

Piperazine-Based Homo- and Copolymers Containing Trivalent and Quaternary Nitrogen Functionalities

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ABSTRACT: The synthesis and solution properties of poly(1,1-diallyl-4-hydropiperazine dichloride) [poly(DAHPD)] (**3**), a dicationic polymer, and poly(1,1-diallylpiperazinium chloride), [poly(DAPC)] (**4**), a bifunctional polymer with trivalent and quaternary nitrogens, and their corresponding copolymers with sulfur dioxide, poly(DAHPD-SO₂) (**6**) and poly(DAPC-SO₂) (**7**), are discussed. Dicationic polymers (**3**) and (**6**) were found to have less pronounced polyelectrolyte effects than their monocationic counterparts (**4**) and (**7**). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1329–1334, 1998

Key words: dicationic polymer; bifunctional polymer; polyelectrolyte effects; piperazine; homopolymer; copolymer

INTRODUCTION

Pioneering work by Butler,¹ involving homo- and copolymerization of diallyl quaternary ammonium salts, led to the synthesis of a variety of water-soluble polymers with extensive industrial applications.^{2,3} Polydiallyldimethylammonium chloride alone accounts for over 200 patents and publications. Hydrophobic modifications of the unsaturated quaternary ammonium monomers resulted in polymers with enhanced viscosity due to hydrophobic association.⁴ The dialkyldiallylammonium salts and sulfur dioxide copolymers are also manufactured commercially and are useful as textile additives, coagulants, and thickeners. Recently we reported^{5,6} on the homopolymerization and copolymerization with sulfur dioxide of 1,1-diallyl-4-formylpiperazinium chloride (DAFPC) (**1**) to yield a homopolymer (polyDAFPC) (**2**) and copolymer (polyDAFPC-SO₂) (**5**), respectively (Scheme 1). Polymerization, as expected, proceeded via alternating intra- and intermolecular chain propagation, termed cyclopolymeriza-

tion, to yield water-soluble (hence, linear) cyclopolymers containing little or no residual unsaturation.^{1,7,8}

The piperazine moiety occurs in a wide range of compounds with interesting biological activities.⁹ Piperazine is inexpensive and is used as the starting material for various pharmaceuticals, polymers, dyes, corrosion inhibitors, and surfactants. Piperazine and some of its derivatives are useful in the treatment of filariasis, travel sickness, and high blood pressure. Herein we report the synthesis and solution properties of poly(1,1-diallyl-4-hydropiperazine dichloride) [poly(DAHPD)] (**3**), a dicationic polymer, and poly(1,1-diallylpiperazinium chloride) [poly(DAPC)] (**4**), a bifunctional polymer with trivalent and quaternary nitrogens (Scheme 1). The corresponding copolymers with sulfur dioxide, poly(DAHPD-SO₂) (**6**) and poly(DAPC-SO₂) (**7**), were also prepared and their solution properties are discussed.

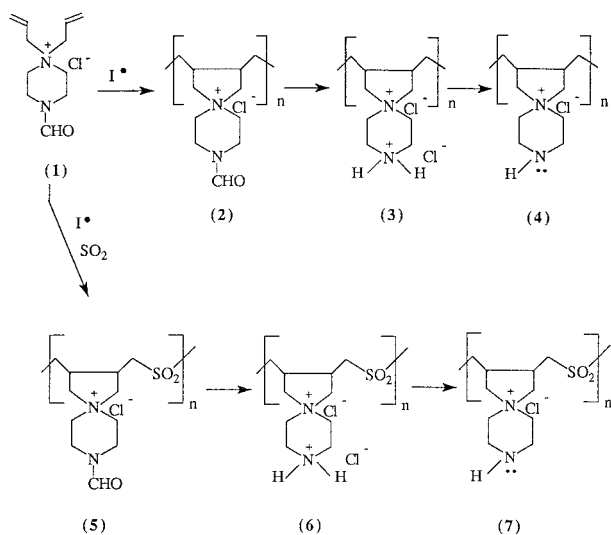
EXPERIMENTAL

Materials

The homopolymers (**2**) and copolymers (**5**) used in this work were prepared as described in the literature.^{5,6}

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Scheme 1 Structures of copolymers.

Physical Methods

Elemental analyses were carried out on Carlo Erba elemental analyzer model 1106. IR spectra were recorded on a Nicolet model 5DX FTIR spectrophotometer and are reported in wave numbers (cm^{-1}). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured in D_2O on a Varian XL 200 spectrometer. Viscosity measurements were made by Ubbelohde (K 0.005989) viscometer. Deionized water was used in the preparation of the polymer solutions. All glassware was cleaned using deionized water.

General Procedure for Preparation of Dicationic Polymers 3 and 6

A solution of homopolymer **2** (10 g) in 10% aqueous HCl (115 cm^3) was stirred at 20°C for 24 h. The homogeneous solution was then precipitated in methanol (600 cm^3). After filtration the hygroscopic white powder was dried under a high vacuum at 50°C for 6 h (or until constant weight of the polymer was achieved) to give the dicationic polymer **3** (9.2 g, 89%). The polymer started to turn brownish at 300°C and melted with decomposition to black materials at around $360\text{--}370^\circ\text{C}$ (closed capillary). The polymer was stored under anhydrous conditions.

ANAL. Calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{Cl}_2$: C, 50.21%; H, 8.43%; N, 11.72%. Found: C, 49.8%; H, 8.55%; N, 11.5%. ν_{max} (KBr): 3425, 2929, 2733, 1630, 1461, 1451, 1324, 1092, 1046, 1017, and 931 cm^{-1} .

Likewise, copolymer **5** was hydrolyzed following the same procedure as above to also give the

dicationic copolymer **6** as a white hygroscopic powder in over a 90% yield.

The polymer started to turn brownish black at 300°C and did not melt even at 380°C (closed capillary). The polymer was stored under anhydrous condition.

ANAL. Calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{Cl}_2 \cdot \text{SO}_2$: C, 39.61%; H, 6.65%; N, 9.24%; S, 10.57%. Found: C, 38.9%; H, 6.8%; N, 9.0%; S, 10.2%. ν_{max} (KBr): 3425, 2940, 2730, 1630, 1459, 1307, 1262, 1129, and 932 cm^{-1} .

Procedure for Preparation of polymers 4 and 7

To a mixture of the dicationic polymer **3** (6.00 g, 25.1 mmol) in water (30 cm^3) was added NaHCO_3 (2.40 g, 28.5 mmol), and it was stirred at 20°C for 12 h during which CO_2 gas was evolved. NaCl (1.46 g, 25 mmol) was added to the polymer mixture and then it was dialyzed against water until it gave a negative test with AgNO_3 . Excess NaCl was added to ensure the removal of any bicarbonate anion as a counterion of the polymer. The polymer solution was then freeze-dried and the resultant white polymer (**4**) was dried under a high vacuum at 50°C until constant weight.

Dicationic copolymer **6** was treated similarly with NaHCO_3 , and following the same procedure the basic quaternary copolymer **7** was obtained as a white powder. The yield of polymers **4** and **7** was in the range of 85–90%. The hygroscopic polymers were stored under anhydrous condition.

Polymer **4** started to turn brownish at 300°C and did not melt even at 380°C (closed capillary).

ANAL. Calcd for $\text{C}_{10}\text{H}_{19}\text{N}_2\text{Cl}$: C, 59.24%; H, 9.45%; N, 13.82%. Found: C, 58.7%; H, 9.39%; N, 13.5%. ν_{max} (KBr): 3430, 2930, 2855, 1653, 1578, 1560, 1459, 1419, 1365, 1280, and 960 cm^{-1} .

Polymer **7** started to turn brownish black at 280°C and did not melt even at 350°C (closed capillary).

ANAL. Calcd for $\text{C}_{10}\text{H}_{19}\text{N}_2\text{Cl} \cdot \text{SO}_2$: C, 45.02%; H, 7.18%; N, 10.50%; S, 12.02%. Found: C, 44.7%; H, 7.25%; N, 10.2%; S, 11.7%. ν_{max} (KBr): 3425, 2967, 2920, 1655, 1576, 1457, 1303, 1278, and 1128 cm^{-1} .

RESULTS AND DISCUSSION

The polymers were white hygroscopic salts, and they started to turn brownish black at around 300°C . The differential thermal analysis and the thermogravimetric analysis of the polymers are

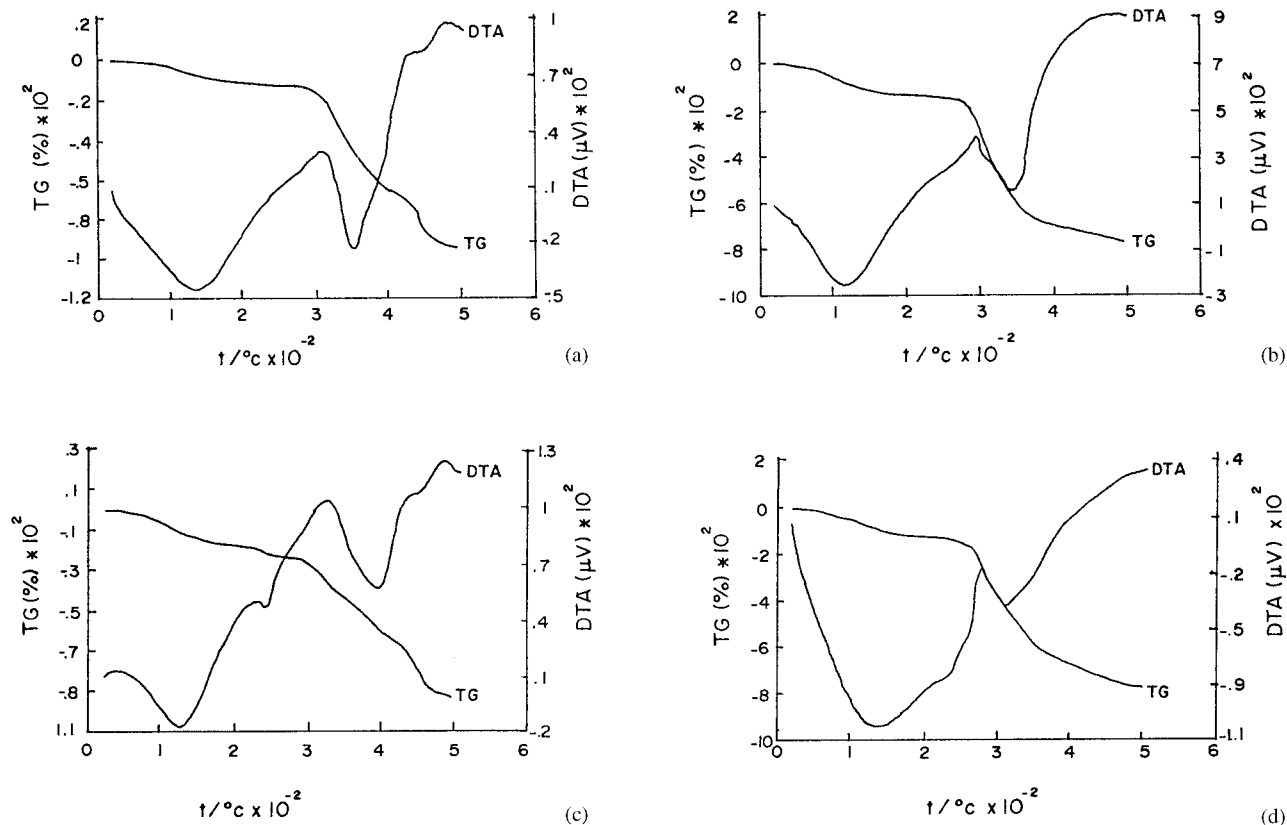


Figure 1 Differential thermal and thermogravimetric analysis (scanning rate, 10°C/min) of (a) poly(DAHPD) (**3**) (entry 1, Table I), (b) poly(DAPC) (**4**) (entry, Table I), (c) poly(DAHPD-SO₂) (**6**) (entry 4, Table I), and (d) poly(DAPC-SO₂) (**7**) (entry 4, Table I).

shown in Figure 1. The polymers showed some predecomposition weight loss, which was attributed to the loss of moisture. Thermal degradation appeared to happen at around 300°C for all the polymers. The IR spectra indicated strong absorption around 3425 cm⁻¹. The presence of strong bands around 1305 and 1128 cm⁻¹ were indicative of the presence of an SO₂ unit in polymers **6** and **7**.

The ¹H- and ¹³C-NMR spectra of these polymers are shown in Figures 2 and 3. For the dicationic polymers **3** and **6** the proton signals are shifted downfield in comparison to their monocationic counterparts **4** and **7**. This is expected due to the presence of additional positive centers in the former polymers. The hydrolysis of the formyl group was complete as indicated by the absence of the CHO proton at an δ of 8 ppm. Assignment of the ¹³C chemical shifts are based on our earlier work.⁶ The C-a and C-b carbon resonances in the cis isomer were expected to split into equal intensity peaks; this was observed only in polymer **7** for a C-a carbon, and splitting was not observed in

the other three cases. The splitting of the C-3 signal into approximately equal intensity peaks for cis and trans isomers in **7** and **6** can be attributed to the different configurations of the adjacent rings: the adjacent rings can add in two ways (*R* or *S*) with equal probabilities. Integration of relevant peaks showed the percentage trans to be 20–25% in these polymers.

Polymers **3**, **4**, **6**, and **7** were found to be insoluble in various organic solvents, including methanol, but were readily soluble in water, as expected. The aqueous solutions remained stable and transparent for months with no discoloration and very little change in their viscometric behavior. A 0.5% solution of the dicationic polymer **3** (entry 2, Table I) was found to have pH values of 2.98 (in the absence of NaCl) and 3.44 (in the 0.1N NaCl). The corresponding pH of the copolymer (**6**) (entry 4, Table I) was determined to be 2.85 and 3.27. The basic polymer **4** (entry 2, Table I), however, had the pH values of 8.40 and 8.10 in the absence and presence of NaCl (0.1N), respectively. In the

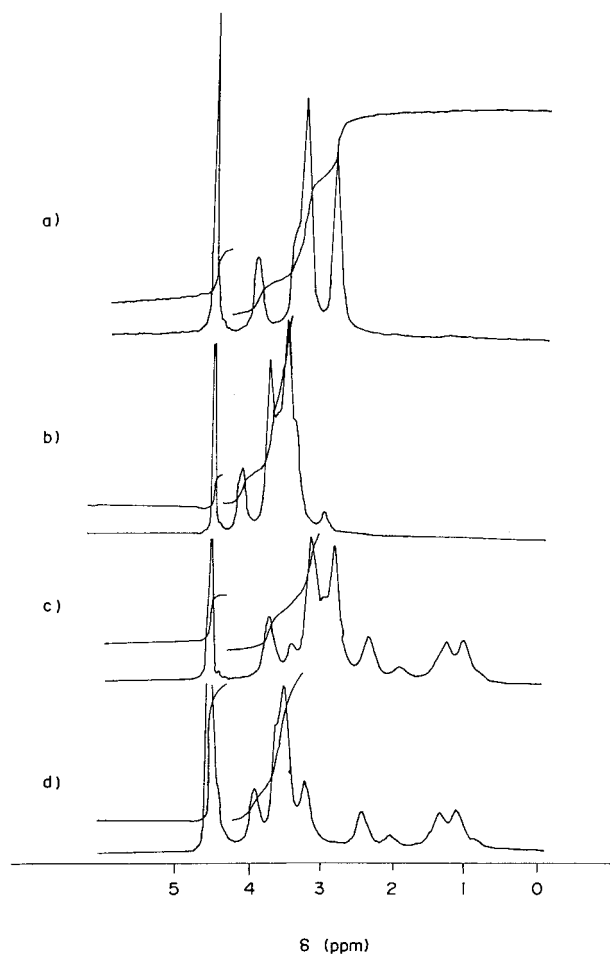


Figure 2 $^1\text{H-NMR}$ spectrum in D_2O of (a) poly(DAPC- SO_2) (**7**), (b) poly(DAHPD- SO_2) (**6**), (c) poly(DAPC) (**4**), and (d) poly(DAHPD) (**3**).

presence of added salt, the dissociation of the NH_2^+ group was suppressed, thereby decreasing the acidity of the dicationic polymer solutions. The basicity of the basic polymer decreased in the presence of salt because it suppressed the dissociation of OH^- in the solution.

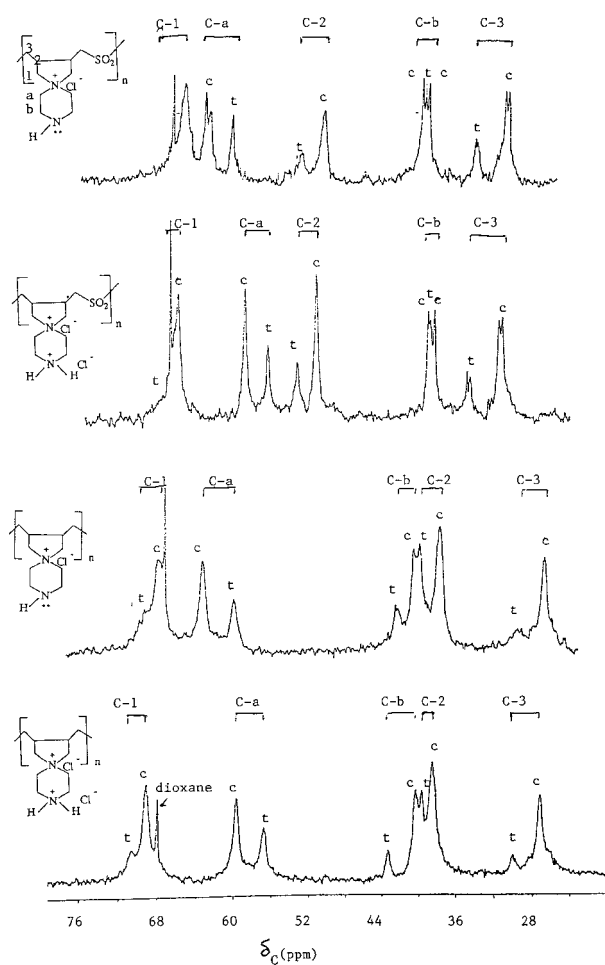


Figure 3 $^{13}\text{C-NMR}$ spectrum in D_2O (using dioxane as the internal standard) of (a) poly(DAPC- SO_2) (**7**), (b) poly(DAHPD- SO_2) (**6**), (c) poly(DAPC) (**4**), and (d) poly(DAHPD) (**3**).

The intrinsic viscosities of polymers **3**, **4**, **6**, and **7** and that of the parent polymers **2** and **5** (from which they were derived) in 0.1N NaCl at 30°C are given in Table I. Although there was

Table I Intrinsic Viscosity of Homo- and Copolymers 2–7

Entry ^a No.	Polymer	Intrinsic Viscosity ^b (dL/g)	Polymer	Intrinsic Viscosity (dL/g)	Polymer	Intrinsic Viscosity (dL/g)
1	2	1.12	3	1.30	4	1.58
2	2	1.68	3	1.89	4	1.78
3	5	0.950	6	2.42	7	2.24
4	5	1.11	6	2.90	7	2.35

^a Polymers **3** and **4** are derived from polymer **2** of entry 1 and 2. Likewise polymers **6** and **7** are derived from polymer **5** of entry 3 and 4.

^b Viscosity of the polymer solution was measured in an Ubbelohde viscometer (K 0.005989) using a 1–0.03125 g/100 cm³ solution in 0.1N NaCl at 30°C.

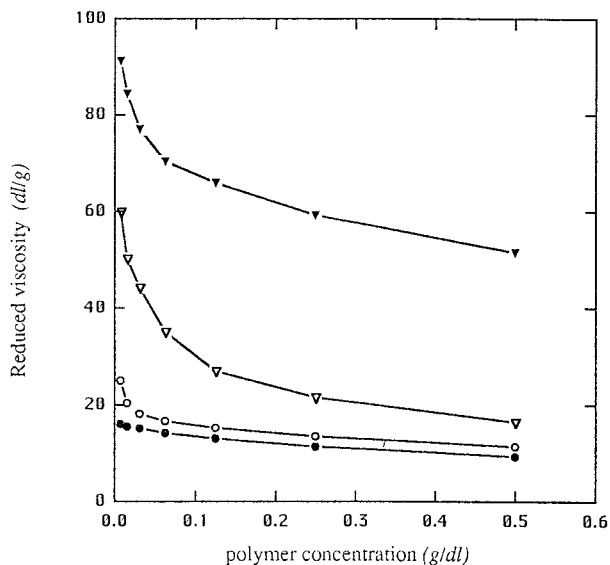


Figure 4 Viscosity behavior in deionized water at 30°C at a shear rate of $\sim 7.5 \times 10^3 \text{ s}^{-1}$ of (●) poly-(DAHDP) (3) (sample: entry 1, Table I), (○) poly-(DAHDP) (3) (sample: entry 2, Table I), (▽) poly-(DAPC) (4) (sample: entry 1, Table I), and (▼) poly-(DAPC) (7) (sample: entry 4, Table I).

a slight increase in the intrinsic viscosity of the homopolymers in going from 2 to 3 and 4, the sulfur dioxide copolymers 6 and 7 were found to have substantially higher intrinsic viscosity than that of the parent polymer 5 from which they were prepared. The viscosity curves are presented in Figures 4–7. The plots are typical for polyelectrolytes in general, unlike the behavior of uncharged linear polymers. The reduced viscosity (η_{sp}/C) versus concentration (C) of the quaternary ammonium polymers are concave upward (Fig. 4); however, in the presence of 0.1N NaCl, the viscosity behavior becomes normal as shown in Figure 5. The polyelectrolyte effects in dicationic polymers 3 and 6 are not as pronounced as in the monocationic polymers 4 and 7. Polymer 2 (entry 1, Table I) has a concentration range of 0.5–0.0078 g/dL and has reduced viscosity in the range of 20–70 dL/g; the range for the corresponding dicationic polymer 3 (entry 1, Table I) was found to be 9–16 dL/g (Fig. 4). Similar viscosity behavior was observed for polymer 3 (entry 2, Table I). For the dicationic copolymer 6, the reduced viscosity (in absence of NaCl) for a concentration range of 0.0313–0.00781 g/dL varied from 32.8 to 36.4 dL/g (entry 4, Table I) and 36.5–45.2 dL/g (entry 3, Table I). The parent polymer 5 (entry 3, Table I) has a viscosity of 54.8–76.0 in

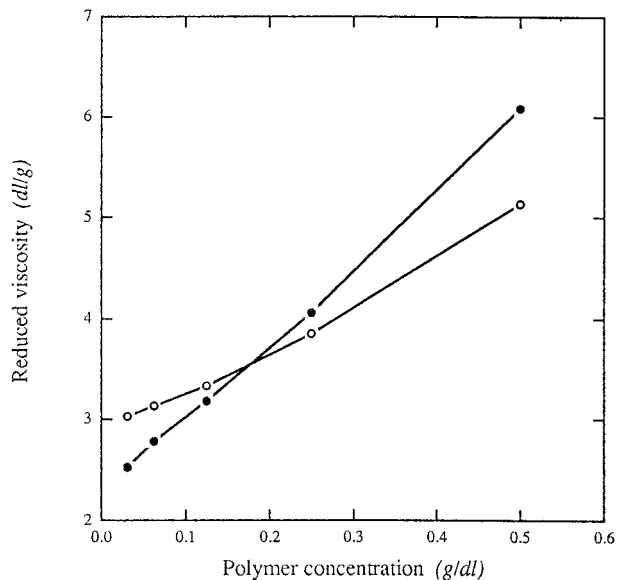


Figure 5 Viscosity behavior in 0.1N NaCl solution at 30°C at a shear rate $\sim 7.5 \times 10^3 \text{ s}^{-1}$ of (●) polymer sample 6 (entry 3, Table I) and (○) polymer sample 6 (entry 4, Table I).

the same concentration range. The monocationic polymers 4 and 7, like their parent polymers 2 and 5, showed similar pronounced polyelectrolyte effects. For instance polymer 4 (entry 1, Table I) and 7 (entry 4, Table I) have reduced viscosities

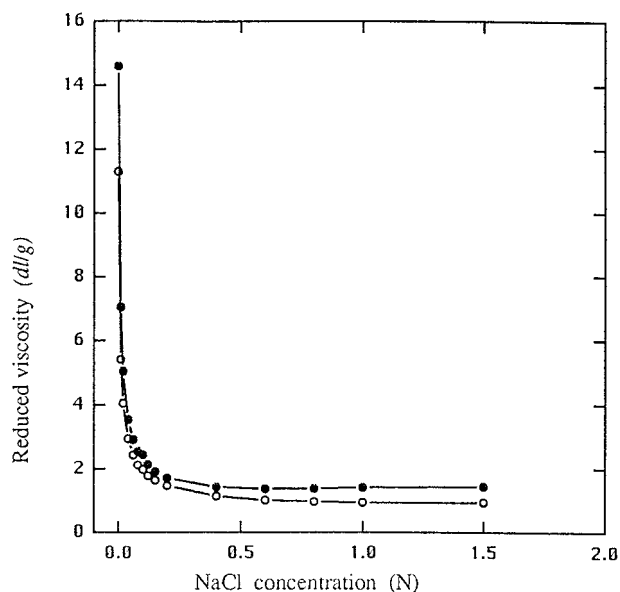


Figure 6 Viscosity behavior of polymer (0.5 g/100 cm^3) at 30°C in different concentrations of NaCl solution: (○) polymer sample 3 (entry 1, Table I) and (●) polymer sample 4 (entry 1, Table I).

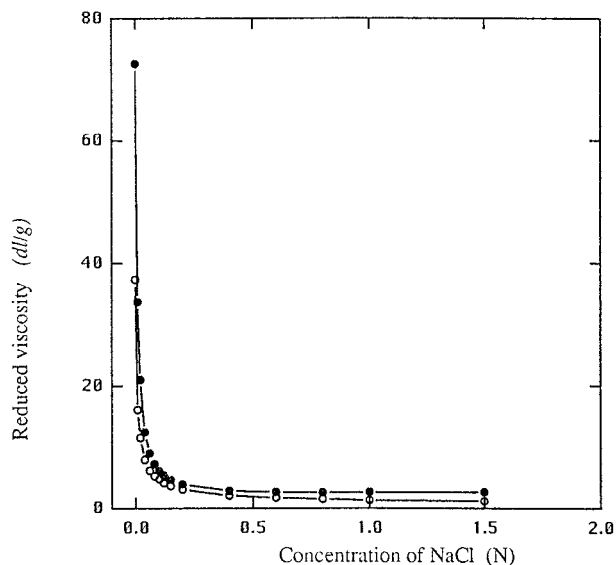


Figure 7 Viscosity behavior of polymer (0.5 g/100 cm³) at 30°C in different concentrations of NaCl solution: (○) polymer sample 6 (entry 3, Table I) and (●) polymer sample 7 (entry 3, Table I).

of 16.4–59.9 and 51.2–91.2 dL/g, respectively, in the concentration range of 0.5–0.0078 g/dL (Fig. 4). Figures 6 and 7 display the reduced viscosity behavior of the polymers in different salt (NaCl) concentrations. Presumably the presence of an additional appended cationic center in each monomer unit suppresses the ionization of the cation in the polymer backbone to such an extent that on further dilution the degree of ionization does not change appreciably. The chloride ions remain in the vicinity of the cationic charge, thereby minimizing repulsive interaction between positive charges and hence suppressing the usual increase in the hydrodynamic volume of the polymers.

These interesting new classes of polymers may find their way into biomedical and industrial applications. As drug carriers, for those molecules

unable to dissolve in aqueous media, the development of polyethyleneimines, polyacrylates, and other types of water-soluble polymers as components of pharmaceutical preparations has been hampered by the problems of nonbiodegradability along with toxicity associated with these polymers.¹⁰ Piperazine and several of its derivatives are used as drugs for treatment of several diseases. The presence of a basic amino group in these water-soluble polymers may be suitable for reversible bond formation with biologically active agents. The presence of quaternary, as well as basic, nitrogen makes these new series polymers especially attractive in water treatment as potential flocculants.

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