1. Introduction

It is difficult to imagine an aspect of our modern world not touched by polyacrylamides and poly(acrylic acids). These hydrophilic polymers, their copolymers with other hydrophilic monomers, and their metallic salts are utilized in many applications. Polyacrylamides are used in applications, such as mining, water treatment, sewage treatment, papermaking, oil well drilling, oil production, and agriculture. Poly(acrylic acids) are used in boiler-water additives, superabsorbent diapers, paints, detergents, industrial coatings, cosmetics, ceramics, textiles, ion-exchange resins, industrial adhesives, cements, and drug delivery [1]. The term polyacrylamide is used for homopolymers as well as for copolymers of acrylamide. Common comonomers for acrylamide are acrylic acid and its salts (“anionic polyacrylamide”) as well as cationic ester of acrylic acid (“cationic acrylamide”).

The utility of these polymers is directly related to their chemical structure, functionality, and molecular mass. The acid and amide functions are highly solvated by water, and are responsible for the solubility of the polymers in aqueous solutions. When cross-linked, the polymers swell in water without dissolving. The properties of polymers containing acrylic or methacrylic acid are dependent on the pH of the aqueous solution in contact with the polymer. Because the metal ion salt interacts with more water molecules than the unneutralized acid group, higher viscosity or higher swelling is observed at elevated pH, which is useful in thickeners or absorbent polymers. The proximity of the carboxyl groups to one another in poly(acrylic acid) gives rise to chelating properties with di- and trivalent metal ions, which is exploited in boiler-scale control and detergent builders. The high polymerizability of the monomers allows the preparation of high molecular mass polymers, which are useful as flocculants and thickeners. When the molecular mass is reduced, the polymers can be used as dispersants and scale inhibitors. The reactivity of the amide and acid groups allows simple chemical modifications that change the polymer properties and amplify the number of applications.

2. Raw Materials

Some useful physical properties of the water-soluble monomers used in the production of polyacrylamides, poly(acrylic acid), and poly
(methacrylic acid) are listed in Table 1. All the monomers are toxic and should be handled with great care. Contact with the skin, eyes, and mucous membranes should be avoided. Breathing of vapors should also be avoided; operations should be conducted in vessels vented to scrubbers or in laboratory fume hoods. The monomers are quite reactive; their contamination can lead to uncontrolled polymerization and must be avoided. Dedicated storage vessels are used for the monomer. Manufacturers’ data should be consulted for the safe handling and use of the products, e.g., [2, 3]. The best sources are material safety data sheets of the raw material producers, which are updated if new information is available.

**Acrylic acid** is described in detail elsewhere (→ Acrylic Acid and Derivatives). It is manufactured via oxidation of propene and has the largest production volume of the hydrophilic monomers. Significant progress has been made towards bio-based acrylic acid [4]. 3-Hydroxypropionic acid (3-HP) is the most likely precursor in a fermentation process. Acrylic acid is very corrosive to the skin and eyes, and its vapors are irritating to the eyes and lungs. Personal protective equipment, such as rubber gloves, goggles, impervious body coverings, and an organic vapor respirator should be used in the case of possible contact with acrylic acid. Commercial acrylic acid is normally inhibited against polymerization with 4-methoxyphenol (methyl ether hydroquinone, MEHQ). As this inhibitor requires oxygen for long-term effectiveness, air should be added to storage containers. The monomer should not be allowed to freeze because this causes the inhibitor to separate from the monomer by fractional crystallization. The resulting uninhibited acrylic acid is hazardous due to the significantly increased potential for uncontrolled polymerization.

Runaway polymerizations have occurred. A rail car of acrylic acid exploded in Teesside (UK) in 1976 as a result of too rapid thawing of frozen acid. The highly exothermic, adiabatic vinyl polymerization can become so hot that decarboxylation of the polymer occurs, with concomitant production of large volumes of carbon dioxide. A less violent, unplanned, runaway polymerization has been described [5].
Here the major product of the vigorous reaction was polyester, which is formed in a Michael-type reaction between molecules of acrylic acid. In 2012 an explosion occurred at the Nippon Shokubai Himeji Plant. The explosion and subsequent fire in an acrylic acid intermediate tank killed one person and injured 36 [6].

**Methacrylic acid** is similar to acrylic acid in most regards and should be handled accordingly. For a detailed description of this compound, see →Methacrylic Acid and Derivatives.

**Acrylamide** is described elsewhere (→Acrylic Acid and Derivatives). It has toxic effects on the nervous system. A low-dose, long-term exposure study in rats showed an increased incidence of tumors. For a review on the toxicity of acrylamide see [7]. At higher doses, laboratory animals experienced reproductive deficiencies [2]. Contact with the monomer should be strictly avoided. Solid acrylamide sublimes readily so that contact with the vapor is a likely route for exposure. Therefore, acrylamide is supplied commercially as an aqueous solution to make handling simpler and to reduce potential exposure to vapors. Nowadays, most of the acrylamide monomer is produced by a biological process. Acrylonitrile is enzymatically hydrolyzed to acrylamide [8]. This process is cheaper and more selective than the copper-catalyzed hydrolysis of acrylonitrile. As with acrylic acid, oxygen is critical for inhibition of polymerization and dissolved oxygen should be present during storage because MEHQ is used as a free-radical scavenger. Acrylamide monomer is readily absorbed through the skin so that rubber gloves and impervious body clothing are required when contact with the aqueous solution is likely.

**N,N-Dimethylacrylamide.** At elevated temperatures and at high pH acrylamide can be hydrolyzed to acrylic acid. Therefore, in some special applications, acrylamide is replaced by the more stable \( N,N \)-dimethylacrylamide. However, this monomer is more expensive and used only in niche applications [9].

### 3. Production

#### 3.1. Free-Radical Polymerization

**Kinetics.** An understanding of the polymerization kinetics of the monomers is essential for the control of polymer production. The molecular mass and molecular mass distribution of the polymers are key determinants of their physical properties and are influenced strongly by polymerization kinetics.

Advanced physical methods and modeling give a deeper insight to the kinetics, i.e., initiation, propagation, and termination [10]. Polymerization kinetics have been studied extensively for acrylic acid, its salts, and acrylamide. Less extensive data are available for the other monomers although some are available for methacrylic acid [11].

The kinetics of free-radical polymerization of acrylic acid, methacrylic acid, acrylamide, and methacrylamide have been investigated in water, dimethyl sulfoxide, tetrahydrofuran, and formamide at 30–60°C with azobisisobutyronitrile as initiator [12]. The polymerization rate is proportional to the monomer concentration and to the square root of the initiator concentration. The acrylics react faster than the methacrylics under identical conditions. The polymerization rate depends on the nature of the solvent; values of the kinetic constants for each monomer in each solvent were determined [12].

The polymerization kinetics for the acid monomers become complicated as the pH of the system changes. At constant overall monomer concentrations, the polymerization rate initially falls as the pH is increased from 2 to 7, then rises slowly from pH 7 to 12 [13, 14]. This has been attributed to a change in the propagation rate constant as the degree of ionization increases [15]. At pH 7 to 12, rates increase with an increase in the ionic strength of the medium [16]. This is accomplished either by adding simple monovalent salts or by increasing the ionized monomer concentration. Methacrylic acid shows a similar behavior [17].

Initiators play a complex role in polymerization kinetics, and initiator fragments can be important in the subsequent use of the polymer: For example, solution properties can deteriorate with time, depending on impurities [18]. Thermal initiators (e.g., azo compounds and
peroxides) produce free radicals in a homolytic scission reaction. The reaction, producing a pair of radicals, is characterized by the temperature at which the specific initiator is half consumed in 10 h. With those initiators the polymerization rate generally depends on the monomer concentration and the square root of the initiator concentration [19, 20]. The monomer may react with the initiator prior to the reaction of the free radical with monomer, and induce the decomposition of the initiator. In such cases (e.g., acrylic acid and sodium persulfate), the polymerization rate depends on the 1.5 power of monomer concentration and the square root of the initiator concentration [15, 16, 21]. Redox initiators produce free radicals in a reaction between a reducing agent and an oxidizing agent. Examples include the persulfate–thiosulfate reaction [22] and the manganic ion (Mn$^{3+}$)-isobutyric acid reaction [23]. For redox initiators not involving metal ions, the polymerization rate usually depends on the first power of the monomer concentration. The rate also depends on the concentration of oxidant and reductant, the stoichiometry of their reaction, and the extent to which the initiators (usually the reductant) participate in radical termination reactions [22, 24–26]. When metal ions are involved in the redox reaction, the kinetics are more complex because the metal ion also participates in the termination step of the polymerization [23, 27, 28].

Copolymerization. See also →Polymerization Processes. The monomers listed in Table 1 are frequently copolymerized with one another and with other monomers. The relative reactivities of the monomers affect the microstructure and thus the physical properties of the polymer. When a comonomer is more reactive than its partner, it tends to be used up earlier in the reaction. The final product then has a distribution of composition as well as a distribution of molecular masses.

Reactivity ratios are derived from measurements of polymer composition as a function of conversion. Data from the entire conversion range of the copolymerization of acrylamide (AAm) and acrylic acid (AA) were utilized to calculate the following reactivity ratios [29]:

$$r_1(\text{AA}) = 1.45 \pm 0.33, \quad r_2(\text{AAm}) = 0.57 \pm 0.04$$

Reactivity ratios for acrylic or methacrylic acid copolymerized with acrylamide have also been determined as a function of pH [30], and the copolymerization has been studied [31]. Selected data are given in Table 2. Reactivity ratios for these and many other potential comonomers have been tabulated [32].

### 3.2. Polymerization Processes

The techniques described in this section are described in detail elsewhere (→Polymerization Processes).

#### 3.2.1. Solution Polymerization

**Batch Polymerization.** The batch polymerization of the water-soluble monomers in solution is straightforward. The monomers are dissolved in water (or another solvent for both the monomer and polymer) at a desired concentration (usually 10–70%). Although acrylamide and acrylic acid have been polymerized in various organic solvents [12], water is used in industrial processes more or less exclusively. One of the very few exceptions is the polymerization of acrylic acid in 2-propanol, which introduces besides the carboxylic function additional functional groups into the molecule by acting as chain transfer agent [33]. The monomer

<table>
<thead>
<tr>
<th>pH</th>
<th>Acrylic acid</th>
<th>Acrylamide</th>
<th>Methacrylic acid</th>
<th>Acrylamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.32 ± 0.046</td>
<td>0.57 ± 0.067</td>
<td>2.80 ± 0.44</td>
<td>0.20 ± 0.069</td>
</tr>
<tr>
<td>6</td>
<td>0.33 ± 0.20</td>
<td>0.85 ± 0.62</td>
<td>0.19 ± 0.08</td>
<td>0.55 ± 0.078</td>
</tr>
<tr>
<td>8</td>
<td>0.63 ± 0.004</td>
<td>0.12 ± 0.004</td>
<td>0.32 ± 0.004</td>
<td>0.53 ± 0.003</td>
</tr>
</tbody>
</table>
solution is deoxygenated by bubbling an inert gas through the solution or by a series of evacuations and repressurization with an inert gas. The desired free-radical initiator is then added and the temperature, usually 40–80°C depending on the specific initiator used, is brought to the appropriate point for polymerization to begin.

The initial monomer concentration is limited because polymerization of the undiluted monomers is extremely dangerous due to the high heat of polymerization and rapid polymerization kinetics [34]. The concentration is also limited by the capacity of the equipment for removing the heat of polymerization and by the molecular mass of the desired polymer. If no heat can be removed from the reactor, the adiabatic temperature rise can be calculated for a given monomer concentration [35]. A suitable monomer concentration can then be calculated, based on the desired initial and final temperatures [36]. To have a better temperature control semibatch polymerizations are used: Part of the monomer solution is charged and the rest of the monomer solution is fed over a period of time [37]. The viscosity of the reaction mass is also important with regard to the equipment available for pumping the product. Higher molecular mass products generally dictate a lower monomer concentration because of their high viscosities, whereas low molecular mass products allow higher monomer concentrations.

Low molecular mass, water-soluble polymers are often desired, and several processes have been developed to produce them industrially. In one such process, sodium hydrosulfite is added continuously to an aqueous monomer solution in a stirred tank while introducing fine air bubbles; polymerization occurs below 80°C [38]. The sulfite acts as a chain-transfer agent to lower the molecular mass. Sodium hypophosphite and 2-mercaptoethanol are commonly used for the same reason [39–41]. In another industrial process, poly(acrylic acid) of molecular mass 1 000–20 000 is prepared at 55 wt% concentration by polymerization with hydrogen peroxide and transition-metal activators, such as copper, iron, or manganese [42].

For some applications solid, dried products are preferred, e.g., powder detergents. The water may be evaporated using hot, rotating drum dryers or continuous belt, hot-air ovens, spray drying, or granulation devices. The dry flakes or lumps are then milled to the desired particle size and packaged in bags ranging in size from 22 to 1 000 kg. Depending on the process conditions, spray drying leads directly to powders or granules without further treatment [43]. Granules are more and more preferred over powders because of the much lower dust level.

Continuous Polymerization. Polymers can often be produced more efficiently by using a continuous polymerizer. An aqueous solution of monomers, initiators, and other additives is fed into one end of the polymerizer, and the polymeric product removed from the other. Low molecular mass copolymers of acrylic acid and acrylamide of controlled molecular mass (10 000 to 100 000) were produced in a packed-tube reactor operating at elevated pressure [44].

When a higher molecular mass is needed the aqueous monomer solution rapidly forms a gel after low conversions. This polymer gel is transformed by cutting, drying, and grinding into a powder. These powders contain up to 90 mass% of polymer. Such products can be used directly as powders (e.g., superabsorbents in diapers) or they are dissolved in water and used as diluted solutions (e.g., as flocculant in sewage plants). The production of superabsorbents is described elsewhere (→ Superabsorbents, Chap. 4). In principle the same processes can be used for the production of polyacrylamides [45]. Common are endless belt and tube-like reactors. If the molecular mass is less than 10^6 the gel is sticky after polymerization and not processable. Therefore, a minimum molecular mass is needed for gel polymerization.

A more flexible process is based on so-called smart scale production (SSP). It has a modular design and setup, and product switches can be handled in a shorter time frame [46]. In another process, 30–40 wt% aqueous monomer solution is pumped onto a continuous moving belt. Angled rollers at the edges of the belt cause a trough to be formed over a section of the belt. The trough holds the liquid monomers. As polymerization proceeds, a gel is formed from the reagents. The belt section flattens after it
passes the final set of rollers, and the gel is released from the belt and is finally discharged from the end of the conveyor. Superabsorbent polyacrylates are prepared industrially in this manner [45]. Another process for superabsorbent polymers is based on kneader technology. The monomer solution is fed at one end into a twin shaft reactor and discharged at the other end [47]. A quite different process, the so-called drop polymerization is currently under development. A droplet generator at the top of a reaction chamber releases droplets of a monomer solution into a gaseous atmosphere [48].

### 3.2.2. Inverse Emulsion Polymerization

In inverse emulsion polymerization, tiny droplets of aqueous monomer solution are dispersed in a continuous organic phase (usually aromatic or aliphatic hydrocarbons) prior to polymerization. The droplets are stabilized by surfactants. Free-radical polymerization of the monomers is conducted similarly to that described for solution polymerization (Section 3.2.1) [49, 50].

An obvious reason for using this technique instead of solution polymerization is to simplify the handling of the polymer product. The low-viscosity dispersion of monomer and polymer droplets is easy to agitate and pump and allows more efficient heat removal during polymerization. In addition, the particle size of the product is more easily controlled because it depends on the nature and amount of the emulsifier used to form the droplets prior to polymerization. Droplet size is typically 0.1–10 μm. However, the process is more complicated; several more ingredients need to be controlled and recycled, especially the hydrocarbon phase (unless the product is sold in emulsion form). It is less efficient on a volumetric basis compared to a powder product, due to the presence of the continuous organic phase. However, it is possible to make such inverse emulsions with a high active content. For a cationic polyacrylamide it is possible to use up to 70 wt% of aqueous monomer phase that itself has a monomer concentration of 30–70 wt% [50]. The overall content of the polymer can reach nearly 50 mass%.

It is possible to increase the active content by removing the volatile byproducts and water [51]. Such products are more expensive due to the distillation step and are used for special applications, such as personal care and pharmaceutical formulations [52].

Modern inverse emulsion products are self-inverting. The monomer emulsion is made using a water-in-oil emulsifier (HLB 3.5–7.5). After polymerization a second emulsifier with higher HLB is added (9 to 14), which acts as an oil-in-water emulsifier [53]. If the product is added to a large amount of water, the oil is emulsified in the water, and the polymer is released. This process is very rapid, and the polymer is dissolved completely within a very short time so that inline dosage is feasible. This is an advantage of inverse emulsions over powder products.

Inverse emulsions can be converted into a powder by a spray-drying process [54]. However, this process causes additional costs and is, if at all, used for niche applications.

### 3.2.3. Suspension Polymerization

In suspension polymerization, small droplets of aqueous monomer solution are dispersed in a hydrocarbon phase, generally with the aid of water-in-oil emulsifier or other polymers [55, 56]. Poly(acrylic acid) (linear and cross-linked) and polyacrylamides can be made by this process. Free-radical polymerization of the monomers is then conducted in a manner similar to that described for emulsion systems (see Section 3.2.2). After the polymerization, the polymer is dried by boiling off the water. The beads are filtered from the organic phase using a centrifugal or other industrial filter. The residual organic phase is then evaporated from the beads using an explosion-proof dryer. The droplet size is controlled by the amount of dispersant used; more dispersant generally yields smaller particle size. Larger polymer particles can be obtained than with emulsion processes. Typically, 15–500 μm spherical beads are formed. Cellulose esters or cellulose ethers are used as protective colloids in the suspension polymerization of sodium acrylate, acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, or sodium styrenesulfonate [57]. A mixed suspending agent for watersoluble monomers consisting of hydrophobic
fumed silica and a copolymer of acrylic acid and lauryl methacrylate yields a controlled particle size distribution [58]. A copolymer of cetostearyl methacrylate and methacrylic acid is beneficial for the polymerization of cationic polyacrylamide [59].

### 3.2.4. Precipitation Polymerization

In precipitation polymerization, the monomer is polymerized in a medium which is a solvent for the monomer but a nonsolvent for the polymer. As the polymer forms, it precipitates from the monomer phase. With the proper choice of medium, polymer isolation and purification is simplified. For example, cross-linked polymers can be produced by copolymerizing acrylic or methacrylic acid with small amounts of an allyl phosphate or phosphite with free-radical initiators in a solvent, such as benzene, hexane, acetone, or chloroethane at ca. 20–90°C [60]. This technology is the basis for the process used industrially to produce Carbopol poly(acrylic acid) resins. The precipitating polymerization of poly(acrylic acid) has been accomplished in methyl ethyl ketone [61].

### 3.2.5. Polymer-Analogous Reactions

The term polymer-analogous reactions denotes reactions that are used to modify the functional groups of polymers. Such reactions are complex from a practical perspective because of the high viscosities of polymer solutions and the changing solubilities of the polymers as they are converted to a different functionality. Polymers of acrylate esters can be hydrolyzed to the corresponding acid polymers and their salts. Polyacrylate esters can also be reacted with amines to yield polyacrylamide or polymethacrylamide derivatives. Polyacrylonitrile can be saponified to a copolymer of acrylic acid salt and acrylamide.

Poly(acrylic acid) undergoes reactions typical of other organic carboxylic acids. It has been reacted with diazomethane to yield poly(methyl acrylate) and with thionyl chloride to yield the acid chloride, which has increased reactivity in acylation reactions, such as amidation. A direct amidation of polyacids is carried out in water at elevated temperature to obtain partially sulfonated polymers [62, 63]. Poly(acrylic acid) can also be dehydrated above 200°C to yield a polyanhydride. The polyacids are generally reacted with neutralizing agents, e.g., alkali-metal hydroxides, carbonates, or amines, to yield the salt. Esterifications and transesterifications have been carried out in organic media using enzymes as catalyst [64]. Polyacrylamides can also be chemically derivatized [65]. Polyacrylamide reacts with formaldehyde in aqueous solution to yield a partially hydroxymethylated polymer. It is also readily hydrolyzed with aqueous sodium hydroxide or sodium carbonate solution to give a polymer with a maximum of ca. 86% acrylic acid moieties [66]. Main issue for this process is the large amount of ammonia that is released. Amide groups are converted to amine groups via the Hofmann reaction [67]; the amide is reacted with sodium hydroxide and hypochlorite to yield the amine. Amine groups can also be introduced into polyacrylamide by the Mannich reaction. Polyacrylamide is reacted with formaldehyde and an amine to produce an N-aminomethylated polymer. Intramolecular imidization occurs when polyacrylamide is heated with a strong acid catalyst.

Due to the processing difficulties encountered in conducting polymer-analogous reactions, such reactions are not typically used to convert a polymer to one with different functional groups. Nevertheless, the technique is used widely for cross-linking polyacrylamides and poly(acrylic acids). Polyacrylamide is cross-linked by reaction of its amido groups with glyoxal (→ Glyoxal). Alternatively, a reactive monomer can be synthesized from acrylamide and glyoxylic acid, copolymerized with acrylamide, and used as a reactive site for subsequent cross-linking (→ Glyoxylic Acid). Poly(acrylic acid) is cross-linked by reaction of its carboxylic acid groups with glycols; this technique is used industrially to cross-link the surface of superabsorbent polymers (→ Superabsorbents, Chap. 4).

### 3.2.6. Residual Monomer Scavenging

An important part of the production of these polymers is the reduction of residual monomers, especially residual acrylamide as it is
carcinogenic. Depending on the application, different types of polyacrylamides are available. For drinking water application, special grades are offered with very low residual acrylamide.

The residual monomer content can be reduced by sulfite solution or gaseous sulfur dioxide [68, 69]. The principle is the Michael addition of a scavenger to the double bond of the residual monomer [70]. Another option is the use of initiator combinations containing one component that reacts at later stage of the production process, e.g., a UV initiator is activated in the drying by irradiation [71].

For solution polymers and inverse emulsions a reshoot with additional polymerization initiator is possible. Simple distillation [72] and solvent extraction [73] have also been employed.

4. Properties

The properties of the polymers as solids and in solution (particularly aqueous solution) determine their applications. Their hydrophilic nature and molecular mass are key determinants of the usefulness of the polymers for specific applications. The molecular mass and the molecular mass distribution can be measured by light scattering, osmometry, and ultracentrifugation. Intrinsic viscosity is the most useful and widely used method of correlation between molecular mass and viscosity: Appropriate equations are given below for individual polymers. Molecular masses are also correlated to the radius of gyration of the molecules in solution by gel permeation chromatography (size-exclusion chromatography) or hydrodynamic chromatography. Very high molecular mass polymers are susceptible to degradation by high shear [74], oxidation [75], and conformational changes [76], which can be induced by impurities introduced as polymerization modifiers. The above methods are useful for measuring the extent of such changes.

Analysis of the polymers and determination of their content of comonomer residues are of practical importance. These can be determined by infrared spectroscopy [77] and nuclear magnetic resonance (NMR) spectrometry [78]. The tacticity of the polymers is also measured by NMR spectrometry [79]. Thermal transitions and polymer chemistry are investigated with differential scanning calorimetry, thermogravimetric analysis (TGA), and TGA-mass spectrometry.

**Poly(acrylic acid)** [9003-04-4] is soluble in many polar and usually hydrogen-bonded solvents such as water, methanol, ethanol, dioxane, dimethylformamide, 2-propanol, formamide, ethylene glycol, and acetic acid. The value of the glass transition temperature \( T_g \) is still in dispute because it is difficult to obtain a solventfree sample. \( T_g \) has been reported at 106°C [80], at 118°C [81], and at 126°C [82]. Mark–Houwink–Sakurada relationships for determining the weight-average molecular mass \( M_W \) from the intrinsic viscosity \([\eta]\) have been determined in many solvents but the following two are widely used:

\[
[\eta] = 0.085 M_W^{0.5} \text{ mL/g} \quad \text{dioxane, } 30^\circ\text{C} [83] \\
[\eta] = 0.1062 M_W^{0.5} \text{ mL/g} \quad 0.2 \text{ mol/L HCl, } 14^\circ\text{C} [84]
\]

The exponents of 0.5 indicate theta conditions for the polymer. Under theta conditions, a given polymer–solvent pair behaves as if it were an ideal solution. This is because the attraction between polymer chain segments just equals the loss of entropy brought about by interpenetration of polymer molecules. If conditions for solvation are made any poorer than those at the theta condition, the polymer precipitates. For poly(acrylic acid), lowering the temperature from the upper critical solution temperature, UCST, causes phase separation. Poly(acrylic acid) is stable in acid or base solution. The solid polymer slowly liberates water upon heating above 100°C, forming the anhydride. The polymer decomposes slowly above 250°C, liberating carbon dioxide.

The simple alkali-metal salts have been characterized extensively, especially poly (sodium acrylate) [9003-04-7]. Poly(potassium acrylate) [25608-12-2] and poly(ammonium acrylate) [9003-03-6] are also known. These polymers are soluble in water and in aqueous salt solutions. Small amounts of organic solvents dissolved in water are sometimes tolerated. The fully neutralized sodium salt has a
glass transition temperature at about 250℃ [81]. Obtaining an accurate value is difficult because of the hygroscopic nature of the polymer. Mark–Houwink–Sakurada relationships have been determined in many aqueous solutions; for example

\[
[n] = 1.24 \times 10^{-3} M_J^{0.53} \text{ mL/g} \\
[n] = 0.146 \times 10^{-3} M_J^{0.80} \text{ mL/g}
\]

1.5 mol/L NaBr, 15℃ [85] 
0.1 mol/L NaCl, 25℃ [86]

Poly(acrylic) salts are more stable to heat than the acid polymer. Anhydride formation is not observed above 50 mol% neutralization of acid groups and up to 250℃, where carbon dioxide evolution is observed.

Polyacrylamide [9003-05-8] is soluble in polar, hydrogen-bonded solvents, such as water, aqueous salt solutions, ethylene glycol, formamide, ethanolamine, dimethyl sulfoxide, and morpholine. For cationic and anionic copolymers, water is the main solvent. The glass transition temperature is again difficult to determine, because it is difficult to prepare a solvent-free sample; \( T_g \) is reported as 170℃ [87] and 188℃ [82]. The density of the polymer is 1.302 g/cm³ [88]. The diffusion coefficient \( D \) and the sedimentation coefficient \( S_0 \) have been determined as a function of molecular mass [89]:

\[
D = 1.24 \times 10^{-4} M_J^{-0.53} \text{ cm}^2/\text{s} \\
S_0 = 1.07 \times 10^{-15} M_J^{0.48} \text{ svedberg}
\]

Mark–Houwink–Sakurada relationships have been determined in many solvents [90]:

\[
[n] = 9.33 \times 10^{-3} M_J^{0.75} \text{ mL/g} \\
[n] = 7.19 \times 10^{-3} M_J^{0.77} \text{ mL/g} \\
[n] = 1.36 \times 10^{-1} M_J^{0.51} \text{ mL/g}
\]

water 
0.5 mol/L NaCl 
ethylene glycol

A theta condition has been established in a 2 : 3 ratio of methanol : water at 20℃ [91], and has been estimated at −38℃ in aqueous solution.

Solutions of polyacrylamide in strong acid gradually become turbid due to imide formation from amide groups. The amide groups hydrolyze to ammonia and carboxylic acid above pH 9. The solid polymer is stable below 210℃, but the amide groups decompose to ammonia above 210℃.

The determination of the molecular mass is quite difficult as most of the polymer have a molecular mass above the exclusion of GPC. Field-flow fractionation has been established as a method to evaluate molecular masses [91]. Very important for the characterization of polyacrylamides are rheological methods [92].

Poly(methacrylic acid) [25087-26-7] is soluble in ethanol, methanol, water, dimethylformamide, dioxane, and 2-ethoxyethanol. The polymer and its sodium salt [54193-36-1] have been characterized because of curiosity about the conformational change that occurs upon neutralization of the acid polymer to about 30 mol%. The glass transition temperature occurs at 185℃ [93]. Mark–Houwink–Sakurada relationships are:

\[
[n] = 22.4 \times 10^{-3} M_J^{0.679} \text{ mL/g} \text{ methanol, 25℃ [94]} \\
[n] = 6.6 \times 10^{-3} M_J^{0.68} \text{ mL/g} \text{ 0.002 mol/L HCl, 30℃ [95]}
\]

The above theta condition at 30℃ in dilute hydrochloric acid is questionable in light of experiments that show phase separation in poly(methacrylic acid) solutions when the temperature is raised to 56℃ [84].

The stability of poly(methacrylic acid) and its salts to acids and bases is similar to that of poly(acrylic acid). The solid polymer evolves water above 180℃, forming an anhydride.

Polymethacrylamide [25014-12-4] is soluble in methanol, water, ethylene glycol, and mixtures of acetone and water. A Mark–Houwink–Sakurada relationship has been established as

\[
[n] = 2.1 \times 10^{-3} M_J^{0.76} \text{ mL/g} \text{ water [96]}
\]

Stability of polymethacrylamide, either in solution or as dry solid, has not been reported.

The major copolymers are those of acrylic acid and acrylamide, prepared either by partial hydrolysis of polyacrylamide [97] (hydrolyzed, sodium salt [25987-30-8] and hydrolyzed, potassium salt [31212-13-2]) or by copolymerization of the respective monomers [82]. The properties of the copolymers depend on the mole fractions of the two monomer residues [98] and on the distribution of molecular masses of the sample [99]. The intrinsic
viscosity (and the second virial coefficient) of the copolymers shows a maximum at 33 mol% acrylic acid residues [98]. Flocculation rate increases with molecular mass; maximum activity was observed with a 70 mol% acrylate copolymer [100]. Solution characteristics of heterodisperse copolymers were determined at various compositions in salt solutions by viscometry, light scattering, and gel permeation chromatography. Mark–Houwink–Sakurada relationships have been determined over the entire composition range with corrections for heterodispersity [99]. Copolymers of methacrylic acid and acrylamide have been similarly characterized as a function of pH [101]. The sudden increase in intrinsic viscosity observed at pH 4–5.5 has been attributed to a sudden unfolding of the chains when the electrostatic repulsion of the ionic groups is just sufficient to overcome the hydrophobic bonding of the α-methyl groups.

Poly(N-isopropylacrylamide) [25189-55-3] is of interest because of a lower critical solution temperature (LCST) of just 31°C in aqueous solution [102]. Dissolved poly(N-isopropylacrylamide) precipitates and its cross-linked gels deswell when the temperature is raised above the LCST. It is soluble in water, methanol, and tetrahydrofuran. The glass transition temperature has been measured at 130°C [103]. A Mark–Houwink–Sakurada relationship has been determined:

\[ [\eta] = 0.112 M_\text{w}^{0.51} \text{mL/g} \quad \text{water, 20°C} \]  

Poly(N,N-dimethylacrylamide) [26793-34-0] is soluble in water, methanol, 2-methoxyethanol, methyl ethyl ketone, diethyl ether, toluene, chloroform, and dioxane. It has a low glass transition temperature (89°C) [105]. The polymer has been extensively characterized only in methanol and water. The Mark–Houwink–Sakurada relationships are [106]:

\[ [\eta] = 17.5 \times 10^{-3} M_\text{w}^{0.58} \text{mL/g} \quad \text{methanol, 25°C} \]
\[ [\eta] = 23.2 \times 10^{-3} M_\text{w}^{0.81} \text{mL/g} \quad \text{water, 25°C} \]

Poly(2-acrylamido-2-methylpropanesulfonic acid) [27119-07-9] is soluble in water, aqueous salt solutions, and dimethylformamide. The sodium salt is soluble in aqueous solution. Mark–Houwink–Sakurada relationships for the homopolymer and its sodium salt are [107]:

\[ [\eta] = 2.11 \times 10^{-3} M_\text{w}^{0.55} \text{mL/g} \quad \text{H}^+ \text{ form, 5 mol/L NaCl} \]
\[ [\eta] = 1.95 \times 10^{-3} M_\text{w}^{0.65} \text{mL/g} \quad \text{Na}^+ \text{ salt in 0.5 mol/L NaCl} \]

Solution properties of carboxylated and sulfonated copolymers have been compared [108].

5. Uses

The molecular mass of a polymer is a key factor in determining its usefulness for a particular application. Polymers of molecular mass less than 20 000 are used as sequestrants and scale inhibitors. Polymers of molecular mass between 20 000 and 80 000 are useful as pigment dispersing agents. Polymers with molecular mass between 10^5 and 10^6 are used as textile finishing agents and retention aids for papermaking. Molecular masses exceeding 10^6 are necessary for flocculants and thickening agents [109]. High molecular mass, cross-linked polymers are used as fluid absorbents. Uses of functional polymers in general and in particular of poly(acrylic acids) and polyacrylamides have been described [1]. The ionic character of the polymer is another important factor in determining its applications. Choices range from nonionic polyacrylamides to partially hydrolyzed polyacrylamides or copolymers of acrylic acid and acrylamide and finally to the salts of poly(acrylic acid). The appropriate choice of ionic content depends on the pH, ionic strength, surface charge of any substrate with which the polymer interacts, and other conditions specific to the application.

The polymers are supplied as solutions, emulsions, and powders. Low molecular mass polymers are typically supplied as viscous, aqueous solutions containing 20–50 wt% polymer. Above a molecular mass of 2×10^5, the high viscosity of such solutions makes them too difficult to meter into processes and mix well; they are supplied as powders packaged in 22 kg bags. The powders are difficult to
dissolve in water because the particles hydrate exceedingly fast, forming gelatinous clumps. Special mechanical dispersers are available from the suppliers to aid dissolution [110]. High molecular mass polymers are also supplied as inverse emulsions; micrometer-sized polymer particles are dispersed in a liquid hydrocarbon with the aid of surfactants. These emulsions are of relatively low viscosity and readily pumped and metered. When the emulsion is added to water the emulsion inverts and the small polymer particles quickly dissolve. Emulsion products are supplied in drums or tank trucks. Cross-linked polymers, such as superabsorbsents are supplied as granules in 1-t sacks that empty from the bottom to make addition of the polymer into hoppers easier.

5.1. Poly(Acrylic Acids) and Their Salts

Water-soluble poly(acrylic acid) and its neutralized salts with a molecular mass of 2 000–5 000 are used as scale inhibitors, sludge (mud, silt, clay) dispersants in cooling water systems, and as dispersants for preparing CaCO₃ or clay slurries as fillers, pigments, or paper-coating materials [111].

Homo- or copolymers of acrylic acid and methacrylic acid and mixtures with up to 10 wt % alkyl acrylate comonomers prevent soil redeposition in liquid detergent formulations [112]. The polymer, neutralized or not, has a molecular mass of 10⁶–10⁷. Relatively small amounts of polymer prevent soil redeposition, improve cleaning performance and viscosity control.

Copolymers having small amounts of pendant hydrophobic groups are also useful as hydraulic fracturing fluids for oil well drilling [113]. The fluids are readily formulated to give an initial viscosity that is retained for long periods at high temperatures and under high shear rates; this is due to hydrophobic bonding between the pendant groups. The polymer molecular mass can be below 10⁶ and yet provide high viscosity in solution because the associating hydrophobic groups create a high pseudomolecular mass.

Cross-linked poly(sodium acrylate) is used as an absorbent in baby diapers [114–116]. Other applications include adult incontinent products [117], feminine hygiene products [118], absorbents in transmission cables [119], and agricultural mulches [120]. Cross-linked polymers of acrylic or methacrylic acid, neutralized to greater than 50 mol%, may also be used to provide high water retention capacity and high viscosity in plaster [121]. A cross-linked, water-absorbent acrylic acid polymer can be used in formulations for sustained-release tablets for oral administration [122]. A blend of waterswellable particles of anionic polymer of acrylic acid or methacrylic acid and their soluble salts and cationic polymers of amino acrylate and aminoalkyl acrylamide is used in prepasted wall-covering adhesive [123] to reduce water absorption. Cross-linked poly(acrylic acid) is also used as a weakly acidic, cation-exchange resin (→ Ion Exchangers).

5.2. Polyacrylamides and Hydrolyzed Polyacrylamides

Polyacrylamides are typically high molecular mass products (>10⁶) made by gel polymerization or inverse emulsion polymerization. Less common products are inverse suspension polymers, which are used in some special applications.

Slightly hydrolyzed polyacrylamide with molecular mass (1–5)×10⁵ is useful as a strengthening agent in finished paper. Polymers with molecular masses up to 10⁶ add wet strength in paper production. Polyacrylamides with molecular masses of (1–2)×10⁶ are used as retention aids in papermaking. The polymer binds the smaller fibers and any filler particles to the larger fibers.

Polyacrylamides and molecular masses of (1–2)×10⁶ are used as retention aids in papermaking. The polymer binds the smaller fibers and any filler particles to the larger fibers.

Polyacrylamides and hydrolyzed polyacrylamides having molecular masses of (2–20)×10⁶ are used in applications involving floculation or to increase the viscosity of aqueous systems. Flocculation is the major use for polyacrylamides [124] (→ Water, 4. Treatment by Flocculation and Filtration) and (→ Acrylic Acid and Derivatives). Flocculant applications include clarification of water used in industrial processes (e.g., as pretreatment of boiler water), in treatment of effluent from paper mills, and in
sewage treatment. In sewage treatment, polyacrylamides increase the removal of solids in the primary settling step, improve clarification of the discharged water, aid in sludge thickening, and increase water removal during sludge dewatering [125]. Molecular mass and mole fraction of ionic groups are optimized to obtain maximum performance. Copolymers of acrylamide and acrylic acid of different compositions were prepared and their flocculation activity toward kaolin clay suspensions studied [100]. Flocculation rate increased with molecular mass, maximum flocculation activity are observed with 70 mol% acrylate copolymer.

In the exploration and production of mineral oil, there are several applications for polyacrylamides. They are used as rheology modifier for aqueous drilling fluids (water-based muds) and shale inhibitors in drilling of boreholes [126]. The water-based mud is used to power and cool the drill bit and to stabilize the formation. Additionally, the water-based mud transports the cuttings to the surface. To be most efficient a complex rheology is necessary. Low molecular polyelectrolytes are used as fluid loss control agents. These products prevent the loss of water from the drilling into the formation. The same principle applies to the cementing of the borehole in which similar products are employed.

During the life-cycle of an oil field the enhancement of the gas or oil-flow might be necessary. This process is called stimulation. If the permeability of the reservoir rock is too low, a so-called fracturing might be applied. During this operation, aqueous solutions are pressed under very high pressure into the formation, which induces fractures. To minimize energy losses during pumping, so-called friction reducers (drag reducers) are used. Liquid inverse emulsions of anionic polyacrylamides are frequently used in this application. If the aquifer of the oil reservoir is too close to the producing well, high amounts of water are pumped with the oil. To reduce the amount of produced water, aqueous solutions of polyacrylamides are pumped with gelling agents through the production well into the formation. Common gelling agents are chromium and zirconium salts. This operation is called water shut-off.

With maturity of an oil field, the reservoir pressure is maintained by injection of water from the sides of the reservoir (secondary oil recovery). During this operation, water channels through the oil banks and thus increases the fraction of water in the produced fluid (mixture of oil and water). To reduce the channeling, the viscosity of the injection fluid is increased to that of the oil by the addition of polymers (tertiary oil recovery). Anionic polyacrylamides are used nearly exclusively for this application. For high salinity or high temperature oil fields sulfonated and/or hydrophobically modified polymers are used.

Some superabsorbents containing acrylamide as comonomer are used in special applications, such as soil conditioning or cable insulation (→ Superabsorbents, Chap. 6). Dust is controlled on roads, in mines, and particularly on surfaces of pulverized coal and mineral piles within open transit cars or trucks by applying oil-continuous emulsions of highly branched, cross-linked, water-swellable polymers of acrylamide and acrylic acid [127]. The polymers are in the form of microgelatinous particles (<1 mm diameter) that swell dramatically in water and then bind dust particles.

5.3. Other Polymers

The polymers described in this section are generally experimental products, some of which are available in developmental quantities.

Lightly cross-linked poly(N-isopropylacrylamide) hydrogels have a phase transition at 31°C. This property has been suggested to be useful in separations, such as concentration of soy protein from aqueous extracts [128] or in controlled drugs release [129].

The good balance of hydrophobic and hydrophilic groups in poly(N,N-dimethylacrylamide) and copolymers of N,N-dimethylacrylamide with other water-soluble monomers makes these materials soluble in a wide range of solvents. This suggests utility as thickeners in formulations with high concentrations of organic chemicals. The homopolymer is mutually soluble with poly(vinyl acetate), poly(methyl methacrylate), and polystyrene.
Appropriate copolymers may serve as polymer compatibilizers [130]. The homopolymers of 2-acrylamido-2-methylpropanesulfonic acid and copolymers with acrylamide [131] and the corresponding alkali-metal salts have been used in applications where the chelation tendencies of carboxylate copolymers toward di- and trivalent ions are detrimental, and for thickening aqueous solutions of strong acids [132] (e.g., in the acidification of oil wells [133]).

6. Economic Aspects

The homo- and copolymers of acrylic acid, its salts, and acrylamide make up the majority of the production volume of these polymers. Manufacturers and trade names are listed in Table 3. In 2008, worldwide production of poly(acrylic acid) and polyacrylamide amounted to $1.58 \times 10^9$ kg and $750 \times 10^6$ kg, respectively.

The market for poly(acrylic acid) was divided as follows: 69.6% as superabsorbent polymers, 10.5% as detergent additives, 11.7% as industrial dispersants, 4.6% as water treatment chemicals (primarily sequestrants and scale inhibitors), and 3.8% as coatings components and drilling muds. The polyacrylamide market was divided as follows: 37% for water treatment (primarily flocculants, 22% for municipal and 15% for industrial water treatment), 25% for additives in pulp and paper, 20% for oil recovery, 10% for mineral processing, and 8% other. Geographically, 48.2% of the poly(acrylic acid) was used in the United States and Canada, 31.3% in Western Europe and 20.5% in Japan. For polyacrylamide the breakdown was 28% United States and Canada, 27% Europe, and 45% Asia.

Annual growth for all segments of the polyacrylamide market was expected to be 5–7% in 2008. The poly(acrylic acid) market is dominated by the superabsorbent polymers which is expected to grow by 3 to 4 % in 2006. For the other polymer a slightly lower growth is expected (around 3%)

7. Toxicology, Occupational Health, and Environmental Aspects

Polyacrylamides, hydrolyzed polyacrylamides, poly(acrylic acids) and their salts are relatively nontoxic materials. Care should be taken in the finishing of the polymers to strictly limit the content of any unreacted monomers because they are toxic [135]. Handling of the monomers is described in Chapter 2.

Poly(acrylic acid) showed low toxicity in acute screening tests indicated by an LD$_{50}$ of 5 000 mg/kg (rat, oral) and 3 000 mg/kg (rabbit, dermal) [109, 136]. Screening tests for toxicity to aquatic wildlife showed that the LC$_{50}$ was greater than 1 000 ppm for daphnia, sunfish, and trout [137]. Neutralized products of high alkalinity can be irritating to the eyes and skin.

The toxicity of polyacrylamide and hydrolyzed (anionic) polyacrylamide containing only 500–800 ppm residual monomers has been evaluated in rats, dogs, and fish [138]. Low toxicity is indicated by the single oral dose LD$_{50}$ which is greater than 4 000 mg/kg in rats. The results from two-year feeding studies in rats showed no effect at 1% dietary concentration and a slight retardation in growth at the 5% dietary level. Dogs were unaffected by

---

**Table 3. Manufacturers and trade names of poly(acrylic acids) and polyacrylamides**

<table>
<thead>
<tr>
<th>Company</th>
<th>Trade name</th>
<th>Type*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Poly(acrylic acids)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Akzo Nobel</td>
<td>Alcosperse</td>
<td>b</td>
</tr>
<tr>
<td>BASF SE</td>
<td>Dispex</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>Sokalan</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>Hysor</td>
<td>a</td>
</tr>
<tr>
<td>BF Goodrich</td>
<td>Carpol</td>
<td>d</td>
</tr>
<tr>
<td>Dow Chemical</td>
<td>Acusol</td>
<td>b</td>
</tr>
<tr>
<td>Evonik</td>
<td>Favor</td>
<td>a</td>
</tr>
<tr>
<td>Nippon Shokubai K.K.</td>
<td>Aquatic</td>
<td>a</td>
</tr>
<tr>
<td>Sanyo Chemical Industries</td>
<td>Sanwet</td>
<td>a</td>
</tr>
<tr>
<td><strong>Polyacrylamides</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alco Chemical</td>
<td>Aquatreat</td>
<td>b</td>
</tr>
<tr>
<td>BASF SE</td>
<td>Magnafloc, Zetag</td>
<td>c, d</td>
</tr>
<tr>
<td></td>
<td>Percol</td>
<td>c, d</td>
</tr>
<tr>
<td></td>
<td>Alcoflood</td>
<td>d</td>
</tr>
<tr>
<td>Beijing Hengiu</td>
<td>Hengfloc</td>
<td>c</td>
</tr>
<tr>
<td>Kemira</td>
<td>Superfloc</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>Fennopol</td>
<td>e</td>
</tr>
<tr>
<td>Mitsubishi Rayon Co, Ltd.</td>
<td>Diaplac</td>
<td>c</td>
</tr>
<tr>
<td>Nalco</td>
<td>Ultimer</td>
<td>c, d, e</td>
</tr>
<tr>
<td>SNF Floerger</td>
<td>Aquasorb</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>Flopam</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>Floret</td>
<td>e</td>
</tr>
<tr>
<td>Solenis</td>
<td>Praestol</td>
<td>c, d</td>
</tr>
<tr>
<td></td>
<td>Praestarete</td>
<td>e</td>
</tr>
</tbody>
</table>

* a = superabsorbent; b = dispersant, scale inhibitor; c = flocculant; d = thickener; e = retention aid.
feeding diets containing up to 6% of these polymers. Fathead minnows, bluegills, and rainbow trout were unaffected by up to 100 ppm of these polymers in the water for 90 days. Minnows were all killed by a solution of 2 500 ppm of hydrolyzed polyacrylamide; the fish had extreme difficulty swimming due to the high viscosity of this test solution. Cationic derivatives of polyacrylamides can kill fish and should not be allowed into natural waterways. Polyacrylamide, cationic- and anionic-modified polyacrylamides, and poly(acrylic acid) and its salts strongly adsorb to many solids. They are thereby effectively removed from sewage in a waste treatment plant as a component of the sludge. Polyacrylamides show no evidence of toxicity at a dosage of $10^4$ mg/kg in rabbits [65]. The fate of polyacrylamides in hydroystems is reviewed in [139].

References


36 American Cyanamid, AU8818380-A, 1989 (W.B. Davies).


Further Reading


