

## Chapter 2

# Synthetic Methods for Water-Soluble Monomers and Polymers Nonpolyelectrolytes and Polyelectrolytes

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This review is based on a lecture that has been presented over the past several years by one of us (GBB) in connection with certain well-established short courses. Although the major water-soluble non-polyelectrolytes are covered briefly in this review, the major emphasis is placed on well-studied and either commercially available polyelectrolyte monomers or such monomers which have the potential for commercial development. The latter judgment is based on availability of raw materials, monomer and polymer yields, and/or quality of derivable polymers or copolymer. In many cases, only the monomers are emphasized, since methods for their polymerization generally parallel each other, all being predominantly initiated and polymerized via free radical mechanisms. No distinction is generally made among the several polymerization techniques such as aqueous or other solution processes, suspension or emulsion processes. In many cases all types have been studied. In most of the others, success in the application of the several techniques to the polymerization process can reasonably be predicted.

Organic compounds having hydrophilic groups are soluble in water provided the hydrophobic-hydrophilic balance is favorable. Alcohols of low molecular weight are soluble in water; however, those of higher molecular weight are no longer soluble. The same principles apply to polymers. Table I includes the more common functional groups which impart water-solubility to organic compounds as well as to polymers.

### Non-polyelectrolytes

Aside from the naturally occurring water-soluble polysaccharides or their synthetically modified derivatives, the major contributors to the non-polyelectrolyte group of water-soluble polymers are: poly(acrylamide), poly(acrylic) or (methacrylic acids), poly(ethylene oxides), poly(methyl vinyl ether) and poly(vinyl alcohols).

Polyacrylamide (PAM). Acrylamide polymerizes easily in aqueous solution in presence of a wide variety of free-radical initiators (1). Many added salts affect polymerization rate and molecular weight. Often, commercially produced poly(acrylamides) may contain a fraction that appears to be insoluble in water, a property which presents a problem for many uses. Much attention

TABLE I. Some Functional Groups Which Impart Water-Solubility to Organic Polymers

-NH <sub>2</sub>	HO- Alcohols	-CH = N - O <sup>-</sup>	
-NHR	Phenols		
-NR <sub>2</sub>	Enols	-PO <sub>3</sub> <sup>-</sup>	
<sup>+</sup> -NR <sub>2</sub> H X <sup>-</sup>	-C = O	-SO <sub>3</sub> <sup>-</sup>	
<sup>+</sup> -NR <sub>3</sub> X <sup>-</sup>		-NH - C(=O) - NH <sub>2</sub>	Water-Soluble Polymers
<sup>+</sup> -PR <sub>3</sub> X <sup>-</sup>		-NH - C(=O) - NH <sub>2</sub>	$-(\text{-CH}_2 - \text{CH-})_n\text{-}$
<sup>+</sup> -OR <sub>2</sub> X <sup>-</sup>	-C = O		$-(\text{-CH}_2 - \text{CH-})_n\text{-}$
-SR <sub>2</sub> X <sup>-</sup>			$-(\text{-CH}_2 - \text{CH-})_n\text{-}$
			$-(\text{-CH}_2 - \text{CH}_2\text{-O-})_n\text{-}$

has been given to water-in-oil emulsion polymerization where a concentrated solution is polymerized as the dispersed phase and the continuous phase consists of a liquid hydrocarbon.

**Poly(acrylic acid) and Poly(methacrylic acid).** Linear polymers of acrylic and methacrylic acids can be prepared by use of free-radical initiation, generally in aqueous solution (2). However, nonaqueous media, inverse phase emulsion or suspension techniques may also be used. Salts of acrylic and methacrylic acids can also be polymerized in aqueous solutions. The rate of polymerization is dependent on pH, being high at low pH, dropping to a minimum at pH 6-7 for both monomers, and rising again to a maximum of pH 10 for acrylic acid and near pH 12 for the methacrylic acid.

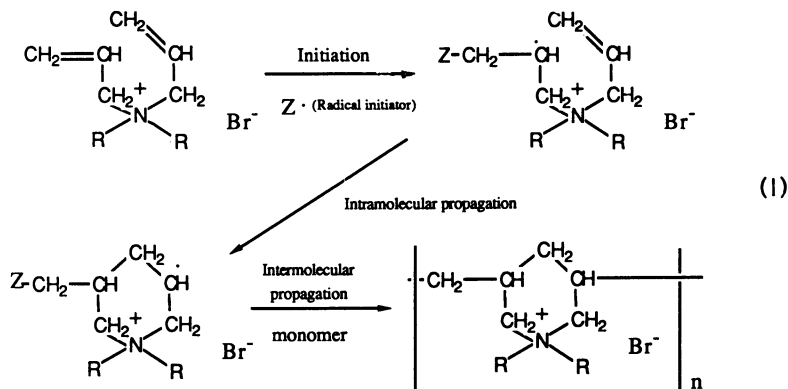
**Poly(methyl vinyl ether).** The only vinyl ether polymer which is completely miscible with water is methyl vinyl ether (3). The vinyl ethers are generally converted to polymers via use of Friedel-Crafts type (or cationic) initiators. The most important commercial materials derived from vinyl ethers are their copolymers with maleic anhydride. These copolymers are hydrolyzable to the corresponding polycarboxylic acids.

**Poly(vinyl alcohol) (PVA).** Polyvinyl alcohol is the largest volume synthetic water-soluble polymer produced in the world. Vinyl alcohol does not exist to any substantial extent in the free state, since it is the enol tautomer of acetaldehyde. Consequently, PVA is commercially produced by hydrolysis of poly(vinyl acetate) (4).

**Polymers of Ethylene Oxide.** Polymeric derivatives of ethylene oxide are divided into classes which are defined by molecular weight. Low mol. wt. polymers of average mol. wts. less than 20,000 are generally defined as poly(ethylene glycols), while polymers with av. mol. wt. up to five million are generally referred to as ethylene oxide polymers. The distinction is based on limitations on mol. imposed by the method of synthesis. All appear to be miscible with water at room temperature in all proportions (5).

PolyelectrolytesCationic Polymers

**Quaternary Ammonium:** The most important and extensively used cationic polymers are the quaternary ammonium polymers. The quaternary ammonium function is highly hydrophilic, and organic compounds containing this group are extensively hydrated. The same is true for the polymers. Among the first water-soluble quaternary ammonium polymers was that shown in Equation 1 (6-7). This polymer, as the chloride salt, is now manufactured under the trade name "Cat-Floc" and was also the first such polymer to be approved by the Food and Drug Administration for use in potable waters. It is extensively used as a flocculating agent, but has many other uses.



The monomer, dimethyldiallylammonium chloride, known as DMDAC or DADMAC, can be synthesized by either of the methods shown in Equation 2, as well as by several other methods. The second method is the most economical and is used commercially. The monomer generally is not isolated, but is purified and polymerized as a 62-70% solution.

The mechanism for polymerization of a non-conjugated diene such as DADMAC is generally referred to as cyclopolymerization. This process does not conform to the theory of Staudinger (8) which postulates that non-conjugated dienes will produce cross-linked polymers on polymerization. Structure 1 shows two alternative structures for the polymer. Structure Ia is predicted by the theory of Flory (9) that states that the more stable intermediate will predominate in vinyl polymerization, which in this case is the secondary radical and would lead to Structure Ib. It has been shown (10) that Structure Ia is the almost exclusive structure obtained in polymerization of DADMAC which requires the less stable primary radical to be the predominant propagating species, contradictory to the theory of Flory.

## Monomer Synthesis:

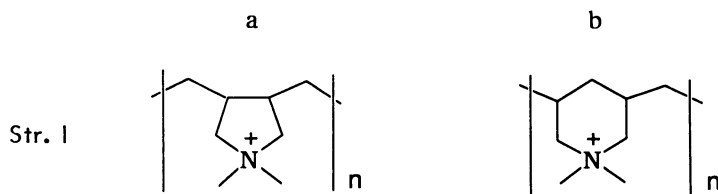
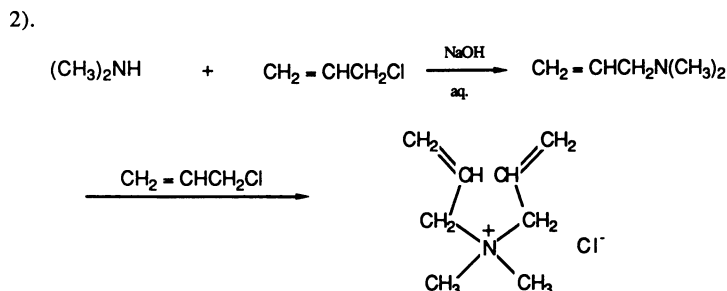
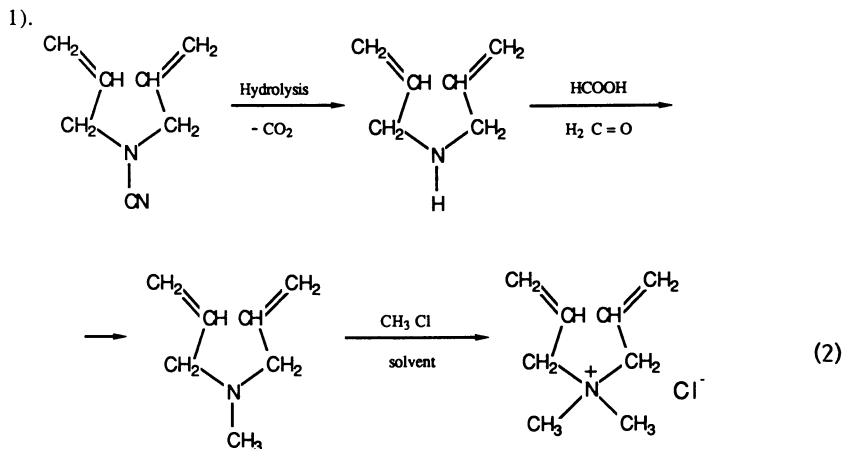


Figure 1 confirms that poly(DADMAC) contains essentially one nitrogen structure, and thus predominantly one ring size (11).

Poly(DADMAC) has been fractionated and its solution properties studied. Figure 2 shows the dependence of intrinsic viscosity of various fractions of the polymer upon temperature at a constant 0.5 ionic strength of the medium (12-13).

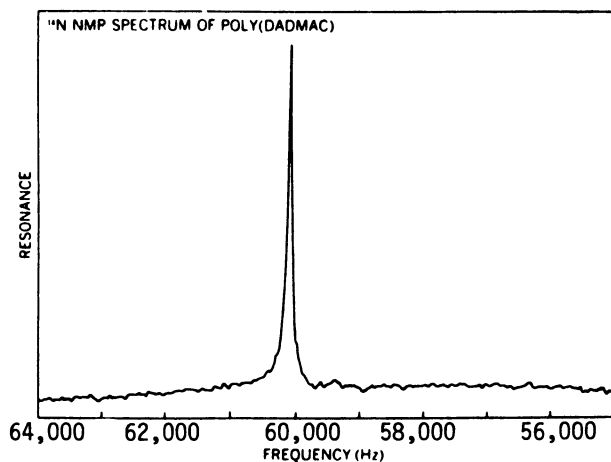


Figure 1.  $^{14}\text{N}$ -NMR spectrum of poly(DADMAC) in water in the scan range 56 000–63 000 Hz at 25 °C. (Reprinted with permission from ref. 11. Copyright 1979 John Wiley & Sons, Inc.)

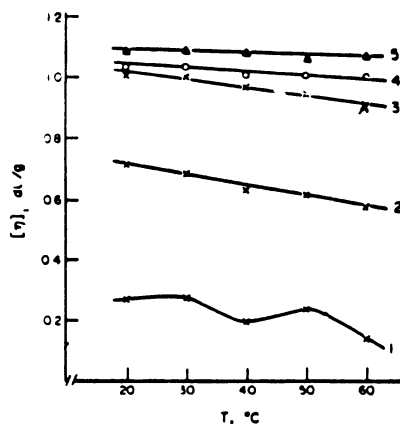


Figure 2. Dependence of intrinsic viscosity upon temperature and molecular weight for an ionic strength of 0.5. Curve 1,  $\bar{M}_w = 0.0835 \times 10^6$ ; curve 2,  $\bar{M}_w = 0.426 \times 10^6$ ; curve 3,  $\bar{M}_w = 0.981 \times 10^6$ ; curve 4,  $\bar{M}_w = 1.943 \times 10^6$ ; curve 5,  $\bar{M}_w = 0.701 \times 10^6$ . (Reprinted with permission from ref. 12. Copyright 1977 Pergamon.)

Figure 3 shows the dependence of intrinsic viscosity of a sample of constant molecular weight on ionic strengths of medium varying from 0.1 to 0.5. From Mark-Houwink plots, the following equations which relate intrinsic

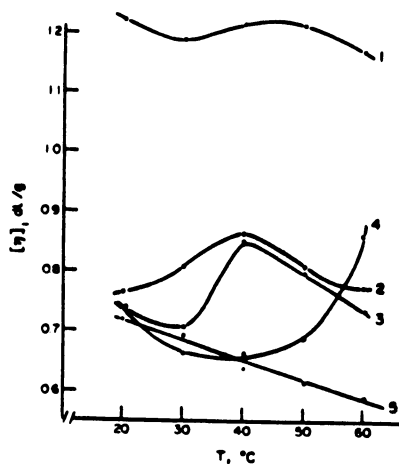


Figure 3. Dependence of intrinsic viscosity of a sample with  $\bar{M}_w = 0.0835 \times 10^6$ , on ionic strength ( $i$ ): 1.  $i=0.1$ ; 2.  $i=0.2$ ; 3.  $i=0.3$ ; 4.  $i=0.4$ ; and 5,  $i=0.5$ . (Reprinted with permission from ref. 13. Copyright 1977 Pergamon.)

viscosity to weight average molecular weight of the polymer at 20°C for the various ionic strengths were obtained:

(0.1 M NaCl solution)	$[\eta] = 3.98 \times 10^{-4} \bar{M}_w^{0.660}$
(0.2 M NaCl solution)	$[\eta] = 2.512 \times 10^{-4} \bar{M}_w^{0.638}$
(0.3 M NaCl solution)	$[\eta] = 2.510 \times 10^{-4} \bar{M}_w^{0.620}$
(0.4 M NaCl solution)	$[\eta] = 1.390 \times 10^{-4} \bar{M}_w^{0.542}$
(0.5 M NaCl solution).	$[\eta] = 3.982 \times 10^{-4} \bar{M}_w^{0.566}$

Poly(DADMAC) can be fractionated and characterized by size exclusion chromatography (SEC) as shown in Figure 4. The column substrate in this case was a chloromethylated and quaternized (with trimethylamine) sample of the ion exchange resin, Amberlite 900 (14).

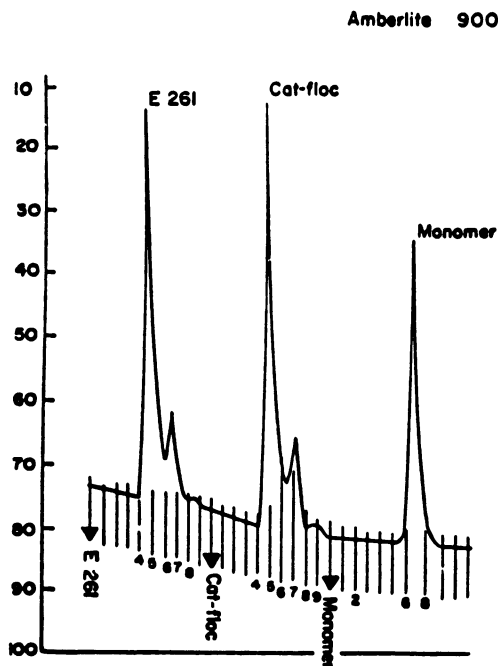


Figure 4. Fractionation of poly-(diallyldimethylammonium chloride) on chloromethylated and quaternized styrene-divinylbenzene gels. (Reprinted from ref. 14.)

The polymer can also be fractionated and characterized by SEC by use of a quaternized silicious substrate as shown in Figure 5 (15).

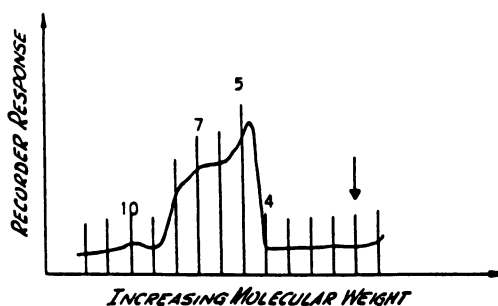
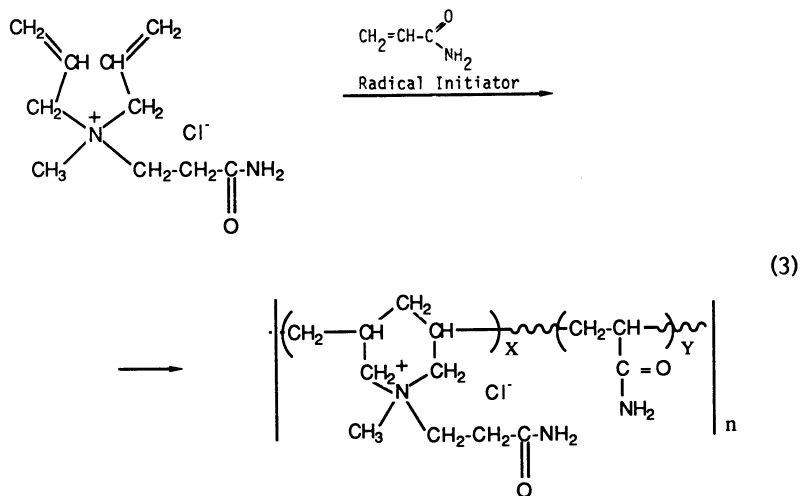


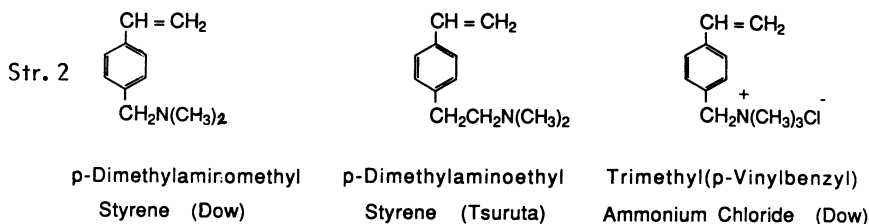
Figure 5. GPC fractionation of a high MW poly-(diallyldimethylammonium chloride) on a quaternized silicious support. (Reprinted from ref. 15.)

Diallylmethyl  $\beta$ -propionamido ammonium chloride monomer and homopolymers have been prepared (16). The polymers as shown in Equation 3 were

found to be useful as primary coagulants and in many flocculation applications. Copolymers with acrylamide have excellent flocculation properties (17).

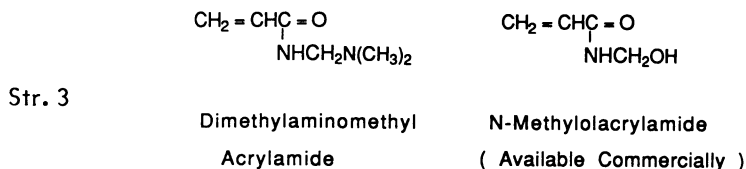


Structure 2 shows some readily polymerizable tertiary amino monomers as well as the corresponding quaternized monomers. The Dow monomers are probably a mixture of the *m*- and *p*-isomers. The three amine monomers polymerize most effectively in aqueous solution at the pH of the hydrochloride salt. The "Tsuruta" monomer can readily be prepared by addition of one mole of dimethyl amine to *p*-divinylbenzene.

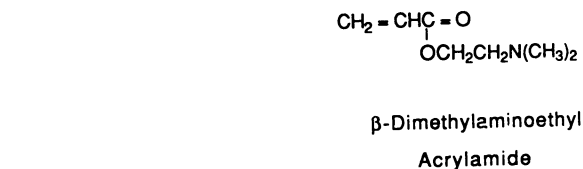


Structure 3 shows types of monomers available by the Mannich reaction of acrylamide with formaldehyde and dimethylamine. The methylol monomer is useful as a post-cross-linking site. The corresponding polymer or copolymer when treated with acid converts methylol containing chains to the methylene-bis-acrylamide cross-links (18).





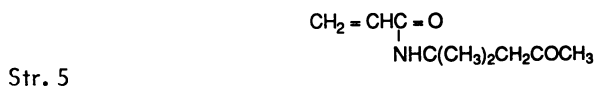
Structure 4 shows some tertiary amino acrylate monomers which are available (19-20). However, the ester linkage is not sufficiently stable to hydrolysis to make this monomer too attractive. The amide monomers are more stable and are extensively used. All can be quaternized.



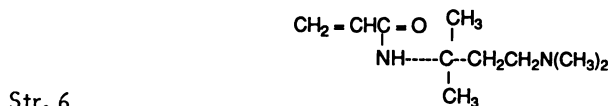
Str. 4



Structures 5 and 6 show some interesting tertiary amino monomers which are synthesized via the Ritter reaction, first developed in 1951 (21). Diacetone acrylamide can be synthesized from the relatively inexpensive raw materials, acetone and acrylonitrile (22-29).



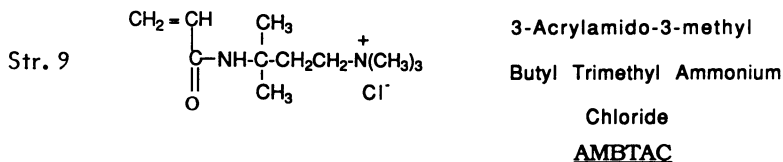
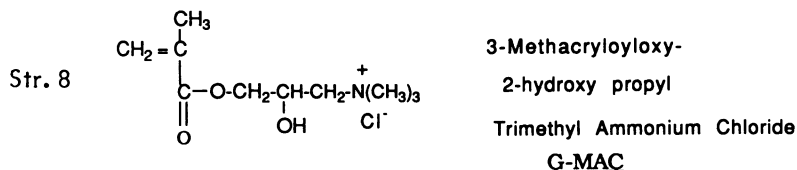
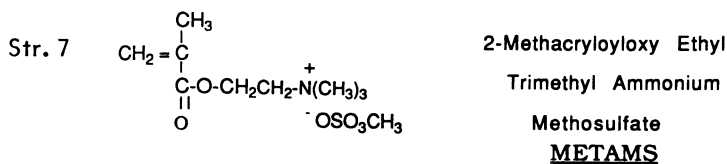
Diacetone Acrylamide



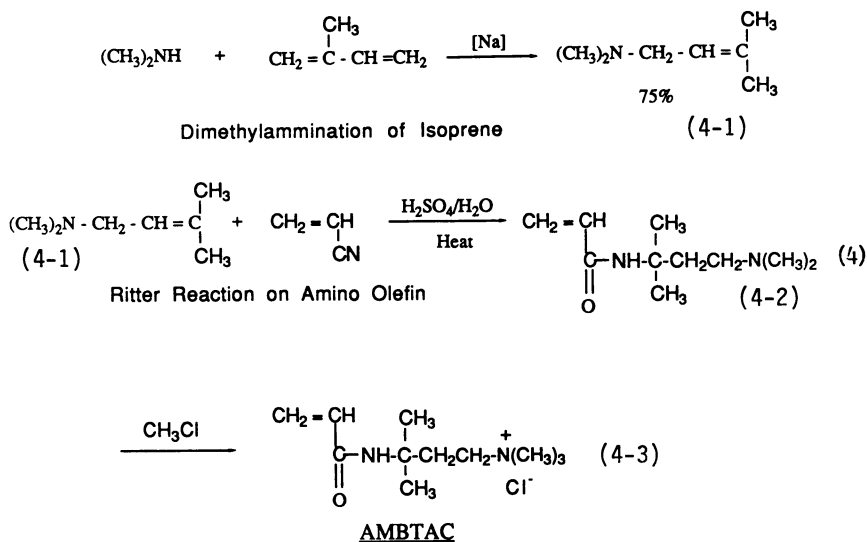
N-(1,1-Dimethyl-3-dimethylamino-  
propyl) Acrylamide

Cationic quaternary ammonium monomers, as shown in Structures 7-9, and their polymers have attained considerable importance because of their exceptionally wide range of applications. The N-substituted acrylamides offer significant advantages over the N-alkyl acrylate esters because of their increased reactivity and hydrolytic stability.

### Cationic (Quaternary) Monomers



The N-(dialkylaminoalkyl)acrylamides have been known for many years; however, the only convenient synthesis of these materials, the reaction of a suitable N,N-dialkyldiamine with acryloyl chloride, is expensive. The synthesis of AMBTAC is shown in Equation 4.



3-Acrylamido-3-methylbutyltrimethylammonium chloride (AMBTAC) has been synthesized by a novel synthetic route which utilizes the sodium catalyzed reaction of dimethylamine with isoprene, to give N,N-3-trimethyl-2-butenylamine and other by-products. The reaction mixture consists of about 75% of N,N-3-trimethyl-2-butenylamine (4-1). The Ritter reaction with acrylonitrile and sulfuric acid yield 85-90% of N-(1,1-dimethyl-3-dimethylaminopropyl) acrylamide (4-2) (30-31).

This amine (4-2) can be homo- or copolymerized and then subsequently quaternized or quaternized directly to give 3-acrylamido-3-methylbutyl trimethylammonium chloride (AMBTAC) (4-3).

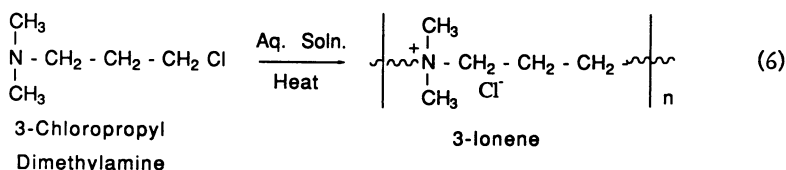
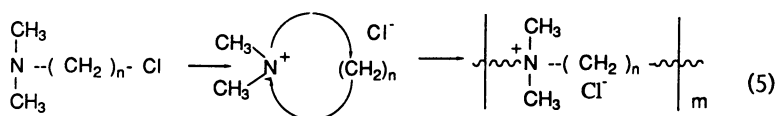
Polyquaternary ammonium compounds with the ammonium ion integral to the backbone of the polymer chain, have been known for about 40 years since the work of Marvel (32-36). Other researchers (37-41) have used the Menshutkin reaction to form linear, unsymmetrical polyquaternary ammonium compounds by reacting ditertiary amines with dihalides.

The generic name "lonenes" was proposed (42) for this class of compounds. This term has been widely accepted and is generally used to describe this type of polymer. They can be derived either from reaction of A-A/B-B monomers (ditertiary amines and dihalides) or by the reaction of an A-B monomer (aminoalkyl halide) with itself to form the linear polyquaternary ammonium compounds.

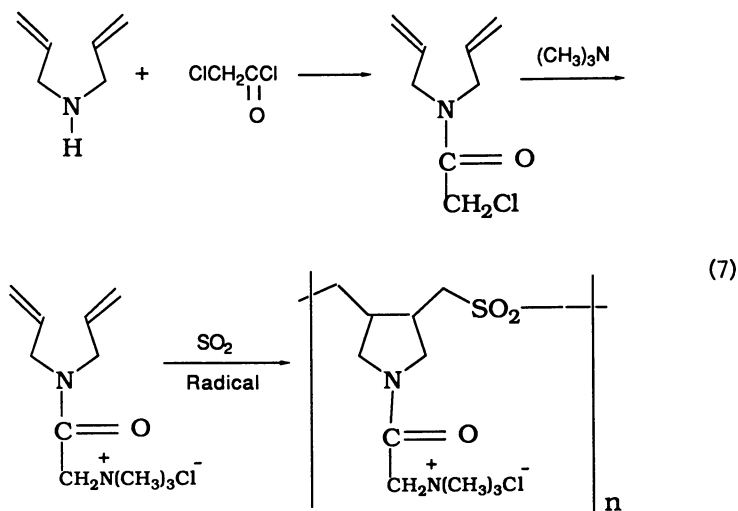
Investigators in this field have elucidated the mechanism (43-58) involved in the step growth polymerizations of both the A-A/B-B reaction sequence and the A-B reaction to form ionenes of well defined character. The highest charge density and the highest molecular weight ionene polymer is the

3-3-ionene. This was first synthesized by Marvel from 3-dimethylamino-n-propyl bromide. Polymerization of dimethylamino propyl chloride in a concentrated aqueous solution (59) yields a reasonably high molecular weight polymer which has properties as a flocculant (Equation 5). Cyclic intermediates have been observed in mechanistic studies of these reactions (Equation 6).

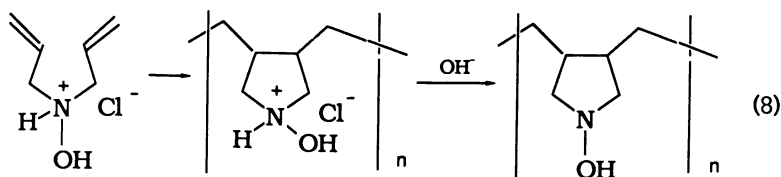
### 3-ionene



A novel approach to quaternary ammonium polymers and copolymers is shown in Equation 7. This group in Japan pioneered in the alternating copolymers of DADMAC monomer with sulfur dioxide (60-61).

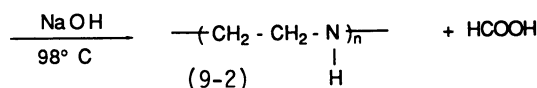
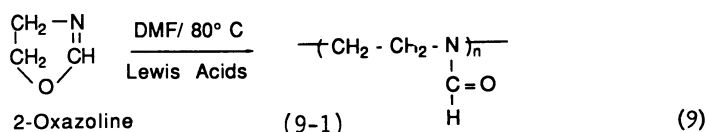


A novel monomer and its polymer are described in Equation 8. N-Hydroxysuccinimide has extremely useful properties as a "catalyst" for low temperature esterification reactions. The potential for the polymer described is obvious (62).



Equation 9 illustrates the synthesis of linear and crystalline polyethylenimine. Polyethylenimine (PEI), produced by the ring opening cationic polymerization of ethylenimine monomer (aziridine), has a highly branched structure. The secondary amine groups in the main polymer chain cause the monomer to "graft" onto the already formed polymer. The preparation of linear PEI from aziridine monomer has yet to be accomplished. Synthesis of linear, crystalline polyethylenimine (9-2) has been accomplished (63-64) by an isomerization polymerization of 2-oxazoline, and alkaline hydrolysis of the intermediate, poly(N-formylethylenimine) (9-1).

#### Linear Crystalline Polyethylenimine

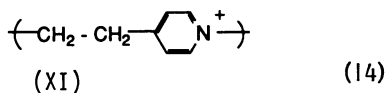
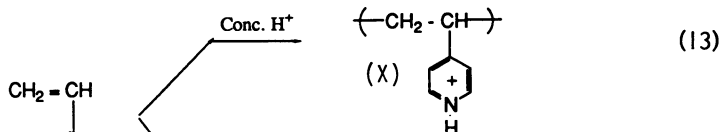
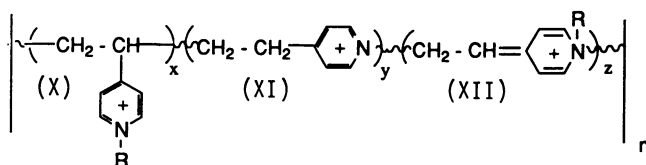
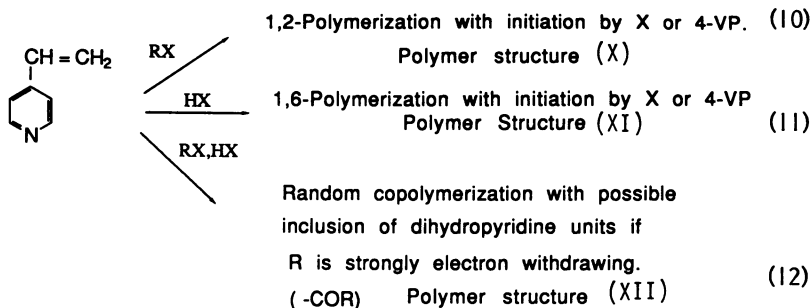


Previously, Fuhrmann (65) had prepared poly(N-acylethylenimines) from 2-substituted-2-oxazolines but did not report the hydrolysis of these materials to the free polyethylenimine. Continued work (66-69) has resulted in elucidation of the mechanism of 2-oxazoline polymerization.

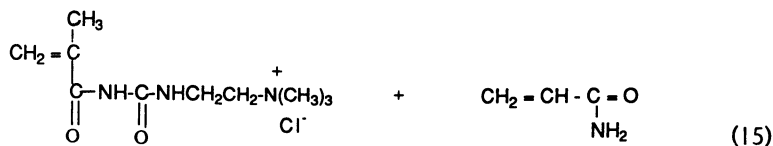
By DSC analysis the melting point of this polyethylenimine (9-2) was shown to be  $58.5^\circ\text{C}$  and the glass transition point was  $-23.5^\circ\text{C}$ . The polymer is insoluble in water at room temperature but soluble in hot water. This solubility behavior is quite different from that of the conventional polyethylenimine which is readily soluble in cold water.

Extensive investigations on the poly(2- and 4-vinylpyridinium salts) have been carried out. Several monomeric quaternary ammonium salts are known to spontaneously polymerize in aqueous solutions when their concentration is above about 25% by weight.

Both 2- and 4-vinylpyridine have been reported (70-82) to undergo spontaneous polymerization either upon attempted quaternization with alkyl halides or protonation with mineral acids. Further discussion of the extensive mechanistic studies reported on this problem is beyond the scope of this summary (Equation 10-14).

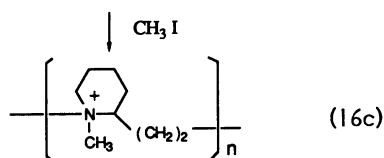
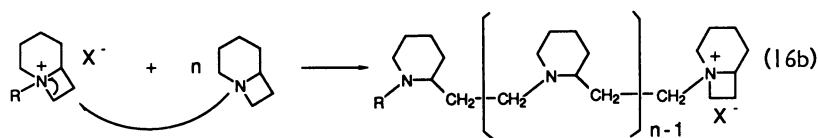
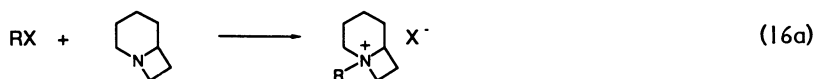


Equation 15 shows some recently claimed methacryloyl urea derivatives containing quaternary ammonium groups and their copolymers with acrylamide (83).

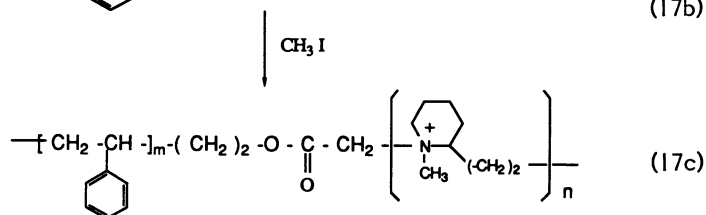
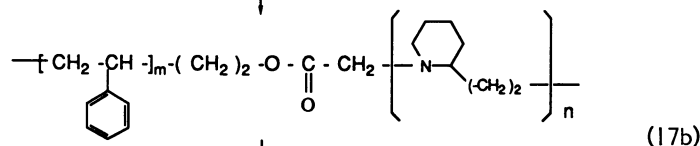
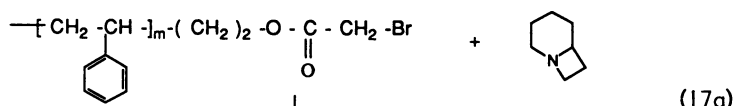


Radical Initiator  
 Copolymer,  $M_w = 2.2 \times 10^6$ , Useful as Flocculation and Sedimentation Agent

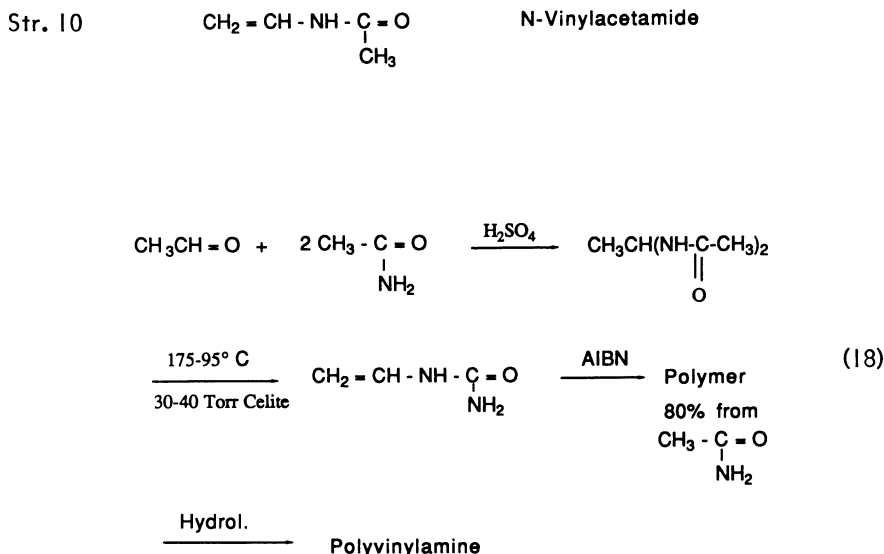
A polymeric tertiary amine is available by cationic ring-opening polymerization of 1-azabicyclo[4.2.0]octane (the so-called condine) (Equation 16). The synthesis and homopolymerization of this monomer was first published in 1960. Several authors studied the mechanism (Equation 16a,b) and kinetics of the polymerization (84-86).



The initiation of the polymerization proceeds by an alkylation and the alkylation agent is fixed at the chain end. Therefore, using a polymeric initiator - for instance, a polystyrene with a bromoacetyler end group (Equation 17a) - a diblock copolymer is obtained (Equation 17b) (87) which can be quaternized (Equation 17c).

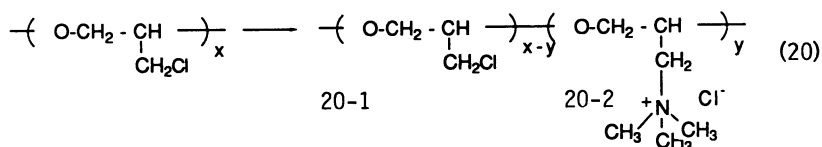
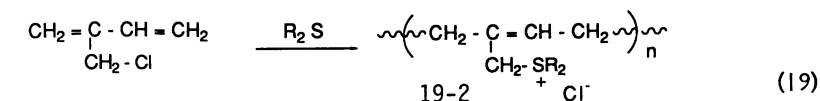


The second monomer shown as Structure 10 provides an excellent route to polyvinylamine. Many efforts have been made over the years to find an economical source of this polyamine of low repeat unit; however, most have been disappointing. N-Vinylacetamide is synthesized as follows (Equation 18) (88):



Sulfonium Monomers and Polymers: 2-Methylene-3-butenyl ammonium and sulfonium monomers and their polymers have been synthesized from 2-chloromethylbutadiene by reaction with a tertiary amine or sulfide, followed by polymerization (Equation 19) (89-91). Polymer modification as shown in Equation 20 can also lead to water-soluble (20-2) polymers.

Dialkyl-(2-Methylene-3-Butenyl) Sulfonium Chloride

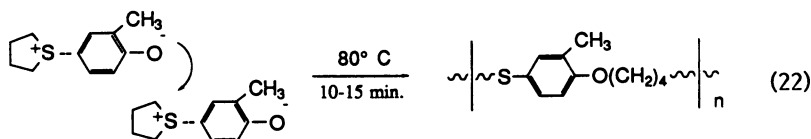
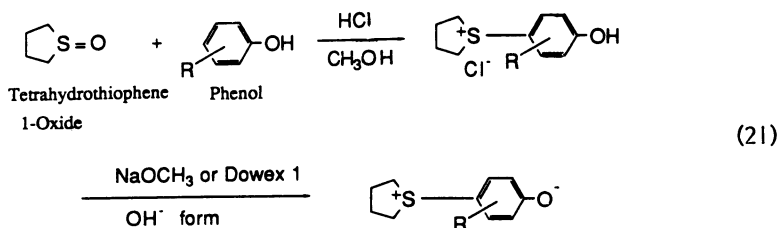




The corresponding cationic polymers (19-2, or 20-2) could be obtained by either polymerization of the ammonium or sulfonium monomers or by reaction of poly(2-chloromethyl-1,3-butadiene) or polymer 20-1 with an appropriate tertiary amine or sulfide (92). These quaternary monomers can be homopolymerized or copolymerized for use as flocculants, dispersants, electroconductive paper coatings and wet strength additives for paper. The sulfonium polymers are water soluble and, upon heating or treatment with a base, tend to decompose and crosslink and become hydrophobic and water insoluble. Chiu (93) disclosed their use in this regard as durable antistatic coatings.

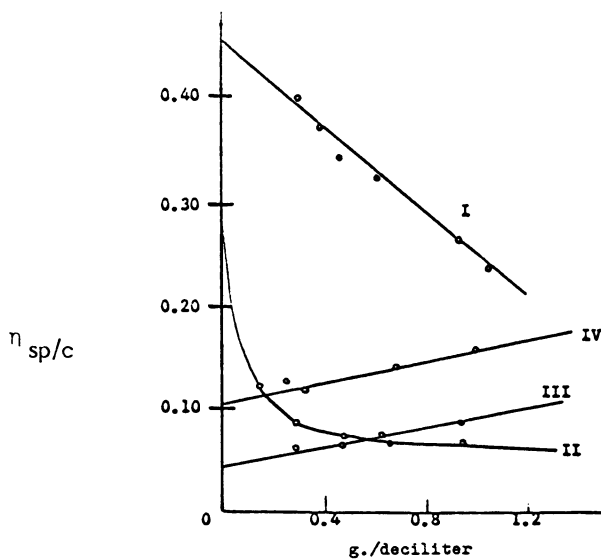
Water soluble monomers containing the sulfonium cation have been extensively studied. The hydrolytic instability of the sulfonium group, however, makes the polymeric materials unstable. This instability has been turned to good use in that these polymers can be applied, e.g., as coatings and the sulfonium function subsequently decomposed to yield hydrophobic and thus water resistant coatings. A new class of coatings has been developed on this basis (Equations 21 and 22) (94-96). A detailed discussion of these monomers and their polymerization was presented by Schmidt and co-workers (97).

#### Preparation of Aryl Cyclic Sulfonium Zwitterions



Polymerization of these cyclic sulfonium zwitterions proceeds by a novel mechanism involving both ring opening and a loss of charge to form nonionic polymers.

Phosphonium Monomers and Polymers: A variety of phosphonium polymers were synthesized via cyclopolymerization of a variety of diallylphosphonium salts (98). The viscosity data (Figure 6) for the poly-phosphonium



Plots of  $\eta_{sp}/c$ :

- I. Poly-(diallyldiphenylphosphonium bromide) in 95% ethanol.
- II. Poly-(diallyldiphenylphosphonium chloride) in a 1.0 M 1:1 ethanol-water solution of potassium chloride.
- III. Poly-(diallyldiphenylphosphonium bromide) in 1:1 ethanol-water 0.1 M in potassium bromide.
- IV. Poly-(diallylphenylphosphine oxide) in 95% ethanol.

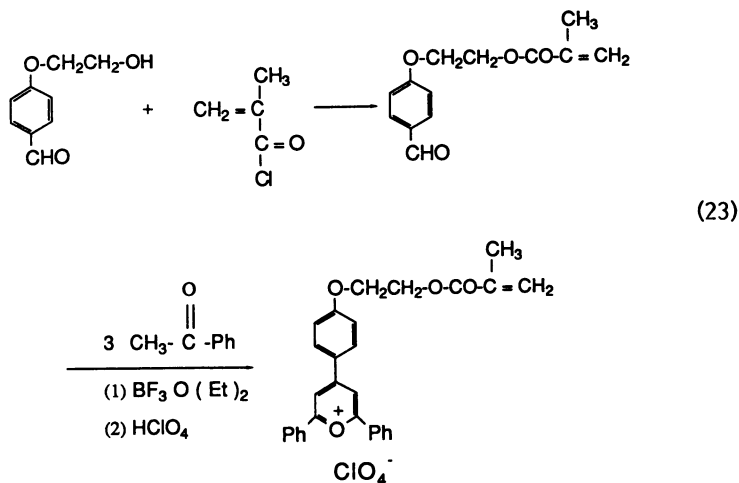
Figure 6. Intrinsic viscosity determinations of phosphonium polymers. (Reprinted from ref. 98. Copyright 1969 American Chemical Society.)

salts were typical of the data for polyelectrolytes in general. The viscosity curves ( $\eta_{sp}/c$  vs.  $c$ ) of polyelectrolytes are strongly concave upward, in contrast to the behavior of uncharged linear polymers. This is due to the dissociation of the ionic bond in the solution which leads to large repulsive forces between the positively charged groups remaining on the chain. These forces give rise to greatly expanded configurations and very large intrinsic viscosities. At high concentrations, the molecules in the polyelectrolyte are not significantly ionized and tend to partially overlap; thus, they are not appreciably expanded. As the solution is diluted, the molecules no longer fill all the space and some of the halide ions leave the region of the chain. This causes a development of charge and extension of the chains. The addition of a strong electrolyte suppresses the loss of halide ion and the viscosity behavior becomes more normal. However, the intrinsic viscosity is dependent on the volume of the polymer in the solution and added electrolyte compresses the hydrodynamic unit corresponding to the polyelectrolyte. The compression changes the shape of the polymer and causes a marked decrease in the viscosity of the solution. Thus, the term intrinsic viscosity, for a polyelectrolyte can not be used in the same sense as for an uncharged polymer since it is dependent largely on the concentration of added salt. This type of behavior was

exhibited by the poly-phosphonium compounds and is illustrated in Figure 6. Line I, represents poly-(diallyldiphenylphosphonium bromide) dissolved in ethanol, and as was expected,  $\eta_{sp}/c$  tended to increase with dilution. Addition of a strong electrolyte, such as a potassium halide, provided a common ion effect which repressed the ionization of the polymer. At this time the viscosity behaved similar to a linear uncharged polymer, as shown by line III. Line II represents poly-diallyldiphenylphosphonium chloride rather than the bromide; but demonstrates an intermediate change between line I and III where insufficient common ion was present to completely repress ionization. Line IV represents the viscosity of the phosphine oxide, which was produced from the same sample of diallyldiphenylphosphonium bromide used for the determination of line III.

**Oxonium Monomers and Polymers:** Of the several possibilities of introducing cations into polymers, perhaps the pyrylium function has been given least attention. However, in order to use most organic photoconductors as the photosensitive layer in electrophotography and electrographic copying processes, it is necessary to increase their sensitivity (e.g., the speed of electrical response) and to extend their photosensitive region to the longer wavelength end of the visible spectrum. To meet these requirements many sensitizers have been investigated and typical materials found useful in this regard are triphenylmethane dyestuffs such as crystal violet and rhodamine, pyrylium salts, benzopyrylium salts, and electron acceptor compounds such as anthraquinone, chloranil and TCNQ (99-101).

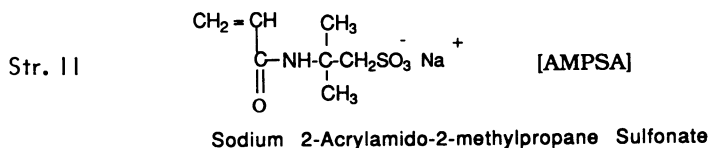
Interest in polymers containing this function followed naturally. A synthesis (102) of vinylpyrylium salts and polymeric benzopyrylium salts for applications in both photosensitizers and photopolymerizable monomers is now available (Equation 23).



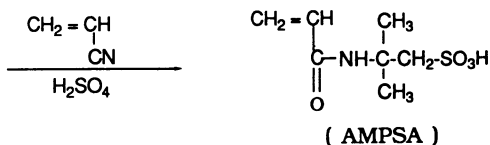
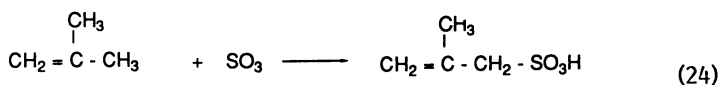
### Anionic Polymers.

**Polysulfonic Acids and Their Salts:** We now turn our attention to some acidic monomers capable of polymerizing to anion containing polymers rather

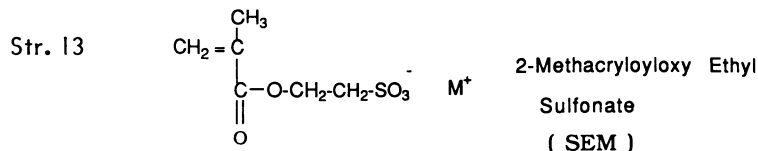
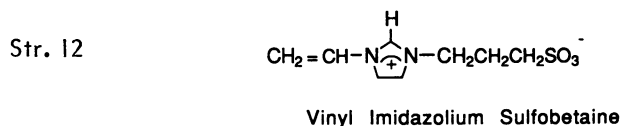
than cation containing polymers as are derived from the quaternary ammonium monomers. Four such monomers are shown as Structures 11-14 (103-116). AMPSA is derived via the Ritter reaction as illustrated in Equation 24.



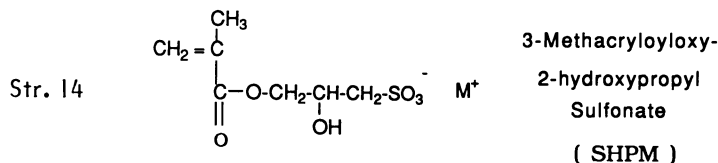
2-Acrylamido-2-methyl Propane Sulfonic Acid



Extensive development work has been done (105-106) on 2-sulfoethyl methacrylate (Structure 12) which has proven to be of limited commercial value due to the hydrolytic instability of the ester linkage. This same hydrolytic instability has been a serious problem with 3-sulfo-2-hydroxypropyl methacrylate reported by Schaper (107) (Structure 13).



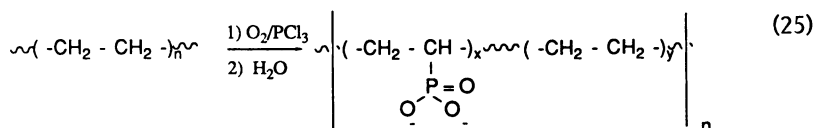
AMPSA was reported by Murfin and Miller (108-109) who prepared this monomer by the reaction of  $\text{SO}_3$  with isobutylene followed by the Ritter reaction with acrylonitrile to yield AMPSA (Structure 14, Equation 24).



AMPSA is highly reactive in both homo- and copolymerizations and can be incorporated into many polymer systems either by homogeneous, solution, or emulsion polymerization techniques. It is used in several industrial polymers and copolymers which have many applications, including improving the affinity for basic dyes in acrylonitrile fibers (110), improving emulsion stability (111), flocculants (112), improving dry strength in paper (113), sludge dispersant in boiler water treatment (114), silt control in cooling water systems (115), and secondary oil recovery (116). AMPSA homopolymers form excellent polysalts with polycations.

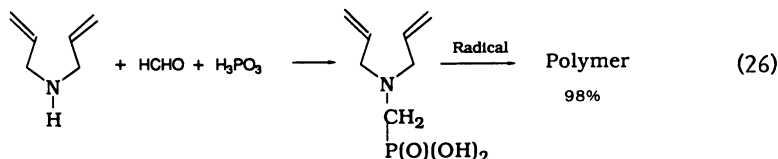
**Polyphosphonic Acids and Their Salts:** Equation 25 shows an example of polymer modification to yield ion containing products. It has been shown (117-118) that bubbling oxygen through a solution of polyethylene in phosphorus trichloride, followed by hydrolyzing the product leads to a series of polymers containing pendant phosphonic acid groups. The original work indicated that solubility in aqueous sodium hydroxide solutions could be attained at only 12 molar % of phosphonic acid substitution.

#### Phosphonated Polyethylene



The mechanical and dielectric relaxation behavior as well as thermal characteristics of a series of ethylene-phosphonic acid copolymers have been reported (119-120).

The use of the Mannich reaction in modification of acrylamide for commercial production of useful polymers has been described earlier (Structure 3). A similar reaction is utilized in the second case of Equation 26 to produce novel phosphonic acid polymers (121).

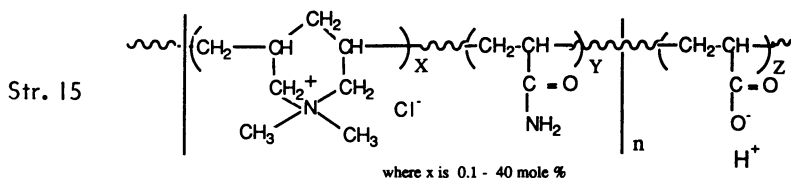


Some problems associated with the exceptionally high molecular weight polymers necessary for satisfactory flocculation characteristics are high viscosities at low concentrations, and times required for dissolution of the solid polymers. Both of these problems can be overcome by synthesis as water-in-oil emulsions followed by inversion and rapid dissolution of the polymer. The details of this procedure are beyond the scope of this review;

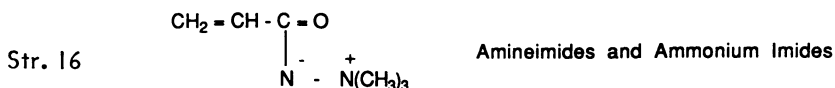
however, a few of the many references dealing with this topic are given (122-125).

### Amphoteric Polymers.

**Quaternary Ammonium-Carboxylates:** Polyampholytes have been synthesized (126) by terpolymerizing dimethyldiallylammonium chloride with acrylamide and acrylic acid. The polymers were used as dry strength resins in paper (Structure 15) (127).



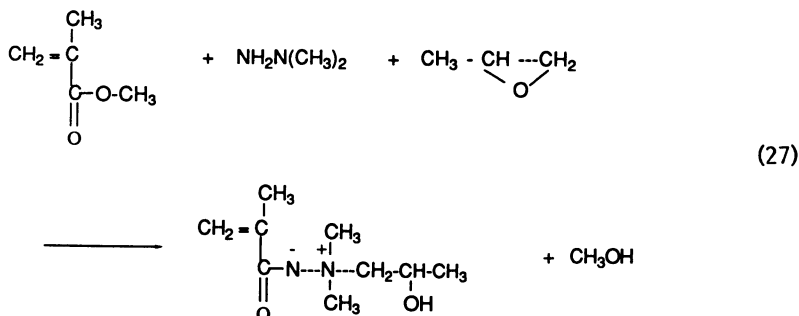
**Amineimides:** Structure 16 illustrates a novel monomer type which imparts interesting properties to polymers. Structure 16 is an amphoteric monomer, a derivative of hydrazine, and has been discussed in a review of water-soluble polymers (103).



The aminimides represent a highly functional class of organic compounds which have been exploited for their unique properties in polymers. An aminimide moiety is both a di-polar ion and an isocyanate precursor. The dipolar ion characteristics contribute toward their water solubility, and as isocyanate precursors, they offer many opportunities for incorporation into polymers where this serves as a latent crosslinking or branching site and can provide a desirable route to adhesion.

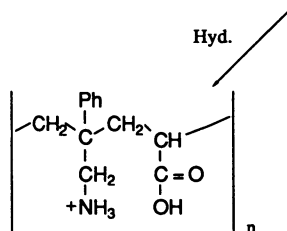
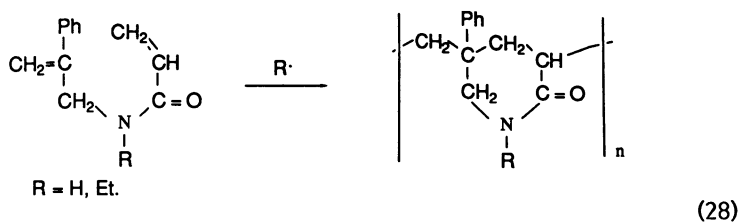
A convenient synthesis of the monomeric methacrylimides was first disclosed by Slagel (128) (Equation 27). A variety of aminimide monomers have been prepared and their polymerization characteristics reported. Culbertson and Slagel (129-131) first reported the polymerization of trimethylamine-4-vinylbenzimidate. Culbertson, Sedor and Slagel (132) also reported the preparation and polymerization of 1,1-dimethyl-1-(2-hydroxypropyl) amine methacrylimide (I) and other derivatives. An excellent review of the chemistry of aminimides was recently prepared by McKillip, et al. (133).

Culbertson, et al. (134-136) have shown that the hydrochloride salt (the hydrazinium form) of 1,1-dimethyl-1-(2-hydroxypropyl) amine methacrylimide more readily copolymerizes with styrene to produce soluble polymers containing pendent quaternary ammonium groups. These polymers can then be treated with base to provide modified polystyrenes containing pendent aminimide residues. The latter polymers can then be thermolyzed in solution or in a solid phase to produce modified polystyrenes containing pendent isocyanate functions. If the thermolysis is carried out in the presence of isocyanate reactive moieties, high molecular weight crosslinked polymers can be synthesized. Several methacrylimide monomers find valuable industrial uses (137).



These monomers are generally used in copolymer systems as isocyanate precursors since they thermolyze to the isocyanate group upon heating. They are very effective in crosslinking and bonding reactions for use in polymeric coatings on metal, rubber (such as for tire cord adhesives) and textiles (such as in shrink-proofing of wool) (138).

**Regular Polyampholytes:** Regular polyampholytes are polymers which contain equal concentrations of both basic and acidic functional groups. There are many reports in the literature on the copolymerization of acid-containing monomers with base-containing monomers, e.g., acrylic acid and vinylpyridine. However, recent studies have shown that some of the original work in this field did not yield polyampholytes at all under the experimental conditions used, but rather homopolymers of one of the ionic monomers with the other present as the counterion. Although many interesting methods (139-142) have been used to synthesize regular polyampholytes, one of the most interesting involves cyclopolymerization of the monomer shown in Equation 28 (143).



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### Some Applications of Water-Soluble Polymers

**Flocculation:** Flocculation of suspended solids from aqueous solutions represents an important area of application of polyelectrolytes. In a laboratory method used to measure the flocculation characteristics of polymers based on that developed by Vilaret (144) a specially prepared kaolinite clay suspension was treated with varying concentrations of polymer, and measurements were made of the equilibrium residual turbidity. Figure 7 shows the results obtained with two polymers of different intrinsic viscosity (145). Residual turbidity is plotted as per cent of initial turbidity ( $T/T_i \times 100$ ) against dosage in micrograms per liter. The turbidity decreases with increasing dosage, reaches a minimum, then increases because of redispersion caused by overtreatment. From these curves one obtains the optimum dosage for coagulation (in this system only) for a particular polymer sample. In the cases shown, the sample with an intrinsic viscosity of 1.36 dl/g has an optimum dosage of 60  $\mu$ g/liter and the sample with an intrinsic viscosity of 0.36 dl/g has an optimum dosage of 125  $\mu$ g/liter.

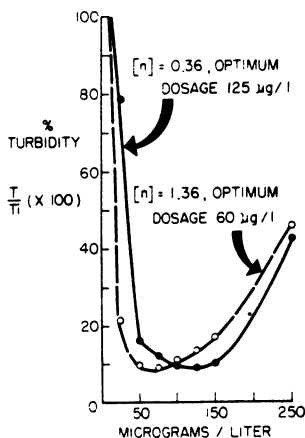


Figure 7. % Residual turbidity vs. poly-DMDAAC dosage. (Reprinted with permission from ref. 145. Copyright 1970 Marcel Dekker, Inc.)

**Sludge Dewatering:** A series of DMDAC-acrylamide copolymers were evaluated for sludge dewatering (145-150). The method of evaluating these polymers was the standard Buchner Funnel Vacuum Filtration Test used in the sewage treatment field. Figure 8 shows the dewatering curves for the copolymers. On the left, volume of filtrate in milliliters is plotted against time in seconds. On the right are the various weight ratios of DMDAAC to acrylamide in the monomer feed. The bottom curve is that obtained with 100% polyacrylamide, which gave identical results to that obtained with no treatment. The third curve from the bottom is that obtained with 100% poly-DMDAAC. Several mixtures of 100% polyacrylamide and poly-DMDAAC were evaluated and in no case were the results as good as that obtained from 100% poly-DMDAAC alone. However, all of the copolymers having >10 mole % of DADMAC were more effective.

The dosage used to obtain these curves was the optimum for each sample and varied from 250 to 350 ppm. The dosage for the top three curves



was 250 ppm, the next two 300, and the rest 350. The curves clearly demonstrate that there is an optimum charge density for a polyelectrolyte used in dewatering digested sewage sludge.

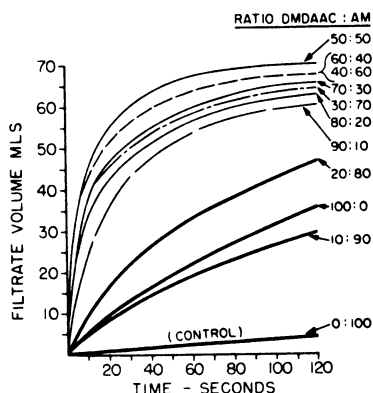


Figure 8. Sewage sludge dewatering curves. (Reprinted with permission from ref. 145. Copyright 1970 Marcel Dekker, Inc.)

Sedimentation of Suspended Polymers: Goodman, et al. (151-152) and others (153), on the basis of a plant-scale study, concluded that the application of a cationic copolymer to the biological oxidation process at a rate of 0.1 lb./ton of secondary effluent dried suspended solids increased the overall BOD removal efficiency of the plant to 95% and decreased the loss of suspended solids in secondary effluent by 99%. At the beginning of this study (153-154) (Figure 9), the secondary effluent suspended solids were 700 mg/l.

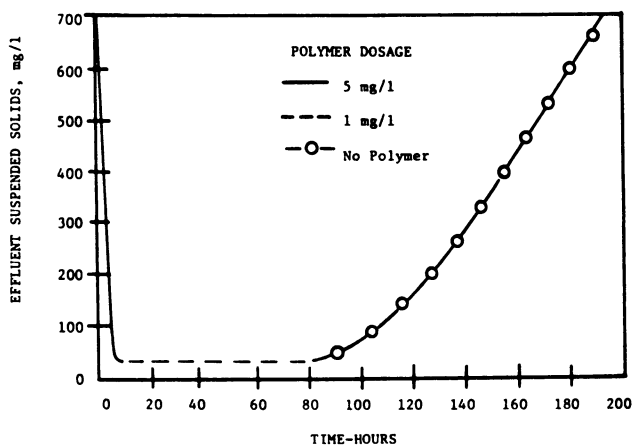


Figure 9. Effect of a cationic polyelectrolyte on secondary sedimentation basin performance. (Reprinted with permission from ref. 150. Copyright 1973 Plenum Press.)

Initially, the copolymer was applied at a treatment dosage of 5 mg/l. Due to the increased capture of suspended solids in the secondary sedimentation basin, the polymer treatment was reduced to 1.0 mg/l and was fed for another 60 hrs. At this treatment dosage, the suspended solids in the secondary effluent remained at 25 mg/l. When the polymer treatment study was stopped at 100 hours, the suspended solids in the secondary effluent gradually increased to 700 mg/l in 90 hours.

**Vacuum Filtration:** Figure 10 illustrates the vacuum filtration of primary sludges. The ferric chloride and lime treatment dosage required to dewater primary sludge is between 3% and 20% (60–100 lb/ton) which results in filtration production rates from a low of 3 lb/ft<sup>2</sup>/hr to a high of 7 lb/ft<sup>2</sup>/hr. The required cationic polyelectrolyte dosage to dewater primary sludge is between 0.2% to 1/2% (4–24 lb/ton), which results in filtration production rates between 6 and 20 lb/ft<sup>2</sup>/hr. (150,154–156).

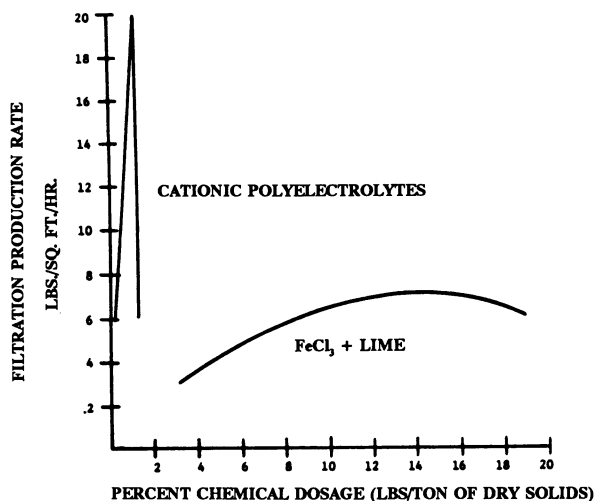


Figure 10. Vacuum filtration of primary sludges. (Reprinted with permission from ref. 150. Copyright 1973 Plenum Press.)

**Electroconductivity in Electrophotography.** The technology associated with electrophotography began with the work of Carlson (157) who developed xerography by utilizing the physics and chemistry of photoconductivity, conductivity, and electrostatics.

An alternative process, developed at RCA (158), involves phenomena similar to xerography, except they all occur on a sheet of specially coated paper. One of the key developments related to this process is the development of commercial electroconductive polymers by several companies. Poly(DADMAC) has been one of the most widely used electroconductive polymers for this purpose. The details of the process are beyond the scope of this review; however, since the conductive polymers conduct via ion transport rather than by an electronic mechanism, the nature of the counter ion affects conductivity. For a series of anions of poly(DADMAC), it was found (Table II) that, in general, the halides are the most conductive and that of these, chloride is the most effective (159). Fortunately, the chloride form of these polymers, typically, is the most economical to produce (160).

TABLE II. Surface Resistivity as a Function of Polymer Anion Form

Anion	Surface Resistivity at 20% RH 0.5 lb/3000 Ft <sup>2</sup> coat weight, ohms
F <sup>-</sup>	$7.4 \times 10^{11}$
Cl <sup>-</sup>	$1.1 \times 10^{10}$
Br <sup>-</sup>	$8.9 \times 10^{10}$
OH <sup>-</sup>	$3.6 \times 10^{12}$
NO <sub>2</sub> <sup>-</sup>	$4.1 \times 10^{10}$
Ac <sup>-</sup>	$2.5 \times 10^{10}$
HSO <sub>4</sub> <sup>-</sup>	$8.2 \times 10^{12}$
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	$4.5 \times 10^{13}$

Figure 11 shows the relative effectiveness of various types of polymers for this application.

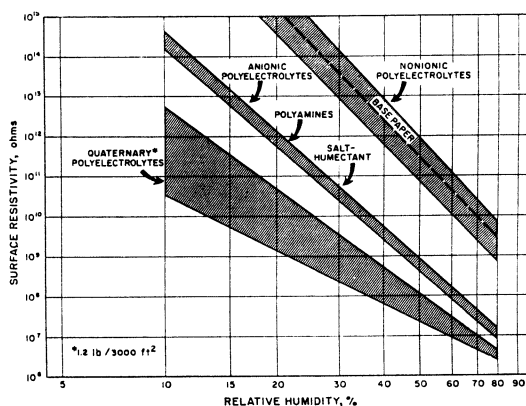


Figure 11. Surface resistivity vs. humidity for polyelectrolytes. (Reprinted with permission from ref. 160. Copyright 1968 Technical Association of the Pulp and Paper Industry.)

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