Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Cationic Quaternary Polyelectrolytes—A Literature Review

M. Fred Hoover[a]
[a] Calgon Corporation, Pittsburgh, Pennsylvania

To cite this Article Hoover, M. Fred(1970) 'Cationic Quaternary Polyelectrolytes—A Literature Review', Journal of Macromolecular Science, Part A, 4: 6, 1327 — 1418

To link to this Article: DOI: 10.1080/00222337008081733

URL: http://dx.doi.org/10.1080/00222337008081733

J. MACROMOL. SCI.–CHEM., A4(6), pp. 1327-1417, October, 1970

Cationic Quaternary Polyelectrolytes — A Literature Review

M. FRED HOOVER

Calgon Corporation
Pittsburgh, Pennsylvania 15230

SUMMARY

This paper is a literature survey of quaternary ammonium, sulfonium, and phosphonium polymers.

Interest in the chemistry of water-soluble polymers (polyelectrolytes) has been continually increasing during the past 20 years. The tremendous scope of utility for water-soluble polymers has led to a vigorous search for new materials and the rapid development of polyelectrolytes into a dynamic field of industrial research. Growth in this field has been especially rapid since 1960; and today, many companies are engaged in synthesis and applications research on polyelectrolytes which are primarily used in four main marketing areas–water treatment, paper, textiles and oil recovery.

Polyelectrolytes are classified into three main groups–nonionic, anionic, and cationic–depending upon the nature of the residual charge on the polymer in aqueous solution (Table 1).

The most versatile and useful type of polyelectrolytes are the cationics, which are comprised again of three classes–ammonium (I°, II°, III° amines and quaternaries), sulfonium, and phosphonium quaternaries as shown in Table 2.

While the polyamines constitute a large class of materials with diverse industrial applications, they vary widely in the starting materials and cookbook recipes used in their synthesis (most are condensation polymers),

Table 1. Polyelectrolytes

Nonionic	Anionic	Cationic
Polyols	Carboxylic	Ammonium
Polyethers	Sulfonic	amines quaternaries
Polyamides	Phosphonic	Sulfonium
Poly (N-vinyl heterocyclics)		Phosphonium

subsequent treatments, and their formulation with other materials for application. They are limited in many applications by their generally low molecular weight and charge-pH dependency. Therefore, in recent years polyelectrolyte monomer/polymer synthesis efforts have been increasingly concentrating on the quaternary polycationics.

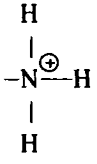
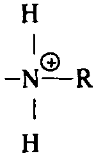
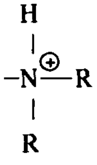
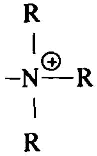
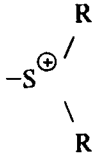
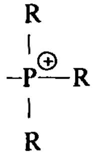
Cationic quaternary polyelectrolytes have many industrial applications; the list in Table 3 is an indication of their varied uses.

In view of the functional utility of these materials and the present interest in quaternary polyelectrolytes, it is surprising that there has not been any form of literature review published on these materials. This may be due, in part, to the great diversity of structural types of polyquaternaries and also to the fact that much of this research is being conducted in highly competitive industrial laboratories.

This paper is an attempt to survey the literature on quaternary polyelectrolytes and to present some of the main literature references to the synthesis and application of the quaternary polyelectrolytes in a systematic manner by structural type. In order to facilitate this review the three basic types of quaternary cationic polyelectrolytes (ammonium, sulfonium, and phosphonium) reported in the literature have been arranged into the structural categories shown in Table 4, according to the position of the quaternary N, S or P heteroatom within the polymer.

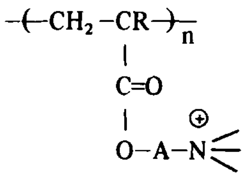
Since almost all of the polyquaternaries reported in the patent and journal literature can be put into one of these structural classes, this classification system provides a suitable guideline for presenting a review on polyquaternaries.

Table 2. Cationic Polyelectrolytes

I. Ammonium I°, II°, III° amines (protonated)	 $H-\overset{\oplus}{N}H_2-H$ (with $-$ bond) I°	 $-\overset{\oplus}{N}H_2-R$ II°	 $-\overset{\oplus}{N}HR-R$ III°
Quaternary		 $-\overset{\oplus}{N}R_2-R$	
II. Sulfonium		 $-\overset{\oplus}{S}R_2$	
III. Phosphonium		 $-\overset{\oplus}{P}R_2-R$	

1. QUATERNARY AMMONIUM POLYMERS

1. Poly[(meth)acryloxyalkyl Ammonium]


$-(CH_2-CR)_n-$, $C{=}O$, $O-A-\overset{\oplus}{N}<$

Amino-containing monomer/polymer systems derived from aminoalkyl-acrylates and methacrylates have been one of the most extensively used types of cationic polymers [1]. The methacrylate monomer is generally preferred for its greater reactivity in polymerizations and, therefore, the majority of references pertain to the use of this monomer type. Most of the published

Table 3. Some Industrial Applications for Cationic Quaternary Polyelectrolytes

1. Primary coagulants
2. Flocculants for solids-liquid separation processes
3. Antistatic agents
4. Soil conditioning
5. Flame retardants
6. Hair sprays, additives to shampoos, soaps, and other cosmetics
7. Sequestering agents and additives to detergents
8. Grease thickening
9. Electroconductive coatings
10. Anion exchange resins
11. Biocides, nematocides, fungicides, etc.
12. Dye mordants and dyeable assists in fibers and photographic film
13. Pigment retention aids and drainage aids in papermaking
14. Wet and dry strength additives in paper
15. Emulsion stabilizers and emulsifiers (also demulsifiers)
16. Corrosion inhibitors
17. Softening agents for fabrics and paper
18. Silver halide peptizers and sensitizers for photographic film
19. Polysalt complexes
20. Permselective membranes
21. Lubricating oil additives
22. Isolation of protein fractions by forming an insoluble complex and regenerating the protein
23. Functional coatings for adhesion, curing, etc.
24. Printing inks
25. Adhesives

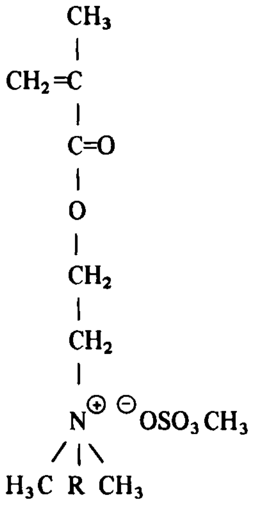
Table 4. Types of Cationic Quaternary Polyelectrolytes

I. Quaternary Ammonium Polymers
  1. Poly(meth)acryloxyalkyl
  2. Poly(meth)acrylamidoalkyl
  3. Polyalkenyl
  4. Polyvinyloxy
  5. Polyvinylbenzyl
  6. Polydiallyl (quaternary ammonium cyclopolymers)
  7. Polyvinylpyridinium
  8. Polyvinylimidazolinium (and other heterocyclics)
  9. Polyalkylation quaternaries "Ionenes")–$N^{\oplus}$ in polymer chain
  10. Polycondensation quaternaries–$N^{\oplus}$ not in polymer chain

II. Sulfonium Polymers
  1. Polyacrylic
  2. Polyvinylbenzyl
  3. Polydiallyl
  4. Polycondensation

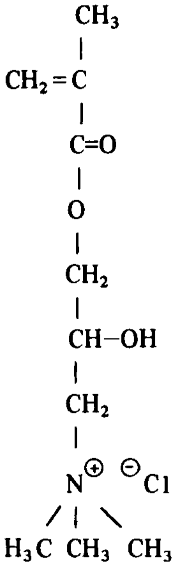
III. Phosphonium Polymers
  1. Polyvinyl
  2. Polyacrylic
  3. Polyvinylbenzyl
  4. Polycondensation

work on the quaternary ammonium methacrylates can be conveniently divided into two areas, depending upon the structure of the methacrylate monomer [2]: 2-methacryloxyethyl trialkylammonium (Structure I) and 3-methacryloxy-2-hydroxypropyl trialkylammonium (Structure II).



I

2-methacryloxyethyl (usually trimethylammonium methylsulfate)



II

3-methacryloxy-2-hydroxypropyl (usually trimethylammonium chloride)

A. Poly(2-methacryloxyethyl Trialkylammonium). Barney [3, 4] first quaternized dimethylaminoethyl methacrylate and prepared homopolymers and copolymers with acrylonitrile containing 1-15% 2-methacryloxyethyl trimethylammonium methylsulfate or ρ-toluenesulfonate to enhance the dyeability of acrylic fibers. Forshey and Kirby [5] also prepared acrylonitrile copolymers with 2-methacryloxyethyl trimethylammonium methylsulfate for enhanced fiber dyeability.

Dimethylaminoethyl methacrylate was quaternized with chloroacetate esters by Winberg [6] to form methacryloxyethyl carboalkoxymethyl dimethylammonium chloride for copolymerization with acrylonitrile for enhanced acid dyeability of fibers.

Maeder [7] prepared water-dispersible copolymers with acrylic esters using quaternary monomers derived from β-diethylaminoethyl acrylate or β-diethylaminoethylfumarate and chloroacetamide.

Jackson and Wilkinson [8] prepared polyampholytes by terpolymerizing 2-methacryloxyethyl trimethylammonium methylsulfate, 2-methyl-2-

propenesulfonate, and acrylonitrile for enhanced acid and basic dye receptivity.

A recent Belgian patent [9] also describes the use of copoly(acrylonitrile-quaternary acrylic esters) in the thiocyanate anion form as an additive to polyacrylonitrile to enhance its dyeability.

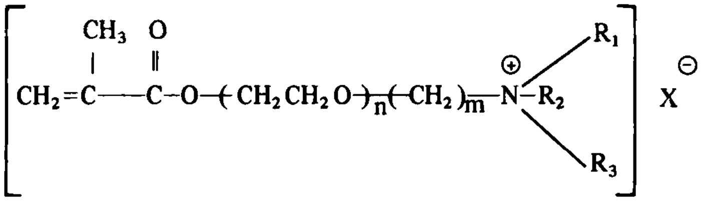
A British patent [10] describes sulfobetaine monomers and polymers of aminoacrylates made by quaternizing dimethylaminoethyl methacrylate with propanesultone and the use of these polymers in various paper and textile coatings.

Hartmann [11] also improved the heat stability of acrylonitrile by copolymerization with 2-methacryloxyethyl trimethylammonium methylsulfate followed by treatment with hydrofluoboric acid.

This type of quaternary polymer has been extensively proposed for antistatic treatment of textiles. Hughes [12] complexed poly(2-methacryloxyethyl trimethylammonium methylsulfate) with fatty alcohol sulfates to prepare an antistatic textile finish, and Bacon and Hughes [13] treated textiles with dilute aqueous solutions of this polyquaternary followed by treatment with a solution of a fatty carboxylate or sulfate salt. Hayek [14, 15] prepared the polyquaternary salts with hydrocarbon sulfates and fatty carboxylic acids for antistatic textile finishes.

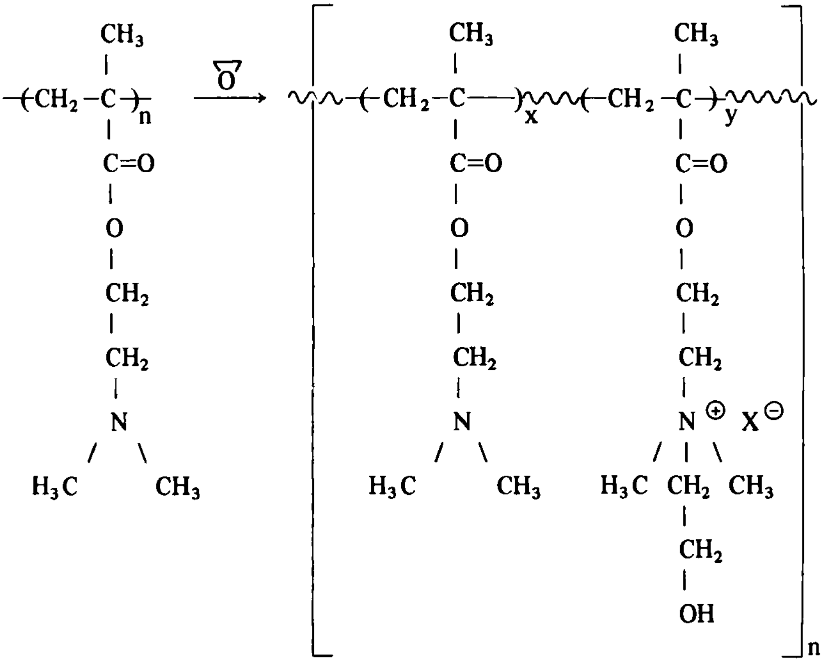
By combining poly(methacryloxyethyl trialkylammonium methylsulfate) with various anionic polyelectrolytes, Jackson [16, 17] prepared durable antistatic finishes for textiles.

Combere and Reed [18] prepared methacrylate esters of β-diethylaminoethyl ether of various ethylene glycols followed by quaternization with dimethylsulfate then polymerization and used the resulting polyacrylic ether quaternaries as antistatic agents (Structure III).



III

Gruntfest and Fordyce [19] partially quaternized poly(dimethylaminoethyl methacrylate) with ethylene oxide to prepare polyquaternaries useful as pigment retention aids in papermaking; Fordyce, Glavis, and Melamed [20] used these same polyquaternaries as flocculants for dewatering aqueous suspensions (Eq. 1).



[19, 20]

(1)

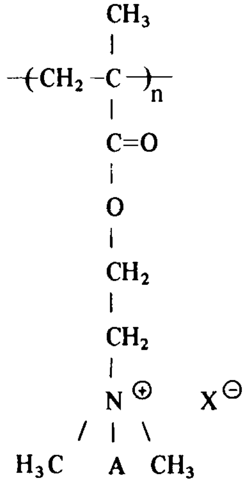
Grey and Webers [21, 22] prepared copolymers of dimethylaminoethyl methacrylate with the trimethylammonium methylsulfate quaternary salt for use as a dye mordant in photographic film.

Melamed prepared a series of poly(trialkylammonium ethyl methacrylates)–N-allyl [23, 24], N-alkoxymethyl [25], N-carbonamido [26], and N-ureido [27]–which are water soluble, but capable of curing to an insoluble form upon heating for textile antistatic and various paper treatments (Structure IV).

Clapp and Yee [28] used poly(2-methacryloxyethyl trimethylammonium methylsulfate) to prepare cationically dispersed vat dyes.

Guenthner [29] prepared oil and water repellent compositions by polymerizing quaternary methacrylates containing the N-perfluoroalkyl sulfonamido group, and Marascia et al. [30] prepared cationic wax emulsions for repellency coatings by using quaternary acrylate polymers. Also Mackenzie [31] used the quaternary aminoalkylmethacrylates to retain perfluoroalkyl phosphates on pulp to produce oil repellent paper.

Nixon, Berrigan, and Williams [32] prepared copolymers of acrolein with 2-methacryloxyethyl trimethylammonium methylsulfate for wet strength



A = $-CH_2-CH=CH_2$

= $-CH_2-O-CH_3$

= $-CH_2CONHCH_2O-$(H or R)

= $-CH_2CONHCONH-$(H or R)

IV [23-26]

agents in paper, and Daniel [33] prepared sizing agents for paper by quaternizing co- and terpolymers of styrene-fatty acrylate-dimethylaminoethyl methacrylate with benzyl chloride to introduce hydrophilic (ionic) sites into the polymer for fiber substantivity.

Copolymers of acrylamide and 2-methacryloxyethyl trimethylammonium methylsulfate have been extensively studied for their use as flocculants, pigment retention aids [34], etc.

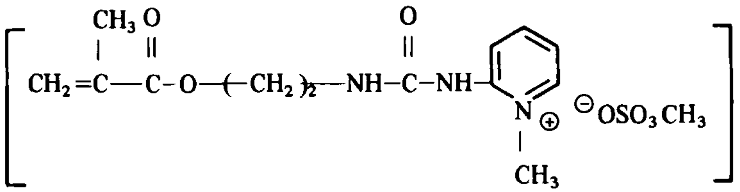
Monagle and Shyluk [35] disclosed a precipitation polymerization process for making acrylamide copolymers with 2-methacryloxyethyl trimethylammonium methylsulfate in a 35-70% tertiary-butanol/water mixture wherefrom the cationic copolymer precipitates as it is formed. Monagle [36] also used various salts along with the tert-butanol/water mixture to provide a solvent media for this precipitation polymerization process.

Recently, Fujimoto [37] prepared antistatic textiles by treating the material with a wide variety of polyquaternary ammonium resins, including poly(2-methacryloxyethyl trimethylammonium methylsulfate), and then polyanionic materials to form an insoluble polysalt-type of film. (See also Jackson [16, 17].)

Szita et al. [38] made quaternary urea-type methacrylate monomers to be copolymerized with acrylonitrile for dye receptivity (Structure V).

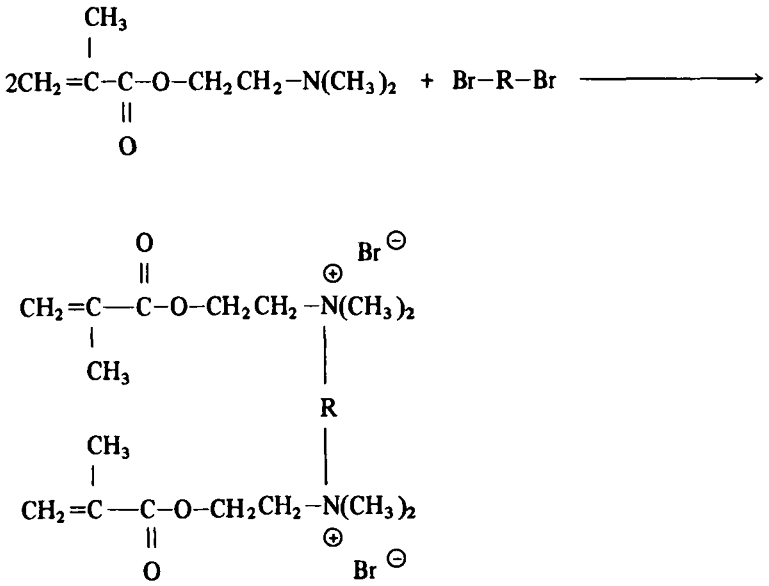
Kirby [39] prepared dye intermediates for photographic film by quaternizing poly(dimethylaminoethyl methacrylate) with dye moieties.

Overberger, Biletch, and Nickerson [40] reported the copolymerization of 2-methacryloxyethyl triethylammonium iodide with 4-vinylpyridine.



V

Rembaum, Singer, and Keyzer [41] made dicationic methacrylic and diallylic compounds for cross-linking agents to make quaternary ammonium group-containing gels, anion exchange resins, permselective membranes, etc. (The analogous compounds were reported in 1951 by Anthes [42] when he synthesized diquaternaries based on γ-dimethylaminopropyl acrylamide with dihalides and used the resulting monomers to make anion exchange resins. Also, Haas and Taylor, U.S. Patent 3,309,376, employed diquaternary dialdehydes to form cross-linked cationic polymers for dye mordants.) (Eq. 2.)



$$2CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2CH_2{-}N(CH_3)_2 + Br{-}R{-}Br \longrightarrow$$

$$\begin{array}{l} CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2CH_2{-}\overset{\oplus}{N}(CH_3)_2 \; Br^{\ominus} \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\quad R \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2CH_2{-}\underset{\oplus}{N}(CH_3)_2 \; Br^{\ominus} \end{array} \qquad (2)$$

[41, 42]

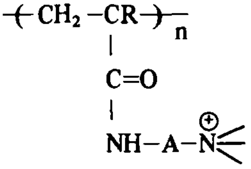
B. Poly(3-methacryloxy-2-hydroxypropyl Trialkylammonium). Recently, Sobolev [43] synthesized another very interesting quaternary acrylate monomer by the reaction of methacrylic or acrylic acid, epichlorohydrin and trimethylammonium chloride. Sobolev [44] also prepared homopolymers and copolymers (using persulfate redox catalyst systems) of 3-methacryloxy-2-hydroxypropyl trimethylammonium chloride with acrylamide, acrolein, etc., which were proposed for wet and dry strength agents in paper, retention aids, flocculants, antistats, etc. Mills [45] prepared terpolymers of 3-methacryloxy-2-hydroxypropyl trimethylammonium chloride with acrolein and other monomers for treating paper–especially for wet strength properties–and textiles.

DeBenedictis and Sobolev [46, 47] discuss the use of poly(3-methacryloxy-2-hydroxypropyl trimethylammonium chloride) as a flocculant in the separation of solids from aqueous suspensions. Both homopolymers and copolymers are used either alone or in conjunction with an anionic polyacrylamide in a dual treatment.

Many years ago, Hwa [48, 49] prepared polymeric anion exchange resins containing the 3-methacryloxy-2-hydroxypropyl trimethylammonium chloride group by treatment of a cross-linked polymer containing glycidyl methacrylate or 3-chloro-2-hydroxypropyl methacrylate with trimethylamine, and Bergmeister and Hackmair [50] used poly(3-methacryloxy-2-hydroxypropyl trimethylammonium chloride) to stabilize cationic emulsion polymers (Eq. 3).

In a recent Belgian Patent, Schaper and Hoover [51] discuss the use of these types of polyacryloxyalkyl and also polyamidoalkyl quaternary ammonium resins for electroconductive coatings on paper.

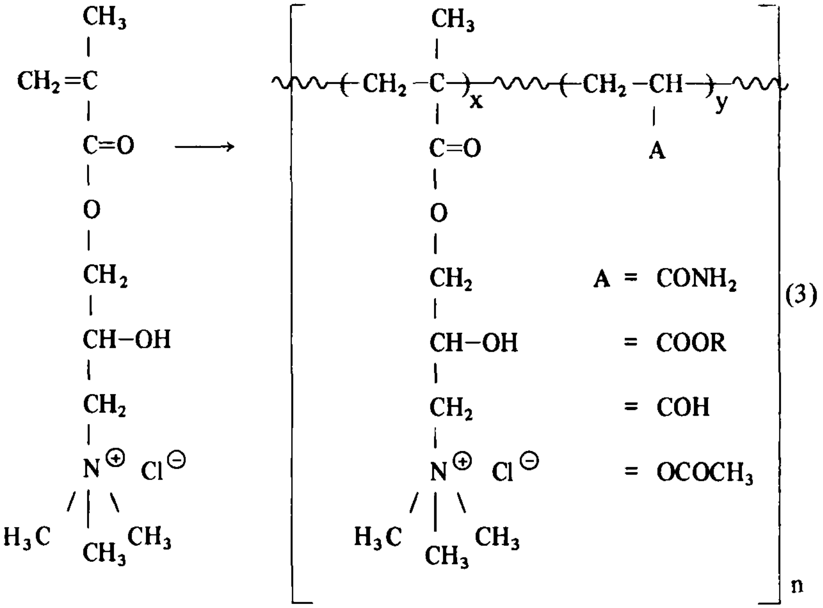
2. Poly[(meth)acrylamidoalkyl Ammonium]



$$\left(CH_2-\underset{\begin{array}{l}|\\ C{=}O\\ |\\ NH{-}A{-}\overset{\oplus}{N}\lessgtr\end{array}}{CR} \right)_n$$

In like manner to the dialkylaminoalkyl(meth)acrylic esters, the N-(dialkylaminoalkyl) acrylamides have been extensively used for making amino-containing polymers for dye receptivity, antistatic coatings, etc. However, not as much work has been reported on the corresponding quaternary aminoalkyl acrylamides as on the quaternary aminoalkyl acrylic esters.

Anthes [42] quaternized N(γ-dimethylaminopropyl)acrylamide with trimethylene dibromide to prepare diquaternary monomers which he polymerized to form gels with anion exchange properties, as mentioned above.



(3)

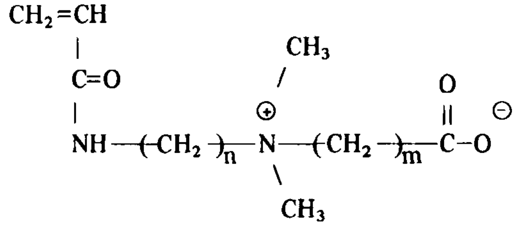
[43-46], 50]

Shacklett [52-54] prepared betaine monomers by quaternizing dimethylaminoethyl and propyl acrylamide and methacrylamide with chloroacetates, β-propiolactone, propanesultone, etc., and terpolymerized these monomers with methacrylamide and dihydroxyalkyl acrylamides to prepare gelatin substitutes for photographic film, protective colloids, dispersing agents, etc. (Structure VI).

Schuller and Thomas [55] also prepared acrylamidopropyl dimethyl carboxymethylammonium betaine. Homopolymers and copolymers of this monomer with acrylamide were proposed as dry strength agents for paper, textile treating agents, soil conditioners, etc., and copolymers with acrylonitrile gave fiber compositions with enhanced dye receptivity.

A British Patent [10] describes sulfobetaine monomers and polymers of aminoalkylacrylamides made by quaternizing dialkylaminoalkyl acrylamides with propanesultone and the use of these polymers in various paper and textile coatings.

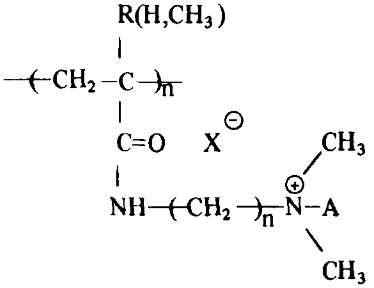
Melamed [23] also prepared a series of quaternary aminoalkyl acrylamides analogous to the acrylic esters, containing reactive N-allyl [24], N-alkoxymethyl [25], N-carbonamido [56], ureido groups [26, 27], which are capable of being rendered insoluble to provide durable antistatic textile finishes and paper strength agents (Structure VII).



$$CH_2{=}CH{-}C({=}O){-}NH{-}(CH_2)_n{-}\overset{\oplus}{N}(CH_3)_2{-}(CH_2)_m{-}C({=}O){-}O^{\ominus}$$

n = 2 or 3
m = 1 or 2

VI [52-55]



$$-(CH_2-C(R)(H,CH_3))_n- \quad C({=}O){-}NH{-}(CH_2)_n{-}\overset{\oplus}{N}(CH_3)_2{-}A \quad X^{\ominus}$$

where A = $-CH_2CH{=}CH_2$
= $-CH_2-O-CH_3$
= $-CH_2CONH_2$
= $-CH_2CONH-CH_2-OH$
= $-CH_2CONH-CH_2-OR$
= $-CH_2CONHCONHR$

VII [23-27, 56]

Melamed [57] also prepared various copolymers with quaternary ammonium alkyl acrylamides, where a benzyl or fatty alkyl group was one of the substituents on the quaternary nitrogen, which had fungicidal and bacteriostatic properties.

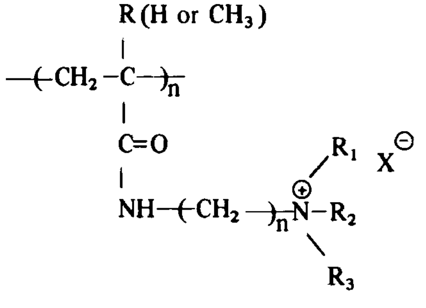
Wilson, Thomas, and Padbury [58] prepared (3-acrylamidopropyl)benzyl dimethyl ammonium chloride homopolymers and copolymers with acrylamide, ethyl acrylate, etc., and used these cationic resins for dry strength agents in paper.

Maeder [59] prepared cationic emulsion copolymers utilizing various quaternary aminoethyl and propyl acrylamides which have epoxypropyl and acetamido functional groups on the nitrogen for textile, paper, and leather coatings.

Fujimoto [37] prepared antistatic textile finishes by first treating the material with a polyquaternary resin, such as poly(acrylamidoethyl and propyl trialkyl ammonium salts), and then with polyanionic resins.

Gustafson and Lirio [60] studied the anion exchange properties of poly(3-acrylamidopropyl trimethylammonium chloride) cross-linked with about 4% divinylbenzene and compared the organic anion adsorption properties of this resin to a poly(vinylbenzyltrimethyl) ammonium chloride resin.

Jones [61] prepared many varieties of monomeric methacrylamido- and acrylamidoalkyl trialkylammonium salts by the reaction of an N,N-disubstituted diamine with acrylyl or methacrylyl chloride and then followed by subsequent quaternization of the tertiary amine. Jones [62] also prepared quaternary ammonium homopolymers from these monomers in 20-50% aqueous solutions using ammonium persulfate at 90-100°C. Baird, Batty, Henshall, and Jones [63] discussed the use of these poly(acrylamidoalkyl quaternary salts) as antistatic finishes for textiles (Structure VIII).



$R_1/R_2/R_3$ = alkyl C_{1-4}
= benzyl
= allyl

n = 2 or 3

$X = \overset{\ominus}{Cl}, \overset{\ominus}{Br}, \overset{\ominus}{OSO_3}CH_3, p-CH_3-\phi-\overset{\ominus}{SO_3}$

VIII [61-63]

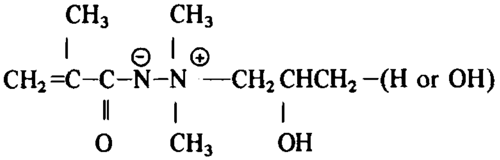
Olaj and Maeder [64] found that terpolymers of quaternized N,N-dialkylaminoalkyl acrylamide (with chloroacetamide) and N-vinylpyrrolidone and acrylic acid were useful as leveling agents for vat dyes.

Poly(aminimides). Another class of compounds that has potential utility in making cationic polyelectrolytes is the aminimides; however, to date these materials have been initially explored for coating applications because of their thermolysis to isocyanates. (See Brit. Patent 1,165,012.)

Culbertson and Slagel [65] reported on the homo- and copolymerization of trimethyl methacrylimide, which when neutralized becomes essentially a poly(acylhydrazinium quaternary salt).

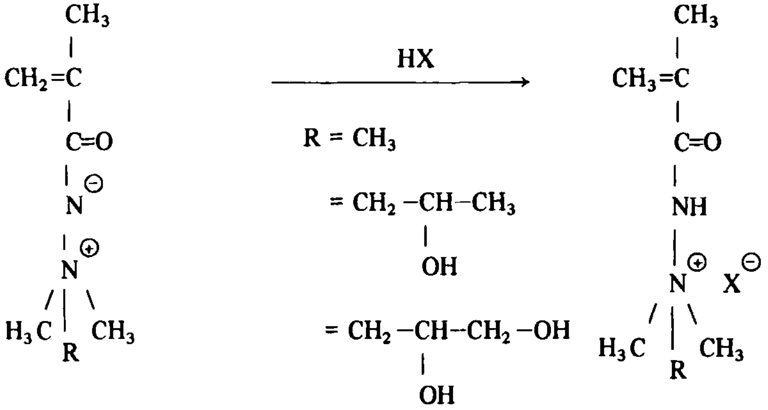
Culbertson et al. [66] reported on trimethylamine-4-vinylbenzimide,

$CH_2{=}CH{-}\phi{-}CO\overset{\ominus}{N}{-}\overset{\oplus}{N}(CH_3)_3$ and Culbertson, Sedor, and Slagel [67] discussed the monomer/polymer properties of two new methacrylimides containing the hydroxypropyl group (Structure IX, Eq. 4).



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{N}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{\oplus}{N}}}-CH_2\underset{\underset{OH}{|}}{C}HCH_2-(\text{H or OH})$$

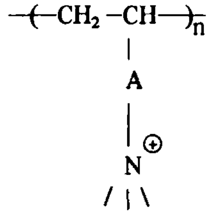
IX



(4)

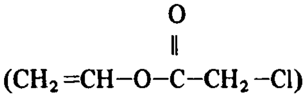
[65-67]

3. Polyalkenyl



$$-\!\left(CH_2-\underset{\underset{\underset{\underset{\underset{/\,|\,\backslash}{\overset{\oplus}{N}}}{|}}{A}}{|}}{CH}\right)_{\!n}\!-$$

Polyvinyl Ammonium. There are many references to the preparation of polyvinyl amines; however, there is little published on quaternary vinylammonium polymers. The carbon-carbon double bond in an α-position to a quaternary ammonium or sulfonium group is not very stable and compounds of this type decompose by disproportionation. Therefore, little progress has been made in the synthesis of polyvinyl quaternary ammonium or sulfonium resins. Two general approaches have been used in attempts to synthesize vinyl ammonium compounds: 1) vinylation of amines with acetylene [68, 69]; 2) dehydration of choline or choline chloride or the dehydrohalogenation of β-chloroethyl-trialkyl amines [70]. Many vinyl ammonium polymers have been prepared, however, where the quaternary nitrogen is not bonded directly to a backbone carbon atom.



Ham and Gann [71] used vinylchloroacetate $(CH_2{=}CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}Cl)$ monomer as a means for introducing a quaternary ammonium group into polyacrylonitrile fibers to enhance their affinity for acid dyes. They prepared acrylonitrile-vinyl chloroacetate copolymers and subsequently reacted the copolymers in DMF with amines. The use of primary and secondary amines resulted in gellation, but tertiary alkyl amines or pyridine gave soluble quaternaries (Eq. 5).

Daniel [72] prepared copolymers of from 1-50% vinyl chloroacetate with vinyl acetate and vinyl stearate followed by quaternization with tertiary amines (specifically, pyridine) in a water miscible organic solvent to obtain quaternary resins for treating cellulosic materials to enhance dyeability and adhesion properties. Sexsmith [73] quaternized the copolymer of vinyl stearate and vinyl chloroacetate with pyridine on a neat basis without the use of solvents at a temperature above the melting point of the copolymer.

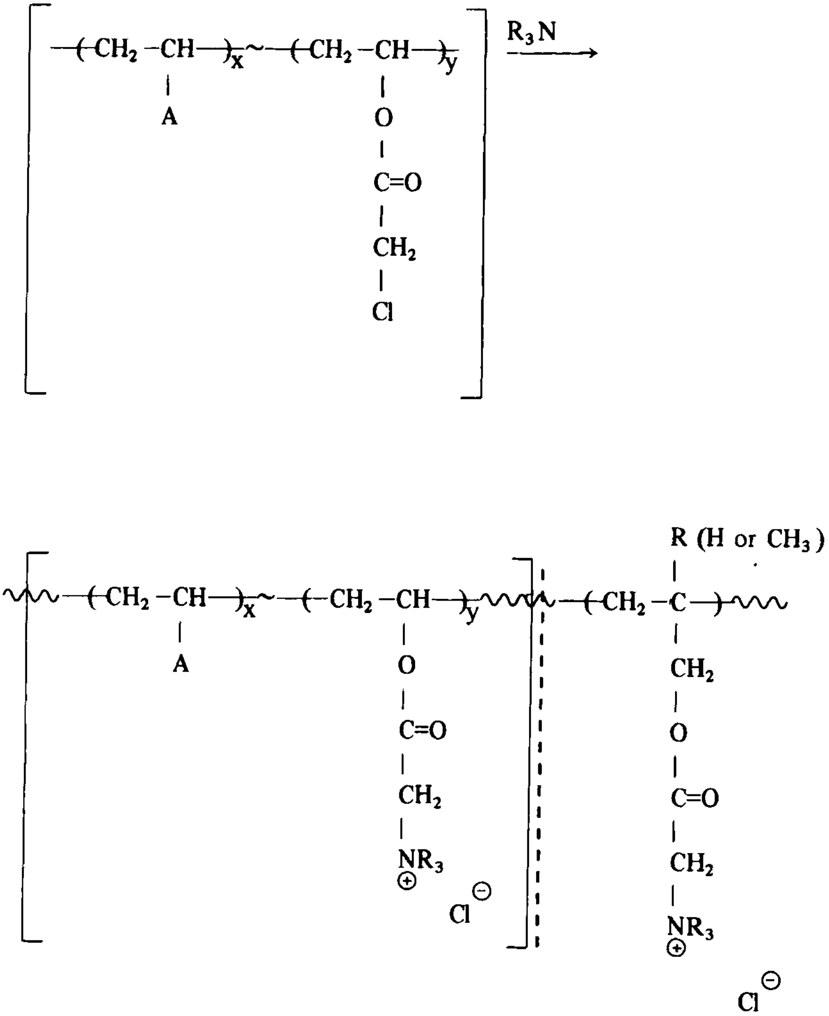
Newport and Reynolds [74] studied the quaternization of poly(vinyl chloroacetate) with pyridine to prepare quaternary polyelectrolytes and also their cross-linking with 4,4′-bipyridine.

Levy, Newport, and Reynolds [75] claim that partially quaternized (30-60%) homopolymers and copolymers of vinyl chloroacetate with vinyl acetate are useful as flocculants.

Heseltine and Brooks [76] used the polyquaternary derived from pyridination of polyvinyl chloroacetate [poly(vinylpyridinium acetate) chloride] as a dye mordant in photographic film.

Because the quaternized vinyl chloroacetate copolymers are not hydrolytically stable and tend to gel or cross-link, Ham, Craig, and Gann [77] investigated the use of allyl- and methallyl chloroacetate copolymers with acrylonitrile. After quaternization with trimethylamine the allyl chloroacetate copolymers gelled, whereas the methallyl chloroacetate copolymers remained stable.

Ham [78] prepared (carbovinyloxymethyl) trimethyl ammonium chloride quaternary monomers by reacting vinyl chloroacetate with tertiary



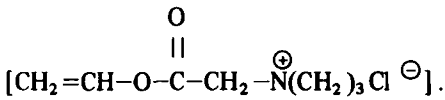
$$\left[-\!\left(CH_2-\underset{\substack{|\\ A}}{CH}\right)_x\!\sim\!\left(CH_2-\underset{\substack{|\\ O\\ |\\ C=O\\ |\\ CH_2\\ |\\ Cl}}{CH}\right)_y \right] \xrightarrow{R_3N}$$

$$\sim\!\left[\left(CH_2-\underset{\substack{|\\ A}}{CH}\right)_x\!\sim\!\left(CH_2-\underset{\substack{|\\ O\\ |\\ C=O\\ |\\ CH_2\\ |\\ \overset{\oplus}{N}R_3 \quad Cl^{\ominus}}}{CH}\right)_y \right]\!\sim\!\left(CH_2-\overset{\substack{R\ (H\ or\ CH_3)\\ |}}{\underset{\substack{|\\ CH_2\\ |\\ O\\ |\\ C=O\\ |\\ CH_2\\ |\\ \overset{\oplus}{N}R_3 \quad Cl^{\ominus}}}{C}}\right)\!\sim$$

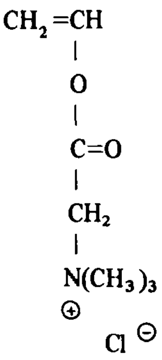
where A = $-CN$, $-OCOCH_3$ or $-CO_2R$

[71-73, 75, 77]

(5)

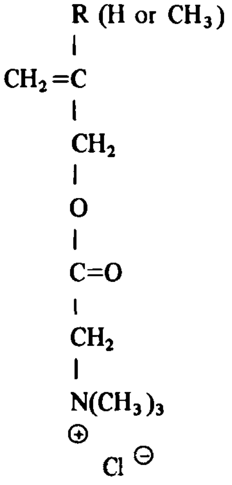
amines  $[CH_2{=}CH{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}\overset{\oplus}{N}(CH_2)_3Cl^{\ominus}]$. Acrylonitrile was then copolymerized with 2-25% of the (carbovinyloxymethyl) quaternary monomer to provide fibers with enhanced acid-dye affinity (Structure X).

In like fashion, Ham [79] copolymerized acrylonitrile with up to 15% (carboallyloxymethyl) trimethylammonium chloride (Structure XI).



$CH_2{=}CH{-}O{-}C({=}O){-}CH_2{-}\overset{\oplus}{N}(CH_3)_3\ Cl^{\ominus}$

X [78]



$R\,(H \text{ or } CH_3)$: $CH_2{=}C(R){-}CH_2{-}O{-}C({=}O){-}CH_2{-}\overset{\oplus}{N}(CH_3)_3\ Cl^{\ominus}$

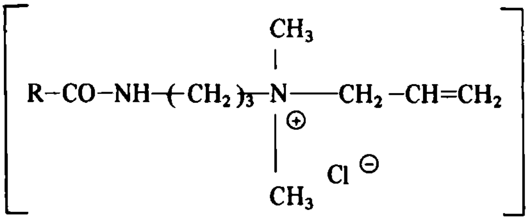
XI [79]

Poly(meth)allyl Ammonium. Butler and Ingley [138] reported that monoallyl trimethyl ammonium bromide, failed to polymerize when subjected to a free radical peroxidic catalyst—which is in accordance with the general observation that monoallyl compounds do not polymerize well due to degradative chain-transfer.

Price [80] reported using allyl γ-myrist(or stear)amidopropyl dimethyl ammonium chloride as a comonomer for dyeable fibers and antistatic compositions. Schuller and Thomas [81] copolymerized allyl dimethyl carboxymethylammonium betaine with acrylonitrile for enhanced dye receptivity and with acrylamide for paper coatings (Structure XIII).

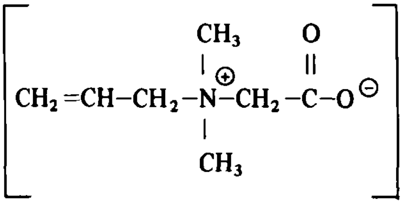
Nixon, Berrigan, and Williams [32] copolymerized acrolein with a variety of quaternary ammonium monomers, including trimethyl allyl ammonium chloride, to prepare cationic polyaldehydes useful for imparting wet-strength to paper.

Naraski [82] quaternized low molecular weight oligomers of allyl chloride



$$\left[R{-}CO{-}NH{-}(CH_2)_3{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{N^{\oplus}}}}}{-}CH_2{-}CH{=}CH_2 \quad Cl^{\ominus} \right]$$

XII

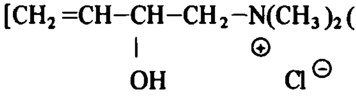


$$\left[CH_2{=}CH{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{N^{\oplus}}}}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}O^{\ominus} \right]$$

XIII

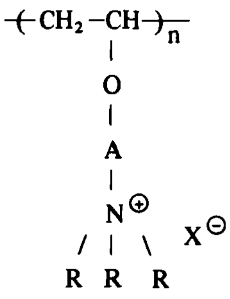
with N-dodecylpiperidine and dimethyldodecylamine to obtain cationic polysoaps and studied their wetting and solubilizing characteristics.

Lytton [83] prepared copolymers of acrylonitrile with dimethylbenzyl (2-hydroxy-3-butenyl) ammonium chloride for increased acid dye receptivity



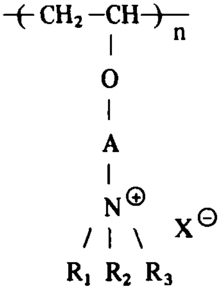
$$[CH_2{=}CH{-}\underset{OH}{\underset{|}{CH}}{-}CH_2{-}\overset{\oplus}{N}(CH_3)_2(CH_2\phi)] \; Cl^{\ominus}.$$

4. Poly(vinyloxyalkyl Ammonium)



$$\left(CH_2{-}\underset{\displaystyle \underset{\displaystyle \underset{\displaystyle \underset{\displaystyle R\;\;R\;\;R}{N^{\oplus}}}{\overset{|}{A}}}{\overset{|}{O}}}{\overset{}{\underset{|}{CH}}} \right)_n \quad X^{\ominus}$$

Barney [84] first prepared homopolymers of vinyloxyalkyl trialkyl quaternary ammonium monomers in the early 1950s and also copolymers with acrylonitrile for fibers with enhanced dye receptivity (Structure XIV). Many other uses for polymers of aminoalkylvinyl ethers have also been proposed [85].



XIV

[84]

$A = -CH_2CH_2-$

$R_1 = R_2 = R_3 = CH_3$

$X^{\ominus} = Cl^{\ominus}$ or $^{\ominus}OSO_3CH_3$

[86]

$A = -(CH_2)_n-$, where n = 2 or 3

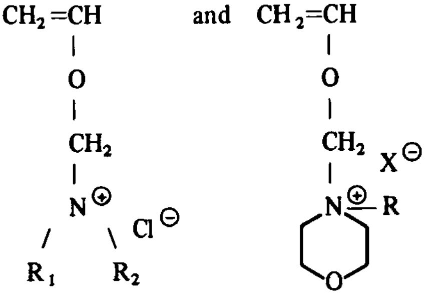
$R_1 = R_2 = CH_3$

$R_3 = -CH_2-\phi, -CH_2CH_2-O-\phi, -CH_2-\phi-(CH_2)_{11}-CH_3$

$= -(CH_2)_n-CH_3$, n = 6-19

Melamed [86] also prepared polymers of quaternary aminoalkylvinyl ethers, where A is ethylene and trimethylene and the substitutents on the quaternary nitrogen are benzyl, phenoxyethyl, and C_{12} to C_{18} fatty tails. These polymers are claimed to have good fungicidal and bactericidal properties and are proposed as additives in chicken feeds, etc.

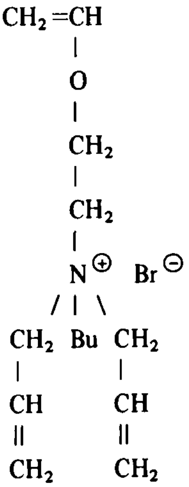
Maeder and Albrecht [87] prepared aqueous emulsion copolymers using styrene or acrylic esters with quaternary vinyl ethers having structures XV which were used for textile, leather, and metal coatings.



XV [87]

$R = R_1 = R_2$ = carboxamidomethyl
= glycidyl
= lower alkyl

Butler and Goette [88] investigated the polymerization of unsaturated (allyl) vinyloxyethyl quaternary ammonium compounds and observed that diallylbutyl-β-vinyloxyethyl ammonium bromide yielded a water-soluble polymer with the vinyloxyethyl group not polymerized. The triallyl analogue produced cross-linked insoluble polymers (Structure XVI).



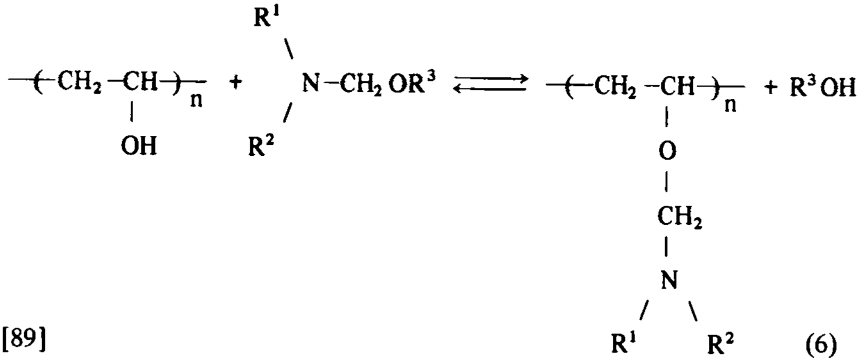
XVI [88]

This is now understood to be due to the cyclopolymerization of the diallyl groups to form a linear cyclic ammonium polymer.

Reynolds [89] has synthesized polyvinyloxymethyl quats by reacting N,N-disubstituted alkoxymethylamines with polyvinyl alcohol followed by subsequent quaternization (Eq. 6). These polyvinyloxymethylammonium quats are said to be useful as dye mordants, silver halide peptizers, sensitizers, and antistatic agents.

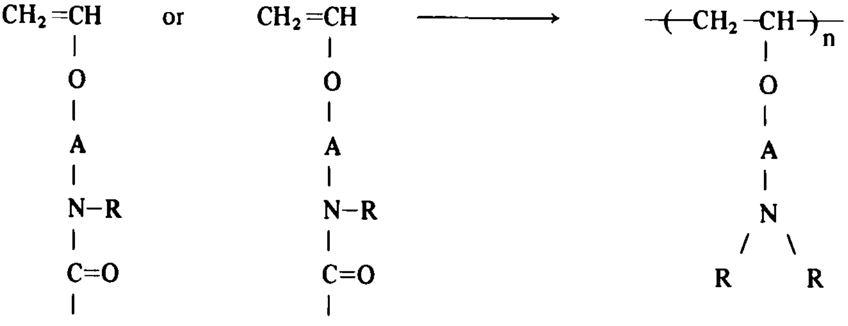
While quaternary aminoalkylvinylethers polymerize quite readily, the tertiary aminoalkylvinylethers cannot be homo- or copolymerized very well. Very high catalyst concentrations (ca. 10-15% BOM) are required and various catalysts have yielded only very low molecular weight polymers with low conversions [90].

Melamed [90] has found that amidoalkylvinylethers are capable of being polymerized to high molecular weight and the resulting polymers can then be hydrolyzed to provide a poly(aminoalkylvinylether) indirectly. The amidoalkylvinylether may be a carbonamidoalkyl or a carbamidoalkylvinylether (ureidoalkylvinylether) (Eq. 7).



$$-\!\!\left(CH_2-\underset{\substack{|\\OH}}{CH}\right)_{\!n}\!- \;+\; \begin{matrix}R^1\\ \diagdown\\ \end{matrix}\!\!N-CH_2OR^3\!\!\begin{matrix}\\ \diagup\\ R^2\end{matrix} \;\rightleftharpoons\; -\!\!\left(CH_2-\underset{\substack{|\\O\\|\\CH_2\\|\\N\\ \diagup\quad\diagdown\\ R^1\qquad R^2}}{CH}\right)_{\!n}\!- \;+\; R^3OH$$

[89] (6)



$$\underset{\substack{|\\O\\|\\A\\|\\N-R\\|\\C=O\\|\\NH_2}}{CH_2=CH} \quad \text{or} \quad \underset{\substack{|\\O\\|\\A\\|\\N-R\\|\\C=O\\|\\R^1}}{CH_2=CH} \longrightarrow -\!\!\left(CH_2-\underset{\substack{|\\O\\|\\A\\|\\N\\ \diagup\quad\diagdown\\ R\qquad R}}{CH}\right)_{\!n}\!-$$

(7)

where A = $(CH_2)_n$; n = 2-3

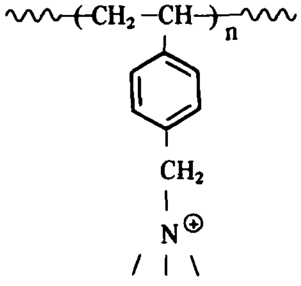
R = H, CH_3

R^1 = H, Alkyl C_{1-4}

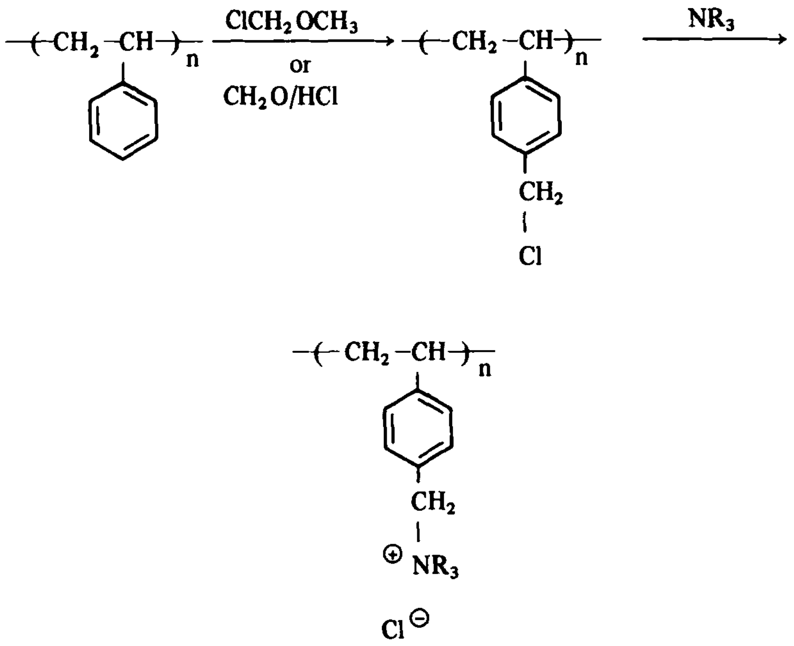
[90]

Cupery and Sauer [91] report the copolymerization of β-vinyloxyethylamine with other comonomers such as styrene and acrylics to prepare primary amino group containing polymers for cross-linkable coating compositions.

5. Poly(vinylbenzyl Ammonium)



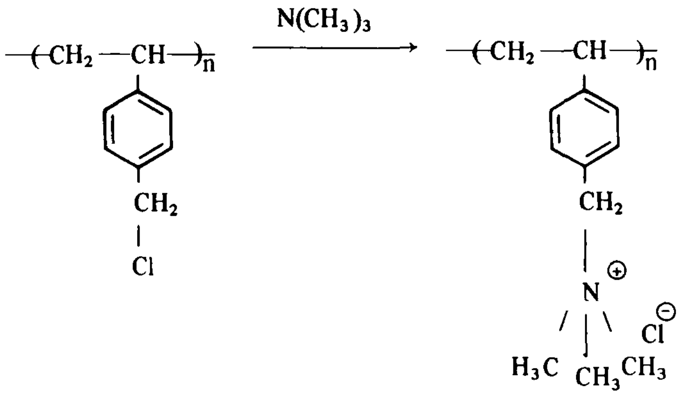
Vinylbenzyl quaternary ammonium polymers were first prepared by Jones [92, 93] by the quaternization of chloromethylated polystyrene and poly-α-methylstyrene with tertiary amines to form a water-soluble polyquaternary (Eq. 8).



(8)

[92, 93]

Lloyd [94] prepared polyvinylbenzyl trimethyl ammonium chloride quats by aminating polymeric chloromethylstyrene latex (prepared by the method of Vitkuski [95]) to obtain a water solution of the polyvinylbenzyl trimethyl ammonium chloride resin. He also prepared the sulfonium salts with sulfides. The chloromethylated polystyrene became water soluble at about 30 mole % quaternization (Eq. 9).



[94, 96-98] (9)

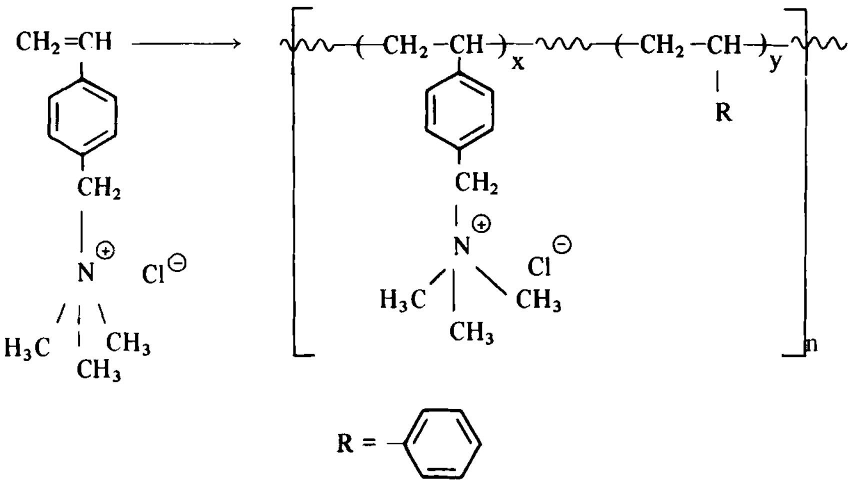
Lloyd and Vitkuski [96] also showed the effects of cross-linking with 0.05 to 1.0% divinyl benzene (which gives interesting microgel structures) on dilute solution viscosities.

Later work by Lloyd and Durocher [97, 98] has shown the quaternization of poly(chloromethylstyrene) with trialkyl amines and disulfides to be an S_N2 nucleophilic displacement reaction.

The aqueous latex emulsion of poly(chloromethylstyrene) is very readily reacted with trimethylamine yielding the water-soluble polyquaternary in a few minutes at 20-30% concentration. Lloyd and Durocher [98] observed a marked decrease in the reaction rate at about 50-60% conversion due to the neighboring group effect and attributed this difference in reactivity to the microtacticity of the polymer segments and the different reaction rate between o- and *p*-chloromethyl groups (this is also discussed by Arends [99]).

In a typical polyquat of this structure, made under optimum conditions, the polymer usually contains 80-85% quaternized units, 2-7% unreacted chloromethyl groups, and 10-13% hydrolyzed groups.

Jones and Goetz [100] reported the synthesis of ρ-vinylbenzyltrimethylammonium chloride monomer, homopolymer, and copolymers with styrene, acrylonitrile, and acrylamide in 1957 (Eq. 10).



$= CONH_2$

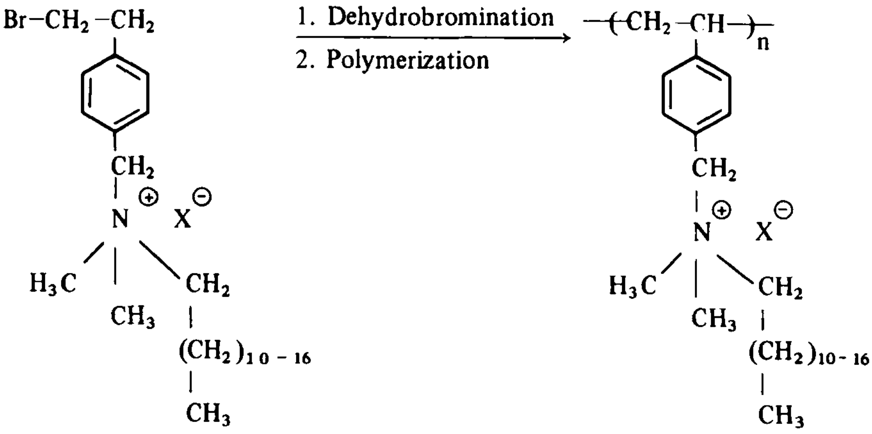
$= CN$

[100] (10)

The method by which ρ-vinylbenzyltrimethylammonium chloride was first obtained involved chloromethylation of phenethyl bromide. Both halogens were replaced by reaction with trimethylamine at room temperature and the difunctional quaternary hydroxide was obtained by ion exchange. This compound readily lost trimethylamine on boiling the aqueous solution under reduced pressure. ρ-Vinylbenzyltrimethylammonium chloride was obtained by HCl neutralization of the aqueous hydroxide quat solution. However, the simplest preparation for these monomers is the aqueous solution amination of ρ-vinylbenzyl chloride with various tertiary amines. The vinylbenzyl quaternary ammonium monomers are also reported to be toxic [100].

Copolymers of acrylamide with ρ-vinylbenzyltrimethyl ammonium chloride were observed to be highly substantive to paper pulp and were proposed by Jones [100] as beater additives; acrylonitrile copolymers for enhanced dyeability; and styrene copolymers for antistatic effects.

Morris [101] also prepared vinylbenzyltrialkyl ammonium chloride monomers and polymers where one of the alkyl groups on the quaternary nitrogen was a C_{12}-C_{18} fatty alkyl chain. He prepared his monomers by dehydrobrominating the (2-bromoethyl)benzyl quaternary ammonium halides (Eq. 11). These polyquats are claimed to be useful for wetting and emulsifying agents, dispersants and antistatic agents.



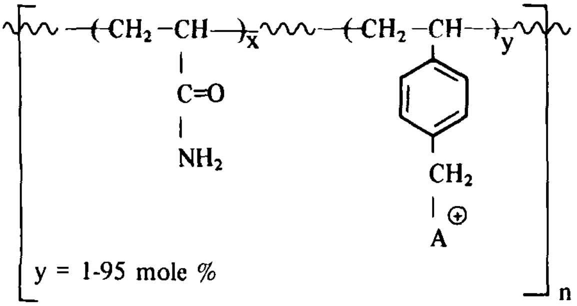
[101] (11)

The vinylbenzyl quaternary ammonium monomers and polymers are the subject of a patent issued to Clarke and Hamerschlag [102] in 1957 where they claim the compositions of linear soluble polyelectrolytes based on these monomers and also cross-linked gels for ion exchange resins and membranes.

Juda and Hamerschlag [103] also discuss the quaternization of chloromethylated polystyrene to yield vinylbenzyl trialkylammonium gel structures.

Repeating the earlier work of Jones, Rassweiler and Sexsmith [104] also worked on acrylamide copolymers of p-vinylbenzyl trialkyl ammonium chloride and cited their use as paper dry strength additives.

Rassweiler and Sexsmith have used all three of the p-vinylbenzyl quaternary monomers (ammonium, sulfonium, and phosphonium) to prepare cationic acrylamide copolymers for use as paper strength additives (Structure XVII).



XVII

where $A^{\oplus}$ is: $NR_3^{\oplus}$: [104]

$PR_3^{\oplus}$: [372]

$SR_2^{\oplus}$: [334]

Jones et al. also quaternized copolymers of vinylbenzyl chloride and isopropenyl chloride [105].

Mäder and Seidel [106] quaternized polyvinylbenzyl chloride with picoline, followed by further condensation with aromatic aldehydes to yield photosensitive poly(N-vinylbenzyl-4-vinylpyridinium) salts.

Jen and House [107] prepared cationic resins for paper sizing and dry strength by partially quaternizing poly(chloromethylstyrene) or copoly (ρ-methylstyrene-chloromethylstyrene) with pyridine to introduce about 2-20% quaternary groups into the polymer while retaining its hydrophobic nature.

By quaternizing chloromethylated styrene-divinylbenzene copolymers, Trostyanskaya et al. [108] prepared quaternary ammonium resins having aminotriacetic and β', β'', β'''-triaminotriethylamine complexogenic groups.

The use of poly(vinylbenzyl trimethylammonium chloride) for electroconductive coatings on paper is discussed by Silvernail and Zembal [109] and Doggett and Cady [110]. These same polyquats are also proposed for antistatic coatings on photographic film and electrostatic recording films by Winchell [111, 112]. Also Geyer [113] discusses the use of polyvinylbenzyl mixed ammonium and sulfonium quats for insolubilizable conductive coatings.

Wahl and Dever [114] propose the addition of both vinylbenzyl trialkyl ammonium and sulfonium polymers to control water-loss from hydraulic cement slurries used in oil well cementing.

The polyvinylbenzyl trialkyl ammonium chloride quats have been proposed extensively for their use as flocculants in many solids-liquid separation processes. Wiley [115] uses polyvinylbenzyltrimethyl ammonium chloride homopolymer and acrylamide copolymers for flocculating ore, clay, and starch slurries, and Priesing and Mogelnicki [116] used a combination of anionic polyelectrolyte and cationic polymer (such as polyvinylbenzyltrimethyl ammonium chloride) to flocculate sewage sludges for dewatering. Zhukovskaya and Vernikova [117] also mention the use of poly(vinylbenzyltrimethyl ammonium chloride) to purify oxytetracycline solutions.

However, the poly(vinylbenzyltrialkylammonium chloride) polyquaternaries have not found commercial utility as flocculants because of their generally low molecular weight.

Polyelectrolyte complexes. Insoluble polyelectrolyte complexes (polysalts) are formed when a cationic quaternary polyelectrolyte is mixed with an anionic polyelectrolyte in solution where mutual interaction (polysalt formation) can occur.

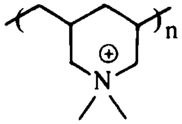
Michaels and Miekka [118-120] and Michaels [121-123] found that membranes consisting of complexes of a polyanion, poly(sodium styrenesulfonate) and a polycation, poly(vinylbenzyltrimethylammonium chloride) could be formed by mixing solutions of the individual polyelectrolytes in a ternary solvent consisting of about 60% water, 20% acetone, and 20% NaBr, casting thin films from the solution, and allowing the acetone to evaporate so that the polysalt complex would precipitate.

Michaels et al. [119, 124-127] also discussed the unusual ion sorption, electroconductive, and mechanical behavior of these polysalts and their use in making membranes for separation processes. These polysalt complexes are also reported to increase the moisture vapor transmission rate of plastics when incorporated as filler material in plastic films [128, 129] and to have biomedical prosthetic utility [130, 131].

The interstitial salt content in the polyelectrolyte complex (gel) can be altered to change its electrical properties for use in various electroconductive applications, such as battery separators [132-135].

Poly(p-vinyl Anilinium). Vinyl trialkyl phenylammonium (anilinium) compounds have been investigated by Price [136] as comonomers for modification of acrylonitrile fibers to enhance their dyeability, and Arcus and Hall [137] investigated the kinetics of the quaternization of poly(4-N,N-dimethylaminostyrene) with methyl iodide.

6. Poly(diallyl Ammonium)



In 1951 Butler and Ingley [138] first reported the observation that diallyl quaternary ammonium bromide salts polymerized with tert-butyl hydroperoxide to form water-soluble polymers–which was quite contrary to the expected insoluble cross-linked resins, as in the case of tri- and tetra-allyl quaternary ammonium compounds. The monoallyl ammonium compounds failed to polymerize. Butler and Goette [139] also observed, contrary to their expectations, that dially butyl β-vinyloxyethyl ammonium bromide yielded a water-soluble polymer with the β-vinyloxy group unpolymerized.

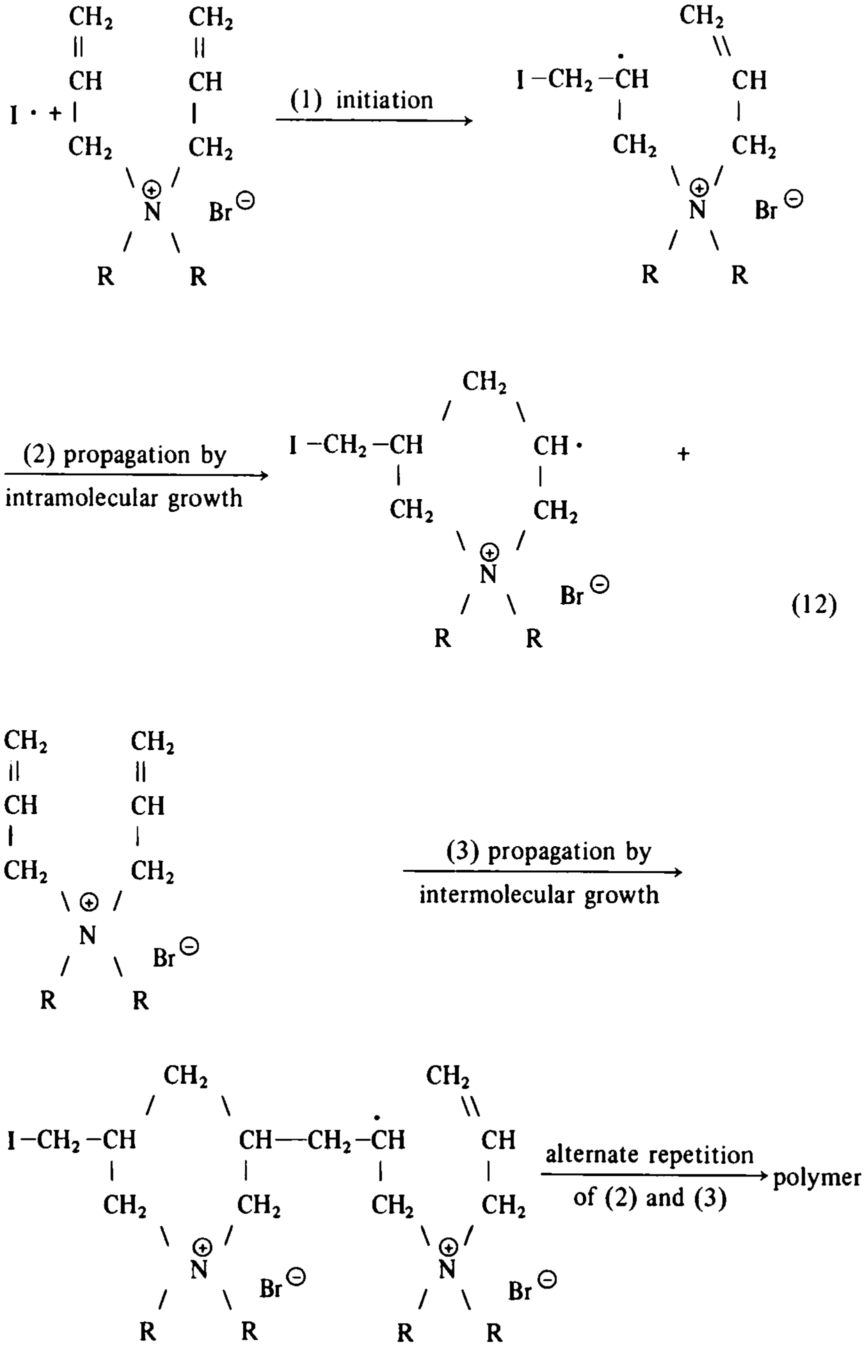
Likewise, Butler and Johnson [140] observed that diallyl propargyl quaternary ammonium compounds produce water-soluble polymers and the propargyl group did not enter the polymerization, and Butler and Goette [141] showed that the 2-butene double bond is also not polymerized in allyl substituted 1,4-diamino-2-butene.

At a Gordon Research Conference in 1955, Dr. Butler proposed a cyclic poly(methylene piperidinium) structure for these diallyl ammonium polymers which is formed by an alternating intramolecular-intermolecular cyclization reaction and propagation into a linear cyclic polymer. The structure of these cycloquats was disclosed in March, 1957 [142] and Butler and Angelo [143] published the 1,6-diene cyclo-polymerization process in June, 1957.

(1,6-Diene)Diallyl Cyclopolymerization (Eq. 12). Butler, Crawshaw, and Miller [144] degraded both poly(diallyl ammonium bromide) and poly(diallyl dimethyl ammonium bromide) and obtained the expected products from cleavage of the piperidinium bromide rings present in the structures, which confirmed the proposed cyclic structure obtained from diallyl ammonium bromide monomers $[(CH_2{=}CHCH_2)_2NR_2]^{\oplus}Br^{\ominus}$. Hydrogenation experiments on purified polymer and infrared data indicate no unsaturation in these polymers.

In 1960, Dr. Butler [145] presented a review of the developments in cyclo polymers up to that time and again in 1966 in the *Encyclopedia of Polymer Science* [146].

Butler, Angelo, and Crawshaw [147] discuss linear homopolymers of diallylamines and Butler [148] disclosed the composition of high molecular



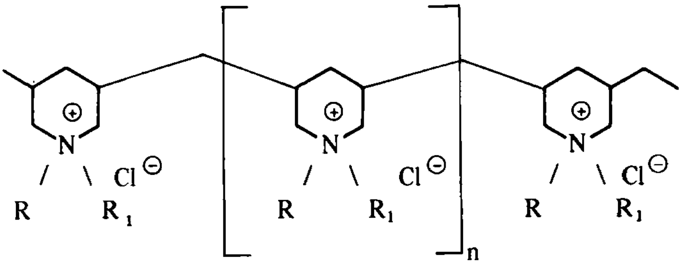
I · +
(1) initiation
(2) propagation by intramolecular growth
(3) propagation by intermolecular growth
alternate repetition of (2) and (3)
polymer
CH₂
CH
N
R
Br
I–CH₂–CH
+

(12)

weight poly(diallylammonium chlorides)—in contrast to the previously prepared low molecular weight poly(diallylammonium bromide) salts.

Poly(N,N-dimethyl-3,5-methylenepiperidinium chloride) (Structure XVIII). Boothe [149, 150] discloses a process for making dimethyldiallylammonium chloride monomer of high purity which is especially suitable for making high molecular weight polymers for flocculants.

Butler also found that many other unsaturated ammonium, sulfonium, and phosphonium compounds containing the 1,6-diene system would also yield water-soluble polymers via cyclopolymerization [148].



XVIII [148, 151, 162, 163]

Recently, Negi, Harada, and Ishizuka [151] studied the polymerization of dimethyldiallylammonium chloride and bromide in DMSO solvent initiated by ammonium persulfate. Their work confirmed Butler's finding that the chloride anion form polymerized much better and gave significantly higher intrinsic viscosities than the bromide anion form.

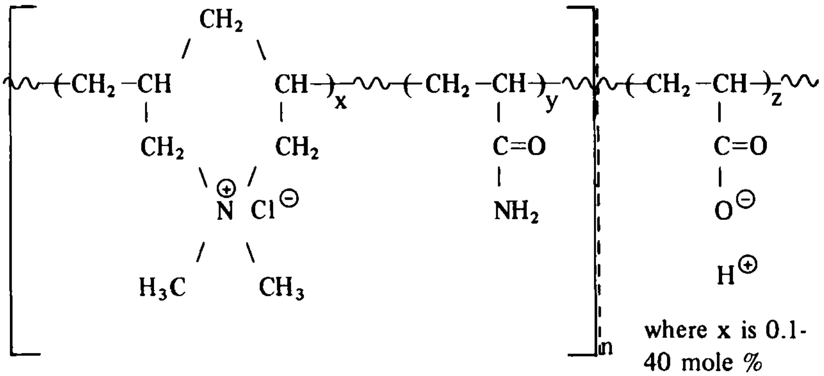
Many studies have been reported on the use of poly(dimethyldiallylammonium chloride) as a primary coagulant or coagulant aid [152] in destabilizing colloidal suspensions and in industrial waste water clarification by Butler [153], Black, Birkner, and Morgan [154, 155], Jones [156], Kleber [157], Posselt et al. [158], Pressman [159], and Dajani [160,161]. This is the only synthetic cationic quaternary ammonium polyelectrolyte approved by U.S.P.H.S. for use in potable water clarification.

It is now recognized that polyquaternary ammonium compounds provide the best materials for electroconductive coatings on paper used in electrographic reproduction processes [163].

Boothe and Hoover [162] proposed the use of poly(dimethyldiallylammonium chloride) as an electroconductive coating for paper and Hoover and Carr [163] elaborated on the optimization, formulation, and commercial use of this polyquat for electroconductive coatings on electrographic papers.

The diallyl quaternary ammonium monomers can also be copolymerized with a wide variety of other monomers to produce cationic copolymers. Schuller et al. [164] reported the copolymerization of dimethyldiallylammonium chloride with acrylamide and acrylonitrile for paper dry strength additives. Schuller and Thomas [165] prepared copolymers of dimethyldiallylammonium chloride with acrylamide, acrylonitrile, styrene, methylacrylate, vinyl acetate, etc. Booth and Linke [166] used copolymers of acrylamide and dimethyldiallylammonium chloride to aid in the separation of aqueous ore pulps and mineral suspensions, and Suen and Schiller [167] used these copolymers to flocculate sewage wastes (Structure XIX).

Schuller, Thomas, Moore, and House [168] made polyampholytes by terpolymerizing dimethyldiallylammonium chloride with acrylamide and acrylic acid which were used as dry strength resins in paper.



where x is 0.1-40 mole %

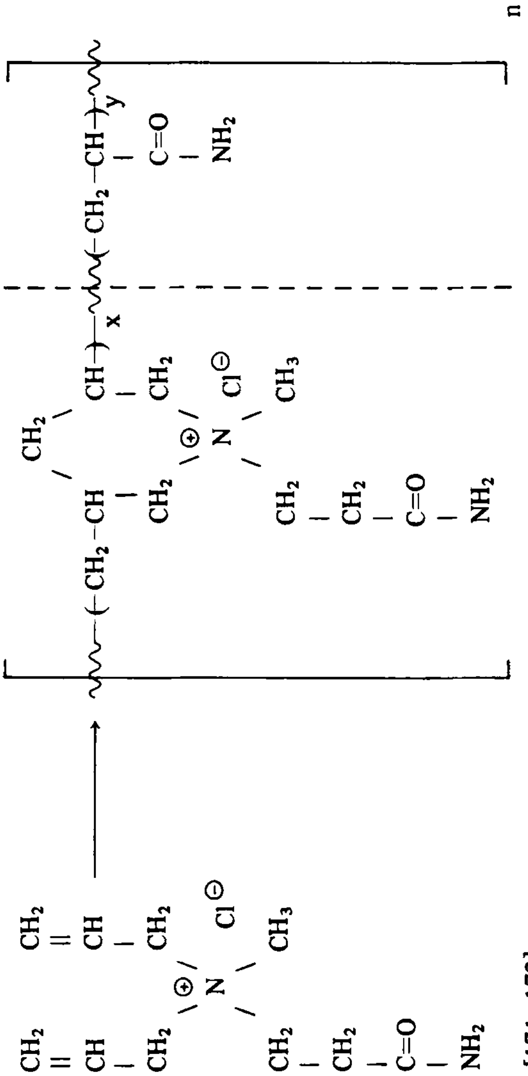
XIX [164-168]

Jen [169] discusses the use of dimethyldiallylammonium chloride to prepare acrylonitrile graft copolymers.

Nixon, Berrigan, and Williams [32] copolymerized dimethyldiallylammonium methylsulfate with acrolein to prepare wet strength resins for paper.

Schuller and Thomas [170] prepared diallylmethyl carboxymethylammonium betaine and copolymerized this with acrylonitrile for enhanced dye receptivity.

Hoover, Schaper, and Boothe [171] prepared diallylmethyl β-propionamido ammonium chloride monomer and homopolymers which are useful

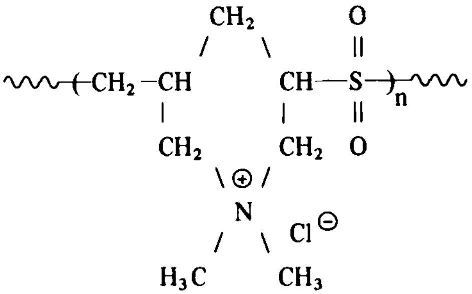


(13)

[171, 172]

as primary coagulants and in many flocculation applications, and Schaper [172] made copolymers of diallylmethyl β-propionamido ammonium chloride with acrylamide which have excellent sewage sludge flocculation properties (Eq. 13).

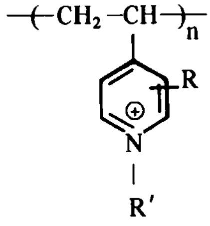
Harada and Katayama [173] and Harada and Arai [174, 175] reported the copolymerization of dimethyldiallylammonium chloride with sulfur dioxide to prepare a quaternary sulfone polymer useful in dye leveling and dye retention, flocculation, and textile treating (Structure XX).



XX [173, 176, 177]

Ueda and Harada [176, 177] discuss the effect of diallylamine substitution on the polymer properties and the use of these polycationic sulfones as flocculants for kaolinite.

7. Poly(vinylpyridinium)



A voluminous amount of research has been done on the vinylpyridine homo- and copolymers in the form of their free tertiary bases; also, since polyvinylpyridine was quaternized and studied by Fuoss and Strauss [190] in 1948, many studies of polyvinylpyridinium systems have been made by these investigators and many others.

Generally, the quaternary pyridinium polymers reported to date can be separated into the following basic structural types:

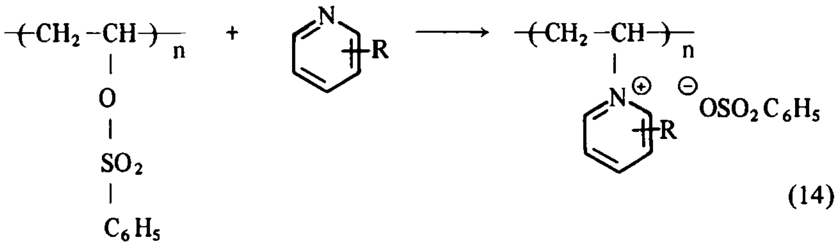
I. Poly(N-vinylpyridinium)
II. Poly(C-vinylpyridinium)

A. Poly-2-vinyl
B. Poly-4-vinyl
C. Poly-2-methyl-5-vinyl

Type 1. Poly(N-vinylpyridinium). Very little work has been reported on the N-vinylpyridinium type polymers but a considerable amount of research has been reported on the C-vinylpyridinium compounds with the vinyl group and substituent alkyl groups in different positions with respect to the nitrogen in the pyridine ring.

Duling and Price [178] studied the homo- and copolymerization of several N-vinylpyridinium fluoroborate salts. Solid state irradiation of N-vinylpyridinium fluoroborate gave a polyelectrolyte with about 150,000 molecular weight.

A series of poly(N-vinylpyridinium sulfonates) were prepared by Reynolds and Kenyon [179, 180] by reacting pyridines with polyvinylsulfonic acid esters, such as polyvinylbenzenesulfonate derived from polyvinyl alcohol (Eq. 14).

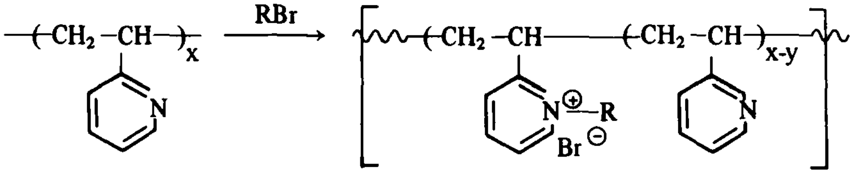


(14)

[179-181]

Williams [181] used these poly(N-vinylpyridiniumsulfonate) resins to prepare light sensitive photographic coatings.

Type IIA. Poly(2-Vinylpyridinium). Maclay and Fuoss [182] prepared poly-2-vinylpyridine, with molecular weight 45,000, by solution polymerization in toluene–in which it was soluble, unlike poly-4-vinylpyridine which precipitates. In their quaternization studies on poly(2-vinylpyridine) with methyl and butyl bromide they found that quaternization was incomplete due to electrostatic and steric screening of some of the ring nitrogens by the polymer. In the poly-2-vinyl-N-methylpyridinium bromide approximately two of every three nitrogens are quaternized, but in the poly-2-vinyl-N-n-butylpyridinium bromide there was only one out of every four nitrogens quaternized. Their viscometric studies also showed that quaternization in the 2-position stiffens and extends the chain to give a more nearly rodlike structure than the corresponding derivative of poly-4-vinylpyridine (Eq. 15).



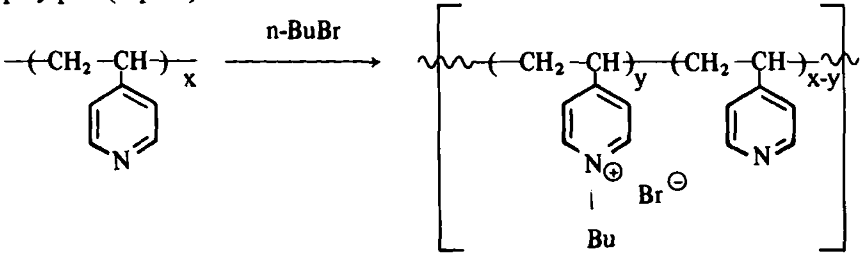
[182] (15)

Several recent references by Matsuzaki and Sugimoto [183] and Weill and Hermann [184] present interpretations of the NMR spectra of poly-2-vinylpyridine, and Gueskens et al. [185, 186] discusses the proton resonance spectra and tacticity of poly-2-vinylpyridine as a function of its method of preparation. Hyde and Taylor [187] presented some data on light-scattering studies of poly(2-vinyl-N-propylpyridinium bromide).

Much work has been done on graft copolymers using poly-2-vinylpyridine [188].

Type IIB. Poly(4-Vinylpyridinium). Richards [189] first made poly-N-alkyl-vinylpyridinium halides in the mid-1940s by quaternizing polyvinylpyridine with alkyl halides in organic solvents.

In 1948, Fuoss and Strauss [190] prepared poly-4-vinyl-N-n-butylpyridinium bromide by quaternizing poly-4-vinylpyridine with n-butyl bromide. The basic poly-4-vinylpyridine was obtained by precipitation from a toluene solution of its monomer upon polymerization (MW 77,000). The polymer was then quaternized with n-butyl bromide in nitromethane to give the polyquat (Eq. 16).



[190-192] (16)

Fuoss and Strauss followed this original paper with a series of papers reporting their work on the aqueous solution conductive [191], viscometric [192, 193], osmotic pressure [194] and light-scattering [195] properties of poly-4-vinyl-N-n-butylpyridinium bromide. Jordan et al. [196] also reported some light-scattering and ultraviolet absorption studies on dilute solutions of poly(4-vinylpyridinium chloride).

Their work showed that the reduced viscosity (η_{sp}/c) and the ratio of osmotic pressure over concentration (π/c) increased with dilution, instead of decreasing linearly with concentration, as is the case for neutral polymers, due to increasing dissociation and electrostatic repulsion with dilution. The addition of excess electrolytes suppressed the dissociation of the polymeric salt and gave linear curves.

Fuoss and Cathers [197, 198] also studied the viscometric and conductive properties of copolymers of styrene and 4-vinylpyridine which were subsequently quaternized to introduce ionogenic sites. They showed that the presence of the ionic groups on the polymer chain gave rise to the typical polyelectrolyte characteristic of an increase in the reduced viscosity with increasing dilution.

Clark [199] also prepared copolymers of vinyl aromatic compounds and quaternary N-alkylvinylpyridinium methosulfates by quaternizing 2-, 4-, and 2-methyl-5-vinylpyridine with dimethylsulfate in alcohol solution and then immediately adding styrene or divinylbenzene and copolymerizing.

Jackson [200] quaternized copolymers of vinylpyridine and di- or trivinylbenzene to form anion exchange resins.

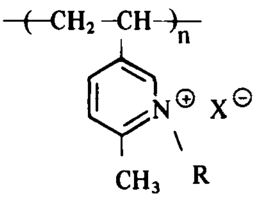
The kinetics of the quaternization reaction on poly-4-vinylpyridine with n-butyl bromide in tetramethylene sulfone, dimethylformamide, and propylene carbonate were investigated by Fuoss, Watanabe and Coleman [201] and Hall [202]. They observed the initial rate to be a rapid second-order reaction, but as the quaternization proceeds, the rate decreases to one-tenth of its initial value due to the positive electrostatic field of high intensity that builds up in the polymer coil. Arends [203] discusses the reasons for the decrease in quaternization rate and lack of 100% conversion due to steric and electrostatic effects and a change in basicity of the pyridine nitrogens. Fuoss and Sadek [204] first demonstrated the mutual precipitation of polycations with polyanions in dilute solutions using poly(4-vinyl-N-n-butyl pyridinium bromide).

Several papers [205-209] have been published on various methods for polymerizing 4-vinylpyridine monomer; however, the corresponding 4-vinylpyridinium quaternary salt monomers have not been obtained. Kabanov et al. [210, 211] have studied the reaction of 4-vinylpyridine with alkyl halides in various organic media. Instead of the monomeric quaternary salts, high molecular weight quaternary polymer is formed. Since strong inhibitors for free radical polymerization did not inhibit this reaction, Kabanov proposed an anionic mechanism to account for the spontaneous polymerization of the quaternary monomer. Quaternary monomeric salts of 2-methyl-5-vinylpyridine are capable of being prepared and isolated, but are subject to spontaneous polymerization on concentrated aqueous solutions.

Strauss, Gershfield, and Spiera [212] observed an anomalous solubility behavior in a polysoap derived from poly-4-vinylpyridine by quaternizing 13.6% of the nitrogens with n-dodecyl bromide and the remainder with ethylbromide. The polysoap was completely soluble in both dilute and concentrated KBr solutions, but insoluble in the intermediate concentration range.

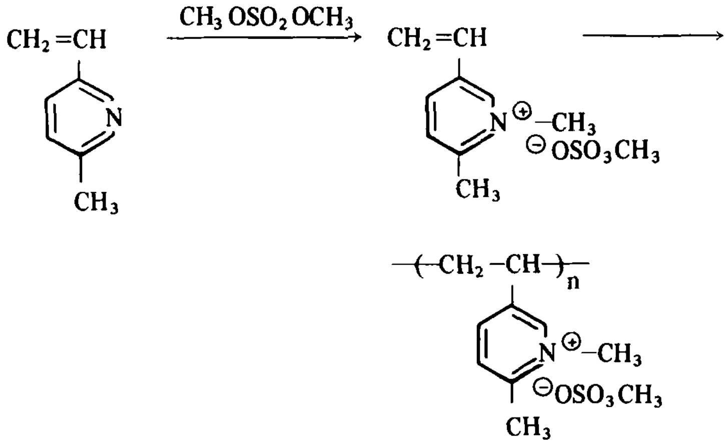
Ruehrwein and Ward [213] used poly-4-vinyl-N-n-butylpyridinium bromide as a soil conditioner.

Type IIC. Poly(2-methyl-5-vinylpyridinium) (Structure XXI). Tabata, Kitano, and Sobue [214] investigated the radiation induced polymerization of 2-methyl-5-vinylpyridine; Gechele et al. [215, 216] investigated the solution properties of poly(2-methyl-5-vinylpyridine); and Lebedev [217] made copolymers with maleic and fumaric acids.



Lincoln and Shyluk [218] disclosed the synthesis of high molecular weight poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) by employing the monomer at a concentration of 65-85% in aqueous solutions and free radical catalysts (Eq. 17). These polymers are claimed to be effective flocculants and retention aids.

Recently, Shyluk [219] discussed some homo- and copolymerization studies on 1,2-dimethyl-5-vinylpyridinium methyl sulfate monomer. It was observed that concentrated aqueous solutions of this pyridinium monomer (above 25%) tended to polymerize spontaneously; reaction temperatures below 25°C give complete polymerization and above this temperature the polymerizations appear to stop at about 70% conversion. They also reported copolymerization studies with acrylamide and methyl methacrylate.



(17)

[218-225]

Kargin et al. [220] and Kabanov et al. [221, 222] also report on the spontaneous polymerization of 1,2-dimethyl-5-vinylpyridine upon quaternization and propose an anionic polymerization mechanism for this process.

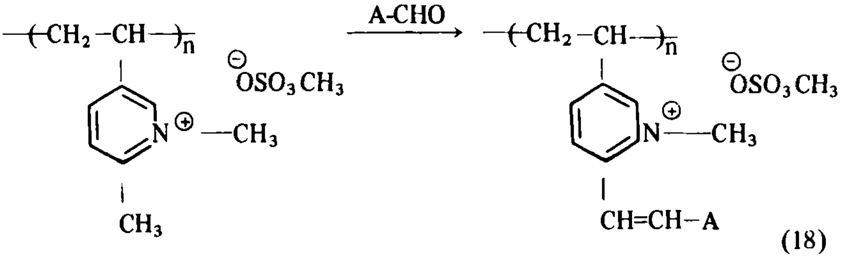
Shyluk [223] reported that water was the only good solvent for poly(1,2-dimethyl-5-vinylpyridinium methyl sulfate) and its aqueous solutions have good viscosity stability at neutral or acidic pH's up to 100°C but the polymer degrades in strongly basic solutions. This behavior seems to be typical of all polyquaternaries.

Shyluk [224] also studied the adsorption of this polyquat on crystalline silica, and Shyluk and Smith [225] discuss its use as a flocculant.

Monagle and Shyluk [35, 36] disclosed a precipitation polymerization process for making acrylamide copolymers with 1,2-dimethyl-5-vinylpyridinium methylsulfate using a tertiary-butanol/water mixture and also with various salts (electrolytes) added from which the polymer precipitates as it is formed.

Strazdins and Kulick [226] use various quaternary polymers, including poly(1,2-dimethyl-5-vinylpyridinium methylsulfate), to increase the retention of a polycarboxylic anhydride sizing emulsions in paper.

Leubner, Williams, and Unruh [227] prepared light-sensitive polymers by reacting poly(1,2-dimethyl-5-vinylpyridinium methylsulfate) with aromatic aldehydes to obtain 4'-(alkoxy or dialkylamino)-1-methyl-5-vinyl-2-stilbazolium methosulfate (Eq. 18).


(18)

[227]

Miscellaneous Pyridinium Polymers. Most synthetic polyampholytes prepared to date have been the amino acid type; few polyampholytes have been reported which contain quaternary cationic groups. Ladenheim and Morawetz [228] prepared N-carboxymethyl-4-vinylpyridinium salts by quaternization of poly(4-vinylpyridine) with ethylbromoacetate followed by hydrolysis to the carboxymethyl betaine polymer (Eq. 19).

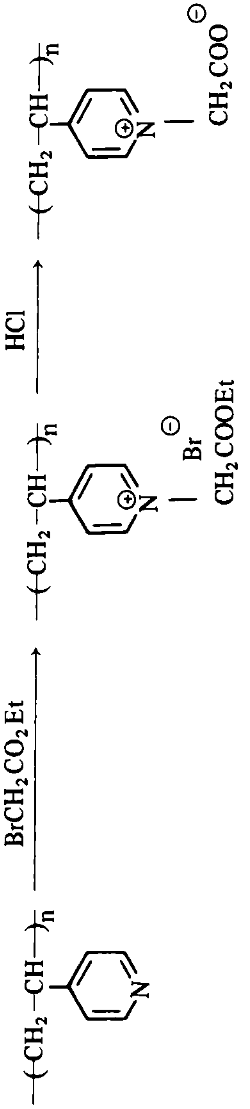
Polysulfobetaines have been made by quaternizing either monomeric or polymeric 2- or 4-vinylpyridine with sultones. Hart and Timmerman [229] prepared poly(4-vinylpyridine-N-butylsulfobetaine) by reacting butane sulfone with 4-vinylpyridine to prepare the monomer, followed by subsequent polymerization, and also by quaternization of poly(4-vinylpyridine) (Eq. 20).

The butylsulfobetaine of poly(2-vinylpyridine) was soluble in water over the whole pH range, while the butylsulfobetaine of poly(4-vinylpyridine) was not soluble in water at any pH but did dissolve in NaCl solutions.

Shen [230] prepared polyquaternary salts of a variety of poly(vinylpyridines) by reacting the polymers with chloroacetic acid to form the N-carboxymethyl betaine quats which are reported to be useful as oil-in-water demulsifying agents and bactericides.

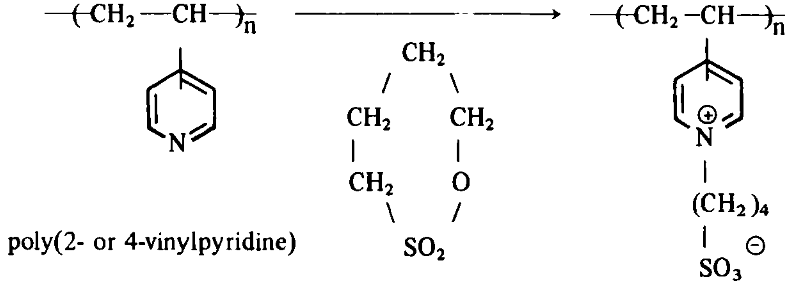
Schuller and Guth [231] quaternized many tertiary amine-containing homo- and copolymers with bromo- and chloroacetates to form the betaines; specifically, they quaternized 2-methyl-5-vinylpyridine homopolymer and acrylamide copolymers. Schuller and Price [232] made several copolymers with 1-carboxymethyl-2-methyl-5-vinylpyridinium betaine monomer.

Sprague and Brooker [233] quaternized poly(2-vinylpyridine) and poly(4-vinylpyridine) by reaction with methyl p-toluenesulfonate to obtain the poly(N-methyl-2- and 4-vinylpyridine p-toluenesulfonate) salts and used these polyquats as dye mordants in photographic film [234]. Minsk and Kenyon [235] and Reynolds and Laakso [236] discuss a method of conducting this quaternization with methyl p-toluenesulfonate in alcohols, ethers, ketones, and other solvents as a reaction media.



(19)

[228]



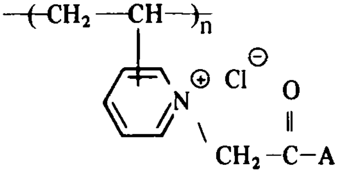
(20)

[229]

Forshey and Kirby [237] copolymerized 1,2-dimethyl-5-vinylpyridinium p-toluenesulfonate with acrylonitrile and prepared the phosphotungstate salts for enhanced dye absorption.

Daniel [238] quaternized 2-methyl-5-vinylpyridine copolymers (with acrylates and styrene) with benzyl chloride for use as sizing agents in paper.

Laakso, Williams, and Garber [239] prepared quaternary vinylpyridine polymers by quaternizing poly(4-vinylpyridine) with compounds containing the chloroacetyl group and used these polymers for antistatic coatings on photographic film [240] (Structure XXI).



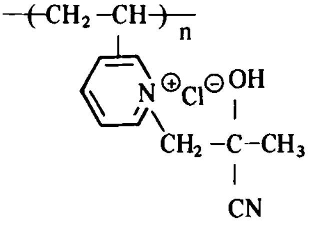
A = Alkyl, $-OR$, $-NR_2$ or $-\phi R$

XXI [239, 240]

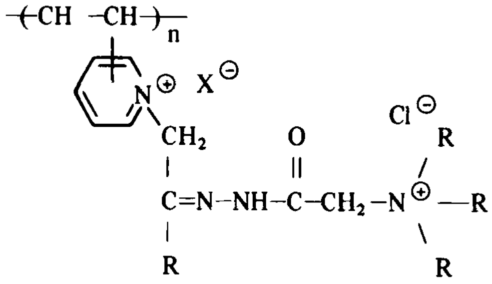
Laakso and Williams [241] quaternized poly(4-vinylpyridine) with chloroacetone cyanohydrin to obtain polyquaternaries useful in making antistatic photographic film [242] (Structure XXII).

Also, Laakso and Williams [243] reacted poly(4-vinylpyridine)haloketone polymers with hydrazides such as Girard reagents "T" and "P" (betaine hydrazide hydrochloride and carbohydrazine-methylpyridinium chloride, respectively) to form quaternaries. These were also used for antistatic photographic film [244] (Structure XXIII).

Price and Thomas [245] found that higher molecular weights and increased conversion could be obtained in the homo- and copolymerization of a variety of quaternary ammonium monomers using a Redox catalyst system comprising nitrate, chlorate, and sulfoxy ions at pH 1-5.

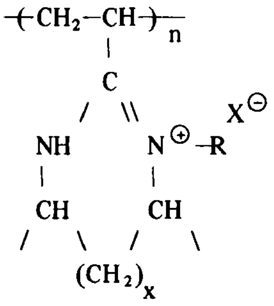


XXII [241, 242]

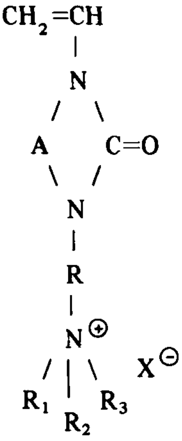


XXIII [243, 244]

8. Poly(vinylimidazolinium) and Other Heterocyclics



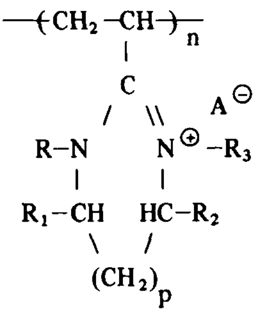
Yost [246] prepared a series of polyvinyl heterocyclic quaternary compounds from such monomers as 1-(β-dialkylaminoethyl)-3-vinylimidazolinone-2 and tetrahydro-pyrimidinone-2, which are reported to be good fungicides, bactericides, softeners, and antistatic agents for cellulosic fabrics (Structure XXIV).



where A is alkylene C_{2-3}

XXIV [246]

Hurwitz and Aschkenasy [247] reacted polyacrylonitrile with diamines to form poly(2-vinylimidazolines) and tetrahydropyrimidines which, upon hydrolysis, yielded poly N-amino-alkylacrylamides. They have prepared both the homopolymers and copolymers by treating acrylonitrile containing copolymers with diamines. These polymers have been evaluated for their utility in hair sprays, retention aids, and as coagulants. The resulting polyimidazolines can be quaternized or used in the form of their acid salts for many flocculation applications as Hurwitz and Aschkenasy [248] and Pollio [249] also discuss (Structure XXV).



R_3 = H, alkyl, or benzyl
p = 0 or 1

XXV [247-249]

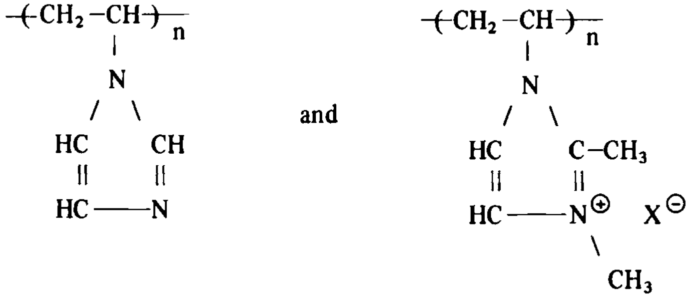
Poly-N-vinylimidazole has been prepared by Poschmann [250] for use as a sizing agent in paper (Structure XXVI). Also, Schickh et al. [251]

prepared terpolymers of N-vinylimidazolinium compounds, such as 1-vinyl-2,3-dimethylimidazolinium methylsulfate, with acrylic esters and acrylonitrile for use as a sizing agent for paper.

Fikentscher et al. [252] prepared cationic emulsion polymers for surface sizing of paper by copolymerizing 1-vinyl-3-methylimidazolinium methylsulfate (and 1,2-dimethyl-5-vinylpyridinium methylsulfate) with other acrylic monomers.

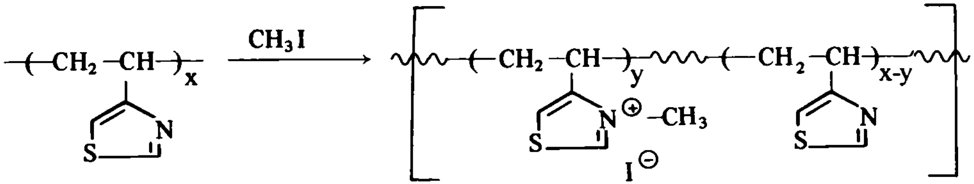
Liu and Gregor [253, 254] investigated metal complexing and electrolyte effects in solutions of poly-N-vinylimidazole.

Copolymers of 2-methyl-1-vinylimidazole with acrylamide were prepared by Machida and Saito [255] and are reported to give good size retention and strength properties to paper. Machida et al. [256] also prepared azo dyes from 2-methyl-1-vinylimidazole homo- and acrylamide copolymers.



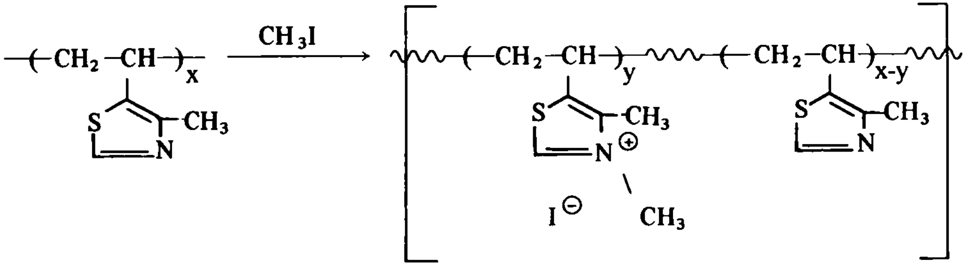
XXVI [250, 253-256]

The catalytic activity of thiamine pyrophosphate, a coenzyme for a number of enzymatic reactions, is known to be due to the presence of the quaternized thiazole ring. Schilling and Mulvaney [257] prepared a series of quaternized poly(vinylthiazoles) to examine for their catalytic activity in the furfural to furoin conversion. The monomer synthesis and polymerization methods for these vinylthiazoles were also reported by Schilling and Mulvaney [258]. Attempts to quaternize 4-vinylthiazole with methyl iodide resulted in the formation of a quaternized thiazolium polymer—just as 4-vinylpyridine is spontaneously polymerized when quaternization with alkyl halides is attempted. Partially quaternized polymers of 4-vinylthiazole and 5-vinyl-4-methylthiazole were obtained by treating the respective poly(vinylthiazoles) with methyl iodide. Surprisingly, these thiazolium polyquats were not water soluble (Eqs. 21 and 22).



(21)

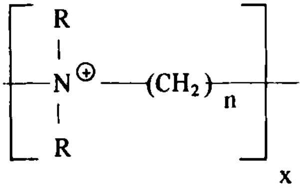
42% quaternized



(22)

[257, 258]

9. Poly(Alkylation Quaternary Ammonium)—"Ionenes"



$$\left[-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{N^{\oplus}}}}}-(CH_2)_n- \right]_x$$

Polyquaternary ammonium compounds with the ammonium ion integral in the backbone of the polymer chain have been known for about 40 years since the work of Marvel in the early 1930s with ω-haloalkyl dialkylamines.

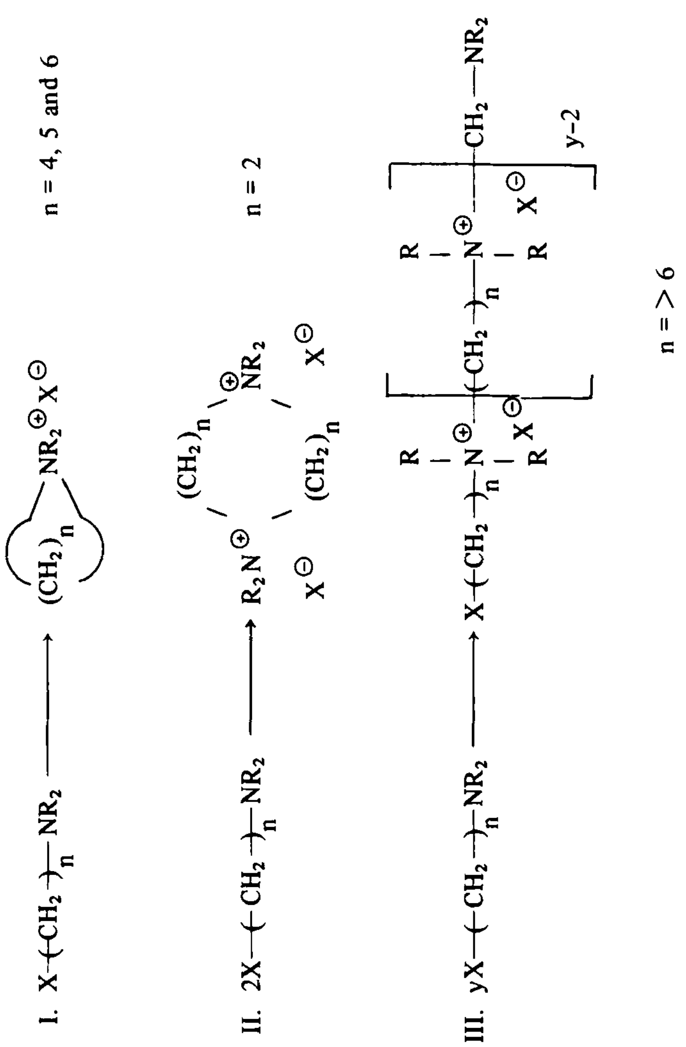
Reaction of ω-Haloalkyl Dialkylamines (Eqs. 23-25). In 1929, Littman and Marvel [259] investigated the reactions of bromodialkylamines of the general formula $Br-(CH_2)_n-N(CH_3)_2$, where n has a value of 4, 5, 6, or 7. All of the amines reacted with themselves to give cyclic quaternary ammonium salts when n has the value of 4, 5, or 6; however, when n = 7, they were unable to obtain any cyclic quat but obtained a chain polyquat.

Gibbs, Littmann, and Marvel [260] also reported linear polyquats from γ-chloropropyldimethylamine. Lehman, Thompson, and Marvel [261] concluded that ω-bromoalkyldimethylamines of the series $Br-(CH_2)_n-N(CH_3)_2$, where n has the number 7, 8, 9, or 10, polymerize to give linear polyquats with molecular weights reported to range from 3,000 to 28,000.

Gibbs and Marvel [262] showed that the size of the alkyl groups on the nitrogen of γ-bromopropylamines influenced the course of the reaction—the dimethyl compound gave predominatly linear polymer while the diethyl gave a cyclic quaternary. Gibbs and Marvel [263] also found that γ-bromopropyldimethylamine in very dilute solution reacts intramolecularly to give the cyclic crystalline salt dimethyltrimethylene ammonium bromide. This salt subsequently rearranges slowly at room temperature or rapidly upon heating to form a linear polyquat.

The reaction of ditertiary amines with dihalides (Menshutkin Reaction [264]) can be made to yield linear polyquaternary ammonium compounds as shown in Eq. (26).

In 1941, Kern and Brenneisen [265] reported the synthesis of a series of polyquaternary ammonium compounds from ditertiary amines and dihalides having molecular weights from 3,000 to 10,000.

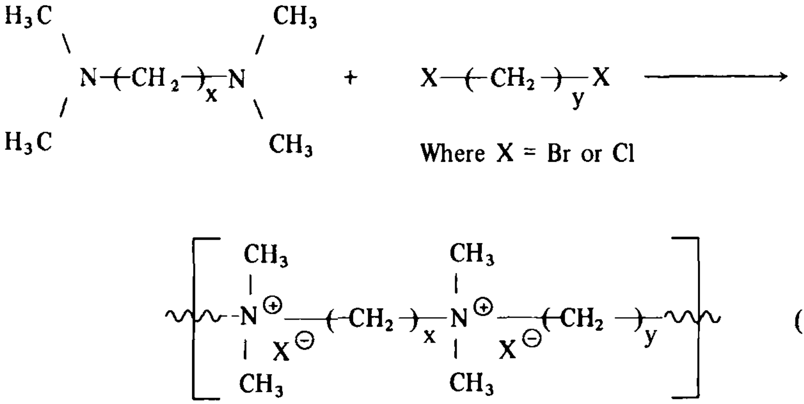


(23)

(24)

(25)

[259-263]



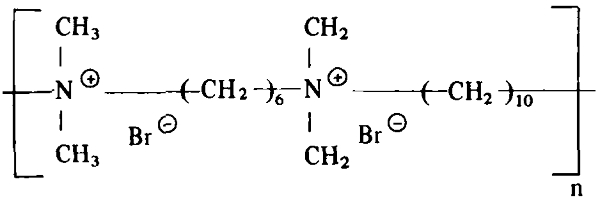
$$(H_3C)_2N\text{-}(CH_2)_x\text{-}N(CH_3)_2 + X\text{-}(CH_2)_y\text{-}X \longrightarrow$$

Where X = Br or Cl

$$\left[\sim\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\, X^{\ominus}\text{-}(CH_2)_x\text{-}\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\, X^{\ominus}\text{-}(CH_2)_y\sim \right] \qquad (26)$$

(26)

Ritter [266] reported the preparation of polyquats derived from decamethylene dibromide and a variety of diamines such as N,N,N′,N′-tetramethylhexamethylenediamine producing a polyquat having this structural unit of Structure XXVII.



$$\left[-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}\, Br^{\ominus}\text{-}(CH_2)_6\text{-}\overset{CH_2}{\underset{CH_2}{N^{\oplus}}}\, Br^{\ominus}\text{-}(CH_2)_{10}- \right]_n$$

XXVII

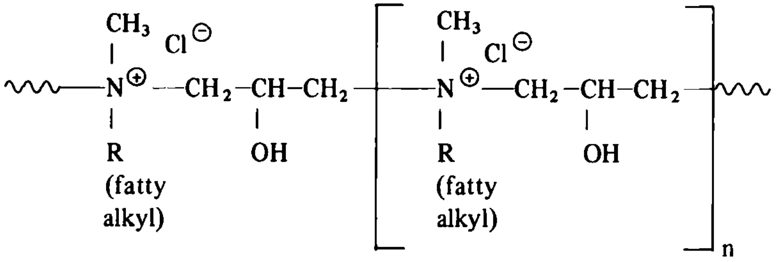
These polyquats are useful as bactericides, dispersing agents, dye fixates, etc., and Searle and Kirby [267] claim the use of these linear polyquaternary compounds where the onium atoms are sulfur, phosphorus, and nitrogen as fungicides and bactericides.

Kirby [268, 269] discusses the preparation of tetraalkyl decamethylenediamines $R_2N\text{-}(CH_2)_{10}\text{-}NR_2$ and their reaction with dihalides to form linear polyquaternaries, useful as bactericides. Coffman [270] reacted diols or dithiols with formaldehyde, ditertiarydiamines, and nonoxidizing acids to obtain polyquaternaries.

Erickson used polyquats derived from diamine-dihalide reactions for soil conditioning [271] and also, when complexed with bentonite, for grease thickening [272].

Taube and Böckmann [273] used ditertiary ethylenediamine and dihalides to prepare linear polyquats as dye fixatives, and Krieg [274] employed polyquaternaries of this type to prevent clay swelling in oil recovery.

The reaction of secondary amines and epichlorohydrin also has been used to form polyquaternary resins. Bock and Houk [275] reacted fatty alkylmethylamines with epichlorohydrin to prepare surface-active polyquaternary ammonium salts with bactericidal properties (Structure XXVIII).



XXVIII [275]

Other surface active polyquaternaries of this general type have been prepared by Gunderson [276] by acylating polyalkylene polyamines with fatty carboxylic acids and then quaternizing with dimethyl sulfate.

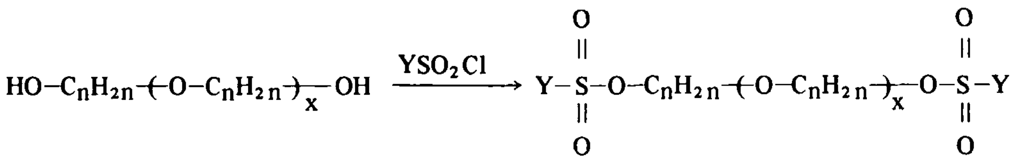
McCarty [277] prepared some interesting quaternary poly(oxyalkylene) alkylbis(diethylenetriamine) compounds for use as flocculants, miticides, and rodenticides. These polymers are prepared by reacting an appropriate polyglycol with chlorosulfonic acid to prepare poly(oxyalkylene) alkybis(diethylenetriamine) which is subsequently quaternized with an appropriate alkylating agent (Eqs. 27 and 28).

Polyethyleneimine$\left(\mathrm{CH_2CH_2NH}\right)_X$ represents the simplest linear polymer with an integral nitrogen and many attempts have been made to quaternize these polymers with varying degrees of success. Mung and Keller [278] quaternized polyalkylenepolyamines with dimethylsulfate for use as dye retention aids.

Feeman [279] prepared a series of polyquats for dye fixation by ethoxylating polyethylenimine and then quaternizing the resulting product with dimethylsulfate. Thewis [280] quaternized polyethylenimine with dimethylsulfate and used this polyquat along with anionic materials for antistatic treatments on plastics and fibers.

Reynolds [281] prepared a series of polyquats both linear and cyclic—containing piperazine rings, which are reported as gelatin hardners.

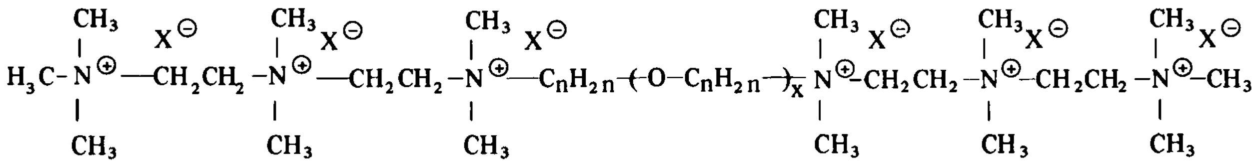
Nordgren and Wittcoff [282, 283] prepared polyquats by reacting dimer



$$HO{-}C_nH_{2n}{-}(O{-}C_nH_{2n})_x{-}OH \xrightarrow{YSO_2Cl} Y{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O{-}C_nH_{2n}{-}(O{-}C_nH_{2n})_x{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}Y \qquad (27)$$

XXIX

$$\text{XXIX} + \text{diethylenetriamine} \longrightarrow \text{XXX} + \text{alkylating agent} \longrightarrow$$



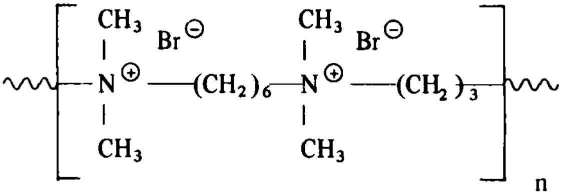
$$H_3C{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\oplus}}}\overset{X^{\ominus}}{-}CH_2CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\oplus}}}\overset{X^{\ominus}}{-}CH_2CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\oplus}}}\overset{X^{\ominus}}{-}C_nH_{2n}{-}(O{-}C_nH_{2n})_x{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\oplus}}}\overset{X^{\ominus}}{-}CH_2CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\oplus}}}\overset{X^{\ominus}}{-}CH_2CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^{\oplus}}}\overset{X^{\ominus}}{-}CH_3$$

(28)

[277]

acid ditertiary amines with dihalides and claim their use as bactericides, flocculants, antistats, etc.

A specific polyquaternary ammonium polymer of this family, hexadimethrine bromide (Polybrene), is used to neutralize the anticoagulant effect of heparin. Polybrene is a polyquat made from N,N,N′,N′-tetramethylhexamethylenediamine and trimethylene bromide. A series of articles [284-290] have been published on the use of this material (Structure XXXI).



$$\left[-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}}\ Br^{\ominus}-(CH_2)_6-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^{\oplus}}}\ Br^{\ominus}-(CH_2)_3- \right]_n$$

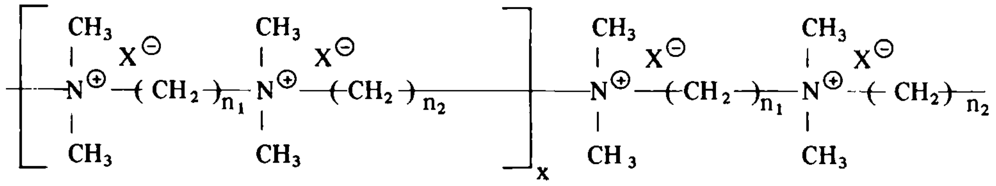
Polybrene, Mol. Wt. ca. 6,000

XXXI [284-290]

The recent work of Rembaum and his associates on these types of polyquaternaries has renewed interest in this area. In 1968, Rembaum, Baumgartner, and Eisenberg [291] proposed the generic name aliphatic "ionenes" for this class of polyquaternary amines. Since then this term has been widely accepted and used to describe this class of linear, polyquaternary ammonium resins derived from ditertiary amines and dihalides (Structures XXXII and XXXIII).

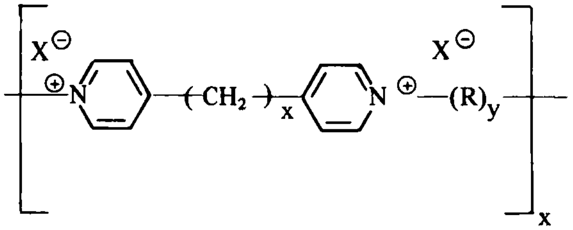
Rembaum [291] describes the synthesis of a series of Ionenes where $n_1 = 6$ and $n_2 = 3\text{-}10$ with molecular weights up to 40,000 and presents data on the mechanism and kinetics of formation of these polyquaternaries. He also proposes their use as electroconductive agents when complexed with 7,7,8,8-tetracyanoquinodimethane (TCNQ) and flocculants; their biocidal properties and ability to form polysalt complexes with polysulfonic materials are also mentioned.

Noguchi and Rembaum [292] reported that unexpected cyclic compounds were formed when tetramethyl diaminomethane was used as one of the reagents ($n_1 = 1$ in above formula). Rembaum concluded from his studies that 3-3 and 2-4 diamine-dihalide combinations yield ionene polymers with the highest density of positive charges; however, they have low molecular weights.



ALIPHATIC
IONENES
$n_1 = 6$
$n_2 = 3\text{-}10$

XXXII



AROMATIC IONENES
x = 2, 3 (Sat. or Unsat.)

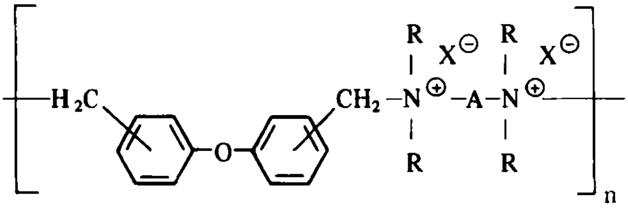
R = $-\!(CH_2)_n\!-$, n = 3-10 (Sat. or Unsat.)

R = o-, m-, p-xylyl

XXXIII [291-295]

Eisenberg and Tokoyama [293] determined the glass transition temperature of some aliphatic ionenes by plasticizing samples with glycerine and extrapolating to zero dilution and obtained very low values of $T_g \approx -90^\circ C$ (for $n_1 = 6$ and $n_2 = 4$ ionene). Rembaum [294] also reported recently on the use of ionenes to form polysalt complexes with anionic polyelectrolytes, and Rembaum et al. [295] discussed the electronic properties of TCNQ complexes with ionenes made from 1,2-bis(4-pyridyl) ethane and the corresponding ethylene compound with p-dibromoxylene.

Lloyd [296] prepared thermoplastic, electroconductive quaternary ammonium ionenes by alkylating ditertiary amines with 4,4′-bis(chloromethylphenyl) ether, and Kraiman and Hasson [297] also prepared polymers of this type by reacting ditertiary amines with chloromethylated diphenyl ethers and proposed their use for antistatic agents, electroconductive coatings for paper, fungicides, etc. (Structure XXXIV).

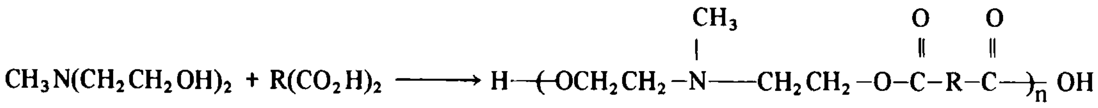


XXXIV [296, 297]

10. Poly(condensation Ammonium)

Alkanolamines can be condensed with dibasic acids to yield aminopolyesters, and Fuoss and Edelson [298] used this type of reaction to prepare a polyquaternary ammonium salt. They condensed methyldiethanolamine with succinic acid to obtain an aminopolyester which they subsequently quaternized with methyl bromide. These polymers offer model systems in which the charge-charge spacing is known and controllable. Fuoss and Edelson synthesized several polymers from different dibasic acids, determined their physical properties, and found that these polyquaternary ammonium polyesters were hydrolytically unstable in water (Eqs. 29 and 30).

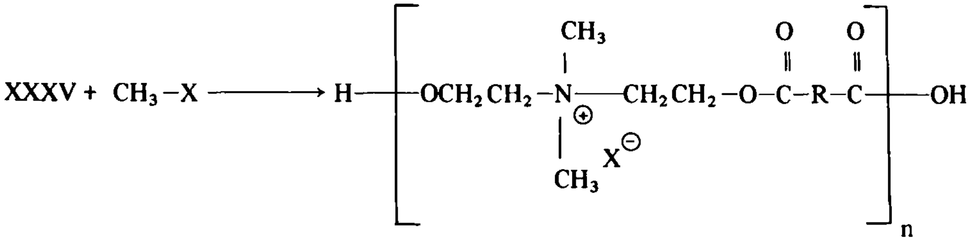
Polyethers can also serve as suitable substrates for the preparation of polyquaternaries. Witcoff [299] prepared a quaternary ammonium polyelectrolyte by quaternizing polyepichlorohydrin with pyridine; Rogers and Woehst [300] extended this to the trialkylamine quats, specifically trimethyl and triethyl. They claim the polymers are useful for modifying epoxy resins and sewage flocculants. Walker and Cambre



$$CH_3N(CH_2CH_2OH)_2 + R(CO_2H)_2 \longrightarrow H\!\left(OCH_2CH_2-\overset{\displaystyle CH_3}{\overset{|}{N}}-CH_2CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-R-\overset{\displaystyle O}{\overset{\|}{C}}\right)_{n} OH$$

(29)

A_{10} Aminopolyester, XXXV



$$XXXV + CH_3-X \longrightarrow H-\left[OCH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{N^{\oplus}}}}}-CH_2CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-R-\overset{\displaystyle O}{\overset{\|}{C}}\right]_{n}-OH \quad X^{\ominus}$$

(30)

[298]

[301] made fatty dodecyl ammonium quats which have antibacterial properties. Voss [302] also used these fatty alkyl ammonium polyethers to prepare cell-free somatic antigens (Eq. 31).

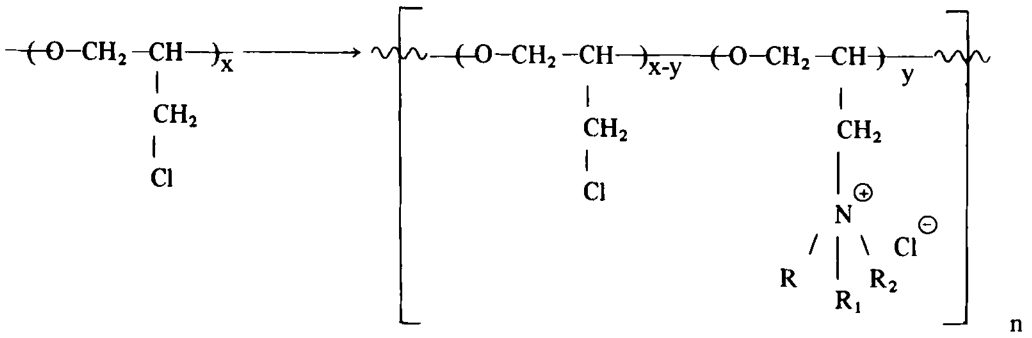
When copolymers containing epoxy groups derived from allyl glycidyl ether or glycidyl methacrylate are reacted with tertiary amines, polyquats are formed as described by Webers [303]. Vandenberg [304] polymerized various quaternary aminoepoxides to obtain polyquats useful as flocculating agents.

Coffman [305] made quaternary ammonium polymers by quaternizing a polytertiaryamine prepared by the reductive amination with dimethylamine of an ethylene/carbon monoxide polyketone.

Polyvinylketones have been condensed with hydrazines containing quaternary nitrogen groups to form polyquats by Laakso and Williams [306]. They react a polyvinylketone with Girard reagents "T" and "P" (betain hydrazide hydrochloride and carbohydrazine-methylpyridinium chloride, respectively) (Structures XXXVI and XXXVII). These polyquats are proposed for antistatic coatings on photographic film [307].

Maleic anhydride copolymers can be reacted with aminoalcohols or diamines to form polyquaternaries. Isaacson and Young [308] reacted styrene-maleic anhydride copolymer with dimethylaminopropylamine and subsequently quaternized the dimethylamino group to yield a polyquaternary which is proposed as a flocculant for oil slicks (Structure XXXVIII).

A common reaction employed to make polyquats is the chloromethylation of aryl-containing polymers (usually the stryl nucleus) followed by quaternization. The condensation polymerization of chloromethyl diphenyl ether provides another good aryl-substrate for polyquats, and Geyer, Hatch and Smith [309, 310] report the preparation of water-soluble mixed cationic ammonium and sulfonium diphenyl ether polymers. They condense chloromethyldiphenyl ether to give a methylene-diphenylether polymer containing residual chloromethyl groups and then quaternize these with trialkylamines and disulfides to form the corresponding polyquaternary ammonium and sulfonium salts. They claim utility for these materials as flocculants, drilling mud additives, anion exchange resins, binders, etc. Geyer [311] also discusses the use of these materials in paper for electroconductive treatments. These polyquaternaries tend to be highly colored due to low molecular weight impurities; therefore, for their utility they must be purified. Roth [312] discusses the use of perchloroethylene extraction to clean up the chloromethylated polymer prior to quaternization.

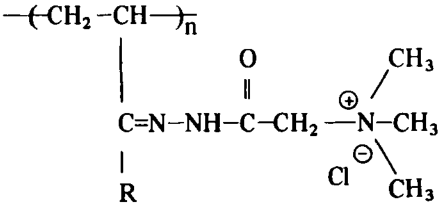


(31)

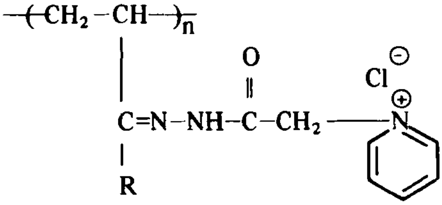
where $R = R_1 = R_2 =$ alkyl C_{1-4} or a ring system containing N

$R = R_1 =$ alkyl C_{1-4} and $R_2 =$ alkyl $C_{8,\ 10\ \mathrm{or}\ 12}$

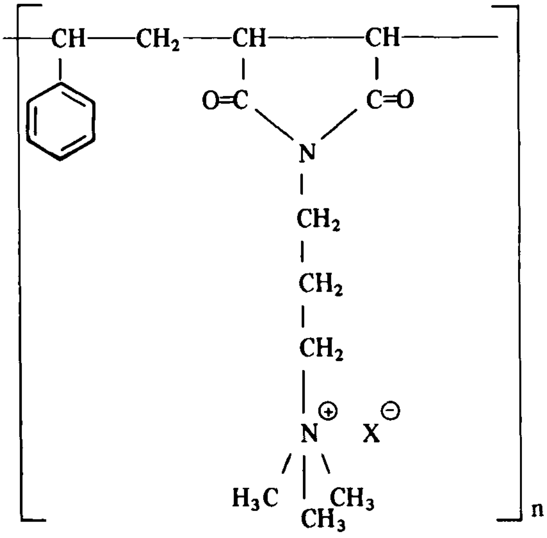
[299-302]



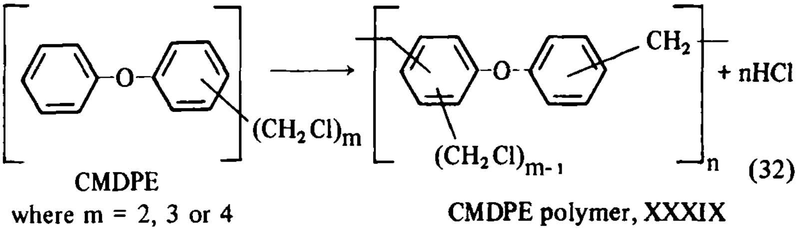
XXXVI [306]



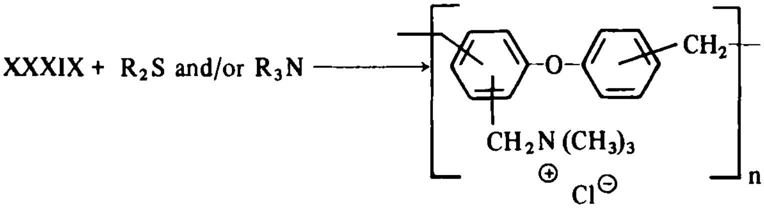
XXXVII [307]



XXXVIII [308]



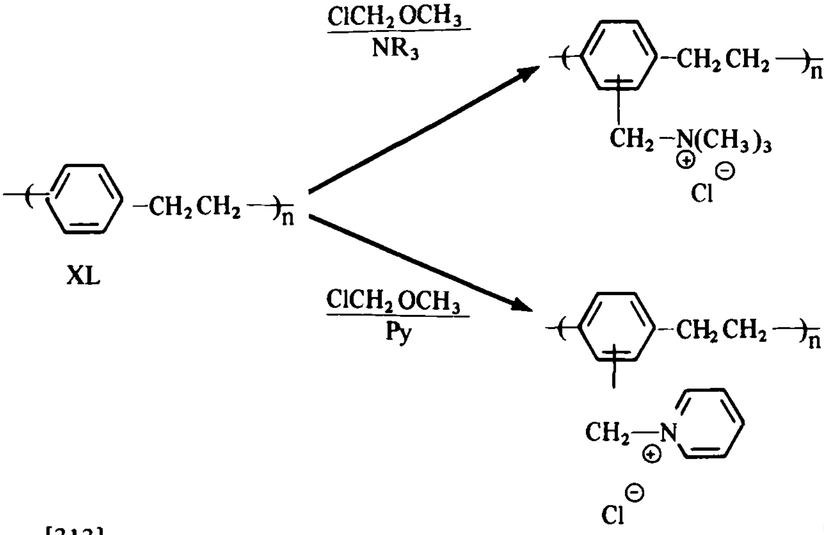
(32)



(33)

[309, 311]

Tevline et al. [313-315] also made similar polyquats by the polycondensation of dibenzyl with $ClCH_2CH_2Cl$ in the presence of $AlCl_3$ to give Structure XL which was modified by chloromethylation and subsequent amination with trialkyl amines or pyridine to provide polyquaternary ammonium salts.



[313]

(34)

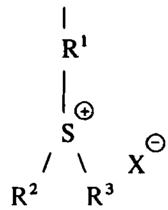
From a practical standpoint, all of the condensation polyquats suffer from three common drawbacks—1) they tend to be very low molecular weight (50,000 max.), 2) they tend to be cross-linked or to gel with storage, and 3) they are not reproducible in charge density or molecular weight. To date, no practically useful, commercial polyquats are made by these processes.

II. POLYSULFONIUM COMPOUNDS

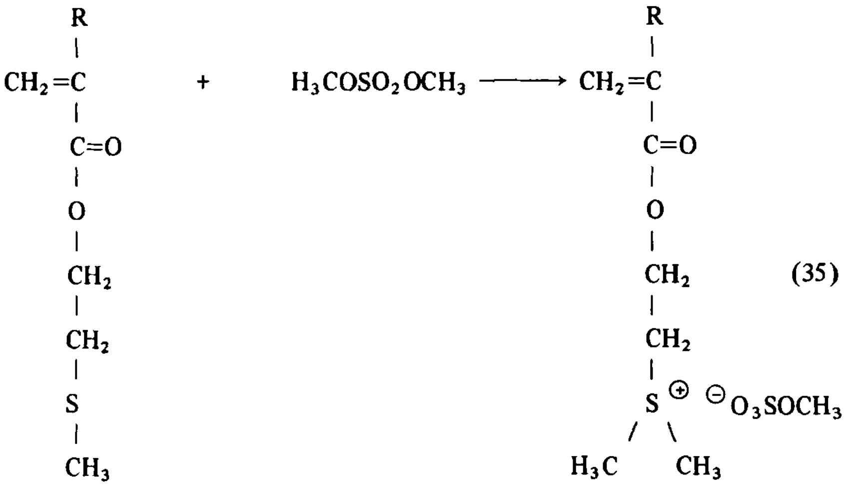
Sulfonium salts have been known for over a century; however, little work has been done on high polymeric sulfonium resins. This is probably due to the fact that sulfonium compounds are relatively unstable and break down to smelly sulfides. The sulfonium quaternary unit does not seem to have any special efficacy over the more readily available ammonium quaternary group.

Attempts to prepare unsaturated sulfonium salts have generally been unsuccessful. From Selkers [316] work, it has been shown that a double bond in the position α to a sulfur is unstable to any alkylating agent and is displaced. In general, sulfonium salts are not very stable and any group larger than methyl is subject to displacement by a smaller group.

1. Poly(meth)acryloxyethyl Sulfonium



LaCombe [317] recently disclosed a series of acrylic and methacrylic sulfonium monomers (sulfines) and their homopolymers (Eq. 35).



$$CH_2{=}C(R){-}C({=}O){-}O{-}CH_2{-}CH_2{-}S{-}CH_3 + H_3COSO_2OCH_3 \longrightarrow CH_2{=}C(R){-}C({=}O){-}O{-}CH_2{-}CH_2{-}\overset{\oplus}{S}(CH_3)_2\ {}^{\ominus}O_3SOCH_3 \qquad (35)$$

[317]

2-acryloxyethyl dimethyl
sulfonium methylsulfate

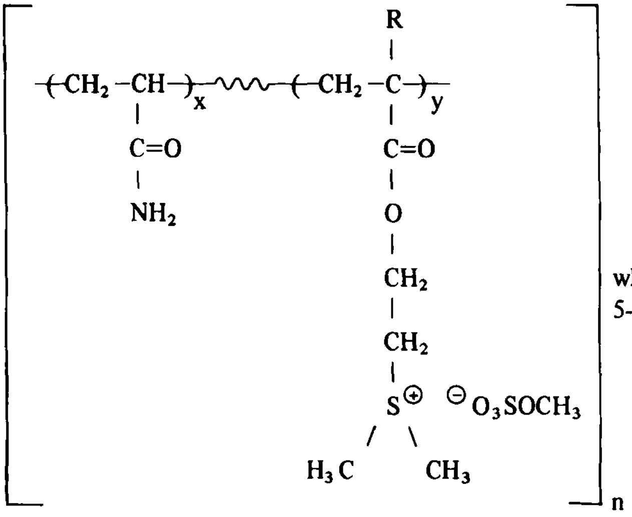
Usually the acrylic sulfonium monomers are prepared by reacting a thioether, 2-methyl thioethylacrylate, with an alkylating agent such as dimethyl sulfate. These monomers are extremely reactive and are usually prepared just prior to conversion to polymer to avoid spontaneous polymerization. The acrylic sulfonium monomer/polymer systems are said to be useful for improving the dyeability of fiber forming compositions and as flocculants.

Fang [318] also prepared the iodide and methosulfate salts of poly(methyl ethyl sulfonium ethyl methacrylate) by the alkylation of poly(2-ethylthioethyl methacrylate). These materials are reported to insolubilize upon heating and thus were used in preparing copolymers for various coating applications.

LaCombe and Bailey [319] also made water-soluble copolymers from these sulfonium acrylate monomers with acrylamide, N-vinylpyrrolidone, styrene, N-methyl-N-vinylacetamide, etc. (Structure XLI).

Bailey and LaCombe [320] disclosed a special process for making high molecular weight, solid copolymers of acrylamide and acrylic sulfonium salts, particularly suitable for use as flocculants, by conducting the copolymerization in acetone or acetonitrile as a solvent media wherein the monomers are soluble and the polymer precipitates as it is formed.

The use of these polymers is discussed by Bailey and LaCombe [321] in more detail in their patent on the use of the acrylic sulfonium homo-



$$\left[-\left(CH_2-\underset{\underset{NH_2}{|}}{\underset{C=O}{|}}{CH}\right)_x \sim\sim\sim \left(CH_2-\overset{R}{\overset{|}{C}}(COOCH_2CH_2\overset{\oplus}{S}(CH_3)_2\ {}^{\ominus}O_3SOCH_3)\right)_y- \right]_n$$

where y is 5-80 mole %

XLI [319-321, 325, 326]

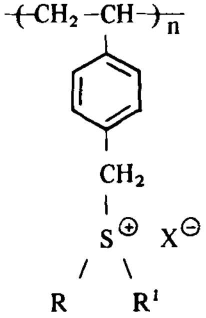
and copolymers as flocculants. Several other references [322-324] also disclose the use of these sulfonium polymers in turbidity removal from water by filtration, etc.

The acrylic sulfonium polymers were also used as paper additives to improve wet and dry strength properties and as pigment retention aids—as discussed by Eldred, Buttrick, and Spicer [325]. Smith [326] used the acrylic sulfonium homopolymers and copolymers along with glyoxal and mineral acid to improve the strength properties of fiberboard. LaCombe [327] also proposes the use of the acrylic sulfonium polymers as additives to fiber-forming compositions to increase their dye-affinity.

Acrylamide copolymers with 2-acryloxyethyl dimethylsulfonium methyl sulfate (60/40 by wt, respectively) are reported by Hansen [328] to stabilize water-in-oil emulsions used for hair dressings. Smith et al. [329] made thermosetting printing inks for tissue paper from sulfonium polymers of both the vinylbenzyl and acrylic type.

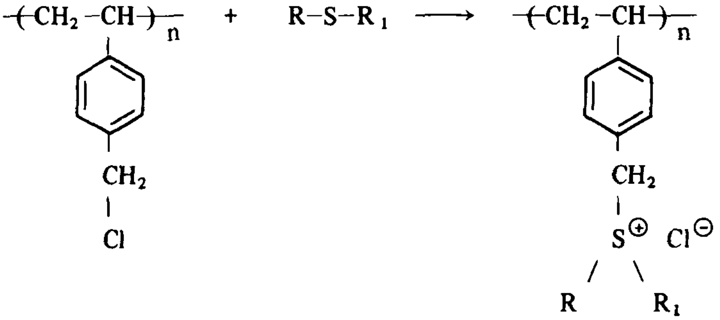
Garrett et al. [330] copolymerized 2-40 mole % of 2-acryloxyethyl dimethylsulfonium methylsulfate with acrylics such as 2-ethylhexylacrylate to obtain pressure-sensitive adhesive compositions.

2. Poly(Vinylbenzyl Sulfonium)



Hatch first prepared vinylbenzyl sulfonium resins by reacting chloromethylated styrene-divinylbenzene beads with dimethyl sulfide to produce anion exchange and chelating resins (by further reaction of nucleophiles with the sulfonium resin).

Hatch and McMaster [331] disclosed the synthesis of a series of vinylbenzyl sulfonium monomers and homopolymers by reacting vinylbenzyl chloride (p-chloromethylstyrene) with various dialkyl sulfides. They claim the vinylbenzyl sulfonium homopolymers are useful for cationic thickening agents and for the flocculation of slimes such as taconite tailings (Eq. 36).



(36)

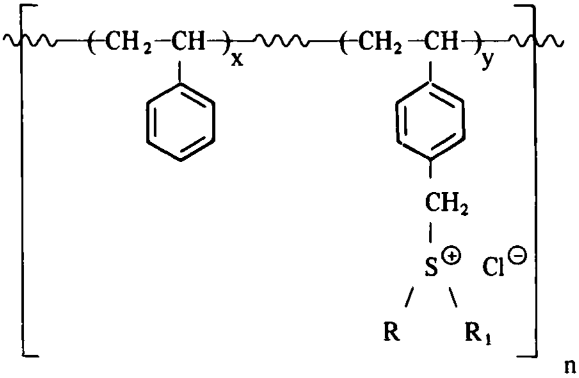
[331-334]

Another way of synthesizing this same polymer structure is to quaternize a chloromethyl styrene containing polymer. Lloyd [332] made vinylbenzyl sulfonium halide resins by reacting a vinylbenzyl halide polymer, either 1) linear, or 2) branched or cross-linked (with 0.01 to 1% divinylbenzene) with an organic sulfide. The vinylbenzyl chloride polymers are most advantageously used in the form of an aqueous latex, which upon treatment with the sulfide is converted to an aqueous solution of the polyvinylbenzyl sulfonium chloride resin.

Hatch and Geyer [333] also prepared polyvinylbenzyl sulfonium polymers by reaction of an organic sulfide with a chloromethylated arylvinyl polymer by using a coupling solvent ("organic transfer solvent") to assist in the phase transition from the organic solvent solution of polychloromethylstyrene to the aqueous solution of the polyvinylbenzyl sulfonium resin.

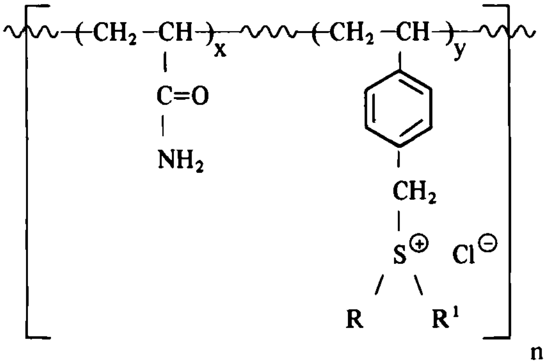
In a recent article, Hatch, Meyer, and Lloyd [334] reviewed sulfonium monomers and polymers derived from Ar-vinylbenzyl chloride.

Sexsmith and Frazza [335] also prepared sulfonium polymers by quaternizing a copolymer of styrene and chloromethylstyrene with sulfides to obtain cationic sulfonium polymers (Structure XLII).



XLII [335, 371]

Rassweiler and Sexsmith [336] made copolymers of acrylamide and vinylbenzyl sulfonium chloride by reacting a copolymer of acrylamide and chloromethyl styrene with dialkyl sulfides (Structure XLIII).



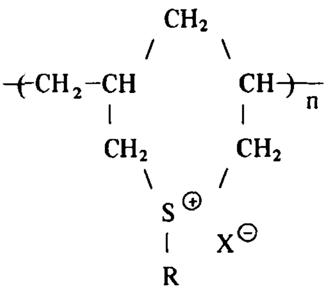
XLIII [104, 336, 337, 372]

They claim the copolymers are useful for soil conditioning and imparting dry strength to paper. Humiston, Meyer, and Kenaga [337] also have used vinylbenzyl sulfonium homopolymers and copolymers (with styrene, acrylamide, and acrylic acid) for increasing the strength properties of paper.

Morgan and Hatch [338] used the combination of a polyvinylbenzyl sulfonium resin and a polycarboxylate resin to increase the wet strength of paper.

Vinylbenzyl trialkylammonium polymers have been proposed as conductive coatings for paper, as previously discussed, and Geyer [339] has found that a mixed copolymer of vinylbenzyl sulfonium and ammonium moieties provides water-soluble conductive coatings which are subject to insolubilization upon thermal treatment to provide water-insoluble conductive coatings.

3. Poly(diallyl Sulfonium)



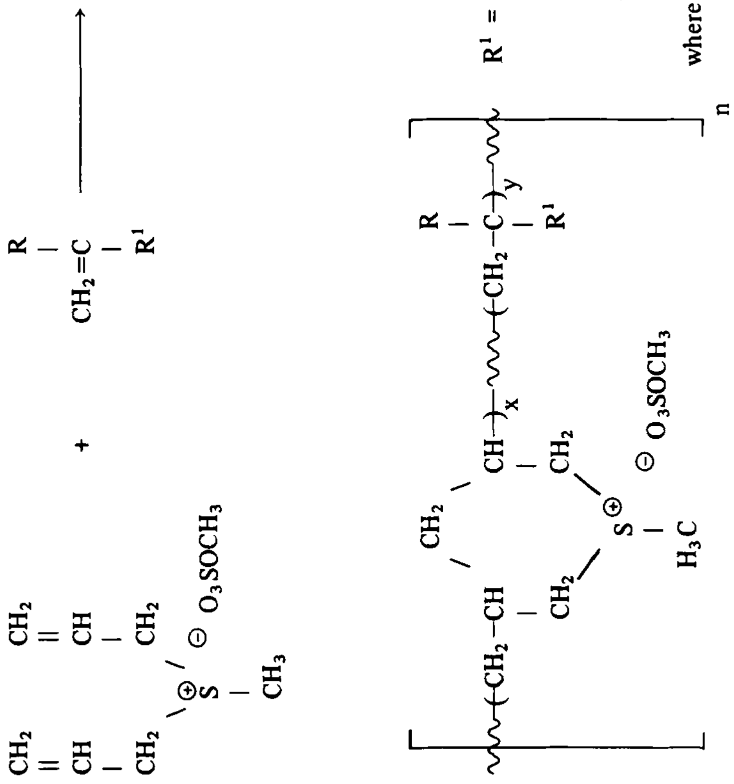
Butler and Benjamin [340] first prepared methyldiallyl sulfonium methylsulfate from diallyl sulfide and dimethyl sulfate in methanol, but they did not report any polymerization studies.

Price and Schuller [341] made linear, soluble copolymers from diallyl sulfonium monomers. The specific sulfonium monomer used in their work was methyl diallyl sulfonium methylsulfate which was copolymerized with other monovinyl materials such as styrene, acrylic esters, acrylonitrile, acrylamide, and vinyl acetate, as shown in Eq. (37).

Schuller et al. [342] published a paper in 1954 disclosing the use of copolymers of methyldiallyl sulfonium methylsulfate and acrylamide as paper treating agents for strength improvement and to provide dye sites. The copolymers were prepared in aqueous solutions by using Redox catalyst systems.

4. Poly(condensation Sulfonium)

Other miscellaneous polyelectrolyte systems containing the sulfonium group have been reported such as the work by Makino and Sugi [343, 344]



(37)

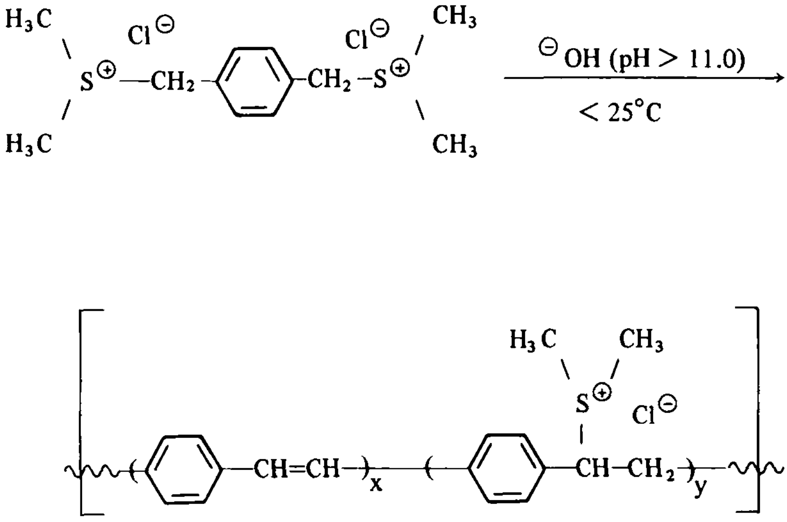
[341]

$$R^1 = -CN,\ -OR,\ -O\overset{O}{\overset{\|}{C}}CH_3,\ -\overset{O}{\overset{\|}{C}}-OR,\ -\overset{O}{\overset{\|}{C}}-NH_2,\ -\overset{O}{\overset{\|}{C}}-R$$

where x = 0.1 to 40 mole %

on the influence of counterion species on the polyelectrolyte behavior (ion-binding and conformation) of poly-L-methionine-S-methylsulfonium salts.

Wessling and Zimmerman [345] disclosed a new fluorescent sulfonium polyelectrolyte (Eq. 38). These sulfonium polymers are made by



(38)

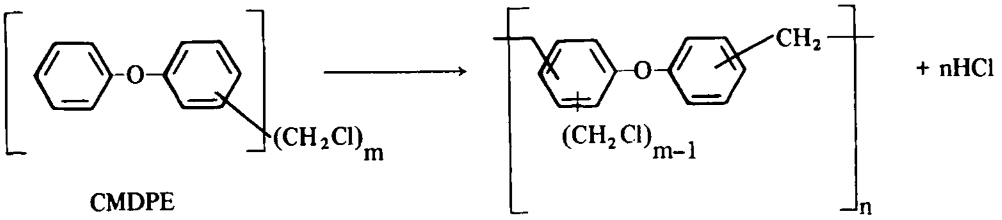
[345, 346]

polymerizing bis-solfonium salts, such as p-phenylene dimethylene bis(dimethyl sulfonium chloride) in a cold, strongly basic aqueous solution. The polymers are reported to be fluorescent under UV and useful as cellulosic dyes and ultraviolet light absorbers.

Further reaction of these sulfonium resins with a mercaptan or thiol produces water-resistant, non-conducting protective coatings [346].

The same reactions were also used by Kanbe and Okawara [347] to prepare poly(p-xylylidenes) from p-xylylene bis(dimethylsulfonium) tetrafluoroborate.

Geyer, Hatch, and Smith [348, 349] describe the preparation of a sulfonium methylenediphenyl ether polymer analogous to the ammonium resins which is made by the condensation polymerization of a chloromethyldiphenylether to give a linear, soluble methylenediphenylether polymer containing residual chloromethyl groups. The residual chloromethyl groups are then reacted with a dialkyl sulfide to form the sulfonium

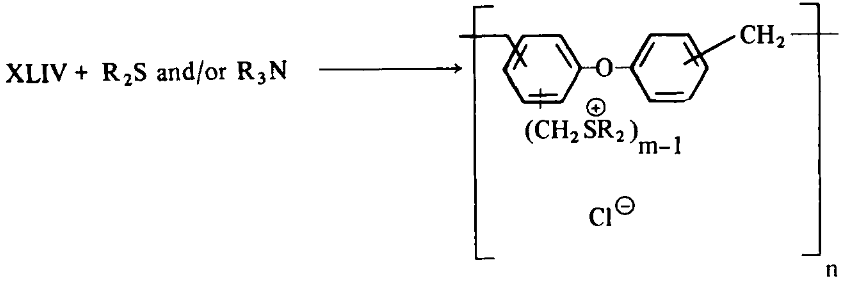


CMDPE

where m = 2, 3 or 4

CMDPE polymer XLIV

(39)



(40)

[348-351]

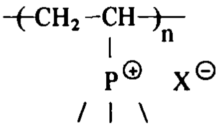
chloride resin. These sulfonium resins are reported to improve the wet and dry strength of paper and provide electroconductive properties [350] (Eqs. 39 and 40).

Geyer [350] also prepared mixed sulfonium-ammonium methylenediphenylether polymers, wherein the sulfonium moiety—[bis(hydroxyethyl sulfonium)]—provides a bonding site for attachment to the cellulose (see Geyer [113] for analogous polymers based on vinylbenzyl).

Recently, Chiu [351] presented data which shows the high degree of retention of these methylenediphenylether sulfonium polymers on pulp.

III. POLYPHOSPHONIUM COMPOUNDS

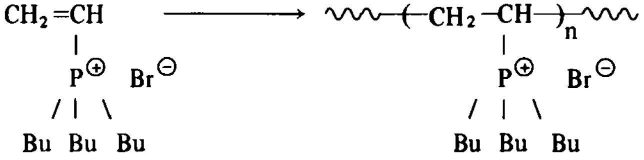
1. Poly(vinyl Phosphonium)



$$-\!\left(CH_2-\underset{\underset{/\ |\ \backslash}{P^{\oplus}}}{\underset{|}{CH}}\right)_n\!-\quad X^{\ominus}$$

Attempts to convert vinyl phosphorus compounds to high molecular weight polymers have been in progress for some time [352]. However, except for an isolated result reported by Tsetlin [353] and co-workers concerning the polymerization of diethyl- and diphenylvinyl phosphine oxide to polymers with molecular weights of 30,000 by ionizing radiation, all efforts have been fruitless, resulting in low molecular weight oligomers.

Although vinylphosphonium salts have been known for more than a century [354], no polymerization work has been reported until recently when Pellon and Valan [355] discovered that tributylvinylphosphonium bromide is converted to a high molecular weight polymer upon irradiation of its aqueous solutions. This was quite unexpected since Gillis [356] has shown that the corresponding vinyl ammonium and sulfonium compounds are not polymerizable (Eq. 41).



$$\underset{\underset{\underset{Bu\ Bu\ Bu}{/\ |\ \backslash}}{P^{\oplus}\ Br^{\ominus}}}{\underset{|}{CH_2{=}CH}} \longrightarrow \sim\!\!\sim\!\left(CH_2-\underset{\underset{\underset{Bu\ Bu\ Bu}{/\ |\ \backslash}}{P^{\oplus}\ Br^{\ominus}}}{\underset{|}{CH}}\right)_n\!\sim\!\!\sim \qquad (41)$$

[355, 357-360]

Further work on the polymerization of tributyl phosphonium bromide in the crystalline state by ionizing radiation was reported by Chen [357, 358].

The mechanism of the ionizing radiation-initiated polymerization of aqueous solutions of tributyl vinylphosphonium bromide to high molecular weight polymers was established to be free radical by Rabinowitz and Marcus [359], and Pellon, Grayson, and Valan [360] also worked on tributyl vinylphosphonium polymers made by various free radical catalysts.

The work of Rabinowitz and Marcus [359] showed that conventional oxidizing peroxide free radical catalysts failed to initiate the polymerization of tributyl vinylphosphonium bromide, but nonoxidizing materials like ditertbutylperoxide and azo compounds did catalyze the polymerization to give high molecular weight polymers. They postulate that the oxidizing peroxides are quickly reduced by the bromide ion before any homolytic cleavage can occur to generate initiating radicals. Rabinowitz and Marcus also observed that tributyl vinylphosphonium chloride was polymerized in aqueous solution using potassium persulfate; the homolytic cleavage of persulfate seems to compete favorably with redox processes involving the chloride ion. This observation is similar to the case of other ammonium halide monomers (e.g., vinyl pyridinium halides, vinylbenzyltrialkyl ammonium halides, and dialkyldiallyl ammonium halides) where the chloride anion form of the monomer polymerizes to much higher molecular weights than the bromides and the iodides do not seem to polymerize well, if at all.

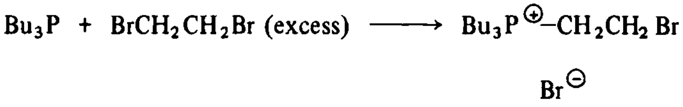
The work of Rabinowitz and Marcus also indicates that polymers from tributyl vinylphosphonium halides seem to be an exception since other trialkyl groups (ethyl, cyclohexyl, phenyl) failed to yield any polymer. Copolymers of tributyl vinylphosphonium halides are also reported.

Poly(tributylvinylphosphonium bromide) is claimed by Gillham and Sherr [361] to be an effective flame retardant for thermoplastic products, and treatment of cellulosic and fibrous materials with a trialkyl vinylphosphonium halide (specifically, the tributyl bromide) monomers or their acetate precursors is claimed to impart both antistatic and flameproof properties [362, 363].

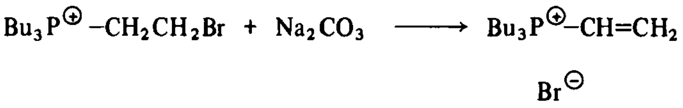
Di-, tri-, or tetra-vinylphosphonium salts are reported to have utility in treating cellulosic materials for improving crease resistance and provide antistatic properties and anionic dye acceptance [364].

The synthesis of vinylphosphonium, arsonium and stibonium monomers is discussed by Maier et al. [365].

The synthesis of vinylphosphonium monomers by the sodium carbonate dehydrobromination of the 2-bromoethyl salt prepared from tributyl phosphine and dibromoethane is discussed by Rabinowitz, Henry, and Marcus [366] (Eqs. 42 and 43).



$$Bu_3P + BrCH_2CH_2Br\ (excess) \longrightarrow \underset{Br^{\ominus}}{Bu_3P^{\oplus}}-CH_2CH_2Br \tag{42}$$

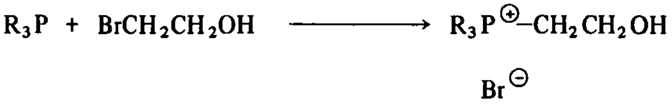


$$\underset{}{Bu_3P^{\oplus}}-CH_2CH_2Br + Na_2CO_3 \longrightarrow \underset{Br^{\ominus}}{Bu_3P^{\oplus}}-CH=CH_2 \tag{43}$$

[366]

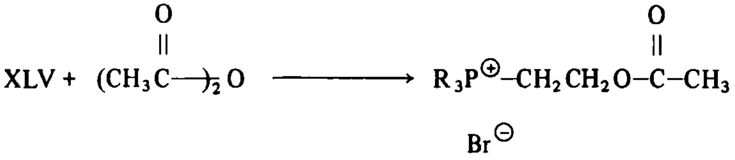
55-72% yield

Rauhut, Borowitz, and Grayson [367] reported the snythesis of trialkyl vinylphosphonium halides by sodium carbonate treatment of the acetate resulting from the acetic anhydride acetylation of the salt formed from the reaction of ethylene bromohydrin and the corresponding phosphine (Eqs. 44-46).



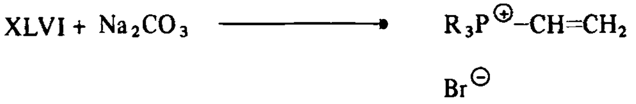
$$R_3P + BrCH_2CH_2OH \longrightarrow \underset{Br^{\ominus}}{R_3P^{\oplus}}-CH_2CH_2OH \tag{44}$$

XLV



$$XLV + (CH_3\overset{\overset{O}{\|}}{C}\!-\!)_2O \longrightarrow \underset{Br^{\ominus}}{R_3P^{\oplus}}-CH_2CH_2O-\overset{\overset{O}{\|}}{C}-CH_3 \tag{45}$$

XLVI



$$XLVI + Na_2CO_3 \longrightarrow \underset{Br^{\ominus}}{R_3P^{\oplus}}-CH=CH_2 \tag{46}$$

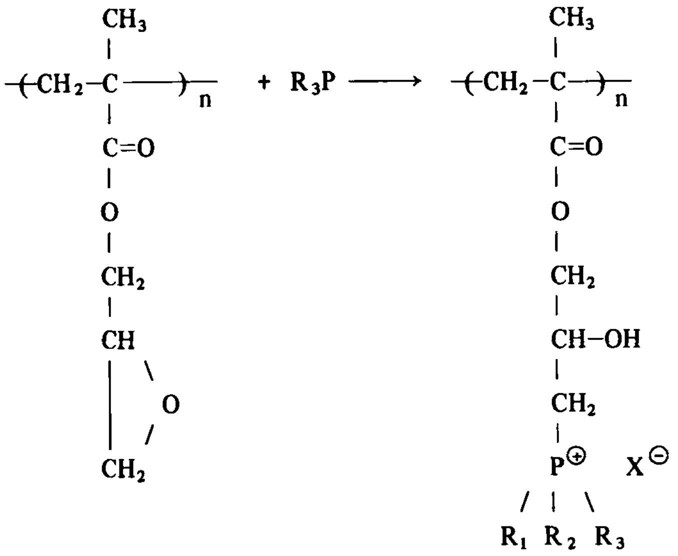
[367]

Attempts to prepare vinylphosphonium salts from vinyl halides and phosphines have been unsuccessful [367].

Analogous to Ham's work with carbovinyloxymethylammonium monomer/polymer systems derived from vinylchloroacetate, Paré and Hauser [368] reacted vinylchloroacetate with phosphines to prepare carbovinyloxymethyl trialkylphosphonium chloride monomers and polymers which displayed flame resistant properties.

2. Poly(acrylic phosphonium)

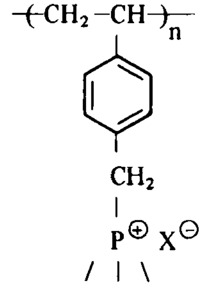
Analogous to Sobolev's work on 2-hydroxypropyl quaternary ammonium methacrylates, Franco [369] prepared polymers containing phosphonium groups by reacting poly (glycidylmethacrylate) with phosphines and used these phosphonium polymers to fix dyes in photographic film (Eq. 47).



(47)

[369]

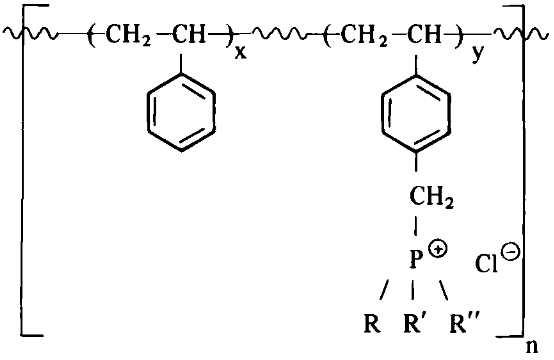
3. Poly(vinylbenzyl Phosphonium)



Polymers containing the vinylbenzyl phosphonium unit can be made by two general techniques: 1) either by direct synthesis of the monomers and subsequent polymerization, or 2) by phosphonation of chloromethylstyrene containing polymers. The latter is preferred due to the difficulty of obtaining the vinylbenzyl phosphonium monomer in good yield and purity without spontaneous polymerization.

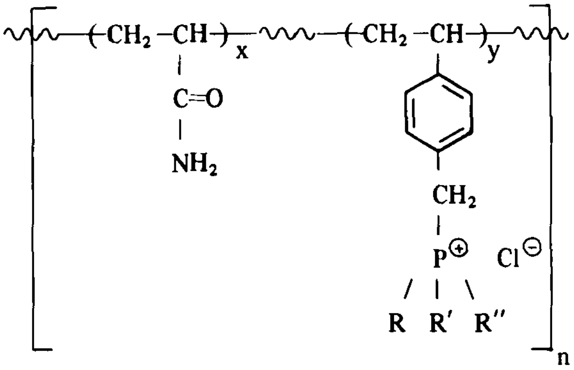
Monomers of this type are usually prepared by the reaction of p-vinylbenzyl halide with the appropriate trialkyl phosphine in alcohol, benzene, or other convenient anhydrous solvent as proposed by Garner et al. [370] who prepared p-vinylbenzyltriphenyl phosphonium chloride.

Salts of these monomeric phosphonium cations with polyacrylate anions are reported to be useful for preparing nonflammable and heat-resistant polymers. Sexsmith and Frazza [371] disclosed water soluble vinylbenzyl phosphonium polymers which they prepared by quaternizing a copolymer of styrene and chloromethyl styrene with a phosphine to obtain cationic phosphonium polyelectrolytes (Structure XLVII).



XLVII [335, 371]

Likewise, Rassweiler and Sexsmith [372] quaternized copolymers of acrylamide and chloromethyl styrene with phosphines to get water-soluble phosphonium polyquaternaries (Structure XLVIII).

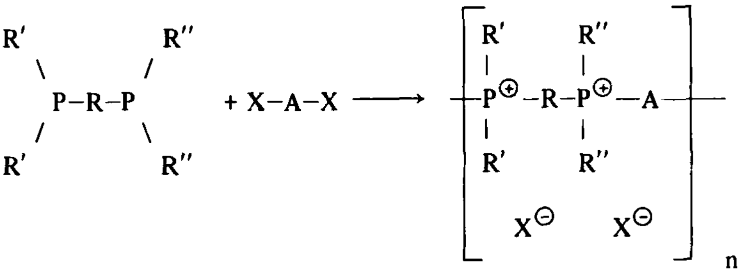


where y = 1-95 mole %

XLVIII [104, 336, 372]

4. Poly(condensation Phosphonium)

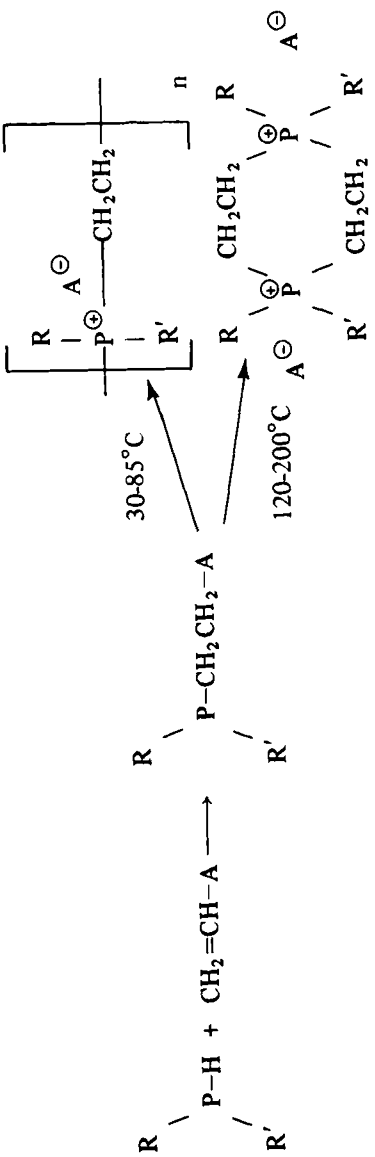
Braye [373] produced a polyphosphonium resin by reacting diphosphines with dihalides to produce an integral polyphosphonium ionene, which is claimed to be useful for antistats, flame retardants, and also to have electroconductive properties when it contians conjugated double bonds (Eq. 48).



(48)

[373]

Rauhut [374, 375] prepared polyphosphonium resins by reacting a secondary phosphine with vinyl esters or halides followed by subsequent conversion of the reaction product to a polydialkylethylenephosphonium salt (Eq. 49).



(49)

$A = \text{halogen or } -O\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

[374, 375]

REFERENCES

Polyammonium

[1] Rohm & Haas Co., T.I.B. SP-84 (April, 1963).
[2] *Mod. Chem.*, 6(2), 14-25 (1969).
[3] A. L. Barney, U.S. Patent 2,677,679 (March 4, 1954) to DuPont.
[4] A. L. Barney, Reissue 24,164 (June 12, 1956) to DuPont.
[5] W. O. Forshey and J. E. Kirby, U.S. Patent 2,680,112 (June 1, 1954) to DuPont.
[6] H. E. Winberg, U.S. Patent 2,744,130 (May 1, 1956) to DuPont.
[7] A. Meader, U.S. Patent 2,965,594 (December 20, 1960) to Ciba Ltd.
[8] H. L. Jackson and W. K. Wilkinson, U.S. Patent 2,794,015 (May 26, 1957) to DuPont.
[9] Belg. Patent 725,882 (June 20, 1969) to American Cyanamid Co.
[10] Brit. Patent 1,077,772 (August 2, 1967) to Rohm & Haas Co.
[11] A. Hartmann, U.S. Patent 2,846,423 (August 5, 1958) to Farbwerke Hoechst A.G.
[12] L. E. Hughes, U.S. Patent 2,694,688 (November 16, 1954) to DuPont.
[13] O. C. Bacon and L. E. Hughes, U.S. Patent 2,729,577 (January 3, 1956) to DuPont.
[14] M. Hayek, U.S. Patent 2,723,256 (November 8, 1955) to DuPont.
[15] M. Hayek, U.S. Patent 2,741,568 (April 10, 1956) to DuPont.
[16] H. L. Jackson, U.S. Patent 2,832,746 (April 29, 1958) to DuPont.
[17] H. L. Jackson, U.S. Patent 2,832,749 (April 29, 1958) to DuPont.
[18] J. P. Combere and F. P. Reed, U.S. Patent 2,824,861 (February 25, 1958) to Hoffman & Co.
[19] I. J. Gruntfest and D. B. Fordyce, U.S. Patent 2,838,397 (June 10, 1958) to Rohm & Haas Co.
[20] D. B. Fordyce, F. J. Glavis, and S. Malamed, U.S. Patent 3,023,162 (February 27, 1962) to Rohm & Haas Co.
[21] R. H. Grey and V. J. Webers, U.S. Patent 2,892,822 (June 30, 1959) to DuPont.
[22] R. H. Grey and V. J. Webers, U.S. Patent 2,839,401 (June 17, 1958) to DuPont.
[23] S. Melamed, U.S. Patent 2,808,349 (October 1, 1957) to Rohm & Haas Co.
[24] S. Melamed, U.S. Patent 2,810,713 (October 22, 1957) to Rohm & Haas Co.
[25] S. Melamed, U.S. Patent 2,843,573 (July 15, 1958) to Rohm & Haas Co.

[26] S. Melamed and R. H. Shimizu, U.S. Patent 3,170,901 (February 23, 1965) to Rohm & Haas Co.

[27] R. H. Zeitschel and S. Melamed, U.S. Patent 3,008,851 (November 14, 1961) to Rohm & Haas Co.

[28] W. S. Clapp and C. M. Yee, U.S. Patent 3,139,321 (June 30, 1964) to DuPont.

[29] R. A. Guenthner, U.S. Patent 3,207,730 (September 21, 1965) to Minnesota Mining and Manufacturing Co.

[30] F. J. Marascia, J. A. Nelson, and C. S. J. Rondestvedt, U.S. Patent 3,248,352 (April 26, 1966) to DuPont.

[31] A. K. Mackenzie, U.S. Patent 3,112,241 (November 26, 1963) to DuPont.

[32] A. C. Nixon, P. J. Berrigan, and P. H. Williams, U.S. Patent 3,278,474 (October 11, 1966) to Shell Oil Co.

[33] J. H. Daniel, Jr., U.S. Patent 2,964,445 (December 13, 1960) to American Cyanamid Co.

[34] *Federal Register,* Vol. 29, No. 117, 1687-1690 (June 16, 1964).

[35] D. J. Monagle and W. P. Shyluk, U.S. Patent 3,336,270 (August 15, 1967) to Hercules, Inc.

[36] D. J. Monagle, U.S. Patent 3,336,269 (August 15, 1967) to Hercules, Inc.

[37] T. Fujimoto, M. Murata, N. Obokata, and S. Kita, U.S. Patent 3,361,718 (January 2, 1968) to Sanyo Chem. Ind. Co., Ltd.

[38] J. Szita, U. Bahr, H. Marzolph, and G. Nischk, U.S. Patent 3,408,338 (October 29, 1968) to Farbenfabriken Bayer, A.G.

[39] J. E. Kirby, U.S. Patent 2,396,275 (March 12, 1946) to DuPont.

[40] C. G. Overberger, H. Biletch, and R. G. Nickerson, *J. Polym. Sci.,* 27, 381-390 (1958).

[41] A. Rembaum, S. Singer, and H. Keyzer, *J. Polym. Sci., Part B,* 7, 395-402 (1969).

[42] J. A. Anthes, U.S. Patent 2,567,836 (September 11, 1951) to American Cyanamid Co.

[43] I. Sobolev, U.S. Patent 3,329,706 (July 4, 1967) to Shell Oil Co.

[44] I. Sobolev, U.S. Patent 3,428,617 (February 18, 1969) to Shell Oil Co.

[45] A. R. Mills, U.S. Patent 3,347,832 (October 17, 1967) to Shell Oil Co.

[46] A. DeBenedictis and I. Sobolev, U.S. Patent 3,321,649 (May 23, 1967) to Shell Oil Co.

[47] A. DeBenedictis, and I. Sobolev, Brit. Patent 1,140,520 (January 22, 1969) to Shell Internationale Res. M.N.V.

[48] J. C. H. Hwa, U.S. Patent 2,630,427 (March 3, 1953) to Rohm & Haas Co.

[49] J. C. H. Hwa, U.S. Patent 2,862,893 (December 2, 1958) to Rohm & Haas Co.

[50] E. Bergmeister and J. Hackmair, U.S. Patent 3,245,939 (April 12, 1966) to Wacker Chemie, G.m.b.H.

[51] R. J. Schaper and M. F. Hoover, Belg. Patent 711,310 (August 26, 1968) to Calgon Corp.

[52] C. D. Shacklett, U.S. Patent 2,777,872 (January 15, 1957) to DuPont.

[53] C. D. Shacklett, U.S. Patent 2,834,758 (May 13, 1958) to DuPont.

[54] C. D. Shacklett, U.S. Patent 2,846,417 (August 5, 1958) to DuPont.

[55] W. H. Schuller and W. M. Thomas, U.S. Patent 2,935,493 (May 3, 1960) to American Cyanamid Co.

[56] S. Melamed and R. H. Shimizu, U.S. Patent 3,166,540 (January 19, 1965) to Rohm & Haas Co.

[57] S. Melamed, U.S. Patent 2,980,657 (April 18, 1961) to Rohm & Haas Co.

[58] L. H. Wilson, W. M. Thomas, and J. J. Padbury, U.S. Patent 2,884,057 (April 28, 1959) to American Cyanamid Co.

[59] A. Maeder, U.S. Patent 3,095,390 (June 25, 1963) to Ciba Ltd.

[60] R. L. Gustafson and J. A. Lirio, *Ind. Eng. Chem.*, 7(2), 116-120 (1968).

[61] G. T. Jones, Can. Patent 595,642 (April 5, 1960) to Imperial Chem. Ind., Ltd.

[62] G. T. Jones, Can. Patent 583,352 (September 15, 1959) to Imperial Chem. Ind., Ltd.

[63] W. Baird, W. Batty, A. E. Henshall, and T. Jones, Brit. Patent 788,079 (December 23, 1957) to Imperial Chem. Ind., Ltd.

[64] O. Olaj and A. Maeder, U.S. Patent 3,178,397 (April 13, 1965) to Ciba Ltd.

[65] B. M. Culbertson and R. C. Slagel, *J. Polym. Sci., Part A-1*, **6**, 363-373 (1968).

[66] B. M. Culbertson, E. A. Sedor, S. Dietz, and R. E. Freis, *J. Polym. Sci., Part A-1*, **6**, 2197-2207 (1968).

[67] B. M. Culbertson, E. A. Sedor, and R. C. Slagel, *Macromolecules*, **1**, 254-260 (1968).

[68] J. W. Reppe, *Government Rept.*, U. S. Dept. Commerce, Rept. PB18852-s, 1949, pp. 66-68.

[69] C. Gardner, V. Kerrigan, J. D. Rose, and B. C. L. Weedon, *J. Chem. Soc.*, **1949**, 789-792.

[70] W. Moore, U.S. Patent 1,797,877 (March 24, 1931) to American Cyanamid Co.

[71] G. E. Ham and P. W. Gann, *Ind. Eng. Chem.*, **45**(10), 2320-2323 (1953).
[72] J. H. Daniel, Jr., U.S. Patent 2,914,513 (November 24, 1959) to American Cyanamid Co.
[73] D. R. Sexsmith, U.S. Patent 3,050,506 (August 21, 1962) to American Cyanamid Co.
[74] J. P. Newport and R. J. W. Reynolds, *Soc. Chem. Ind.* (London) *Monogr.*, **25**, 131-142 (1967).
[75] W. J. Levy, J. P. Newport, and J. W. Reynolds, U.S. Patent 3,432,430 (March 11, 1969) to Imperial Chem. Ind., Ltd.
[76] D. W. Heseltine and D. A. Brooks, U.S. Patent 3,455,693 (July 15, 1969) to Eastman Kodak Co.
[77] G. E. Ham, A. B. Craig, and P. W. Gann, *Ind. Eng. Chem.*, **45**(10), 2323-2326 (1953).
[78] G. E. Ham, U.S. Patent 2,572,560 (October 23, 1951) to Monsanto Chemical Co.
[79] G. E. Ham, U.S. Patent 2,572,561 (October 23, 1951) to Monsanto Chemical Co.
[80] J. A. Price, U.S. Patent 2,654,729 (October 6, 1953) to American Cyanamid Co.
[81] W. H. Schuller and W. M. Thomas, U.S. Patent 2,935,493 (May 3, 1960) to American Cyanamid Co.
[82] H. Narasaki, *Kogyo Kagaku Zasshi*, **65**, 793-804 (1962).
[83] M. R. Lytton, U.S. Patent 2,617,781 (November 11, 1952) to DuPont.
[84] A. L. Barney, U.S. Patent 2,764,578 (September 25, 1956) to DuPont.
[85] Brit. Patent 815,745 (July 1, 1959) to Rohm & Haas Co.
[86] S. Melamed, U.S. Patent 2,980,634 (April 18, 1961) to Rohm & Haas Co.
[87] A. Maeder and O. Albrecht, U.S. Patent 3,198,762 (August 3, 1965) to Ciba Ltd.
[88] G. B. Butler and R. L. Goette, *J. Amer. Chem. Soc.*, **74**, 1939-1941 (1952).
[89] D. D. Reynolds, U.S. Patent 3,345,346 (October 3, 1967) to Eastman Kodak Co.
[90] S. Melamed, U.S. Patent 2,871,203 (January 27, 1959) to Rohm & Haas Co.
[91] M. E. Cupery and J. C. Sauer, U.S. Patent 2,720,511 (October 11, 1955) to DuPont.

[92] G. D. Jones, U.S. Patent 2,694,702 (November 16, 1954) to Dow Chemical Co.

[93] G. D. Jones, *Ind. Eng. Chem.*, **44**, 2686-2693 (1952).

[94] W. G. Lloyd, U.S. Patent 3,178,396 (April 13, 1965) to Dow Chemical Co.

[95] J. F. Vitkuske and F. C. Rutledge, U.S. Patent 3,072,588 (January 8, 1963) to Dow Chemical Co.

[96] W. G. Lloyd and J. F. Vitkuske, *J. Appl. Polym. Sci.*, **6**(24), S57-S59 (1962).

[97] W. G. Lloyd and T. E. Durocher, *J. Appl. Polym. Sci.*, **7**(6), 2025-2033 (1963).

[98] W. G. Lloyd and T. E. Durocher, *J. Appl. Polym. Sci.*, **8**, 953-969 (1964).

[99] C. B. Arends, *J. Chem. Phys.*, **38**(2), 322-324 (January 1963).

[100] G. D. Jones and S. J. Goetz, *J. Polym. Sci.*, **25**, 201-215 (1957).

[101] L. R. Morris, U.S. Patent 2,772,310 (November 27, 1956) to Dow Chemical Co.

[102] J. T. Clarke and A. H. Hamerschlag, U.S. Patent 2,780,604 (February 5, 1957) to Ionics, Inc.

[103] W. Juda and A. H. Hamerschlag, U.S. Patent 2,860,097 (November 11, 1958) to Ionics, Inc.

[104] J. H. Rassweiler and D. R. Sexsmith, U.S. Patent 3,068,213 (December 11, 1962) to American Cyanamid Co.

[105] G. D. Jones, J. R. Runyon, and J. Ong, *J. Appl. Polym. Sci.*, **5**(16), 452-459 (1961).

[106] H. Mäder and B. Seidel, Brit. Patent 1,098,892 (January 10, 1968) to Agfa-Gevaert A.G.

[107] Y. Jen and R. R. House, U.S. Patent 3,015,605 (January 2, 1962) to American Cyanamid Co.

[108] E. B. Trostyanskaya et al., *J. Polym. Sci.*, **59**, 379-387 (1962).

[109] L. H. Silvernail and M. W. Zembal, U.S. Patent 3,011,918 (December 5, 1961) to Dow Chemical Co.

[110] T. Doggett and J. H. Cady, U.S. Patent 3,110,621 (November 12, 1963) to S. D. Warren Co.

[111] A. M. Winchell, U. S. Patent 3,399,995 (September 3, 1968) to GAF Corp.

[112] A. Winchell, Brit. Patent 1,162,156 (August 20, 1969) to GAF Corp.

[113] G. R. Geyer, U.S. Patent 3,335,100 (August 8, 1967) to Dow Chemical Co.

[114] W. W. Wahl and C. D. Dever, U.S. Patent 3,094,501 (June 18, 1963) to Dow Chemical Co.

[115] R. M. Wiley, U.S. Patent 3,055,827 (September 25, 1962) to Dow Chemical Co.

[116] C. P. Priesing and S. Mogelnicki, U.S. Patent 3,259,570 (July 5, 1966) to Dow Chemical Co.

[117] S. A. Zhukovskaya and L. M. Vernikova, *Khim.-Farm. Zh.*, **1**(8), 52-54 (1967).

[118] A. S. Michaels and R. G. Miekka, *J. Phys. Chem.*, **65**, 1765-1773 (1961).

[119] A. S. Michaels and R. G. Miekka, U.S. Patent 3,276,598 (October 4, 1966) to Dow Chemical Co.

[120] R. G. Miekka, Sc.D. Thesis, M.I.T. Dept. of Chem. Eng. (1961).

[121] A. S. Michaels, *Ind. Eng. Chem.*, **57**(10), 32-40 (1965).

[122] A. S. Michaels, U.S. Patent 3,271,496 (September 6, 1966) to Amicon Corp.

[123] Fr. Patent 1,531,592 (July 5, 1968) to Amicon Corp.

[124] A. S. Michaels, G. L. Falkenstein, and N. S. Schneider, *J. Phys. Chem.*, **69**(5), 1456-1465 (1965).

[125] A. S. Michaels, L. Mir, and N. S. schneider, *J. Phys. Chem.*, **69**(5), 1447-1455 (1965).

[126] A. S. Michaels, H. J. Bixler, R. W. Hausslein, and S. M. Fleming, *O. S. W. Res. & Dev. Rept.*, No. 149 (1965).

[127] S. J. Reid, J. Th. G. Overbeek, W. Vieth, and S. M. Fleming, *J. Colloid Interfac. Sci.*, **26**(2), 222-229 (1968).

[128] H. J. Bixler, A. S. Hoffman, and L. A. Spano, *Space/Aeronautics Res.*, **48**, 107-112 (1967).

[129] A. S. Michaels, U.S. Patent 3,467,604 (September 16, 1969) to Amicon Corp.

[130] M. F. Refojo, *J. Appl. Polym. Sci.*, **11**(10), 1991-2000 (1967).

[131] H. J. Bixler, R. A. Cross, and L. L. Markley-Nelson, Ger. Patent 1,806,115 (May 22, 1969).

[132] I. Michaeli and T. Bejerano, *J. Polym. Sci., Part C,* **22**, 909-915 (1969).

[133] A. S. Michaels, U.S. Patent 3,324,068 (June 6, 1967) to Amicon Corp.

[134] A. S. Michaels, U.S. Patent 3,419,430 (December 31, 1968) to Amicon Corp.

[135] A. S. Michaels, U.S. Patent 3,419,431 (December 31, 1968) to Amicon Corp.

[136] J. A. Price, U.S. Patent 2,941,969 (June 21, 1960) to American Cyanamid Co.

[137] C. L. Arcus and W. A. Hall, *J. Chem. Soc.*, **1963**, 4199-4204.

[138] G. B. Butler and F. L. Ingley, *J. Amer. Chem. Soc.*, **73**, 895-896 (1951).

[139] G. B. Butler and R. L. Goette, *J. Amer. Chem. Soc.*, **74**, 1939-1941 (1952).

[140] G. B. Butler and R. A. Johnson, *J. Amer. Chem. Soc.*, **76**, 713-714 (1954).

[141] G. B. Butler and R. L. Goette, *J. Amer. Chem. Soc.*, **76**, 2418-2421 (1954).

[142] *Chem. & Eng. News*, **35**(22), 24 (March 11, 1957).

[143] G. B. Butler and R. J. Angelo, *J. Amer. Chem. Soc.*, **79**, 3128-3131 (1957).

[144] G. B. Butler, A. Crawshaw, and W. L. Miller, *J. Amer. Chem. Soc.*, **80**, 3615-3618 (1958).

[145] G. B. Butler, *J. Polym. Sci.*, **48**, 279-289 (1960).

[146] G. B. Butler, *Encyl. Polym. Sci. & Tech.*, **4**, 568-599 (1966).

[147] G. B. Butler, R. J. Angelo, and A. Crawshaw, U.S. Patent 2,926,161 (February 23, 1960) to Peninsular ChemResearch, Inc.

[148] G. B. Butler, U.S. Patent 3,288,770 (November 29, 1966) to Peninsular ChemResearch, Inc.

[149] J. E. Boothe, U.S. Patent 3,461,163 (August 12, 1969) to Calgon Corp.

[150] J. E. Boothe, U.S. Patent 3,472,740 (October 14, 1969) to Calgon Corp.

[151] Y. Negi, S. Harada, and O. Ishizuka, *J. Polym. Sci., Part A-1*, **5**(8), 1951-1965 (1967).

[152] *Chem. & Eng. News*, **46**(3), 46-47 (January 15, 1968).

[153] G. B. Butler, Brit. Patent 1,084,540 (September 27, 1967) to Peninsular ChemResearch, Inc.

[154] A. P. Black, F. B. Birkner, and J. J. Morgan, *J. Amer. Water Works Assoc.*, **57**(12), 1547-1560 (1965).

[155] A. P. Black, F. B. Birkner, and J. J. Morgan, *J. Colloid Interfac. Sci.*, **21**, 626-648 (1966).

[156] R. H. Jones, Ph.D. Thesis, Univ. of Florida (1966).

[157] J. P. Kleber, *Water & Wastes Eng.*, **6**(6), 42-44 (1969).

[158] H. S. Posselt, A. H. Reidies, and W. J. Weber, Jr., *J. Amer. Water Works Assoc.*, **60**(1), 48-68 (1968).

[159] M. Pressman, *J. Amer. Water Works Assoc.*, **59**(2), 169-182 (1967).

[160] M. T. Dajani and T. G. Cocks, U.S. Patent 3,408,292 (October 29, 1968) to Nalco Chemical Co.

[161] M. T. Dajani, U. S. Patent 3,409,547 (November 5, 1968) to Nalco Chemical Co.

[162] J. E. Boothe and M. F. Hoover, Fr. Patent 1,494,438 (September 8, 1967) to Calgon Corp.

[163] M. F. Hoover and H. E. Carr, *TAPPI,* 51(12), 552-559 (1968).

[164] W. H. Schuller, J. A. Price, S. T. Moore, and W. M. Thomas, *J. Chem. Eng. Data,* 4(3), 273-276 (1959).

[165] W. H. Schuller and W. M. Thomas, U.S. Patent 2,923,701 (February 2, 1960) to American Cyanamid Co.

[166] R. B. Booth and W. F. Linke, U.S. Patent 3,147,218 (September 1, 1964) to American Cyanamid Co.

[167] T. J. Suen and A. M. Schiller, U.S. Patent 3,171,805 (March 2, 1965) to American Cyanamid Co.

[168] W. H. Schuller, W. M. Thomas, S. T. Moore, and R. R. House, U.S. Patent 2,884,058 (April 28, 1959) to American Cyanamid Co.

[169] Y. Jen, U.S. Patent 2,958,673 (November 1, 1960) to American Cyanamid Co.

[170] W. H. Schuller and W. M. Thomas, U.S. Patent 2,935,493 (May 3, 1960) to American Cyanamid Co.

[171] M. F. Hoover, R. J. Schaper, and J. E. Boothe, U.S. Patent 3,412,019 (November 19, 1968) to Calgon Corp.

[172] R. J. Schaper, Can. Patent 820,379 (August 12, 1969) to Calgon Corp.

[173] S. Harada and M. Katayama, U.S. Patent 3,375,233 (March 26, 1968) to Nitto Boseki Co.

[174] S. Harada and K. Arai, Paper Presented at the 15th Annual Meeting of the Society of Polymer Science, Nagoya, Japan, May, 1966.

[175] S. Harada and K. Arai, Paper Presented at the 15th Annual Meeting of the Society of Polymer Science, Nagoya, Japan, May, 1966.

[176] T. Ueda and S. Harada, *J. Appl. Polym. Sci.,* 12(11), 2383-2393 (1968).

[177] T. Ueda and S. Harada, *J. Appl. Polym. Sci.,* 12(11), 2395-2401 (1968).

[178] I. N. Duling and C. C. Price, *J. Amer. Chem. Soc.,* **84**, 578-583 (1962).

[179] D. D. Reynolds and W. O. Kenyon, U.S. Patent 2,571,761 (October 15, 1951) to Eastman Kodak Co.

[180] D. D. Reynolds and W. O. Kenyon, U.S. Patent 2,701,243 (February 1, 1955) to Eastman Kodak Co.

[181] J. L. R. Williams, U.S. Patent 2,908,667 (October 13, 1959) to Eastman Kodak Co.

[182] W. N. Maclay and R. M. Fuoss, *J. Polym. Sci.*, **6**(5), 511-521 (1951).

[183] K. Matsuzaki and T. Sugimoto, *J. Polym. Sci., Part A-2,* **5**, 1320-1322 (1967).

[184] G. Weill and G. Hermann, *J. Polym. Sci., Part A-2,* **5**, 1293-1295 (1967).

[185] G. Geuskens, J. C. Lubikulu, and C. David, *Polymer,* **7**(1), 63-65 (1966).

[186] C. Loucheux and Z. Czlonkowska, *J. Poly. Sci., Part C,* **10**, 4001-4010 (1968).

[187] A. J. Hyde and R. B. Taylor, *Chem. Soc.* (London) *Spec. Publ.*, **23**, 325-333 (1968).

[188] A. B. Gosnell et al., Paper Presented at International Symposium on Macromolecular Chemistry, Brussels, Louvain, Belgium, 1967.

[189] L. M. Richards, U.S. Patent 2,487,829 (November 15, 1949) to DuPont.

[190] R. M. Fuoss and U. P. Strauss, *J. Polym. Sci.*, **3**(2), 246-263 (1948).

[191] R. M. Fuoss and U. P. Strauss, *J. Polym. Sci.*, **3**(4), 602-603 (1948).

[192] R. M. Fuoss, *J. Polym. Sci.*, **3**(4), 603-604 (1948).

[193] U. P. Strauss and R. M. Fuoss, *J. Polym. Sci.*, **8**(6), 593-598 (1951).

[194] U. P. Strauss and R. M. Fuoss, *J. Polym. Sci.*, **4**, 457-472 (1949).

[195] R. M. Fuoss and D. Edelson, *J. Polym. Sci.*, **6**, 767-774 (1951).

[196] D. O. Jordan, T. Kurucsev, and R. L. Darskus, *Polymer,* **6**(6), 303-310 (1965).

[197] R. M. Fuoss and G. I. Cathers, *J. Polym. Sci.*, **4**, 97-120 (1949).

[198] G. I. Cathers and R. M. Fuoss, *J. Polym. Sci.*, **4**, 121-133 (1949).

[199] J. T. Clark, U.S. Patent 2,732,350 (January 24,1956) to Ionics, Inc.

[200] E. F. Jackson, U.S. Patent 2,540,985 (February 6, 1951) to Monsanto Chemical Co.

[201] R. M. Fuoss, M. Watanabe, and B. D. Coleman, *J. Polym. Sci.*, **38**, 5-15 (1960).

[202] C. L. Arcus and W. A. Hall, *J. Chem. Soc.*, **1964**, 9595-9599.

[203] C. B. Arends, *J. Chem. Phys.*, **39**(7), 1903-1904 (1963).

[204] R. M. Fuoss and H. Sadek, *Science,* **110**, 552-554 (1949).

[205] E. B. Fitzgerald and R. M. Fuoss, *Ind. Eng. Chem.*, **42**(8), 1603-1606 (1950).

[206] P. P. Spiegelman and G. Parravano, *J. Polym. Sci., Part A*, **2**, 2245-2273 (1964).

[207] S. Tazuke and S. Okamura, *J. Polym. Sci., Part B*, **3**(2), 135-138 (1965).

[208] D. Laurin and G. Parravano, *J. Polym. Sci., Part B*, **4**, 797-801 (1966).

[209] C. David, A. Verhasselt, and G. Geuskens, *Polymer*, **9**(10), 521-526 (1968).

[210] V. A. Kabanov, K. V. Aliev, O. V. Kargina, T. I. Patrikeeva, and V. A. Kargin, *J. Polym. Sci., Part C*, **16**, 1079-1094 (1967).

[211] V. A. Kabanov, K. V. Aliev, and V. A. Kargin, *Vysokomol. Soedin., Ser. A*, **10**(7), 1618-1632 (1968).

[212] U. P. Strauss, N. L. Gershfeld, and H. Spiera, *J. Amer. Chem. Soc.*, **76**, 5909-5911 (1954).

[213] R. A. Ruehrwein and D. W. Ward, *J. Soil Sci.*, **73**, 485-492 (1952).

[214] Y. Tabata, H. Kitano, and H. Sobue, *J. Polym. Sci., Part A*, **2**, 3639-3648 (1964).

[215] G. B. Gechele and L. Crescentini, *J. Polym. Sci., Part A*, **3**(10), 3599-3611 (1965).

[216] C. Garbuglio, L. Crescentini, A. Mula, and G. B. Gechele, *Makromol. Chem.*, **97**, 97-112 (1966).

[217] V. S. Lebedev and R. K. Gavurina, *Vysokomol. Soedin.*, **6**(8), 1353-1358 (1964).

[218] D. C. Lincoln and W. P. Shyluk, U.S. Patent 3,095,404 (June 25, 1963) to Hercules Powder Co.

[219] W. P. Shyluk, *J. Polym. Sci.*, **2**, 2191-2206 (1964).

[220] V. A. Kargin et al., *Proc. Acad. Sci. U.S.S.R.*, **160**, 604 (1965).

[221] V. A. Kabanov, T. I. Patrikeeva, and V. A. Kargin, *Dokl. Akad. Nauk SSSR*, **168**(6), 1350-1353 (1966).

[222] V. A. Kabanov, T. I. Patrikeeva, O. V. Kargina, and V. A. Kargin, *J. Polym. Sci., Part C*, **23**, 357-363 (1968).

[223] W. P. Shyluk, *J. Appl. Polym. Sci.*, **8**, 1063-1076 (1964).

[224] W. P. Shyluk, *J. Polym. Sci., Part A-2*, **6**, 2009-2019 (1968).

[225] W. P. Shyluk and R. W. Smith, *J. Polym. Sci., Part A-2*, **7**, 27-36 (1969).

[226] E. Strazdins and R. J. Kulick, U.S. Patent 3,409,500 (November 5, 1968) to American Cyanamid Co.

[227] G. W. Leubner, J. L. R. Williams, and C. C. Unruh, U.S. Patent 2,811,510 (October 29, 1957) to Eastman Kodak Co.

[228] H. Ladenheim and H. Morawetz, *J. Polym. Sci.*, **26**(113), 251-254 (1957).

[229] R. Hart and D. Timmerman, *J. Polym. Sci.*, **28**(118), 638-640 (1958).

[230] K. T. Shen, U.S. Patent 2,771,462 (November 20, 1956) to Petrolite Corp.

[231] W. H. Schuller and D. C. Guth, U.S. Patent 2,958,682 (November 1, 1960) to American Cyanamid Co.

[232] W. H. Schuller and J. A. Price, U.S. Patent 2,977,341 (March 28, 1961) to American Cyanamid Co.

[233] R. H. Sprague and L. G. S. Brooker, U.S. Patent 2,484,430 (October 11, 1949) to Eastman Kodak Co.

[234] R. H. Sprague and L. G. S. Brooker, U.S. Patent 2,548,564 (April 10, 1951) to Eastman Kodak Co.

[235] L. M. Minsk and W. O. Kenyon, U.S. Patent 2,484,420 (October 11, 1949) to Eastman Kodak Co.

[236] D. D. Reynolds and T. M. Laakso, U.S. Patent 2,725,381 (November 29, 1955) to Eastman Kodak Co.

[237] W. O. Forshey and J. E. Kirby, U.S. Patent 2,680,112 (June 1, 1954) to DuPont.

[238] J. H. Daniel, Can. Patent 577,917 (June 16, 1959) to American Cyanamid Co.

[239] T. M. Laakso, J. L. R. Williams, and C. S. Garber, U.S. Patent 3,125,550 (March 17, 1964) to Eastman Kodak Co.

[240] T. M. Laakso, J. L. R. Williams, and C. S. Garber, U.S. Patent 2,972,535 (February 21, 1961) to Eastman Kodak Co.

[241] T. M. Laakso and J. L. R. Williams, U.S. Patent 3,068,215 (December 11, 1962) to Eastman Kodak Co.

[242] T. M. Laakso and J. L. R. Williams, U.S. Patent 2,972,536 (February 21, 1961) to Eastman Kodak Co.

[243] T. M. Laakso and J. L. R. Williams, U.S. Patent 3,062,785 (November 6, 1962) to Eastman Kodak Co.

[244] T. M. Laakso and J. L. R. Williams, U.S. Patent 2,972,538 (February 21, 1961) to Eastman Kodak Co.

[245] J. A. Price and W. M. Thomas, U.S. Patent 2,840,550 (June 24, 1958) To American Cyanamid Co.

[246] R. S. Yost, U.S. Patent 2,840,546 (June 24, 1958) to Rohm & Haas Co.

[247] M. J. Hurwitz and H. Aschkenasy, U.S. Patent 3,406,139 (October 15, 1968) to Rohm & Haas Co.

[248] M. J. Hurwitz and H. Aschkenasy, U.S. Patent 3,288,707 (November 29, 1966) to Rohm & Haas Co.

[249] F. X. Pollio, U.S. Patent 3,300,406 (January 24, 1967) to Rohm & Haas Co.

[250] F. Poschmann et al., U.S. Patent 3,323,980 (June 6, 1967) to Badische Anilin & Soda-Fabrik Ak.

[251] O. V. Schickh et al., U.S. Patent 3,329,560 (July 4, 1967) to Badische Anilin & Soda-Fabrik Ak.

[252] H. Fikentscher et al., U.S. Patent 3,174,874 (March 23, 1965) to Badische Anilin & Soda-Fabrik Ak.

[253] K. J. Liu and H. P. Gregor, *J. Phys. Chem.*, **69**(4), 1248-1251 (1965).

[254] K. J. Liu and H. P. Gregor, *J. Phys. Chem.*, **69**(4), 1252-1259 (1965).

[255] S. Machida and H. Saito, *Sen-I Gakkaishi*, **23**(7), 301-305 (1967).

[256] S. Machida, M. Araki, and K. Matsuo, *J. Polym. Sci.*, **12**, 325-332 (1968).

[257] C. L. Schilling, Jr., and J. E. Mulvaney, *Macromolecules*, **1**(5), 452-455 (1968).

[258] C. L. Schilling, Jr., and J. E. Mulvaney, *Macromolecules*, **1**(5), 445-451 (1968).

[259] E. R. Littmann and C. S. Marvel, *J. Amer. Chem. Soc.*, **52**, 287-293 (1930).

[260] C. F. Gibbs, E. R. Littmann, and C. S. Marvel, *J. Amer. Chem. Soc.*, **55**, 753-757 (1933).

[261] M. R. Lehman, C. D. Thompson, and C. S. Marvel, *J. Amer. Chem. Soc.*, **55**, 1977-1981 (1933).

[262] C. F. Gibbs and C. S. Marvel, *J. Amer. Chem. Soc.*, **56**, 725-727 (1934).

[263] C. F. Gibbs and C. S. Marvel, *J. Amer. Chem. Soc.*, **57**, 1137-1139 (1935).

[264] N. Menschutkin, *Z. Physik. Chemie*, **5**, 589 (1890).

[265] W. Kern and E. Brenneisen, *J. Prakt. Chem.*, **159**, 194-217 (1941).

[266] D. M. Ritter, U.S. Patent 2,261,002 (October 28, 1941) to DuPont.

[267] N. E. Searle and J. E. Kirby, U.S. Patent 2,271,378 (January 27, 1942) to DuPont.

[268] J. E. Kirby, U.S. Patent 2,375,853 (March 15, 1945) to DuPont.

[269] J. E. Kirby and J. F. Lontz, U.S. Patent 2,388,614 (November 6, 1945) to DuPont.

[270] D. D. Coffman, U.S. Patent 2,191,753 (February 27, 1940) to DuPont.

[271] J. G. Erickson, U.S. Patent 2,807,910 (October 1, 1957) to General Mills, Inc.

[272] J. G. Erickson, U.S. Patent 2,767,176 (October 16, 1956) to General Mills, Inc.

[273] C. Taube and K. Böckmann, U.S. Patent 3,009,761 (November 21, 1961) to Farben. Bayer A.G.

[274] C. D. Krieg, U.S. Patent 3,349,032 (October 24, 1967) to Petrolite Corp.

[275] L. H. Bock and A. L. Houk, U.S. Patent 2,454,547 (November 23, 1948) to Rohm & Haas Co.

[276] L. O. Gunderson, U.S. Patent 2,583,772 (January 29, 1952) to Dearborn Chemical Co.

[277] L. P. McCarty, U.S. Pat. 3,206,462 (September 14, 1965) to Dow Chemical Co.

[278] F. Mung and K. Keller, U.S. Patent 2,040,061 (May 5, 1936) to General Aniline Works, Inc.

[279] J. F. Feeman, U.S. Patent 3,334,138 (August 1, 1967) to Crompton & Knowles Corp.

[280] J. Thewis, Ger. Patent 1,123,282 (February 2, 1962) to Badische Anilin & Soda-Fabrik A.G.

[281] D. D. Reynolds, U.S. Patent 3,370,048 (February 20, 1968) to Eastman Kodak Co.

[282] R. Nordgren, L. R. Vertnik, and H. Wittcoff, U.S. Patent 3,235,596 February 15, 1966) to General Mills, Inc.

[283] R. Nordgren and H. A. Wittcoff, U.S. Patent 3,371,116 (February 27, 1968) to General Mills, Inc.

[284] W. A. Weiss et al., *J. Amer. Med. Ass.*, **166**, 603-607 (1958).

[285] P. Lolezari and T. H. Spaet, *J. Lab. Clin. Med.*, **57**, 868-873 (1961).

[286] P. Lolezari, *Blood*, **19**, 109-114 (1962).

[287] E. T. Kimura, P. R. Young, and G. H. Barlow, *Proc. Soc. Exp. Biol. Med.*, **111**, 37-41 (1962).

[288] G. H. Barlow et al., *Proc. Soc. Exp. Biol. Med.*, **113**, 884-886 (1963).

[289] F. W. Preston and R. P. Parker, *Amer. Med. Ass. Arch. Surg.*, **66**, 545-550 (April, 1963).

[290] A. Zipursky et al., *Can. J. Phys. Tox.*, **43**, 289-297 (1965).

[291] A. Rembaum, W. Baumgartner, and A. Eisenberg, *J. Polym. Sci., Part B*, **6**(3), 159-171 (1968).

[292] H. Noguchi and A. Rembaum, *J. Polym. Sci., Part B*, **7**, 383-394 (1969).

[293] A. Eisenberg and T. Tokoyama, *Polym. Preprints*, **9**(1), 617-622 (1968).

[294] A. Rembaum, *J. Macromol. Sci.-Chem.*, **A3**(1), 87-99 (January, 1969).

[295] A. Rembaum, A. M. Hermann, F. E. Stewart, and F. Gutmann, *J. Phys. Chem.*, **73**(3), 513-520 (March, 1969).

[296] W. G. Lloyd, U.S. Patent 3,265,663 (August 9, 1966) to Dow Chemical Co.

[297] E. Kraiman and A. F. Hasson, U.S. Patent 3,265,734 (August 9, 1966) to Sun Chemical Co.

[298] R. M. Fuoss and D. Edelson, *J. Polym. Sci.*, **6**(5), 523-532 (1951).

[299] H. Wittcoff, U.S. Patent 2,483,749 (October 4, 1949) to General Mills, Inc.

[300] W. A. Rogers and J. E. Woehst, U.S. Patent 3,320,317 (May 16, 1967) to Dow Chemical Co.

[301] G. B. Walker and C. M. Cambre, U.S. Patent 3,428,680 (February 18, 1969) to Procter & Gamble Co.

[302] J. G. Voss, U.S. Patent 3,408,440 (October 29, 1968) to Procter & Gamble Co.

[303] V. J. Webers, U.S. Patent 2,676,166 (April 20, 1954) to DuPont.

[304] E. J. Vandenberg, U.S. Patent 3,403,114 (September 24, 1968) to Hercules, Inc.

[305] D. D. Coffman, U.S. Patent 2,595,225 (May 6, 1952) to DuPont.

[306] T. M. Laakso and J. L. R. Williams, U.S. Patent 3,096,305 (July 2, 1963) to Eastman Kodak Co.

[307] T. M. Laakso and J. L. R. Williams, U.S. Patent 2,972,537 (February 21, 1961) to Eastman Kodak Co.

[308] H. V. Isaacson and D. W. Young, U.S. Patent 3,415,745 (December 10, 1968) to Sinclair Research, Inc.

[309] G. R. Geyer, M. J. Hatch, and H. B. Smith, U.S. Patent 3,316,186 April 25, 1967) to Dow Chemical Co.

[310] Brit. Patent 1,066,771 (April 26, 1967) to Dow Chemical Co.

[311] G. R. Geyer, U.S. Patent 3,248,279 (April 26, 1966) to Dow Chemical Co.

[312] H. H. Roth, U.S. Patent 3,397,179 (August 13, 1968) to Dow Chemical Co.

[313] A. S. Tevlina et al., *Plast. Massy*, 3, 27-29 (1968).

[314] G. S. Kolesnikov, A. S. Tevlina, and A. T. Bzhalilov, U.S.S.R. Patent 231,805 (November 28, 1968).

[315] G. S. Kolesnikov, A. S. Tevlina, A. T. Bzhalilov, and G. M. Koval, *Plast. Massy*, **8**, 17-19 (1968).

Polysulfonium

[316] M. L. Selkers, *Ind. Eng. Chem.*, **40**, 1467 (1948).

[317] E. M. LaCombe, U.S. Patent 3,269,991 (August 30, 1966) to Union Carbide.

[318] J. C. Fang, U.S. Patent, 3,310,540 (March 21, 1967) to DuPont.

[319] E. M. LaCombe and F. E. Bailey, Jr., U.S. Patent 3,280,081 (October 18, 1966) to Union Carbide Corp.

[320] F. E. Bailey, Jr., and E. M. LaCombe, U.S. Patent 3,278,501 (October 11, 1966) to Union Carbide Corp.

[321] F. E. Bailey, Jr., and E. M. LaCombe, U.S. Patent 3,214,370 (October 26, 1965) to Union Carbide Corp.

[322] G. R. Bell, U.S. Patent 3,227,650 (January 4, 1966) to Johns-Manville Corp.

[323] R. Andersen and G. R. Bell, U.S. Patent 3,235,495 (February 15, 1966) to Johns-Manville Corp.

[324] J. Sopoci, U.S. Patent 3,247,106 (April 19, 1966) to Johns-Manville Corp.

[325] N. R. Eldred, G. W. Buttrick, and J. C. Spicer, U.S. Patent 3,207,656 (September 21, 1965) to Union Carbide Corp.

[326] K. L. Smith, U.S. Patent 3,332,835 (July 25, 1967) to Union Carbide Corp.

[327] E. M. LaCombe, U.S. Patent 3,238,276 (March 1, 1966) to Union Carbide Corp.

[328] K. R. Hansen, U.S. Patent 3,377,250 (April 9, 1968) to Colgate-Palmolive Co.

[329] M. L. Smith, G. Roccheggiani, and R. W. Faessinger, U.S. Patent 3,389,108 (June 18, 1968) to Scott Paper Co.

[330] W. F. Garrett, F. E. Bailey, Jr., and R. D. Lundberg, Can. Patent 779,935 (March 5, 1968) to Union Carbide Corp.

[331] M. J. Hatch and E. L. McMasters, U.S. Patent 3,078,259 (February 19, 1963) to Dow Chemical Co.

[332] W. G. Lloyd, U.S. Patent 3,236,820 (February 22, 1966) to Dow Chemical Co.

[333] M. J. Hatch and G. R. Geyer, U.S. Patent 3,287,306 (November 22, 1966) to Dow Chemical Co.

[334] M. J. Hatch, F. J. Meyer, and W. D. Lloyd, *J. Appl. Polym. Sci.*, **13**, 721-744 (1969).

[335] D. R. Sexsmith and E. J. Frazza, U.S. Patent 3,216,979 (November 9, 1965) to American Cyanamid Co.

[336] J. H. Rassweiler and D. R. Sexsmith, U.S. Patent 3,060,156 (October 23, 1962) to American Cyanamid Co.

[337] C. G. Humiston, F. J. Meyer, and D. L. Kenaga, U.S. Patent 3,130,117 (April 21, 1964) to Dow Chemical Co.

[338] R. W. Morgan and M. J. Hatch, U.S. Patent 3,146,157 (August 25, 1964) to Dow Chemical Co.

[339] G. R. Geyer, U.S. Patent 3,335,100 (August 8, 1967) to Dow Chemical Co.

[340] G. B. Butler and B. M. Benjamin, *J. Amer. Chem. Soc.*, **74**, 1846-1848 (1952).

[341] J. A. Price and W. H. Schuller, U.S. Patent 2,923,700 (February 2, 1960) to American Cyanamid Co.

[342] W. H. Schuller, J. A. Price, S. T. Moore, and W. M. Thomas, *J. Chem. Eng. Data*, **4**(3), 273-276 (July, 1959).

[343] S. Makino and S. Sugai, *J. Polym. Sci., Part A-2*, **5**, 1013-1028 (1967).

[344] S. Makino, K. Wakabayashi, and S. Sugai, *Biopolymers*, **6**(4), 551-561 (1968).

[345] R. A. Wessling and R. G. Zimmerman, U.S. Patent 3,401,152 (September 10, 1968) to Dow Chemical Co.

[346] R. A. Wessling and R. G. Zimmerman, U.S. Patent 3,404,132 (October 1, 1968) to Dow Chemical Co.

[347] M. Kanbe and M. Okawara, *J. Polym. Sci., Part A-1*, **6**(4), 1058-1060 (1968).

[348] G. R. Geyer, M. J. Hatch, and H. B. Smith, U.S. Patent 3,316,186 (April 25, 1967) to Dow Chemical Co.

[349] Brit. Patent 1,066,771 (April 26, 1967) to Dow Chemical Co.

[350] G. R. Geyer, U.S. Patent 3,248,279 (April 26, 1966) to Dow Chemical Co.

[351] T. T. Chiu, *TAPPI*, **52**(2), 340-344 (1969).

Polyphosphonium

[352] R. Rabinowitz, R. Marcus, and J. Pellon, *J. Polym. Sci., Part A*, **2**, 1233-1240 (1964).

[353] B. L. Tsetlin et al., *Vysokomol. Soedin.*, **3**, 1117 (1961).

[354] A. W. Hoffmann, *Ann (Suppl.)*, **1**, 145, 275 (1861).

[355] J. J. Pellon and K. J. Valan, *Chem, Ind.* (London), **32**, 1358 (August 10, 1963).

[356] R. G. Gillis, Ph.D. Thesis, Univ. of Notre Dame (1952).

[357] C. S. H. Chen and D. G. Grabar, *J. Polym. Sci., Part C,* 4, 849-868 (1963).
[358] C. S. H. Chen, U.S. Patent 3,269,930 (August 30, 1966) to American Cyanamid Co.
[359] R. Rabinowitz and R. Marcus, *J. Polym. Sci., Part A,* 3(5) 2063-2074 (1965).
[360] J. J. Pellon, M. Grayson, and K. J. Valan, U.S. Patent 3,294,764 (December 27, 1966) to American Cyanamid Co.
[361] H. C. Gillham and A. E. Sherr, U.S. Patent 3,431,324 (March 4, 1969) to American Cyanamid Co.
[362] M. Grayson, U.S. Patent 3,421,834 (January 14, 1969) to American Cyanamid Co.
[363] H. C. Gillham and A. E. Sherr, U.S. Patent 3,309,425 (March 14, 1967) to American Cyanamid Co.
[364] Brit. Patent 1,088,672 (October 25, 1967) to Imperial Chemical Ind.
[365] L. Maier et al., *J. Amer. Chem. Soc.,* 79, 5884-5889 (1957).
[366] R. Rabinowitz, A. C. Henry, and R. Marcus, *J. Polym. Sci., Part A,* 3(5), 2055-2061 (1965).
[367] M. M. Rauhut, G. B. Borowitz, and M. Grayson, U.S. Patent 3,422,149 (January 14, 1969) to American Cyanamid Co.
[368] P. J. Paré and M. Hauser, U.S. Patent 3,125,555 (March 17, 1964) to American Cyanamid Co.
[369] S. Franco, U.S. Patent 3,429,839 (February 25, 1969) to Ferrania Societa per Azioni.
[370] A. Y. Garner, J. G. Abramo, and E. C. Chapin, U.S. Patent 3,065,272 (November 20, 1962) to Monsanto Chemical Co.
[371] D. R. Sexsmith and E. J. Frazza, U.S. Patent 3,168,502 (February 2, 1965) to American Cyanamid Co.
[372] J. H. Rassweiler and D. R. Sexsmith, U.S. Patent 3,068,214 (December 11, 1962) to American Cyanamid Co.
[373] E. H. Braye, Brit. Pat. 1,093,603 (December 6, 1967) to Union Carbide Corp.
[374] Brit. Pat. 898,759 (June 14, 1962) to American Cyanamid Co.
[375] M. M. Rauhut, U.S. Patent 3,206,496 (September 14, 1965) to American Cyanamid Co.

Accepted by editor November 21, 1969
Received for publication January 27, 1970