



Synthesis and solution properties of a new poly(electrolyte-zwitterion)

Mohammad A.J. Mazumder, Yunusa Umar, Sk. Asrof Ali*

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

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Abstract

A novel electrolytic-zwitterionic (EZ) monomer, Sodium *N*-(3-sulfopropyl)-3-(*N,N*-diallylamino)propanesulfonate, on homopolymerization in aqueous solution using *tert*-butylhydroperoxide, afforded the poly(electrolyte-zwitterions) (PEZ). The copolymer of the above monomer and sulfur dioxide was also synthesized in excellent yield. The EZ monomer as well as the PEZs contains structural features common to both polyzwitterions and conventional polyelectrolytes. The solution properties of these polymers were studied in detail. The PEZ, as the name implies, possess dual type of structural character and it is the electrolytic portion of the structure that dictates the solubility and viscosity behavior of the polymers.

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1. Introduction

The homo [1]- and co-cyclopolymerization [2–4] of *N,N*-diallyl quaternary ammonium salts **1** led to the synthesis of an array of water-soluble cationic polyelectrolytes **2** and **3** (Scheme 1) [5–11] of tremendous scientific and technological interest. Poly(diallyldimethylammonium chloride) alone accounts for over 1000 patents and publications. The cyclopolymerizations have been shown to proceed via alternating intra- and inter-molecular chain propagation through the less stable five-membered cyclic structure rather than the thermodynamically favorable six-membered one [12–17]. The monomers **1** with modified R² side chain have also provided entries [18–27] into the amphoteric polymers—polybetaines **4** and polysulfobetaines **5**. The amphoteric polymers, unlike polyelectrolytes, can exhibit antipolyelectrolyte behavior [19,28–32], that is enhancements in the viscosity and solubility in the presence of added electrolytes (e.g. NaCl) due to the neutralization of the ionically crosslinked network in a collapsed coil conformation of polyzwitterions. The development in the cyclopolymerization process has in recent years entered a new stage that deals with synthesis of pH-responsive ionic polymers **4** and **5** (R¹ = H) [33–37] that has demonstrated interesting pH-responsive solution behavior. Recently, the

polyquaternary ammonium salt **6**, containing structural features common to both polybetaines and conventional polyelectrolytes has been synthesized [38].

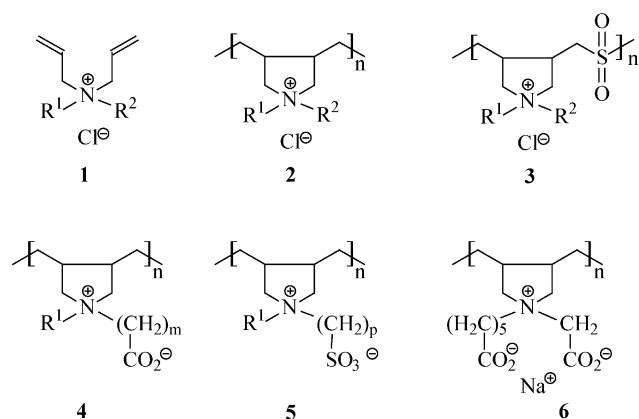
The present paper describes, for the first time, the synthesis of poly(electrolyte-zwitterion) (PEZ) **9** and the corresponding sulfur dioxide copolymer **10** from the highly symmetrical monomer **8** having identical length and chemical structure of the side chains (Scheme 2). The study has provided an interesting opportunity to investigate which structural features—electrolytic or zwitterionic—dictates the solution properties of the new polymers.

2. Experimental

2.1. Physical methods

Melting points are recorded in a calibrated Electrothermal-IA9100-Digital Melting Point Apparatus using heating rates of 1 °C/min in the vicinity of the melting points. Elemental analyses were carried out in a Carlo-Erba elemental analyzer Model 1102. IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer (spectral resolution, 4 cm⁻¹; number of scans, 19). ¹H and ¹³C NMR spectra of the polymers were measured in D₂O using dioxane as internal standard on a JEOL LA 500 MHz spectrometer. Viscosity measurements were made by an

* Corresponding author. Tel.: +966-3-860-3830; fax: +966-3-860-4277.
E-mail address: shaikh@kfupm.edu.sa (S.A. Ali).

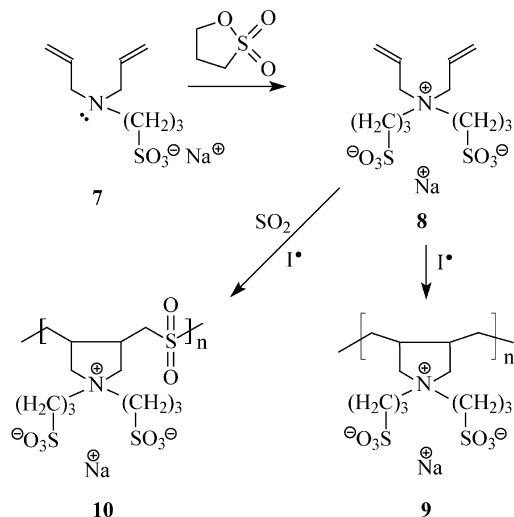


Scheme 1.

Ubbelohde viscometer (having Viscometer Constant of 0.005718 cSt/s at all temperatures) using CO₂-free water under N₂ in order to avoid CO₂ absorption that may affect the viscosity data and kinetic energy corrections was applied to the data. A gentle stream of N₂ was passed through distilled deionized water at 90 °C for 15 min in order to remove dissolved gases. This water was used viscosity measurements.

2.2. Materials

AIBN from Fluka Chemie AG (Buchs, Switzerland) was purified by crystallization from a chloroform–ethanol mixture. 1,3-Propanesultone from Fluka was used as received. Acetonitrile (hplc grade) was dried over Linde 4A molecular sieves. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a bp of 64–65 °C (4 mmHg). All glassware were cleaned using deionized water. Sodium 3-(*N,N*-diallylamino)propanesulfonate (**7**) was prepared as described in a previous report [36].



Scheme 2.

2.3. Sodium *N*-(3-sulfopropyl)-3-(*N,N*-diallylamino)propanesulfonate **8**

A mixture containing the sodium 3-(*N,N*-diallylamino)-propanesulfonate (**7**) (25 g, 104 mmol) and 1,3-propanesultone (25 g, 205 mmol) in dry acetonitrile (500 cm³) was stirred at 70 °C in a closed vessel for 48 h. The sodium salt was partially soluble in the mixture; and as the reaction proceeded, a clear solution was obtained within 6 h. Continued reaction resulted in the formation of more product which settled as a thick liquid at the bottom of the flask. At the end of the elapsed time the mixture was concentrated to an approximate volume of 100 cm³. The supernatant liquid was decanted and the thick liquid was dissolved in methanol (50 cm³) and precipitated in acetone (250 cm³). The process was repeated thrice to obtain the electrolyte-zwitterionic monomer **8** as a highly hygroscopic white solid which was dried to a constant weight (29.9 g, 79.2%) at 60 °C under vacuum. The melting point was 202–207 °C (closed capillary). The monomer was so hygroscopic that a satisfactory elemental analysis was not obtained ν_{\max} (KBr): 3447(s), 2971, 1647, 1545, 1475, 1424, 1364, 1194 (s), 1047, 961, 736 cm⁻¹; δ_{H} (D₂O): 2.12 (4H, quint, $J = 7.9$ Hz), 2.85 (4H, t, $J = 7.1$ Hz), 3.31 (4H, apparent t, $J = 8.6$ Hz), 3.85 (4H, d, $J = 7.4$ Hz), 5.62 (4H, m), 5.91 (2H, m), (HOD: 4.65). δ_{C} (D₂O): 18.26, 47.99, 57.30, 61.68, 124.42, 129.82 (dioxane, 67.40 ppm).

2.4. General procedure for the homopolymerization of the monomer **8**

All the polymerizations were carried out under the conditions described in Table 1. A solution of the monomer **8** in CO₂ and O₂ free deionized water in a 10 cm³ round bottomed flask was purged with N₂, and after adding the initiator the mixture was stirred in the closed flask at 70 °C for 20 h followed by 80 °C for another 20 h. The reaction mixture remained transparent throughout the process. At the end of the specified time, the ¹H NMR spectra of the crude reaction mixture revealed the composition of the PEZ **9** and the unreacted monomer **8**. The reaction mixture was cooled,

Table 1
Effect of monomer concentration on the cylopolymerization

Entry	Monomer concentration (w/w%)	TBHP ^a (mg)	Yield ^b (%)	Intrinsic viscosity ^c (dl/g)
1	65	10	78 (63)	0.145
2	70	10	89 (74)	0.161
3	75	10	85 (72)	0.151

Polymerization reactions were carried out using 11 mmol of the monomer in aqueous medium at 70 °C for 20 h followed by 80 °C for 20 h.

^a Initiator [*tertiary* butylhydroperoxide, (TBHP)].

^b Determined by ¹H NMR analysis. Isolated yields are written in parentheses.

^c Viscosity of 1–0.125% polymer (**9**) solution in 0.1N NaCl at 30 °C as measured with an Ubbelohde viscometer ($K = 0.005718$).

and transferred to a dialysis bag and dialyzed against deionized water for 24 h for the removal of the unreacted monomer. The polymer solution was then freeze-dried and subsequently dried to a constant weight at 70 °C under vacuum. The hygroscopic white polymer was then kept in a desiccator. Onset of thermal decomposition (closed capillary): the color changed to brownish black at 340 °C, and black at 400 °C; (found: C, 37.2; H, 6.6; N, 3.5; S, 16.2. $C_{12}H_{22}NNaO_6S_2 \cdot H_2O$ requires C, 37.79; H, 6.34; N, 3.67; S, 16.81%); the 1H and ^{13}C NMR spectra are displayed in Figs. 1 and 2, respectively; ν_{max} (KBr): 3443 (s), 2923, 1653, 1461, 1191 (s), 1048 (s), 737, 601 cm^{-1} .

2.5. General procedure for the copolymerization of the monomer **8** with SO_2

All the polymerizations were carried out using conditions as described in Table 2. In a typical experiment, required amount of SO_2 was absorbed in a solution of the monomer **8** in DMSO. The required amount of the initiator (AIBN) was then added under N_2 and the closed flask was stirred using magnetic stir-bar at 57 °C for 24 h. Within hours, the magnetic bar stopped stirring, and finally the reaction mixture became cloudy. At the end of the elapsed time, the mixture was soaked in methanol, filtered and washed with liberal excess of hot (50 °C) methanol to ensure the

Table 2

Effect of concentration of monomer and initiator on the monomer **8**/ SO_2 copolymerization

Entry number	DMSO (g)	Initiator ^a (mg)	Yield (%)	Intrinsic viscosity ^b (dl/g)
1	5.2	35	77 (65)	0.553
2	5.2	55	85 (76)	0.285
3	8.5	55	86 (73)	0.293

Polymerization reactions were carried out in DMSO using 11 mmol each of the monomer and SO_2 at 57 °C for 24 h.

^a Azobisisobutyronitrile.

^b Viscosity of 1–0.0625% polymer solution in 0.1N NaCl at 30 °C was measured with a Ubbelohde Viscometer ($K = 0.005718$).

complete removal of the unreacted monomer (as indicated by 1H NMR). The hygroscopic white copolymer PEZ **10**, was then dried to a constant weight at 55 °C under vacuum. The white copolymer was stored in a desiccator. The onset of thermal decomposition (closed capillary): the color suddenly changed to black at 320 °C; (found: C, 31.9; H, 5.6; N, 2.9; S, 20.5. $C_{12}H_{22}NNaO_8S_3 \cdot H_2O$ requires C, 32.35; H, 5.43; N, 3.14; S, 21.59%); the 1H and ^{13}C NMR spectra are displayed in Figs. 1 and 2, respectively; ν_{max} (KBr) 3444 (s), 2961, 2923, 1646, 1464, 1418, 1308, 1188 (s), 1132, 1046, 928, 860, 796, and 736 cm^{-1} .

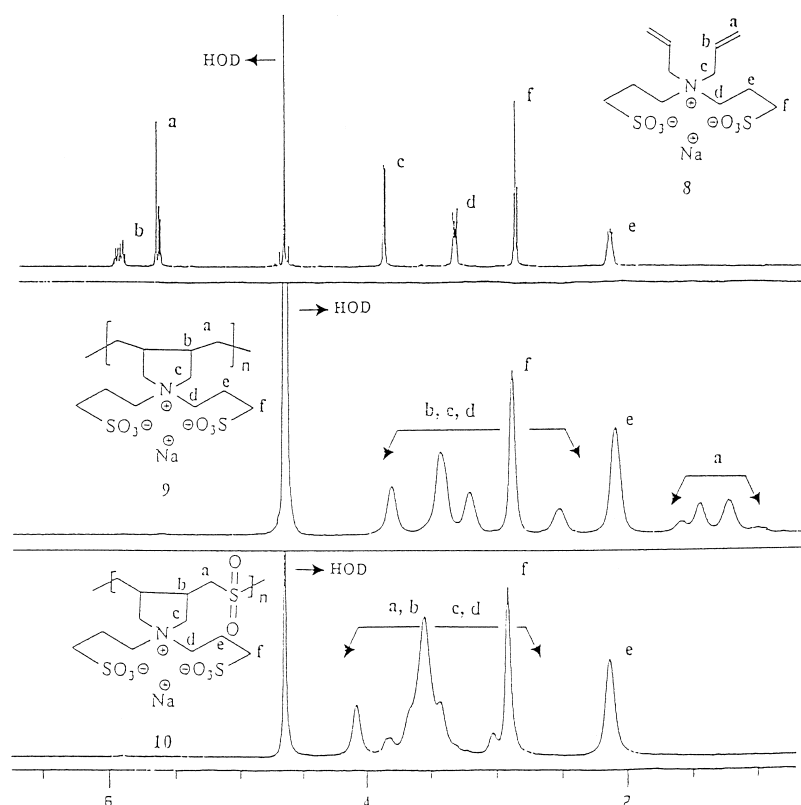


Fig. 1. 1H NMR spectrum of the monomer **8**, PEZ **9** and **10** in D_2O .

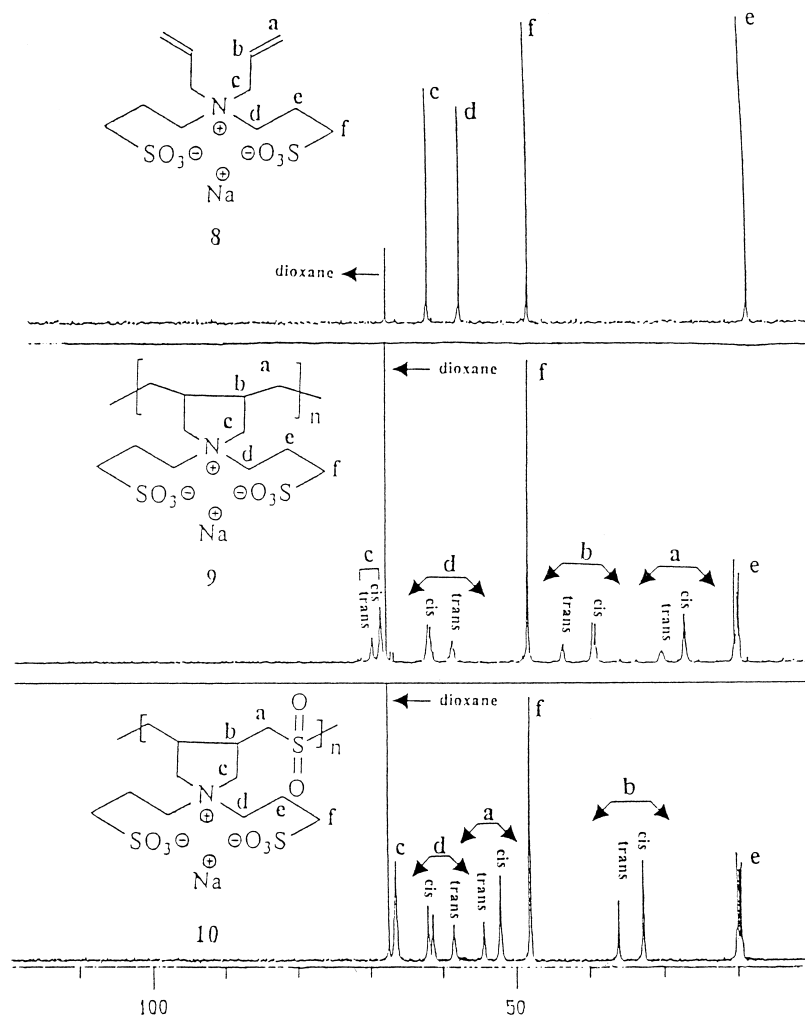


Fig. 2. ^1H decoupled ^{13}C NMR spectrum of the monomer **8**, PEZ **9** and **10** in D_2O .

3. Results and discussion

3.1. Synthesis of the homo- and copolymers

Sodium 3-(*N,N*-diallylamino)propanesulfonate (**7**) on treatment with 1,3-propanesultone afforded the special zwitterionic-electrolytic monomer **8** in excellent yield (90%) (Scheme 2). The monomer was found to be soluble in water, methanol, DMF, DMSO but insoluble in acetone, acetonitrile and many other less polar common solvents. Interestingly, the monomer **8** was found to remain in solution in a 90:10 acetonitrile/methanol mixture at 20 °C but precipitates out as the solution is heated to ~40 °C. The monomer was subjected to cyclopolymerization reaction in aqueous solution using *t*-butylhydroperoxide as an initiator to give the PEZ **9** in very good yields. The results of the polymerizations carried out under various monomer concentration and the intrinsic viscosities of the resultant polymers **9** are given in Table 1. As is evident from Table 1, the highest yield and viscosity value are obtained for the

polymerization reaction under entry 2 with a monomer concentration of 70% (w/w).

Cyclopolymerization of the monomer **8-SO₂** in DMSO using AIBN as the initiator went smoothly to give the copolymer PEZ **10** in excellent yields (Scheme 2). As evident from Table 2, the lower monomer and high initiator concentration lead to polymers with lower viscosity values.

3.2. Infrared and NMR spectra

The IR spectra of the PEZs, **9** and **10**, indicate the presence of the sulfonate group by its strong characteristic bands at ~1190 and ~1047 cm^{-1} . The two strong bands at 1308 and 1132 cm^{-1} were assigned to the asymmetric and symmetric vibrations of SO_2 unit in the copolymer **10**. ^1H and ^{13}C NMR spectra of the monomer and polymers are displayed in Figs. 1 and 2, respectively. The absence of any residual alkene proton or carbon signal in the spectra suggested the degradative chain transfer process [39] for the termination reaction. The proton signals of the copolymer PEZ **10** are, as expected, shifted downfield in compare to

homopolymer **9** due to the presence of electron withdrawing SO_2 group in the polymer backbone. The assignments of the ^{13}C peaks are based on earlier works [13,23,40,41]; the spectral data (specially the number of signals) point to the formation of the pyrrolidine rings rather than the unsymmetrical six-member ring structure. Integration of the relevant peaks in the ^{13}C spectrum yields the *cis/trans* ratio of the ring substituents to be 70/30, which is similar to that observed for the polymers derived from quaternary ammonium salts [23,24].

3.3. Solubility

The solubility behavior of the polymers **9** and **10** is shown in Table 3. Both the homo- and copolymers were found to be very soluble in majority of the protic solvents except methanol, triethylene glycol and acetic acid. The solubility in water is a demonstration of the electrolytic behavior the PEZs since the zwitterionic trait [19,28,29] in the polymers are expected to impart insolubility in water.

3.4. Viscosity measurements

Viscosity data for PEZ **9** (entry 2, Table 1) is presented in Fig. 3. In the absence of added salt (NaCl), the plot for PEZ **9** is typical for polyelectrolyte, i.e. concave upward. In the presence of added salt the viscosity curves become linear as expected of any polyelectrolyte; the intrinsic viscosity values decreases with increase in the NaCl concentration and converge to a minimum at 0.3N NaCl. Viscosity data for the copolymer PEZ **10** (entry 1, Table 2) is presented in Fig. 4. The viscosity plots ascertain the polyelectrolytic behavior of the copolymer. As in the case of the homopolymer, the intrinsic viscosity values decreases with increase in the NaCl concentration; the intrinsic viscosities $[\eta]$, in 0.1, 0.3, 0.5, 1.0, 2.0N NaCl was measured to be 0.556, 0.340, 0.310, 0.302 and 0.289 dl/g, respectively. The typical polyelectrolyte behavior of the present polymers may be explained by the presence of one effective negative charge on a monomer unit, since each unit has two negative charges and one positive charge.

Viscosity behavior of a polyelectrolyte is different from

Table 3
Solubility of PEZ **9** and **10**

Solvent	ϵ	HOMO 9	CO 10
Water	78.4	+	+
Methanol	32.3	–	–
Formic acid	58.5	+	+
Formamide	111.0	+	+
Ethylene glycol	37.3	+	+
Triethylene glycol	23.7	–	–
Acetic acid	6.15	–	–

2% (w/w) of polymer–water mixture (solution) was made after heating the mixture at 70 °C for 1 h and then cooling to 23 °C. ‘+’ indicates soluble; ‘–’ indicates insoluble.

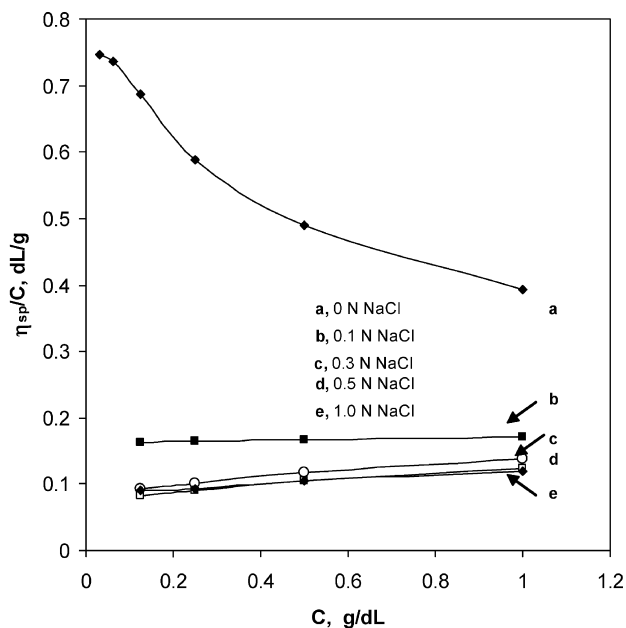


Fig. 3. The viscosity behavior of PEZ **9** (entry 2, Table 1) in salt-free water and various NaCl solutions at 30 °C using an Ubbelohde Viscometer.

that of non-ionic polymers [42]. Application of Huggins viscosity relationship [43] (Eq. (1)) for linear parts of the curves describing the dependence of reduced viscosity (η_{sp}/C) on concentration C for dilute polyelectrolyte solutions free of simple electrolyte leads to ambiguous values of the interaction parameters. In salt-free and low added-salt concentrations (10^{-3} – 10^{-5} M) cases, a useful practical method has been reported [44,45] to obtain $[\eta]$ using Eq. (2). However, the dependence of reduced viscosity on concentration in the presence of sufficient concentration of simple electrolyte (10^{-2} – 10^0 M) becomes linear, similarly

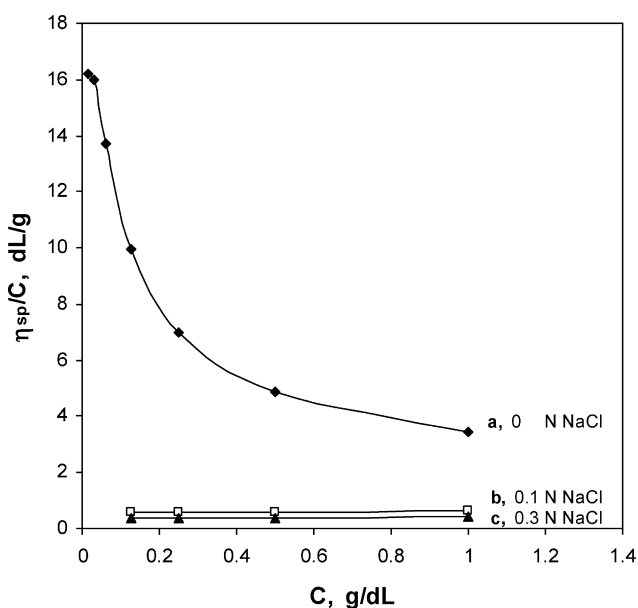


Fig. 4. The viscosity behavior of PEZ **10** (entry 1, Table 2) in salt-free water and various NaCl solutions at 30 °C using an Ubbelohde Viscometer.

to the usual non-ionic polymer solution, and in this case intrinsic viscosity $[\eta]$ can be easily determined [45–47].

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C \quad (1)$$

$$\frac{\eta_{sp}}{C} = \frac{\eta_{intra}}{C} + \frac{\eta_{inter}}{C} \quad (2)$$

In this work, extrapolation was possible for determination of $[\eta]$ for all polymer solutions in the presence of added salt. The variation of $[\eta]$ and Huggins parameter, k' , with temperature for the PEZ **9** (entry 2, Table 1) in 0.1N NaCl, and PEZ **10** (entry 1, Table 2) in 0.1 and 0.5N NaCl are given in Table 4. The intrinsic viscosity for the PEZ **9** passes through a maximum at 30 °C and thereafter decreases with increasing temperature. However, the intrinsic viscosity for the PEZ **10** increases continuously with increasing temperature both in 0.1 and 0.5N NaCl (Table 4). The values (k') vary generally from 0.3 to 0.8 for higher polymers. The lowest values are obtained when the polymer is dissolved in a good solvent. The solvent system (i.e. 0.1N NaCl) for the copolymer **10** in this case seems to be a thermodynamically good one, whereas it is a bad solvent for the homopolymer **9** at higher temperatures (Table 4). It is known that intrinsic viscosity of polymer solutions is a function of temperature; it can increase or decrease or could have a maximum at a characteristic temperature, T_m [48,49]. Theoretically all polymer–solvent systems should have a maximum intrinsic viscosity at a certain temperature which may not always be experimentally achievable [50,51] as in the case of PEZ **10**.

Intrinsic viscosity and Huggins parameter, k' , for the copolymer PEZ **10** (entry 1, Table 2) in various 0.1N salt solutions were determined. The results are shown in Table 5. The viscosity plots are presented in Fig. 5. The intrinsic viscosity is found to decrease in the order NaCl > KCl > CsCl (for common anions) and KI > KBr > KCl (for common cations). It becomes obvious from the Table 5 that the cations as well as anions do not have much of an effect to influence the viscosity behavior of PEZ **10**. This is contrary to what is expected of a polymer containing zwitterions or electrolyte as the sole functionality [23,24].

Table 5

Effect of various salt solutions on the viscosity behavior of PEZ **10** at 30 °C

Salt solution (0.1N)	Common anion		Salt solution (0.1N)	Common cation	
	$[\eta]$ (dl/g)	k'		$[\eta]$ (dl/g)	k'
LiCl	0.528	0.810	KF	0.587	0.368
NaCl	0.553	0.281	KCl	0.483	0.444
KCl	0.483	0.444	KBr	0.492	0.463
CsCl	0.435	0.693	KI	0.515	0.368

While the intrinsic viscosity of cationic polyelectrolytes has been shown [47] to decrease in 0.1N aqueous salt solution in the order KF > KCl > KBr > KI, the order is reversed for polybetaines or polyampholytes [24,28,35–37]. The polarizable (soft) anion I^- , has been shown to be more effective in screening the positive nitrogens on the macromolecular chain of cationic and zwitterionic polymers. In the presence of I^- , the cationic polyelectrolytes, thus, assume a more coiled conformation, whereas in polybetaines the macromolecule becomes extended to some extent [45] in order to relieve the repulsion among the highly exposed negatives charges on the pendants. Unlike X^- , the hydration shell for the M^+ (e.g. Na^+) in water is generally fairly large; hence the distance of closest approach is not sufficient to effectively neutralize the negative charges on the pendants.

In order to extract the zwitterionic behavior, i.e. increase of $[\eta]$ with increasing added salt concentration, the $[\eta]$ of the PEZ **10** was measured in solution containing various concentration of KI; the $[\eta]$ values in 0.01, 0.05, 0.1, 0.3 and 0.5N KI solutions were found to be 1.48, 0.670, 0.515, 0.356 and 0.332 dl/g, respectively. The decreasing values of $[\eta]$ with increasing added-salt demonstrated the inability of even the highly polarizing iodide to overwhelm the electrolytic behavior in favor of the zwitterionic trait.

The PEZ **10** is expected to behave like an anionic polyelectrolyte since each monomer unit has an overall negative charge. For common anions, the lowest viscosity was obtained in CsCl solution (Fig. 5, Table 5). Cesium cation having the smallest charge to radius ratio and relatively smaller hydration shell is most effective in neutralizing the anionic charges on the pendants thus favoring the packing of the polymer chains. Viscosity

Table 4

Dependence of intrinsic viscosity and Huggins parameter k' of homo and copolymer upon temperature in NaCl solutions

Temp (°C)	Homopolymer 9 in 0.1N NaCl		Copolymer 10 in 0.1N NaCl		Copolymer 10 in 0.5N NaCl	
	Intrinsic viscosity (dl/g)	k'	Intrinsic viscosity (dl/g)	k'	Intrinsic viscosity (dl/g)	k'
20	0.153	0.222	0.502	0.329	0.254	1.27
30	0.163	0.346	0.553	0.281	0.316	0.407
40	0.128	2.36	0.575	0.360	0.334	0.512
50	0.122	3.26	0.619	0.309	0.362	0.450
60	0.119	3.48	0.648	0.273	0.407	0.190
70	–	–	0.673	0.254	0.428	0.164

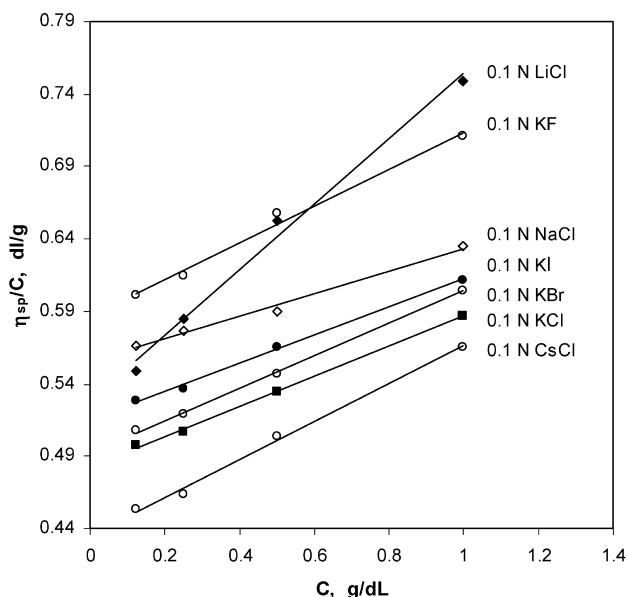


Fig. 5. The viscosity behavior of PEZ **10** (entry 1, Table 2) in various 0.1N salt solutions at 30 °C using an Ubbelohde Viscometer.

values in 0.1N LiCl and KF having smallest cation and anion, respectively; do not fit into the trends observed for various salt solutions. We are unable to offer any rationale at this stage for the observed discrepancy. The PEZ **9** and **10** possess dual type of structural character and it is the electrolytic portion of the structure that dictates the solubility and viscosity behavior of the polymers.

4. Conclusions

The symmetrical monomer, **8**, containing electrolytic and zwitterionic moiety is prepared from inexpensive starting materials. The work described in this paper represents the use of cyclopolymerization technique to provide the first synthetic examples of PEZs having equal size of the electrolytic and zwitterionic pendants. The increase of viscosity with increase in temperature for the PEZ **10** is an interesting property. Hydrophobically modified PEZs could be useful where viscosification of water at higher temperatures is of interest. The work is currently under investigation in our laboratory.

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