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Polyelectrolyte Complexes*,†

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INTRODUCTION

Polyelectrolyte complexes used at present in the formation of a variety of membranes evolved from the investigations of the interactions between acidic polyions and basic polycations [1] as well as from the knowledge acquired during the study of ion exchange resins [2].

The principle used in mixed-bed ion exchange demineralization is illustrated in Fig. 1. Figure 1 represents a mixture of an anionic

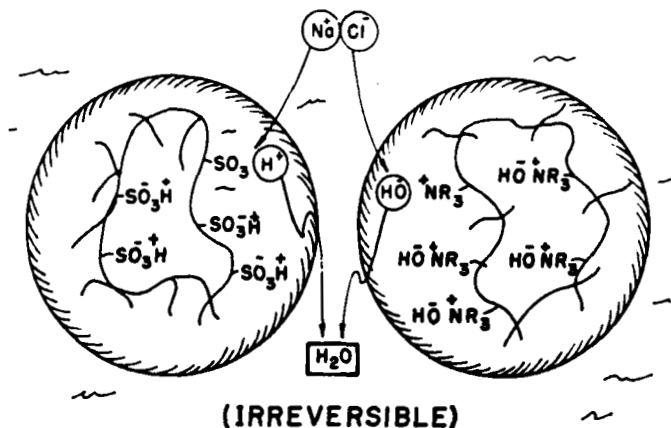


Fig. 1. Mixed-bed ion exchange demineralization [3].

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resin such as cross-linked polystyrene sulfonic acid with a cationic resin such as cross-linked poly(vinylbenzyltrimethylammonium) hydroxide. The sodium ions diffuse into the negatively charged resin and are exchanged for hydrogen ions, while the chloride ions are exchanged in the positively charged resin for hydroxyl groups. The hydrogen and hydroxyl ions diffuse out and neutralize one another through the driving force caused by the neutralization of a strong acid with a strong base; therefore, the demineralization of aqueous solutions is very efficient. However, since the reaction is irreversible, the recovery of the ion exchange resin can be accomplished only by a prior separation of the two types of resins, and the costs of commercial applications of the mixed-bed technique are prohibitive. It was necessary, therefore, to develop a reversible demineralization method, and this was accomplished by means of the so-called "snake cage polyelectrolyte" [3]. The latter consists of a cross-linked resin mixture, or "cage," which holds inside it a long linear polymer, or "snake." Practically, a snake cage polyelectrolyte is prepared, e.g., by swelling a cross-linked polystyrene sulfonic acid resin in acrylic acid and then polymerizing the latter. The polyacrylic acid is trapped inside the cage of sulfonated polystyrene.

The removal of sodium chloride by means of a snake cage polyelectrolyte is illustrated in Fig. 2.

Since the resin is internally neutralized, it absorbs both sodium and chloride ions reversibly and can, therefore, be regenerated simply by water-washing.

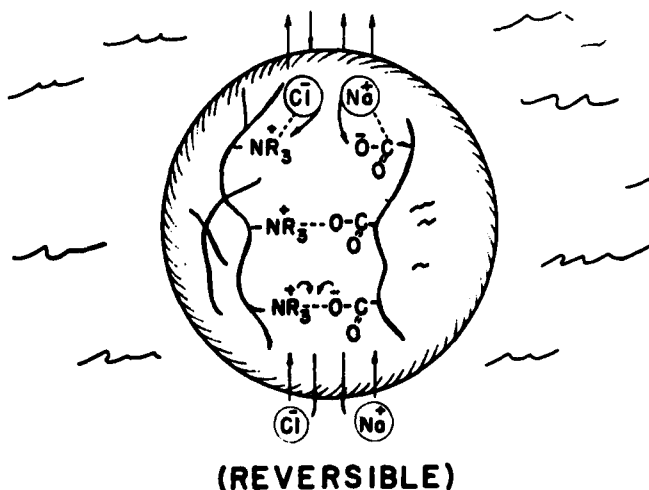


Fig. 2. Snake cage resin demineralization [3].

Table 1. Properties of Polyion Complexes

1. Insolubility in common solvents
2. Dielectric properties very sensitive to moisture and ion content
3. High dc conductance in contact with aqueous electrolytes
4. Permeable to electrolytes
5. Impermeable to macrosolutes
6. Rubbery when wet, hard and brittle when dry

In 1961, Michaels and Miekka [4] reported that the interaction of aqueous solutions of high molecular weight poly(styrene sodium sulfonate) with aqueous solutions of poly(vinylbenzyltrimethylammonium) chloride leads to an insoluble precipitate, the most likely structure of which consists of a cross-linked polymer. The cross-linking is due to the interaction between the negative sulfonate anion and the positive ammonium cation [5]. This type of polyelectrolyte complex, or polysalt, may be freed from sodium chloride, since the latter diffuses out from the polymeric matrix in the presence of water.

The main differences between the polysalts developed by Michaels and the snake cage polyelectrolytes are that (a) soluble polymers are used in the synthesis of the complexes, which may be obtained in neutral form or with an excess of either positively or negatively charged groups; and (b) solvent systems have been developed from which the polysalt may be cast to form a variety of membranes of considerable commercial interest. The properties and possible

Table 2. Possible Applications of Polyelectrolyte Complexes

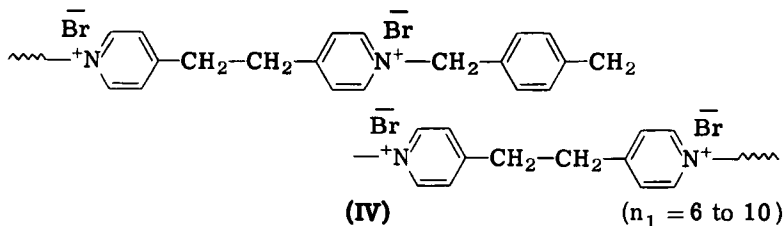
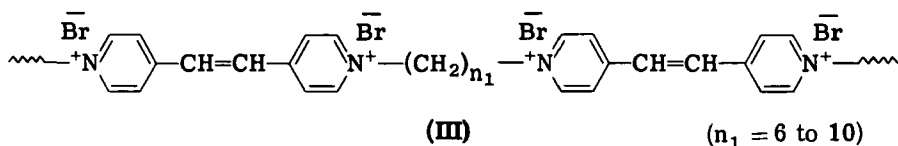
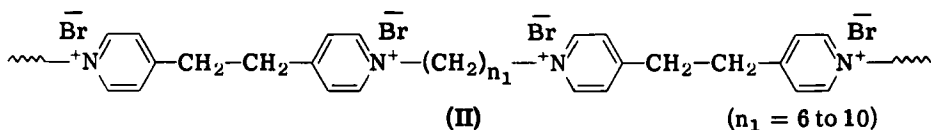
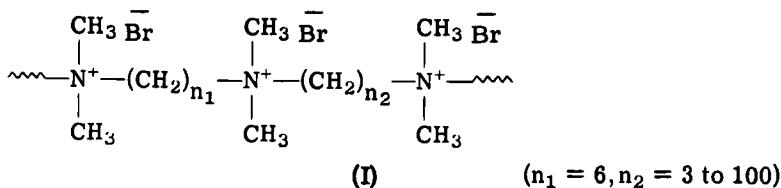
1. Ultrafiltration membranes
2. Battery separators
3. Plastic composites
4. Electrically conductive and antistatic coatings
5. Medical and surgical prosthetic materials

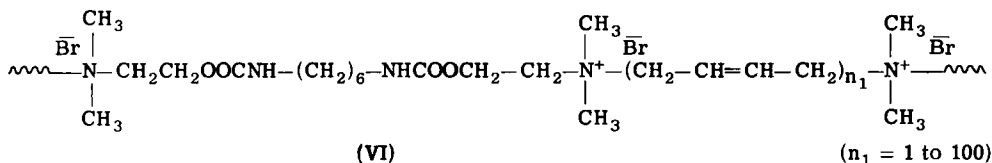
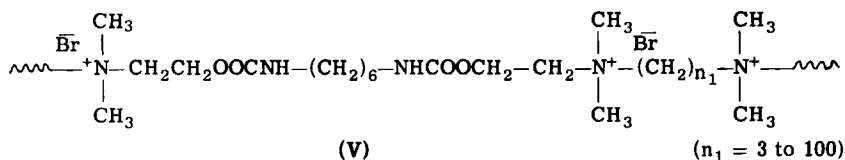
applications of this new type of polyelectrolyte complex were outlined by Michaels [5] and more recently by Markley et al. [6]. Some properties and applications of these polysalts are summarized in Tables 1 and 2.

This paper describes a new series of polyelectrolytes, most of which are water soluble and form polyelectrolyte complexes with negatively charged polyelectrolytes similar to those described by Michaels [5]. Different types of complexes are also formed with 7, 7, 8, 8-tetracyanoquino dimethane (TCNQ). The polymeric TCNQ complexes are characterized by insolubility in common solvents and high electrical conductivity.

SYNTHESIS

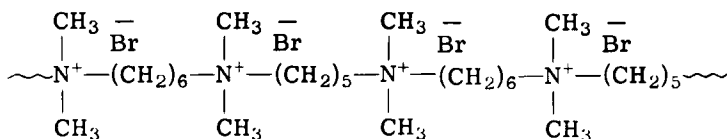
A variety of polymers shown below (I-VI) were synthesized, using benzene, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or mixtures of DMF with water or methanol as solvents.





In this paper the mechanism of formation of polymers represented by structure (I) will be described, and since these consist of ionic amines the generic name of aliphatic ionenes is suggested.

The materials utilized in the synthesis of a typical ionene are N, N, N', N'-tetramethylhexamethylenediamine and 1, 5-dibromopentane, to yield a polymer of the following structure:



To specify the nature of the pendant group on the nitrogen atom as well as the counterion, the prefix "tetramethyl" and the suffix "bromide" will be used, giving a full name of tetramethyl-6, 5-ionene bromide. The pharmacological properties, the molecular weight, and the antiheparin action of tetramethyl-6, 3-ionene bromide were described in the literature [7]. However, to our knowledge, the method or mechanism of formation of this polymer has not been published anywhere.

KINETICS

The synthesis of a variety of ionenes with molecular weight of 10, 000-40, 000 and with yields of over 90% can be achieved at room temperature. To elucidate the mechanism of formation of aliphatic ionenes, a detailed kinetic study was carried out. Most of the kinetic data were obtained using stoichiometric proportions of freshly distilled reagents, in dilatometers and in absence of air. The rates of reaction could also be followed by titration of the halide ion according to the procedure of Mohr [8]. Both methods yielded good

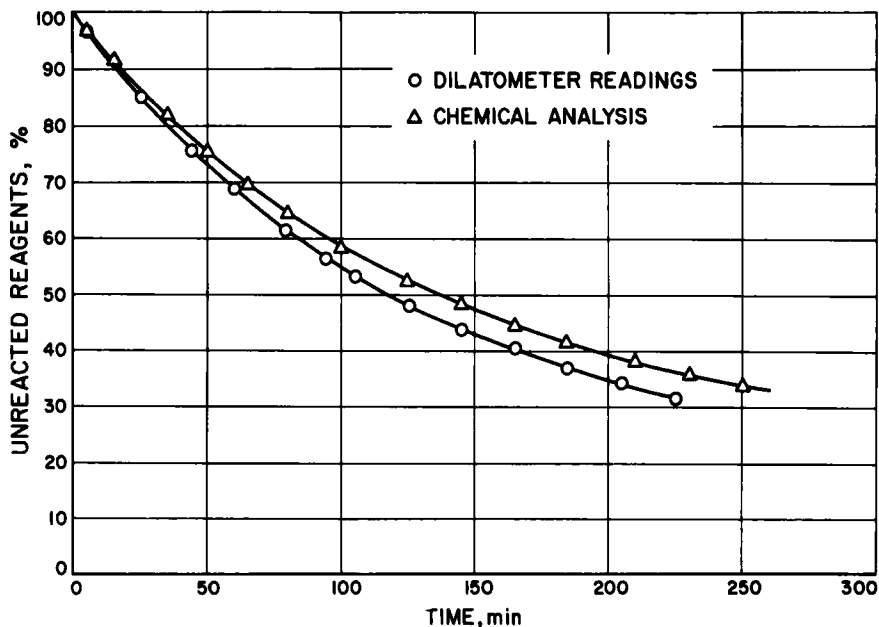


Fig. 3. Rates of formations of 6,5-ionene bromide in dimethylformamide-water (80:20 by volume).

agreement for the reaction order, the rate constant differing by 10%. A comparison of the rate determined dilatometrically and titrimetrically is shown in Fig. 3. The order of reaction as determined from a log log plot of rate against concentration was found to depend on the concentration of reagents and on the nature of the solvent. The kinetic data are summarized in Table 3.

An analysis of Table 3 permits the following conclusions:

1. The reaction order varies from one, in pure DMF, to exactly two, in 20% water: 80% DMF mixture (by volume) but at lower concentration.
2. The rates are greatly solvent dependent and increase in this order: methanol < methanol-DMF < H₂O-DMF; i.e., the higher the dielectric constant of the medium, the higher the rate.
3. The rates do not seem to vary to any considerable extent as a function of the number of methylene groups in either the amine or the dibromide.
4. The rate of formation of an ionene chloride is considerably smaller than that of an ionene bromide.

Table 3. Reaction Kinetics of Aliphatic Ionenes

Run	Reagents	Concentration ^a , moles/liter	Solvent	Reaction rate $\times 10^3 \text{ min}^{-1}$ $\frac{1}{\Delta V} \frac{dv^b}{dt}$	Reaction order
2	1, 3-Dibromopropane + THD ^c	1.32	DMF	—	0.90
6	1, 3-Dibromopropane + THD	0.74	CH ₃ OH + DMF (50 : 50)	0.85	1.25
3	1, 5-Dibromopentane + THD	1.26	DMF	5.1	1.0
5	1, 5-Dibromopentane + THD	1.14	CH ₃ OH	0.5	—
7	1, 5-Dibromopentane + THD	0.72	CH ₃ OH + DMF (50 : 50)	1.2	1.44
12	1, 5-Dibromopentane + THD	0.72	H ₂ O + DMF (20 : 80)	7.3	1.60
13	1, 5-Dibromopentane + THD	0.72	H ₂ O + DMF (20 : 80)	6.0 ^d	1.60
14	1, 5-Dibromopentane + THD in presence of 6, 5-ionene 0.1 mole %	0.72	H ₂ O + DMF (20 : 80)	7.3	1.6
24	1, 5-Dibromopentane + GHD	0.20	H ₂ O + DMF (20 : 80)	2.3	2.0
4	1, 10-Dibromodecane + THD	1.17	DMF	5.8	1.0
8	1, 10-Dibromodecane + THD	0.70	CH ₃ OH + DMF (50 : 50)	1.0	1.33
15	Dibromomethane + TMD ^e	0.76	H ₂ O + DMF (20 : 80)	0.29	—
16	Dibromoethane + TDD ^f	0.76	H ₂ O + DMF (20 : 80)	1.8	1.29
17	Dibromomethane + THD	0.74	H ₂ O + DMF (20 : 80)	1.2	1.43
19	1, 6-Dichlorohexane + THD	0.72	H ₂ O + DMF (20 : 80)	0.42	1.45

^aTotal concentration of reagents present in stoichiometric amounts.

^b dv/dt = rate of decrease of volume, ΔV = the total volume change amounting in most cases to 70 ± 10 ml/mole of product.

^cTHD = N, N, N', N'-tetramethylhexamethylenediamine.

^dFollowed by chemical analysis.

^eTMD = N, N, N', N'-tetramethylmonomethylenediamine.

^fTDD = N, N, N', N'-tetramethyldimethylenediamine.

VISCOSITY AND MOLECULAR WEIGHT

The rates of formation of tetramethyl-6, 5- and 6, 10-ionene bromides were also followed in previously described vacuum viscometers [9]. The specific viscosity at 25°C in 80:20 (by volume) DMF-water and 50:50 (by volume) DMF-methanol mixtures was plotted as a function of time and is shown in Fig. 4. The increase in rate in presence of water is apparent from the figure, the final viscosity reaching similar values in both solvent systems at the end of polymerization. At 75°C the reaction proceeds at a very fast rate (curve 5); however, the specific viscosity reaches a constant value, much smaller than that attained at 25°C. It appears, therefore, that

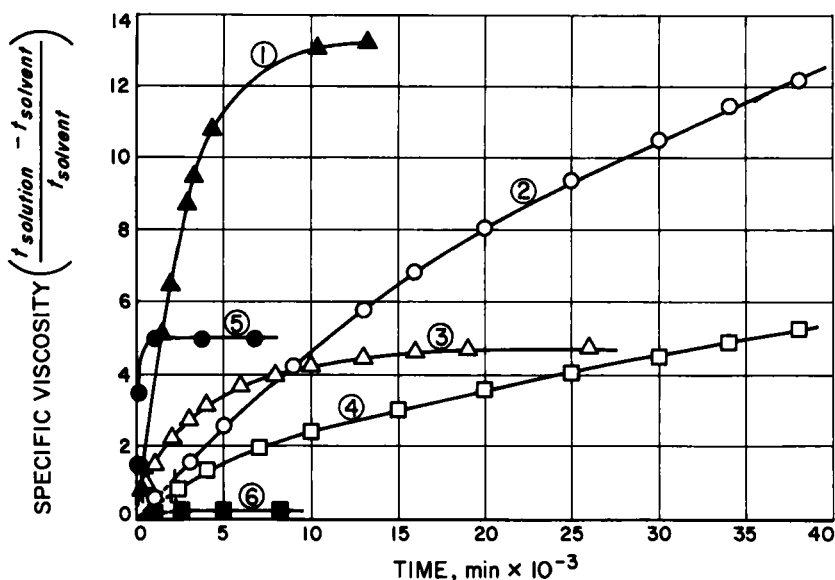


Fig. 4. Specific viscosity of ionene bromides in DMF-H₂O and DMF-CH₃OH mixtures as a function of time. Curve 1: 6, 10-Ionene in DMF-H₂O (80:20 by volume) at 25°C intrinsic viscosity in 0.4M KBr water solution of isolated product = 0.221. Curve 2: 6, 10-Ionene in DMF-CH₃OH (50:50 by volume) at 25°C intrinsic viscosity in 0.4M KBr water solution of isolated product = 0.211. Curve 3: 6, 5-Ionene in DMF-H₂O (80:20 by volume) at 25°C intrinsic viscosity in 0.4M KBr solution of isolated product = 0.170. Curve 4: 6, 5-Ionene in DMF-CH₃OH (50:50 by volume) at 25°C intrinsic viscosity in 0.4M KBr water solutions = 0.189. Curve 5: 6, 10-Ionene in DMF-CH₃OH (50:50 by volume) at 75°C. Curve 6: 2, 1-Ionene in DMF-H₂O (80:20 by volume) at 25°C.

Table 4. Specific^a, ^b and Intrinsic^c Viscosities of Ionenes in Distilled Water and in 0.4 M KBr Water Solutions

Run	Ionene	Solvent used to preparation	Reaction time at 25°C, hr	η_1^a	η_2^b	$[\eta]^c$ g/dl	Remarks
2	6,3	DMF	48	0.13	—	—	Polymer partly insoluble
3	6,5	DMF	48	0.60	0.23	0.12	Polymer partly insoluble
4	6,10	DMF	48	0.96	0.43	0.18	Polymer partly insoluble
5	6,5	CH ₃ OH	385	0.97	0.34	0.17	Complete solubility
6	6,3	DMF + CH ₃ OH (50 : 50)	576	0.82	0.24	0.14	Complete solubility
7	6,5	DMF + CH ₃ OH (50 : 50)	600	1.15	0.37	0.19	Complete solubility
8	6,10	DMF + CH ₃ OH (80 : 20)	480	1.08	0.42	0.17	Complete solubility
9	6,10	DMF + CH ₃ OH (50 : 50)	1080	1.44	0.49	0.21	Complete solubility
10	6,5	DMF + CH ₃ OH (50 : 50)	1200	1.05	0.35	0.19	Complete solubility
11	6,5	DMF + H ₂ O (80 : 20)	300	0.95	0.32	0.17	Complete solubility
21	6,10	DMF + H ₂ O (80 : 20)	456	1.61	0.53	0.22	Complete solubility

$${}^a\eta_1 = \frac{t \text{ solution} - t_{\text{H}_2\text{O}}}{t_{\text{H}_2\text{O}}}, t = \text{time of flow, polymer concentration} = 2 \times 10^{-3}\text{M.}$$

$${}^b\eta_2 = \frac{t \text{ solution} - t_{0.4\text{M aq. KBr}}}{t_{0.4\text{M aq. KBr}}}, \text{polymer concentration} = 2 \times 10^{-3}\text{M.}$$

^cIntrinsic viscosity in 0.4M KBr water solutions.

at higher temperature a termination step is involved. Included in Fig. 4 is the specific viscosity of a 2,1-ionene (curve 6). Although the yield of 2,1-ionene was $>90\%$, curve 6 shows that the propagation step is limited.

To determine the intrinsic viscosities of ionenes and eventually obtain a relation between viscosity and molecular weight, the specific behavior of polyelectrolytes must be taken into account in pure water and in aqueous salt solutions [10]. The specific viscosities of ionenes were found to decrease rapidly when measured in low shear viscometers as a function of potassium bromide concentration in distilled water, reaching an almost constant value in the range of 0.17–0.5 M KBr water solution.

Plots of reduced viscosity versus concentration in 0.4 M KBr water solutions yielded straight lines from which the intrinsic viscosity could be determined. The results are shown in Table 4.

The weight average molecular weight of 6,10-ionene of $[\eta] = 0.22$ was found by light-scattering measurements to be equal to $15,000 \pm 500$.

TCNQ COMPLEXES

A number of ionenes have been allowed to react with LiTCNQ in methyl alcohol-water mixtures, and the electronic conductivity of the precipitated complexes was measured using evaporated gold as electrodes. Table 5 shows the room temperature resistivity of 6,3-,

Table 5. Resistivities (ρ) Ionene TCNQ Complexes

Ionene	$[\eta]$ g/dl	ρ $\Omega\text{m, cm}$
6,3 ^a	0.14	2.1×10^6
6,3 ^b	0.14	1.2×10^2
6,8 ^a	0.17	2.9×10^6
6,8 ^b	0.17	2.0×10^2
6,10 ^a	0.22	3.0×10^6
6,10 ^b	0.22	3.8×10^3

^aReacted with 2 moles of LiTCNQ/unit segment.

^bReacted with 2 moles of LiTCNQ and 1 mole of neutral TCNQ/unit segment.

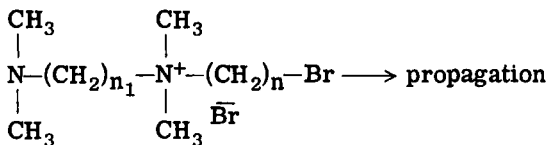
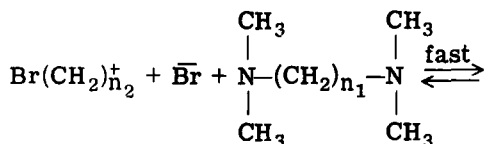
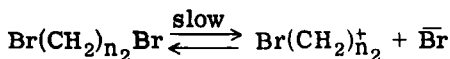
6, 8-, and 6, 10-ionenes combined with TCNQ. Complexes containing neutral TCNQ are also included in Table 5.

The results show that aliphatic ionenes in the form of their TCNQ salts exhibit high conductivity that decreases as n_2 increases.

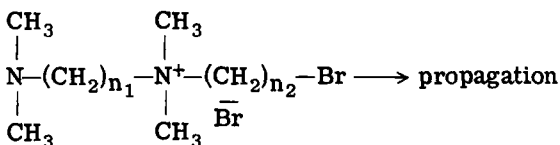
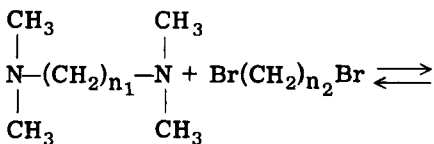
DISCUSSION

The synthesis of ionenes is based on the well-known Menshutkin reaction, which was thoroughly investigated over a number of years and has recently been briefly reviewed [11].

On the basis of the present kinetic study and previous work by Ingold and his collaborators [12], a formulation of the following mechanism is possible.



If the ionization reaction constitutes a slow process it will become rate determining, hence first-order kinetics are observed; but a one-step bimolecular process is also likely:



If the unimolecular and bimolecular processes take place simultaneously, the data take on an intermediate character (see Table 1). An unambiguous second-order process, observed at low concentrations of reactants, indicates that (a) under these conditions the bimolecular process is prevalent, and (b) cyclization, which could possibly accompany the propagation step, does not occur to any significant extent in most of the systems of Table 3, since formation of a cyclic compound would be expected at high dilution and would follow first-order kinetics. Although the rates do not differ greatly, the molecular weight as indicated by the intrinsic viscosity measurements varies considerably. With high positive charge concentration (e.g., 2-1 ionene), the propagation step is limited in spite of a conversion greater than 90%, and only low molecular weight species are obtained. A greater separation of positive charges on the chains (n_1 and $n_2 > 3$) leads to polymers of molecular weight of the order of 10,000-40,000. These low molecular weights are undoubtedly due to side reactions such as reaction of the dibromide with DMF. However, the use of fractionation methods or a different solvent system will probably extend the range of molecular weights.

CONCLUSIONS

The elucidation of the mechanism of ionene formation makes it possible to tailor-make new series of positive polyelectrolytes in which the positive charges on the nitrogen atoms are separated by known distances. The new aliphatic ionenes combine with negative polyelectrolytes, such as polystyrene sulfonic acids, polyacrylic acids, heparin, etc., to form a variety of membranes, the characteristics of which depend on the particular ionene used in the synthesis. Commercial polymers may also be blended or chemically combined with ionenes, thus acquiring desirable physical properties. The study of these polyelectrolyte complexes is now in progress.

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