

Cyclopolymerization Studies of Diallyl- and Tetraallylpiperazinium Salts

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SYNOPSIS

The quaternary ammonium salt 1,1-diallyl-4-formylpiperazinium chloride (**7**) was synthesized in good yields. The monomer (**7**) on cyclopolymerization in the presence of ammonium persulfate in water solution at 90°C afforded water-soluble polymer (**8**) having excellent rheological properties. The synthesis of the polymer (**8**) paves the way for the preparation of a novel class of polymers: dicationic polyelectrolytes (**9**) and cationic polymer (**10**) with a basic nitrogen as well as a quaternary nitrogen. Effects of monomer, initiator, and additives concentration were studied. Cyclopolymerization of (**7**) with 1,1,4,4-tetraallylpiperazinium dichloride (**12**) gave ion-exchange resins with excellent swelling coefficients. © 1996 John Wiley & Sons, Inc.

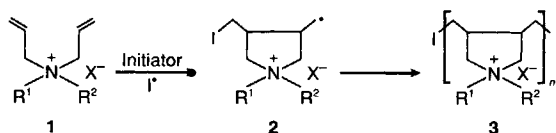
INTRODUCTION

Among the plethora of water-soluble polymers, cationic quaternary ammonium polymers have etched a place of distinction due to their diverse commercial applications.¹ Butler and co-workers led to the polymerization of a variety of diallyl quaternary ammonium salts (**1**) via an alternating intra-intermolecular chain propagation, now termed cyclopolymerization, to yield water-soluble, hence linear, cyclopolymers (**3**) containing little or no residual unsaturation.² Cyclopolymerization has been shown to proceed predominantly through the less stable five-membered cyclic structure (**2**) under conditions of kinetic control³ (Scheme 1).

A review and use analysis of poly(diallyldimethyl ammonium chloride), the most prominent technological cationic ammonium polymer, has been reported.⁴ Even though the polymerization of various diallyl quaternary ammonium salts has been studied in detail, the polymerizations of the corresponding piperazine derivative (**7**), to our knowledge, is not

reported to date (Scheme 2). The piperazine moiety (**4**) occurs in a wide range of compounds having interesting biological activity.⁵ Piperazine is used as an intermediate for various pharmaceuticals, polymers, dyes, corrosion inhibitors, and surfactants. Piperazine itself and some of its derivatives are useful in the treatment of filariasis, travel sickness, and high blood pressure. There are several piperazine-based tranquilizers available. Piperazine is inexpensive yet is conspicuously overlooked by researchers for its inclusion as a starting material in the synthesis of cationic ammonium cyclopolymer. Herein we report the synthesis and solution properties of cyclopolymers of 1,1-diallyl-4-formylpiperazinium chloride (DAFPC) (**7**) and its copolymerization with the corresponding tetraallyl derivative (**12**) (Scheme 2). Obtaining the polymer (**8**) would pave the way to its possible conversion into (**9**), a unique dicationic polymer, and (**10**), a bifunctional polymer with quaternary ammonium and basic trivalent amine groups. Versatility of piperazine will be demonstrated by polymerization and copolymerization of 1,1,4,4-tetraallylpiperazinium dichloride (TAPDC) (**12**) and DAFPC (**7**) to prepare cross-linked polymers for possible application as ion-exchange resins.

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Scheme 1

EXPERIMENTAL

Materials

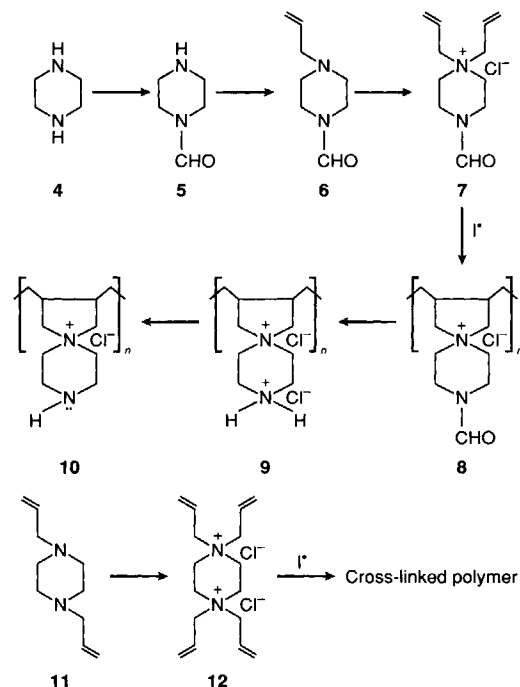
Anhydrous piperazine, allyl chloride, and ethyl formate, obtained from Fluka Chemie AG, were used as received. Ammonium persulfate from BDH Chemical Co. was kept in the freezer and used without further purification. All solvents used were of high-performance liquid chromatography (HPLC) grade.

Physical Methods

Elemental analyses were carried out on Fisons Instruments Model EA 1108 CHNS-O. Infrared spectra were recorded on a Nicolet Model 5DX Fourier transform infrared (FTIR) spectrophotometer and are reported in wave numbers (cm^{-1}). $^1\text{H-NMR}$ spectra were measured in solvents as mentioned using tetramethylsilane (TMS) as internal standard on a Varian XL 200 spectrometer. Viscosity measurements were made by Ubelhode (K 0.005989) and Brookfield DV II viscometer using the Thermocell System. Deionized water was used in polymerization reaction under an N_2 atmosphere. All glasswares were cleaned using deionized water.

1-Formylpiperazine (5)

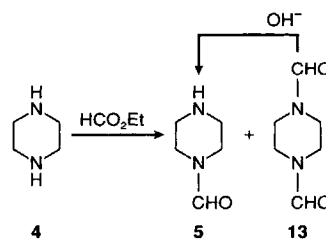
To a round-bottom flask fitted with a condenser and containing piperazine (200 g, 2.32 mol), ethyl formate was added (172 g, 2.32 mmol) in one portion. Within minutes, the exothermic reaction started along with the dissolution of the piperazine. The reaction mixture was heated at 90°C for 5 h. A careful analysis of the $^1\text{H NMR}$ spectrum of the crude products in CD_3OD revealed the presence of (4), (5), and (13) in a ratio of 15 : 60 : 25, respectively (Scheme 3, Table I). The formyl protons of (5) and (13) appeared at δ 8.08 and 8.16, respectively. After the distillation of piperazine (20 g, 10%), 1-formylpiperazine was collected at $85\text{--}87^\circ\text{C}$ (0.2 mbar Hg) (132 g, 50%). The compound (5) is contaminated with 2–3% of piperazine and was used without further purification. The residue after distillation was



Scheme 2

ground to powder and washed several times with ether to give the diformyl compound (13) as white solid (68 g, 21%).

To a stirred solution of compound (13) (68.0 g, 0.478 mol) in water (50 cm^3) at room temperature, a solution of sodium hydroxide was added (0.525 mol) in water (30 cm^3) dropwise over a period of 30 min. The reaction mixture, after stirring overnight, was saturated with anhydrous potassium carbonate and extracted with a 1 : 1 methanol-dichloromethane mixture ($4 \times 100\text{ cm}^3$). The organic layer was dried (Na_2SO_4), concentrated, and distilled as before to give the compound (5) (31 g, 57%). The $^1\text{H-NMR}$ spectrum of the crude products indicated the presence of (4), (5), and (13) in a ratio of 15 : 68 : 17, respectively. The combined procedures thus afforded 1-formylpiperazine in an overall yield of 62%.



Scheme 3

Table I Reaction of Piperazine with Ethyl Formate

Reactants	Solvents	Composition of Reaction Mixture		
		4	5	13
Piperazine + ethyl formate	Bulk	17	58	25
Piperazine + ethyl formate	Methanol	18	42	40
1,4-diformylpiperazine + NaOH	Water	15	68	17

1-Allyl-4-formylpiperazine (6)

To a mixture of sodium bicarbonate (1.2 mol) in water (120 cm³), 1-formylpiperazine (**5**) was added (114 g, 1.0 mol). To the stirred paste, allyl chloride was added (88.0 g, 1.15 mol) dropwise over a period of 30 min at 20°C with frequent ice cooling. The reaction mixture, after stirring for 48 h at 20°C, was extracted with dichloromethane (4 × 100 cm³). The organic layer was dried (Na₂SO₄), and to the concentrated solution 15 cm³ of ethyl formate was added and kept at 50°C for 5 h to convert any piperazine to its diformyl derivative (**13**) and 1-allylpiperazine (if any) to its 1-allyl-4-formylpiperazine derivative (**6**). After removal of the ethyl formate, the residual liquid was distilled with a 12-inch Vigreux column to give (**6**) (133 g, 86%) as a colorless liquid (bp_{3.5 mbar Hg} 114–115°C). An extra pure compound (**6**) was obtained by dissolving it with an equal volume of hexane–ether mixture (4 : 1 v/v) and keeping in the freezer to give low melting crystals.

ANAL: Found C, 62.10; H, 9.08; N, 18.03. C₈H₁₄N₂O requires C, 62.30; H, 9.15; N, 18.17%; ν_{\max} (neat) 3086, 2902, 2866, 2801, 1683, 1451, 1414, 1340, 1303, 1279, 1224, 1203, 1158, 1146, and 930 cm⁻¹; δ_{H} (CDCl₃) 2.46 (4 H, m), 3.04 (2 H, d with fine allylic splitting, J 7.0 Hz), 3.42 (2 H, apparent t , J 5.5 Hz), 3.60 (2 H, apparent t , J 5.5 Hz), 5.26 (2 H, m), 5.78–6.02 (1 H, m), 8.09 (1 H, s).

1,1-Diallyl-4-formylpiperazinium Chloride (7)

A mixture of (**6**) (60.0 g, 0.390 mol) and allylchloride (46.0 g, 0.60 mol) in acetone (250 cm³) was heated at 90°C in a closed vessel for 90 h. The reaction mixture was cooled, filtered, and washed with cold acetone to give the quaternary ammonium salt (**7**) as white solid (76.0 g, 85%). The chloride salt was found to be highly hygroscopic, and it was recrystallized from ethanol–acetone (9 : 1) mixture to give (**7**) as colorless hygroscopic crystals. The monomer was then dried under high vacuum for 10 h at 50°C.

The salt (**7**) was stored under anhydrous conditions, mp 167–169°C (closed capillary).

ANAL: Found C, 57.14; H, 8.44; N, 11.84. C₁₁H₁₉N₂OCl requires C, 57.26%; H, 8.30%; and N, 12.14%; ν_{\max} (KBr) 3085, 2976, 2944, 2861, 1676, 1645, 1479, 1442, 1404, 1246, 1127, 952, 863, and 824 cm⁻¹; δ_{H} (CD₃OD) 3.55 (4 H, m), 3.95 (4 H, m), 4.19 (4 H, d, J 7.0 Hz), 5.84 (4 H, m), 6.17 (2 H, m), and 8.21 (1 H, s).

1,1,4,4-Tetraallylpiperazinium Dichloride (12)

To a saturated aqueous solution of potassium carbonate (150 g, 1.08 mol), anhydrous piperazine (**4**) (43.0 g, 0.50 mol) was added. To the stirred mixture, allyl chloride (84.2 g, 1.10 mol) was added dropwise over a period of 1 h with frequent ice cooling. After stirring at 20°C for 24 h, the reaction mixture was extracted with dichloromethane (3 × 150 cm³). The organic layer was dried (Na₂SO₄), concentrated, and the residual liquid was distilled under vacuum to give the 1,4-diallylpiperazine (**11**) (67 g, 81%) as a colorless liquid (bp_{6.5 mbar Hg}, 75°C).

A solution of the diallylpiperazine (**11**) (30 g, 0.18 mol) and allyl chloride (41.3 g, 0.54 mol) in acetone (240 cm³) was heated in a closed vessel at 87°C for 72 h to give the tetraallyl derivative (**12**) (44 g, 77%). The white hygroscopic salt was crystallized from methanol and stored in a desiccator, mp 210–212°C (closed capillary).

ANAL: Found C, 59.8; H, 9.1; N, 8.6. C₁₆H₂₈N₂Cl requires C, 60.18; H, 8.84; N, 8.78%; ν_{\max} (KBr) 2968, 1481, 1436, 1303, 1279, 1115, 1024, 988, 967, 875, 858, 776 and 689 cm⁻¹; δ_{H} (CD₃OD) 4.05 (8 H, s), 4.26 (8 H, d, J 7.0 Hz), 5.84–6.36 (12 H, m).

General Procedure for the Polymerization Reactions

In a 5 cm³ round-bottom flask containing a magnetic stirrer, the dry monomer (**7**) (3.00 g) was taken. The

appropriate concentration of the monomer was achieved by adding deionized water. The flask was flushed with nitrogen by evacuation and introduction of nitrogen at -15°C . A solution of ammonium persulfate (15.0 mg) in 0.10 cm^3 of water was added with a syringe over a period of 15 min (approximately 1 drop per 2 min) under a nitrogen atmosphere to the stirred monomer solution at 80°C . The glass stopper was briefly opened under nitrogen to add each drop of initiator. The weight of the reaction flask containing the reaction mixture at the beginning and end of the reaction remained almost constant, thus ensuring no change in monomer concentration due to any loss of water vapor. The reaction mixture was then stirred at 90°C for an additional 1 h. Toward the end of the reaction, rotation of the magnetic stirrer slowed down or completely stopped in the viscous colorless solution. While hot, the slurry of the polymer in methanol (15 cm^3) was transferred to a flask containing acetone (50 cm^3). The white powder of the polymer was filtered and dried under high vacuum at 60°C for 10 h (or until constant weight of the polymer was achieved) and polymers were obtained in 75–80% yield. The use of a methanol/acetone mixture ensures the complete removal of the unreacted monomer, as indicated by $^1\text{H-NMR}$ spectra (Fig. 1). Polymers started to turn brownish at $\sim 350^{\circ}\text{C}$ and melted with decomposition to black material at $360\text{--}365^{\circ}\text{C}$ (closed capillary). Most of the polymers gave satisfactory elemental analysis (for instance, polymer for entry no. 6).

ANAL: Found C, 56.10; H, 8.75; N, 11.70. $\text{C}_{11}\text{H}_{19}\text{N}_2\text{OCl}$ requires C, 57.26%; H, 8.30%; and N, 12.14%.

Due to the hygroscopic nature the percentage of hydrogen is usually found to be more than the calculated value.

IR DATA: ν_{max} (KBr) 3450, 2956, 1669, 1449, 1409, 1273, 1240, 1127, 1018, and 970 cm^{-1} .

Polymerization of Tetraallylpiperazinium Dichloride (12)

The polymerization of tetraallylpiperazinium dichloride (12) was carried out by using *t*-butylhydroperoxide at 50°C and ammonium persulfate at 80°C , as initiators. For synthesis of a good-quality resin, copolymerization was also carried out with

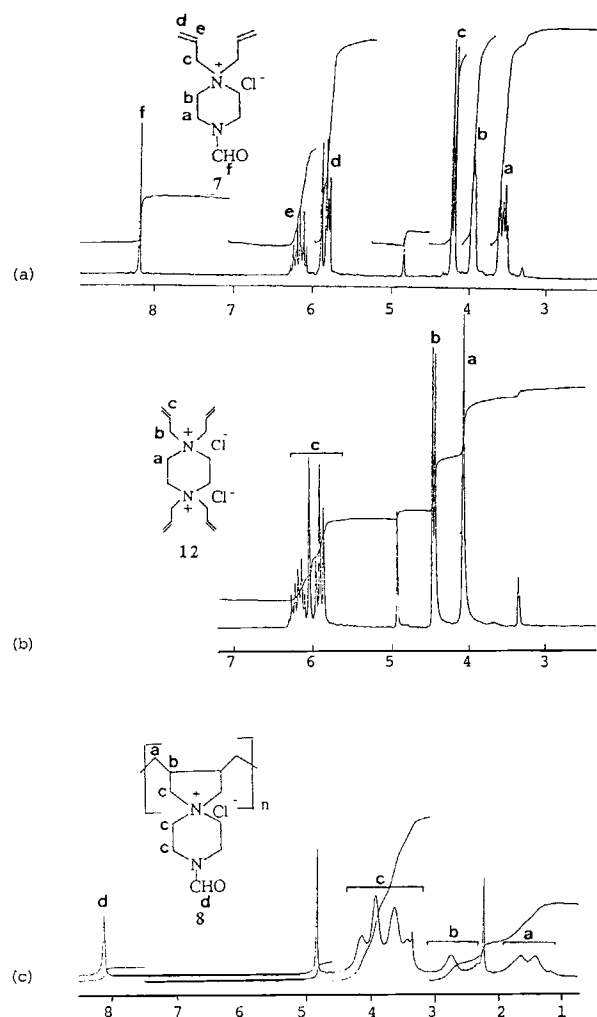


Figure 1 $^1\text{H-NMR}$ spectrum of (a) **7** in CD_3OD , (b) **12** in CD_3OD , and (c) homopolymer **8** in D_2O .

different compositions of (**12**) and (**7**), as described in Table III.

Poly- and Copolymerization of the Tetraallylpiperazinium Dichloride (12) and 1,1-Diallyl-4-formylpiperazinium chloride (7)

Poly- and copolymerization conditions for the monomers (**12**) and (**7**) are described in Table III. At the end of the elapsed time, the hard mass of the resin was thoroughly washed with hot water until the filtrate gave no turbidity with a solution of silver nitrate. The resins were dried under vacuum at 70°C for 12 h. These polymers were ground, and the 20- to 30-mesh fraction was used for the determination of swelling coefficient. The results are tabulated in Table III.

RESULTS AND DISCUSSION

Piperazine contains two basic amine functional groups. As simple as it may seem, selective synthesis of monosubstituted piperazine derivatives has frustrated many a researcher and still poses a significant challenge. Reaction of piperazine with acid chlorides, anhydrides, esters, and alkyl halides gives a mixture of mono- and di-substituted products along with unreacted piperazine, whose separations are most often difficult, if not impossible, to achieve.

Reaction of piperazine (**4**) with one equivalent of ethyl formate afforded a mixture of the unreacted piperazine (**4**), 1-formylpiperazine (**5**), and 1,4-diformylpiperazine (**13**) in a respective ratio of 17 : 58 : 25, as determined by integration of the NMR signal of several protons (Scheme 3, Table I). Distillation under vacuum gave the monoformyl derivative (**5**) in 50% yield, contaminated with a few percent (2–3%) of piperazine. We were not able to obtain (**5**) completely free of piperazine even by repeated distillation. Piperazine is insoluble in ethyl formate in the beginning, but as the exothermic reaction proceeds with the formation of one equivalent of ethanol, the reaction mixture becomes a clear solution. Initially the monoderivative (**5**) is expected to go to the solution and the piperazine would remain in the solid state, and as such the monoderivative (**5**) has a better chance of reacting further with ethyl formate to give (**13**). With this in mind, we carried out the reaction by initially dissolving the piperazine in methanol and then adding ethyl formate. However, the ratio of the compounds in the reaction mixture did not change in favor of the desired derivative (**5**)—rather, it became worse. Reaction carried out either at 0°C or 20°C afforded a mixture of (**4**), (**5**), and (**13**) in a ratio of 18 : 42 : 40, respectively. Surprisingly, a considerable amount of diformyl compound (**13**) is formed in this reaction. Selective deformylation of one of the groups is expected to lead to the desired compound (**5**). It was anticipated that basic hydrolysis of (**13**) should be faster than that of (**5**), since the former having an electron-withdrawing group (CHO) on the other end of the ring should exert additional stability to the negatively charged transition state. Alkaline hydrolysis of (**13**) with one equivalent of sodium hydroxide in water at 20°C afforded a mixture of (**4**), (**5**), and (**13**) in a respective ratio of 15 : 68 : 17. The alkaline hydrolysis thus provided us with an additional amount of desired monoprotected derivative (**5**) (Scheme 3, Table I).

1-Formylpiperazine (**5**), on treatment with 1.2 equivalent of allyl chloride in a sodium bicarbonate–water mixture, afforded 4-formyl-1-allylpiperazine (**6**) (83% yield) (Scheme 2). Our starting material, which contained a few percent of piperazine, was converted to 1,4-diallylpiperazine (**11**) in this process. The compound (**11**) was easily separated from (**6**) during distillation. The compound (**6**) must be free of (**11**) since its presence may induce cross-linking in the polymerization process.

Next we proceeded to synthesize the quaternary ammonium salts (**7**). Unexpectedly, the reaction of (**6**) with allyl chloride in acetone proceeded very slowly even at 80°C. However, the quaternary salt (**7**) was obtained in good yield (over 80%) at 90°C (90 h). Careful analysis of the ¹H-NMR spectrum revealed the presence of a trace (~ 1%) amount of crosslinker tetraallyl derivative (**12**). However, during crystallization the crosslinker was removed, and thus very pure monomer 1,1-diallyl-4-formylpiperazinium chloride (DAFPC) (**7**) was obtained for the polymerization reaction. The formyl proton appeared at δ 8.21 in the ¹H-NMR spectrum (Fig. 1). The allylic protons signals were shifted downfield (δ 4.19) due to the presence of adjacent positively charged nitrogen. The colorless crystalline monomer was found to be highly hygroscopic and liquefies readily on exposure to air due to absorption of moisture. The presence of moisture was also indicated in the IR spectrum.

With the monomer (DAFPC) in hand, we proceeded to carry out the polymerization reaction under different conditions using ammonium persulfate as the initiator. The effects of concentration of initiator, monomer, and sodium salt of ethylenediaminetetraacetate (Na₄EDTA) on the polymerization reactions are given in Table II. The maximum value of reduced viscosity was obtained with 5 mg of ammonium persulfate per gram of the monomer (compare entries 1, 10–12; 6, 16, 17). For the subsequent polymerization, 5 mg initiator per gram of monomer was used. The effects of initial monomer concentration on the viscosity are given in Table II. At 50% monomer concentration, no polymer was obtained. Highest reduced viscosity and intrinsic viscosity was obtained at 65% monomer concentration (entry 6). By increasing the concentration of the monomer to 70%, a small amount of gel formation was observed. Polymerization reactions were carried out in deionized water. Cyclopolymerizations were known⁷ to give quaternary ammonium polymers of high molecular mass. It has been proposed that

Na_4EDTA presumably acts as a chelater in removing trace metals which may otherwise act as a chain transfer agent. The results of the polymerization of our monomer (**7**) in water solution in the presence of various amounts of Na_4EDTA are given in Table II (compare entries 1, 13–15 and 6, 18–21). Highest intrinsic viscosity was obtained in polymerization using deionized water containing 25 ppm Na_4EDTA . An intrinsic viscosity of 1.62 dL/g (entry 20) for a polyelectrolyte does indeed reflect an astonishingly high molecular mass of the polymer. The polymers are found to be insoluble in methanol but readily soluble in water. The $^1\text{H-NMR}$ spectra of the monomer (**7**) and polymer are displayed in Figure 1 along with the NMR spectrum of the tetraallyl monomer (**12**).

Viscosity curves are presented in Figures 2 through 7. The plots are typical for polyelectrolytes in general, unlike the behaviour of uncharged linear polymers. The reduced viscosity (η_{sp}/C) versus concentration (C) of the quaternary ammonium polymers is strongly concave upward (Fig. 2). The addition of a strong electrolytelike sodium chloride

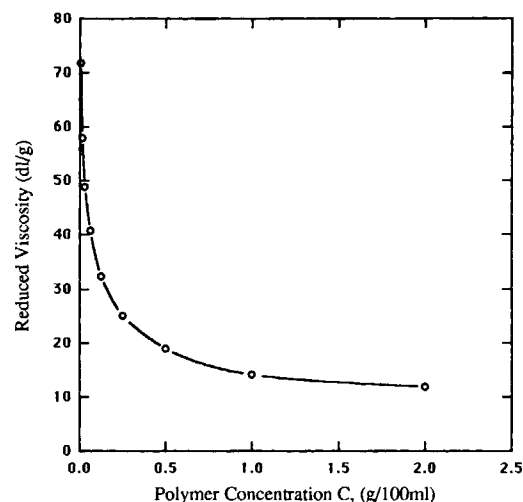


Figure 2 Viscosity behavior of polymer sample (entry 20) in deionized water at 30°C at shear rate $\sim 7.5 \times 10^3 \text{ s}^{-1}$.

suppresses the ionization of the polymer due to the common ion effect, and the viscosity behaviour becomes normal, as can be seen in Figure 3. The term

Table II Effect of Concentrations of Monomer, Initiator, and Na_4EDTA on Cyclopolymerization

Entry No.	Monomer Concentration ^a (% w/w)	Na_4EDTA (\times ppm)	Initiator (mg/g monomer)	Reduced ^b Viscosity (dL/g)	Intrinsic ^c Viscosity (dL/g)
1	50	0	5.0	—	—
2	55	0	5.0	2.37	0.637
3	57	0	5.0	2.56	0.798
4	60	0	5.0	6.60	1.22
5	62.5	0	5.0	6.73	1.25
6	65	0	5.0	6.85	1.36
7	67	0	5.0	6.66	1.23
8	68.5	0	5.0	6.73	1.31
9	70	0	5.0	6.25	1.11
10	55	0	2.5	1.30	0.331
11	55	0	7.5	1.70	0.589
12	55	0	10	1.75	0.534
13	55	5	5.0	3.02	0.735
14	55	25	5.0	5.45	1.01
15	55	50	5.0	3.34	0.875
16	65	0	2.5	2.09	0.605
17	65	0	7.5	4.42	0.903
18	65	5	5.0	4.37	1.33
19	65	10	5.0	11.9	1.43
20	65	25	5.0	11.8	1.62
21	65	50	5.0	11.7	1.60

^a Prepared in deionized water containing \times ppm Na_4EDTA .

^b Viscosity of 2% polymer solution in deionized water was measured in Ubelhode viscometer ($K = 0.005989$) at 30°C.

^c Viscosity of the polymer solution was measured 1–0.0078 g/100 cm³ solution in 0.1 N NaCl at 30°C.

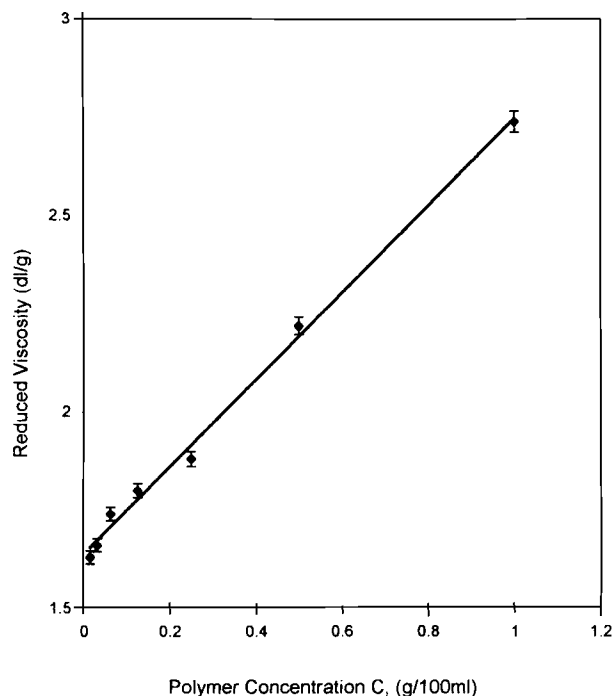


Figure 3 Viscosity behavior of polymer sample (entry 20) in 0.1 N NaCl solution at 30°C at shear rate $\sim 7.5 \times 10^3 \text{ s}^{-1}$.

intrinsic viscosity for the quaternary ammonium polymers cannot be used in the same sense as for uncharged polymers since it is dependent largely on the concentration of the added salt. Figure 4 displays the reduced viscosity behavior of polymer in differ-

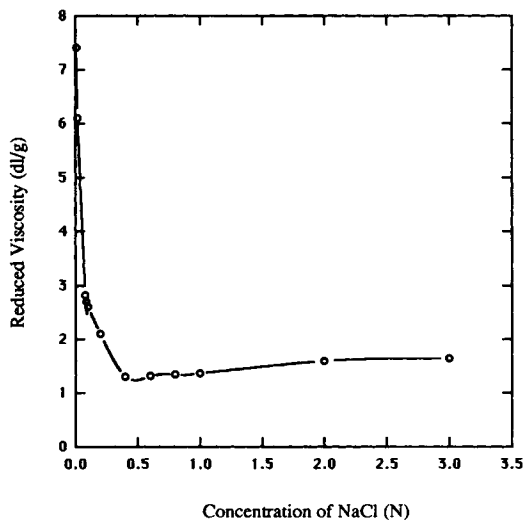


Figure 4 Viscosity behavior of polymer sample (entry 19) (1 g/100 mL) at 30°C in different concentrations of NaCl solution.

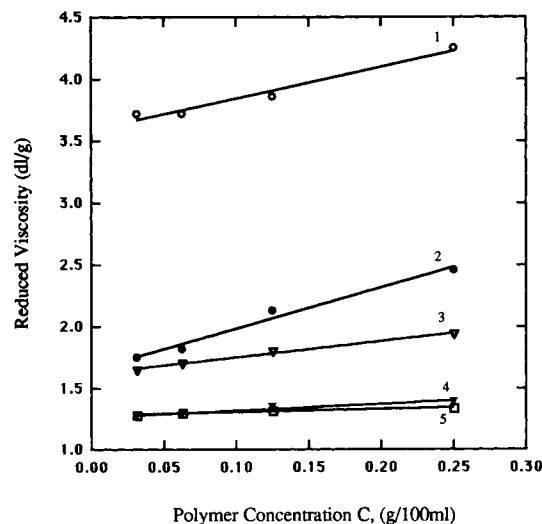


Figure 5 Viscosity behavior of polymer sample (entry 20) in different concentrations of NaCl solution at 30°C. (1) 0.03 N NaCl solution; (2) 0.07 N NaCl solution; (3) 0.10 N NaCl solution; (4) 0.30 N NaCl solution; (5) 0.70 N NaCl solution.

ent salt concentrations. The limiting viscosity numbers decrease with increasing added salt concentration and converge to a minimum at 0.3 N (Fig. 5). Absolute viscosity curves of a polymer sample at various temperatures and shear rates are displayed in Figures 6 and 7. The decrease in the viscosity with increasing shear rate indicates a non-Newtonian shear thinning behavior; however, at a high shear rate it shows almost Newtonian behavior. Viscosity

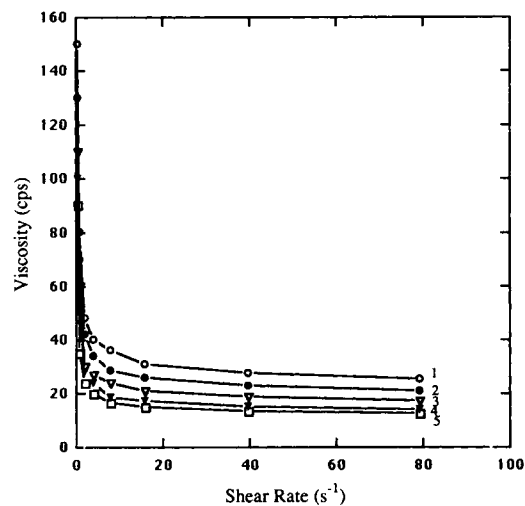


Figure 6 Viscosity of polymer solution (C, 2 g/100 mL) (entry 20) versus shear rate at different temperatures. (1) 30°C; (2) 40°C; (3) 50°C; (4) 60°C; (5) 70°C.

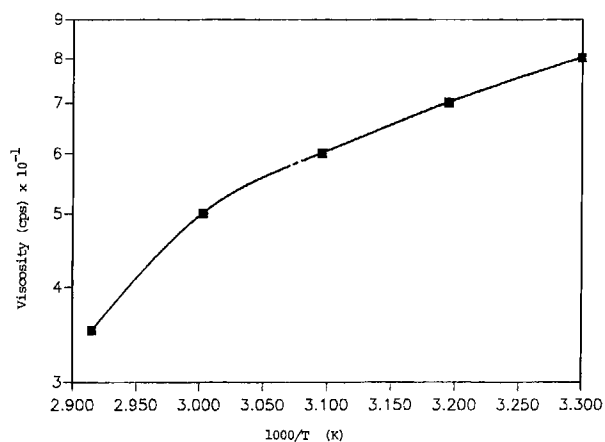


Figure 7 Viscosity behavior of polymer solution (C, 2 g/100 mL) (entry 20) in deionized water at shear rate 0.8 s^{-1} .

was found to decrease with an increase in temperature. Viscosity behavior of the polymer solutions does not change appreciably even after several months—for instance, reduced viscosity of the polymer sample (entry 6) for a 2% solution was changed from 6.85 to 6.53 and of a 1% polymer solution in 0.1 N NaCl solution from 1.91 to 1.82 after 5 months at room temperature. The polymeric solutions are thus found to be stable without any discoloration.

Preparation of Crosslinked Polymer

Unsaturated quaternary ammonium salts offer a convenient way to prepare basic ion-exchange resins. It has been shown that the rate of ion-exchange process is a function of a diffusion factor,⁸ and the diffusion rates depend on the degree of crosslinking of

the polymer network. The degree of swelling of an ion-exchange resin is influenced by the degree of crosslinking. The rate of diffusion of the ions to the ion-exchange centers is also influenced by the degree of swelling. It has been reported⁹ that for polymers having a coefficient of swelling of 5.08 and 1.17, the theoretical exchange capacity attained was 88.8 and 39.4%, respectively. The degree of crosslinking of the polymeric network controls the exchange capacity.¹⁰ The ion-exchange materials with a higher degree of crosslinking do not permit the diffusion of exchanging ions having an effective diameter larger than the diameter of the opening to the internal structure of the polymer. Ion-exchange materials derived from polymerization of quaternary ammonium salts permit a greater homogeneity in the resulting polymer than the technique which requires incorporation of the desired functional group (positively charged nitrogen, in this case) into an existing polymer network.

The polymerization of the monomer (**12**) was carried out in aqueous solutions under various conditions using ammonium persulfate (APS) and *t*-butylhydroperoxide (TBHP) as initiators. The details of polymerization of (**12**) and copolymerization with (**7**) are given in Table III. The tetraallyl monomer has the advantage of having its own crosslinking agent incorporated into it. In most cases, excellent yield of the crosslinked water-insoluble polymers was obtained. As the monomer concentration in the aqueous solution decreases, the yield of the polymer also decreases (entry 24). For the measurements of swelling coefficients, polymers were crushed and a 20- to 30-mesh fraction was used. The coefficient of swelling is defined as the ratio of the settled wet volume of the resin to the dry volume.

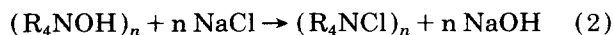
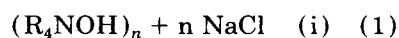
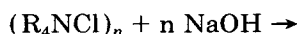
Table III Poly- and Copolymerization of Tetraallylpiperazinium Dichloride (**12**) and 1,1-Diallyl-4-formylpiperazine (**7**) in Aqueous Solutions

Entry No.	Initiator ^a	12 g (mol %)	7 g (mol %)	Monomer Conc. % (w/w)	Polymer Yield (%)	Swelling Coefficient
22	TBHP	5 g (100)	—	69	76	1.75
23	TBHP	5 g (100)	—	53	94	2.00
24	TBHP	5 g (100)	—	36	50	2.80
25	APS	5 g (100)	—	69	82	1.80
26	APS	3.5 g (63)	1.5 g (37)	65	60	2.72
27	APS	2.5 g (42)	2.5 g (58)	65	68	3.15
28	APS	0.5 g (7)	5.0 g (93)	65	87	3.16
29	TBHP	0.5 g (7)	5.0 g (93)	65	97	2.80

^a Polymerization using 0.10 g TBHP (*t*-butyl hydroperoxide) was carried out at 50°C for 48 h; polymerization using APS (ammonium persulfate) was carried out at 80°C for 1 h.

Thus, to a known volume of dry resin, sufficient water was added to cover the resin and the volume of the wet resin, after no further change in the volume occurred, was measured. As is evident from Table III, neither the polymer yield nor the swelling coefficient varies much by changing the initiator from TBHP to APS (entries 22 and 25). Swelling coefficients increased as the monomer (**12**) concentration decreased, indicating that the polymerization in dilute solution proceed to yield polymer with lesser degree of crosslinking. A swelling coefficient of 2.8 (entry 24) is found to be higher than many of the similar crosslinked polymers reported.¹¹

A copolymerization study using the crosslinker (**12**) and the diallyl derivatives (**7**) was carried out in aqueous solution using different mole percents of each of the monomers. A mixture of (**12**) and (**7**) in a respective mole percent ratio of 7 : 93 afforded crosslinked water-insoluble polymers with excellent swelling coefficient and yield (entries 28 and 29). The capacity of these polymers will be investigated in the future. However, the polymers and copolymers of these compounds have been found to undergo ion-exchange reactions, as presented in eqs. (1) and (2):



The crosslinked polymer was treated with 1% NaOH solution and stirred for 10 min at room temperature. The filtrate, after acidification with halogen-free HNO₃, gave a precipitate of AgCl upon treatment with AgNO₃. This indicated that the resin was converted to its hydroxide form by releasing the chloride ions. The washing with 1% NaOH solution was continued until the acidified filtrate was found to be free of chloride ions. The polymer was then washed with distilled water until a neutral filtrate was obtained. Finally, the treatment of the polymer

with a neutral solution of NaCl afforded a strongly basic solution, showing that the chloride ions were exchanged with hydroxide ions.

Finally, to our delight, the quaternary ammonium salt (**7**) on acidic hydrolysis (7% HCl) afforded the dicationic polymer (**9**) cleanly and quantitatively, which on treatment with NaHCO₃ gave the anticipated polymer (**10**) with quaternary as well as basic functionalities. We shall report in due time results of the properties and applications of these interesting polymers.

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