (246) used such changes in the settling rate of kaolin suspensions to assay for low levels of anionic polyacrylamides in runoff water from a soil amendment application involving those polymers. They were able to reliably detect residual polymer in the water at the ppm level.

9. Specifications, Shipping, and Storage

The amount of residual acrylamide is usually determined for commercial polyacrylamides. In one method, the monomer is extracted from the polymer and the acrylamide content is determined by HPLC (247). A second method is based on analysis by cationic exchange chromatography (248). For dry products the particle size distribution can be quickly determined by use of a shaker and a series of test sieves. Batches with small particles can present a dust hazard. The percentage of insoluble material is determined in both dry and emulsion products.

Polyacrylamide powders are typically shipped in moisture-resistant bags or fiber packs. Emulsion and solution polymers are sold in drums, tote bins, tank trucks, and tank cars. The transportation of dry and solution products is not regulated in the United States by the Department of Transportation, but emulsions require a DOT NA 1693 label.

Under normal conditions, dry polymers are stable for 1 y or more. The emulsion and solution products have somewhat shorter shelf lives.

10. Health and Safety Factors

Commercial Polyacrylamides. Dry cationic polyacrylamides have been tested in subchronic and developmental toxicity studies in rats. No adverse effects were observed in either study. Chronic studies of polyacrylamides in rats and dogs indicated no chronic toxicity or carcinogenicity. Dry anionic and nonionic polyacrylamides (249) have acute oral (rat) and dermal (rabbit) LD_{50} values of greater than 2.5 and greater than 10.0 g/kg, respectively. Dry cationic polyacrylamides have acute oral (rat) and dermal (rabbit) LD_{50} values of greater than 5.0 and greater than 2.0 g/kg, respectively. Emulsion nonionic, anionic, and cationic polyacrylamides have both acute oral (rat) and dermal (rabbit) LD_{50} values of greater than 10 g/kg. Dry nonionic and cationic material caused no skin and minimal eye irritation during primary irritation studies with rabbits. Dry anionic polyacrylamide did not produce any eye or skin irritation in laboratory animals. Emulsion nonionic polyacrylamide produced eye irritation in rabbits, while anionic and cationic material produced minimal eye irritation in rabbits. Emulsion nonionic, anionic, and cationic polyacrylamide produced severe, irreversible skin irritation when tested in rabbits that had the test material held in skin contact by a bandage for 24 h. This represents an exaggeration of spilling the product in a boot for several hours. When emulsion nonionic, cationic, and anionic polyacrylamides were tested under conditions representing spilling of product on clothing, only mild skin irritation was noted. Polyacrylamides are used safely for numerous indirect food packaging applications, potable water, and direct food applications.

Experimental Polyacrylamides. It is wise to treat any laboratory-prepared "experimental" polyacrylamide as if it contains substantial amounts of unreacted monomer unless it has been isolated and purified as described above.

Acrylamide is commercially available as a 50% solution in water with a copper salt as a polymerization inhibitor. Polymerization is very exothermic and autopolymerization can occur under certain conditions. In the interest of safety, acrylamide solutions should be stored under the following conditions:

1. Maintain the storage temperature below 32°C (90°F) and above the solubility point.
2. Keep the solution free of contaminants.
3. Maintain the proper level of oxygen and Cu^{2+} inhibitors.
4. Maintain the pH at 5.2–6.0.
5. Store the solution in a container that is opaque to light.

It is recommended that these solutions be stored for no more than 3 mo due to depletion of the dissolved oxygen. All containers must be dated and no more than 93% full. Packaged acrylamide solutions should be consumed on a first-in, first-out basis.

11. Economic Aspects

Worldwide, there are many suppliers of polyacrylamides. Some of these are producers and some are repackagers. Suppliers are listed in Table 6. Selling prices for polyacrylamides vary considerably depending on the product form (solution, emulsion, dry), type (anionic, nonionic, cationic), and other factors. Prices on a polymer basis can range from as low as about \$2/kg for simple dry nonionic polyacrylamides to \$8/kg and more for highly charged cationic polymers. Prices in recent years have dropped due to price erosion and due to

Table 6. **Suppliers of Polyacrylamides**

Region	Companies
United States	Axchem
	Baker-Petrolite Co.
	BetzDearborn, Inc.
	Buckman Laboratories International, Inc.
	Calgon Corp.
	Callaway Chemical Co.
	Chemtall, Inc.
	CIBA Specialty Chemicals Corp. (Allied Colloids, Ltd.)
	Cytec Industries, Inc.
	Delta Chemical Corp.
	The Dow Chemical Co.
	Drew Chemical Corp. (Ashland Chemical, Inc.)
	Exxon Chemical Co.
	Hercules Inc.
	Nalco Chemical Co.
	Polydyne, Inc.
	S.N.F. Floerger SA
	Stockhausen, Inc.
Canada	Cytec Canada, Inc.
	Nalco Canada, Inc.
	Raisio Chemicals Canada, Inc.
	Rhodia Canada, Inc.
Mexico	BASF Mexicana, S.A. de C.V.
	Cytec, Atequiza Jalisco
	Nalco, Toluca

Table 6 (*Continued*)

Region	Companies
South America	Dispersol San Luis S.A. (Argentina)
	LaForestal Quimica S.A.I.C. (Argentina)
	Henkel Argentina S.A.
	Industrias Quimicas del Valle S.A. (Argentina)
	Proquima Productos Quimicos (Argentina)
	Adesol Produtos Quimicos Ltda. (Brazil)
	Quimicos Nacional Quiminasa S/A (Brazil)
	Cyquim de Columbia
	Quimicos Cyquim, C.A. (Venezuela)
Europe	BASF AG (Germany)
	Ciba Specialty Chemicals PLC (UK)
	Cytec Industries BV (Netherlands)
	Cytec Industries UK Ltd. (UK)
	Deutsche Nalco-Chemie GmbH (Germany)
	Kimira Oyj (Finland)
	Röhm GmbH (Germany)
	S.N.F. Floerger S.A. (France)
	Stockhausen GmbH (Germany)
Japan	Arakawa Chemical Industries, Ltd.
	Dai-Ichi Kogyo Seiyaku Company, Ltd.
	Diafloc Co., Ltd.
	Harima Chemicals, Inc.
	Hymo Corporation
	Kurita Water Industries, Ltd.
	Japan Polyacrylamide Ltd.
	Konan Chemical Industry Co., Ltd.
	Mitsubishi Chemical Industries Co., Ltd.
	Mitsui-Cytec, Ltd.
	Nippon Kayaku Company, Ltd.
	Sankyo Kasei Company, Ltd.
	Sanyo Chemical Industries, Ltd.
	Sumitomo Chemical Company, Ltd.
	Toa Gosei Chemical Industry Company, Ltd.
Republic of Korea	Cytec Korea, Inc.
	E-Yang Chemical Co., Ltd.
	Kolon Industries, Inc.
	Unico (Seoul)
Taiwan	Cytec Taiwan Corp.
	Taiwan Arakawa Chemical Ind., Ltd.
	Young Sun Chemical Works, Ltd.
China	China Petrochemical Corp.
India	Engineer's Poly-Chem
	Kaushal Aromatic Chemicals Pvt. Ltd.
	Somnath Products

lower manufacturing costs of AETAC and DADMAC cationic monomers. In many applications, such as sludge dewatering in waste treatment, the need for increased performance has lead to increased functionalization (eg, higher cationicity) and increased cost.

In the United States the major uses for polyacrylamides are in water treating and paper manufacturing. For water treating the best growth is expected to be for cationic copolymers due to use in dewatering equipment like belt presses that produce high-solids sludge cakes that can be more easily incinerated or disposed of in scarcer landfills. For paper manufacturing, glyoxalated cationic copolymers for paper wet strength, high-molecular-weight retention aids, and drainage aids are considered to grow in use. Increased use of PAM flocculants in recycled paper mills, particularly in deinking mills where better process water clarification is necessary because of closed water circuits, is also expected. Polyacrylamides are beginning to be used along with surface sizes in paper to improve the control of ink adsorption and print quality. In the mineral process industry in the United States (and Australia) there has been a great increase in the use of hydroxamated polyacrylamides in alumina manufacture. The market for polyacrylamides in enhanced oil recovery has decreased steadily in the United States In 1985, the total market exceeded 10 million metric tons, but in 1999 the use has been almost none. Total consumption of polyacrylamides is expected to increase about 4% per year during the next few years after 1999 in the United States. In Europe the use of water-treating chemicals on municipal sludge treatment will increase due to European Union legislation preventing sewage dumping. The treatment of wastewater is intensive, and many waste treatment plants and paper mills have closed circuits due to environmental concerns. The total consumption of PAMs is expected to increase about 3% per year in Europe. In Japan, the major consumption has been in paper manufacture (anionic and nonionic polyacrylamides) and water treatment (cationic and amphoteric copolymers). In municipal sludge treatment, highly cationic polyacrylamides are used for rapid flocculation in high-speed centrifuges. The use of cationic copolymers is expected to grow at higher rates. Japan exports a considerable amount of polyacrylamides (and acrylamide monomer) to Asian and other markets. Another potential market will be enhanced oil recovery in China. Table 7 gives an estimated breakdown of polyacrylamide consumption (1).

Table 7. **Consumption of Polyacrylamides**[a]

Year	Paper (%)	Water treating (%)	Mining (%)	EOR (%)	Other (%)	Total (10^3 t)
			United States			
1989	21.9	59	7.9	6	5.4	68.5
1993	18.3	63	13.6	0	5.1	86.0
1997	25	60	10.8	0	4.2	120.0
			Western Europe			
1997	38.4	53.5	5.8	0	2.3	86
			Japan			
1985	62	38				42
1989	57.7	42.3				52
1993	51	49				53
1997	52.4	47.6				63

Source: Ref. 1.

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