An Exceptionally Salt Tolerant Copoly(maleimide sulfobetaine) – Structural Requirements for Ultra-salt Tolerance

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Abstract

Zwitterionic polymers are an important class of polymers with far ranging applications. In the widely studied poly(meth)acrylate and poly(meth)acrylamide based zwitterions, properties can be tuned predominantly by changing the nature of substituents attached to ammonium ions. However, these changes influenced the salt tolerance of zwitterionic polymers only to a limited extent. Upon adding salt these polymers expanded in solution initially. Further increase in salt concentration caused the polymer chains to shrink similar to the common water soluble, uncharged polymers thereby deteriorating the viscosity of aqueous solutions. In contrast to the conventional poly(meth)acrylate and poly(meth)acrylamide-based zwitterions, zwitterionic copolymaleimides showed substituent dependent salt tolerant nature. In the absence of any substituent on the polymer backbone such as zwitterionic poly(ethylene-alt-maleimide) (ZI-PEMA) the viscosity of salt solutions increased both with the increasing salt concentration as well as the concentration of polymer. This is likely due to the continuous expansion of polymer coil in salt solutions with increasing salt concentration caused primarily by the rigidity of polymer backbone. ZI-PEMA also enhanced the saturation limit of mono- and divalent salts like sodium chloride and hydrated calcium bromide in water. This property is useful for various applications like fish curing, for making high density fluids, refrigeration, etc. across various industrial sectors.

1. Introduction

Water-soluble polymers have many applications as dispersants, flocculating agents, rheology modifiers, thickeners, etc. In some of these applications, the water-soluble polymers also need

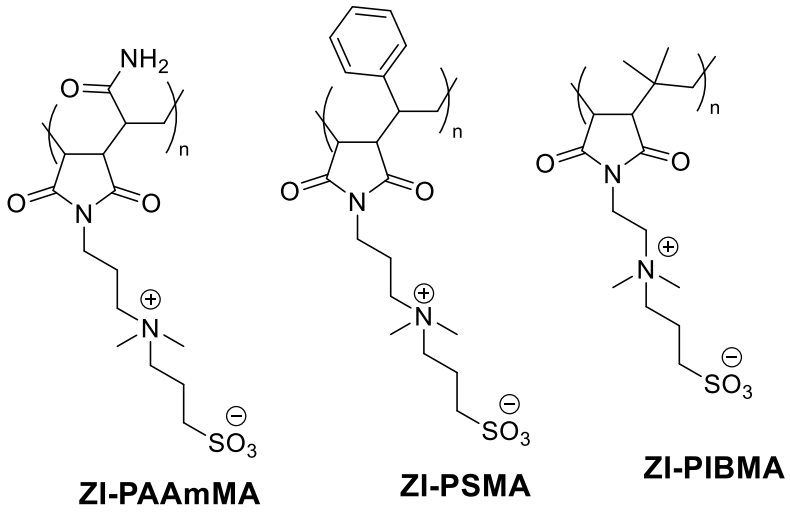
to be salt tolerant because salt is either intentionally added into the formulation for enhancing some properties or these aqueous polymer solutions encounter salt in the field of application.[1-3] For example, salts may be added in cosmetic formulations as moisturizing agent and the added salt could pose problems for the colloidal stability of polymers added as thickening agents. In the oil and gas industry, it is a common practice to inject polymer solutions into the oil well to displace residual crude oil.[4,5] Often these polymer solutions would encounter salt solutions of varying salinity in the ground or off-shore where it is injected. In general, upon encountering salt, many undesired changes occur in these aqueous polymer solutions. The solubility of polymer may be reduced or as a result, polymers may precipitate out of the aqueous solution.[6-8] This in turn will have a deleterious effect on the rheological properties of the aqueous polymer solution.[9] It may be noted that polymers were used in the first place to improve the viscosity of aqueous medium. Aqueous salt solutions are widely used in fishing industry as refrigerants and fish curing agents. Salt solutions are used as high-density fluids and in large industrial refrigeration installations for a variety of commercial uses.[10] These solutions are also extensively used in oil and gas industry to separate hydrocarbon from aqueous sediments. Therefore, polymers that exhibit high salt tolerance are industrially relevant materials.

Ionic polymers in particular zwitterionic polymers are an important class of polymers that show salt tolerance to some extent.[11-17] However, the salt tolerance of zwitterionic polymers is dependent on the concentration of salt solution and the nature of salt. In general, the salt tolerance of zwitterionic polymers is directly related to its chemical structure and composition. Since zwitterionic polymers possess strong interchain interactions of attraction between counterions and repulsion between charges of similar nature, addition of salt interferes with these interactions. This is generally referred to as antipolyelectrolyte effect.[18] The extent of zwitterionic polymer-salt interaction is dependent primarily on the strength of interactions prevailing within the zwitterionic polymer. This in turn predominantly depends on the chemical structure of the zwitterionic polymer since factors like backbone rigidity, polarity, etc. are determined by the chemical structure. Backbone rigidity could play a vital role in regulating the ionic clusters as well its size by controlling the solution conformation of polymer chains. Thus, chemical structure of zwitterionic polymer is the ultimate determining factor in controlling the solution behaviour of polymers.

Zwitterionic polymers have been extensively studied as antifouling materials. Because of the ease of preparation and the ease of availability of starting materials, zwitterionic polymers in the beginning were largely derived from poly(meth)acrylates and (meth)acrylamides. The

structural diversity has been expanded to introduce various additional characteristics. Since the flexibility of polymer backbone is comparable, the property variations that can be obtained with these polymers were limited. Therefore, the behaviour in salt solution remained similar or comparable and varied within a narrow range. Often the rheological properties of these zwitterionic polymers deteriorate in salt solutions with increasing concentration of salt. Thus, there is a need to further enhance the salt tolerant nature of these polymers.

Interestingly, there are not many reports on copolymaleimide based sulfobetaines. Until now, only a few zwitterionic copolymaleimides shown in Scheme 1 have been reported. Other than these, there is also an article on zwitterionic polysoaps.[19] This does not qualify in the aforementioned category of zwitterionic copolymaleimide because of the presence of zwitterion in the vinyl comonomer i.e., not part of the cyclic imide unit and hence would fall under zwitterionic copolyacrylamide. Another report involving the uncyclized amic acid has not been considered due to the more flexible nature of such ring opened zwitterionic copolymaleiamic acid.[20]



Scheme 1. Chemical structure of Zwitterionic copolymaleimides ZI-PAAmAM,[21] ZI-PSMA,[22] and ZI-PIBMA[23] reported in literature.

Considering the ability of maleic anhydride to copolymerize with vinyl monomers, the structural diversity possible for zwitterionic copolymaleimides is immense. As observed in the case of polysulfobetaines derived from poly(meth)acrylates and poly(meth)acrylamides, the properties may vary within a narrow range. Unlike the sulfobetaines of poly(meth)acrylates and poly(meth)acrylamides, sulfobetaines of copolymaleimides would possess certain rigidity of polymer backbone and this would depend on the nature of substituents present as part of the vinyl comonomer. Presence of cyclic units as part of the backbone normally provides rigidity to the polymer backbone. The combination of backbone rigidity and electrostatic interactions

could induce these polymers to exist as rigid rods i.e. in expanded conformation in solution. This rigid rod like nature would dictate ionic interactions and ionic clusters formed upon adding salt. Thus, zwitterionic polymers derived from such cyclic units being present as part of the polymer backbone could help to enhance the rheological properties particularly in salt solutions. This was confirmed earlier in a copolymaleimide sulfobetaine (ZI-PIBMA) derived from poly(maleic anhydride-alt-isobutene) where the viscosity of zwitterionic polymaleimide increased with increasing concentration of sodium chloride in water.[23] Upon further expanding the structural variations within the class of copolymaleimide sulfobetaines, it was found that the zwitterionic polymer derived from poly(ethylene-co-maleimide) (ZI-PEMA) possessed the ability to increase the solubility limit of mono and divalent salts in water well above its saturation limit. Such aqueous salt solutions with enhanced salt concentrations have dual benefits. These solutions depress the freezing temperature of water and simultaneously help to increase the density of fluids thus making these zwitterionic copolymaleimides useful for a variety of applications.[10, 24-26]

2. Experimental Section

2.1 Materials. Poly(ethylene-alt-maleic anhydride) [PEMA, av. molecular weight 100,000-500,000 Da], Poly(methyl vinyl ether-alt-maleic anhydride) [P(MVE-MA), av. molecular weight 1,080,000 Da], 1,3-propane sultone (1,3-PS, 98%), N,N-dimethyl ethylene diamine (DMED, 95%) and hydrated calcium bromide ($CaBr_2.xH_2O$) were purchased from Sigma-Aldrich and used without further purification. N,N-Dimethylformamide (DMF) used as common solvent was of HPLC grade. Aqueous salt solutions of polymer were prepared using deionized (DI) water.

2.2 Characterization. Nuclear magnetic resonance (NMR) spectra were recorded at room temperature on 400 MHz Bruker UltraShield AVANCE 400SB spectrometer using deuterium oxide (D_2O) as the solvent. Fourier transform infrared (FT-IR) Spectra were recorded with KBr pellets using PerkinElmer Frontier FT-IR instrument. The aggregate sizes of polymers in aqueous media were determined by dynamic light scattering (DLS) studies. DLS was performed by using a Zetasizer Nano ZS Instrument (Malvern Instruments, UK) equipped with a He−Ne laser (633 nm) and with noninvasive backscattering (NIBS) detection at a scattering angle of 173°. The autocorrelation function was converted to intensity averaged particle size distribution using Dispersion Technology Software from Malvern Instruments. Each measurement was repeated at least three times, and the average result was reported as the final Z average diameter (nm). The measurements were performed by heating the sample from 20° to 85 °C and then cooling the sample from 85° to 20° C. Rheology measurements were

performed using a strain-controlled Physica (Anton Paar) MCR-501 instrument equipped with a double gap cylinder and geometry set up. The experiment consisted of viscosity measurement of 5 wt % polymer in aqueous salt solutions of varying concentrations at increasing rotational shear rate from 0.1 to 1000/s. Each solution was measured three times. Thermogravimetric analysis was performed using TA instruments TGA Q500 under nitrogen atmosphere at a heating rate of 10 °C/min.

2.3 Experimental

Preparation of ZI-PEMA

Poly(ethylene-alt-maleic anhydride) (av. Molecular weight 100,000-500,000) (11.5439g, 0.09154 mol) was dissolved in N,N-dimethylformamide (120 mL) by heating the mixture at 100 °C in a round bottom flask fitted with a reflux condenser. To this solution, N,N-dimethyl ethylenediamine (DMEDA) (8.07g, 0.09155 mol) was added dropwise. An off-white solid separated upon adding DMEDA. Toluene (50 mL) was added and the reflux condenser was replaced with a Dean-Stark apparatus. The temperature was raised to 160 °C and the water formed in the reaction along with toluene was removed overnight (18h). Then the pale yellow solution was cooled down to 80 °C. About 2 ml of solution was withdrawn and precipitated in diethyl ether, washed with diethyl ether and dried for analysis. Propane sultone (PS) (11.4543g, 0.09381 mol) was added to the remaining solution. An off-white solid separated from the reaction solution after completing the addition of PS. The reaction mixture was heated at 80 °C with stirring for 24 h. After cooling down to room temperature (25 °C), the reaction mixture was transferred to a beaker containing ethyl acetate (500 mL). It was stirred well and the solid was allowed to settle down. The liquid was decanted off and the procedure was repeated two more time. Then the solid was dried in a hot air oven maintained at 60 °C for 48 h. Yield: 22g. The solid (PEMA-DA) obtained by precipitating the DMF solution in diethyl ether after imidization could not be redissolved in organic solvents after drying. The following is the FT-IR analysis of the intermediate PEMA-DA:

KBr pellet (cm^{-1}): 3448, 2948, 2865, 2826, 1777, 1697, 1583, 1456, 1400, 1340, 1229, 1152, 1101, 1040, 928, 862, 775, 623.

Av. MW of ZI-PEMA: 250,000 – 1,260,000.

FT-IR analysis of ZI-PEMA (KBr pellet, cm^{-1}): 3447, 3041, 2959, 1772, 1700, 1490, 1400, 1358, 1191, 1043, 919, 796, 733, 666, 605, 527.

^{1}H-NMR of ZI-PEMA (D_2O containing traces of NaCl) (δ) ppm: 1.45-2.19 (b, 4H), 2.21-2.38 (b, 2H), 2.82-2.91 (b, 2H), 2.96-3.01 (b, 2H), 3.2-3.4 (b, 6H), 3.5-3.7 (b, 4H), 3.85-4.1 (b, 2H).

^{13}C-NMR of ZI-PEMA (D_2O containing traces of NaCl, δ) ppm: 180.75, 60.27, 59.56, 51.16, 47.38, 45.21, 37.13, 27.04, 18.37.

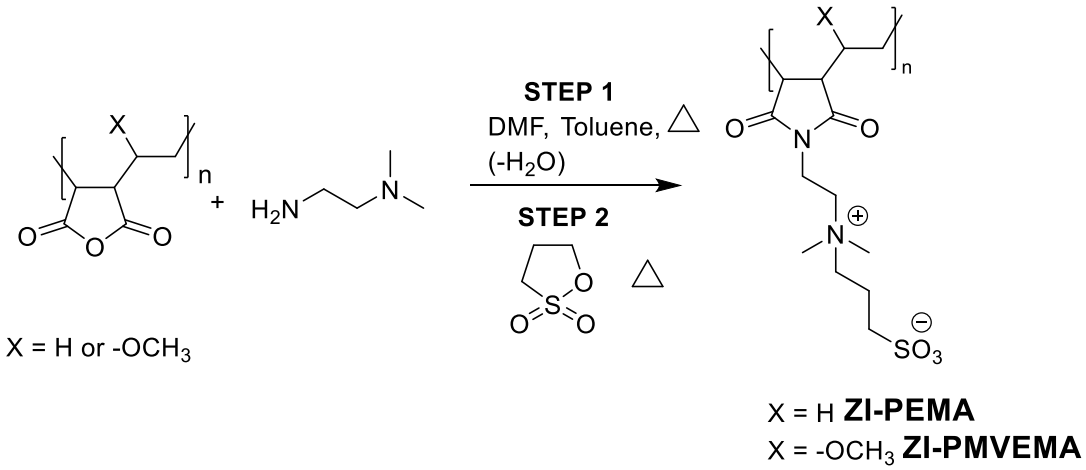
ZI-PMVEMA (Scheme 2) was prepared in the same way as ZI-PEMA.

Av. MW of ZI-PMVEMA: 2,410,000.

FT-IR analysis of ZI-PMVEMA (ATR mode): 3049, 2937, 2854,1740, 1694, 1489, 1433, 1392, 1187, 1093, 1033, 907, 781, 726, 647.

^{1}H-NMR of ZI-PMVEMA (D_2O containing traces of NaCl) (δ) ppm: 2.1-2.3 (b, 4H), 2.9-3.01 (b, 4H), 3.1-3.3 (b, s, 9H), 3.4-3.6 (b, 6H), 3.7-3.8 (b, 1H).

3. Results and Discussion



Scheme 2. Preparation of zwitterionic copolymaleimides.

The zwitterionic copolymaleimides, ZI-PEMA and ZI-PMVEMA were prepared from poly(ethylene-alt-maleic anhydride) and poly(methyl vinyl ether-alt-maleic anhydride) respectively as shown in Scheme 2 by a two-step one pot process. In the first step, the water formed due to imidization was removed as an azeotrope with toluene overnight. After collecting the water overnight, the reaction mixture was cooled down to 80 °C and propane sultone was added to form the zwitterionic polymers. ZI-PEMA was obtained as an off-white solid that was insoluble in water. ZI-PMVEMA was dark in colour and highly soluble in water. The polymers were characterized by spectroscopic and thermal techniques. Since preformed polymers were used and the reactions only involved functional group conversion, the molecular weight of ZI-PEMA and ZI-PMVEMA were determined using a reported method.[23,27] Figure S1 shows the FT-IR spectrum of intermediate PEMA-DA. The completeness of imidization can be noticed by the absence of absorption corresponding to anhydride carbonyl groups in Figure S1. In addition, unlike the starting polymer PEMA, the thermogravimetric analysis (TGA) of the intermediate PEMA-DA showed a one-step degradation. Figure S2 shows the thermogravimetric and differential thermal analysis of PEMA-DA. Figure 1 shows the ^{1}H-

NMR spectrum of ZI-PEMA. The spectrum conformed to the expected chemical structure of ZI-PEMA. Figure S3 shows the FT-IR spectrum of ZI-PEMA. Upon conversion of PEMA-DA to ZI-PEMA, minor shift in absorption of asymmetric and symmetric stretching of imide carbonyls were noticed. The absorption of imide carbonyl groups in PEMA-DA shifted from 1777 and 1697 cm^{-1} to 1772 and 1700 cm^{-1} in ZI-PEMA. Figure S4 shows the thermogravimetric and differential thermal analysis of ZI-PEMA. Similar to PEMA, ZI-PEMA also showed a two-step degradation curve in the TGA. However, the shift in peak position is apparent from the differential thermal analysis shown in Figure 2. Among PEMA and its derivatives, the thermal stability decreases in the order PEMA-DA>PEMA>ZI-PEMA. Cyclic imide is well known to impart thermal stability to polymers, polyimides being one of the most thermally stable polymers. Thus, the conversion of cyclic anhydride to imide enhanced the thermal stability of intermediate PEMA-DA. The lower thermal stability of ZI-PEMA is likely due to the instability of sulfobetaine functionality with quaternary ammonium species being thermally poorly stable. Polymers bearing functionalities / groups with contrasting thermal stability typically show step wise degradation curves in TGA.[28-30] Figure S5 shows the ^{1}H-NMR spectrum of ZI-PMVEMA. As shown in Figure S6, the absorption corresponding to asymmetric and symmetric stretching of imide carbonyl groups were observed at 1740 and 1694 cm^{-1} respectively.

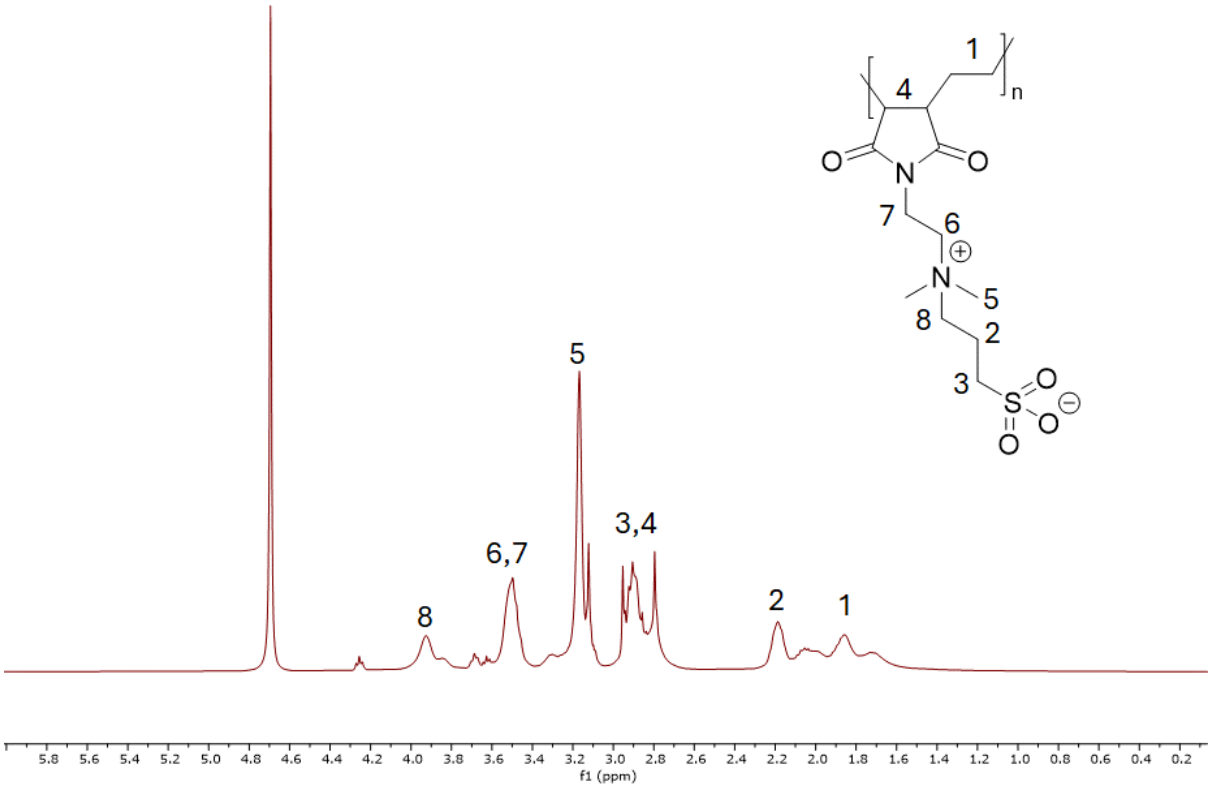


Figure 1. ^{1}H-NMR spectrum of ZI-PEMA in D_2O containing NaCl.

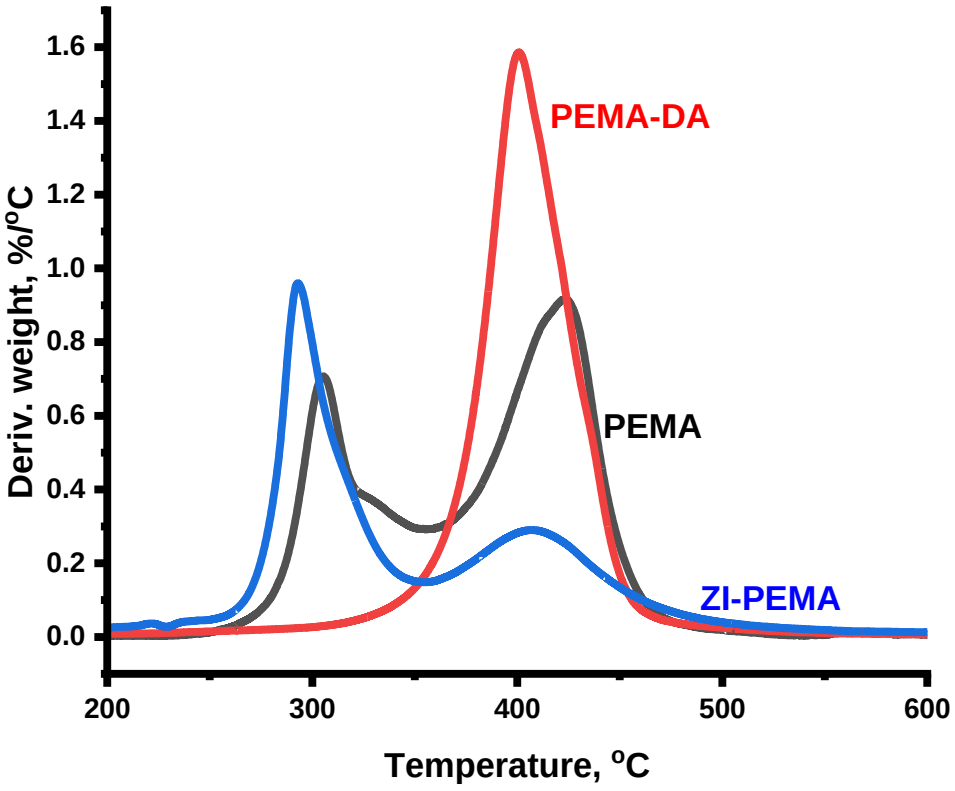


Figure 2. Comparison of differential thermal analysis of PEMA, PEMA-DA and ZI-PEMA.

3.1 Enhancing solubility limit of salts in water

Sodium chloride in water reaches saturation at a concentration of about 26 wt%. The limit for salt concentration near saturation for sodium chloride in water is reported to be 25.58%.[10] However, ZI-PEMA enhanced this limit to above 35 wt% of sodium chloride with 4 wt% of polymer. This limit increased further to 38.5 wt% of sodium chloride with 14.5 wt% of polymer. As shown in Figure 3, this also resulted in depression of freezing temperature of salt solution. As noticed in Figure 3, the depression of freezing point of water caused by the increased sodium chloride concentration was 7.7 $^{\circ}$C. The darkness of solution formed by ZI-PMVEMA prevented any visual observation for its ability to enhance the solubility limit of sodium chloride beyond saturation limit. However, as shown in Figure 3 the aqueous solution of ZI-PMVEMA containing 38.5 wt% of sodium chloride showed only a moderate reduction in freezing point depression that was comparable to that of 23% sodium chloride solution indicating that ZI-PMVEMA did not increase the solubility of sodium chloride beyond its saturation point.

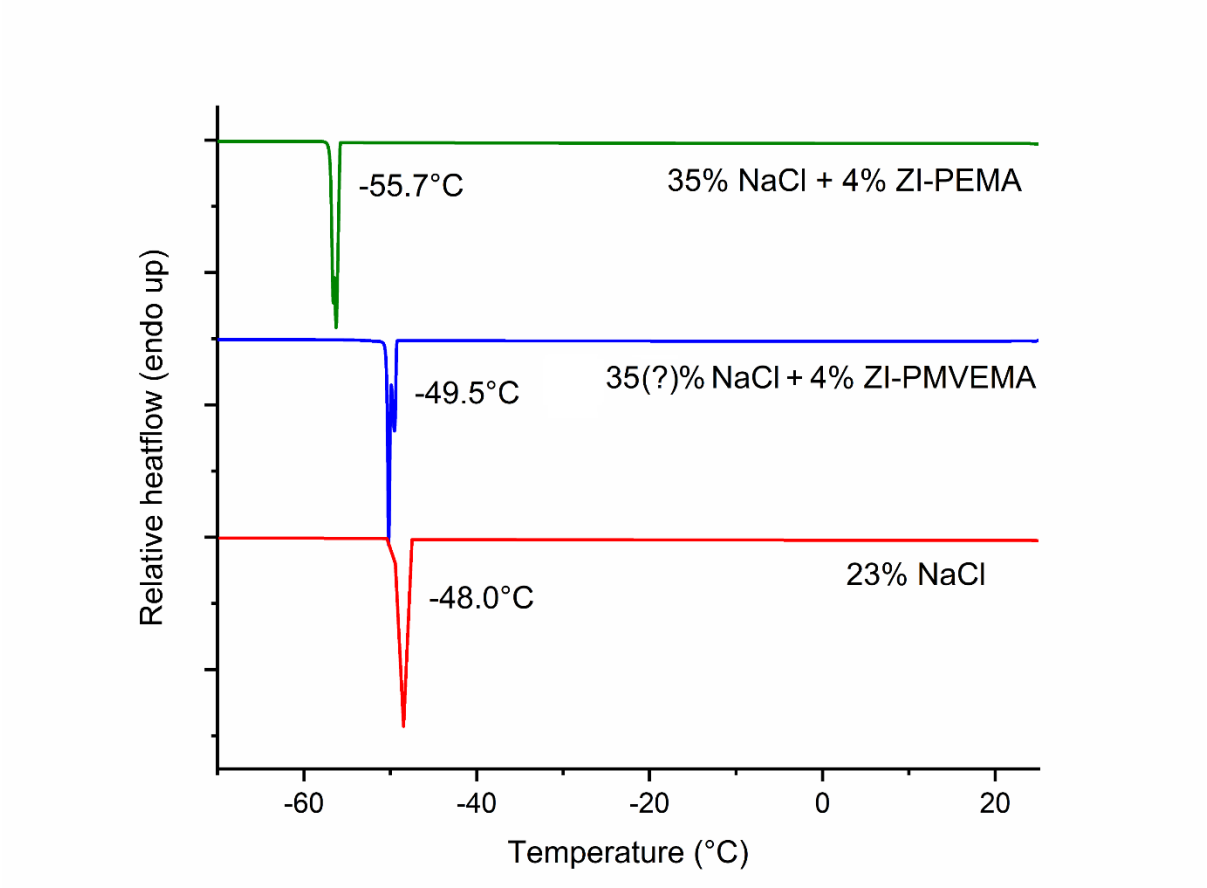


Figure 3. Low temperature differential scanning calorimetric analysis of sodium chloride solutions with and without ZI-PEMA and ZI-PMVEMA (onset of transitions are indicated) (Note: 35(?). ? Due to the dark colour of solution of 35 wt% NaCl + 4 % ZI-PMVEMA, the presence of undissolved solid could not be verified).

Table 1 shows the crystallization and melting temperature of aqueous sodium chloride solution as studied by low temperature differential scanning calorimetry.

Table 1. Crystallization and melting transitions of aqueous sodium chloride solutions.

Component	**Concentration of salt, wt%**	**T_{exo}, °C**	**T_{endo}, °C**
DI water	0	-13.27	2.61
NaCl	8	-24.74, -35.47	-5.39, -19.86
NaCl with ZI-PEMA	8	-16.08, -39.56	-4.94, -21.24
NaCl	15	-29.99, -36.49	-18.96
NaCl with ZI-PEMA	15	-32.43, -37.82	-20.41
NaCl	23	-45.82	-18.85
NaCl with ZI-PEMA	23	-36.85, -41.46	-19.65
NaCl with ZI-PEMA	35	-54.07	-19.91

T_{exo} – exothermic transition (midpoint) observed upon cooling from 20 °C to -70 °C in low temperature differential scanning calorimetric analysis at a rate of 2 °C/min.

T_{endo} – endothermic transition (midpoint) observed upon heating from -70 °C to 20 °C in low temperature differential scanning calorimetric analysis at a rate of 2 °C/min.

Deionized water upon cooling at a rate of 2 °C per minute from 20 °C showed a freezing temperature (T_{exo}) (crystallization) of -13 °C and upon subsequent warming at the same rate a melting temperature (T_{endo}) of 3 °C was observed. Due to the ability of ZI-PEMA to increase the solubility of sodium chloride in water these transitions were shifted respectively to -54 °C and -20 °C. Unlike two transitions noticed for the crystallization in intermediate salt concentrations, the transition noticed in 35 wt% of sodium chloride solution with ZI-PEMA is like polymer free 23 wt% sodium chloride solution. The presence of two exothermic transitions may be an indication of presence of water bound to the salt to varying degrees. Even though

the depression of freezing point occurred nearly linearly with increasing polymer and salt concentration, not much variation was noticed in the melting transition (T_{endo}) beyond a sodium chloride concentration of 15 wt%.

This trend of increasing salt concentration beyond the normal saturation point accompanied by the depression of freezing point of salt solution was also observed in hydrated calcium bromide solution. Calcium bromide reaches saturation at 57 wt% and the salt concentration at near saturation for calcium bromide is 55.9 wt%.[10] Since ZI-PEMA is insoluble in deionized water and readily dissolves in sodium chloride solution, at first 3 wt% polymer was dissolved in 1 wt% sodium chloride solution. In this solution, it was possible to dissolve calcium bromide to make 90.5 wt% of aqueous calcium bromide solution. The freezing point of water continued to lower with increasing concentration of salt. Unlike the sodium chloride, the amount of ZI-PEMA required to shift saturation limit in the case of hydrated calcium bromide was lower. In the absence of polymer, sodium chloride alone did not enhance the solubility limit of calcium bromide.

Figure 4 shows the low temperature differential scanning calorimetry analysis of calcium bromide solutions at various concentrations. The exothermic transition corresponding to the crystallization of water continued to lower with increasing salt concentration and no crystallization was noticed until -70 ^{o}C at calcium bromide concentration of above 90 wt%.

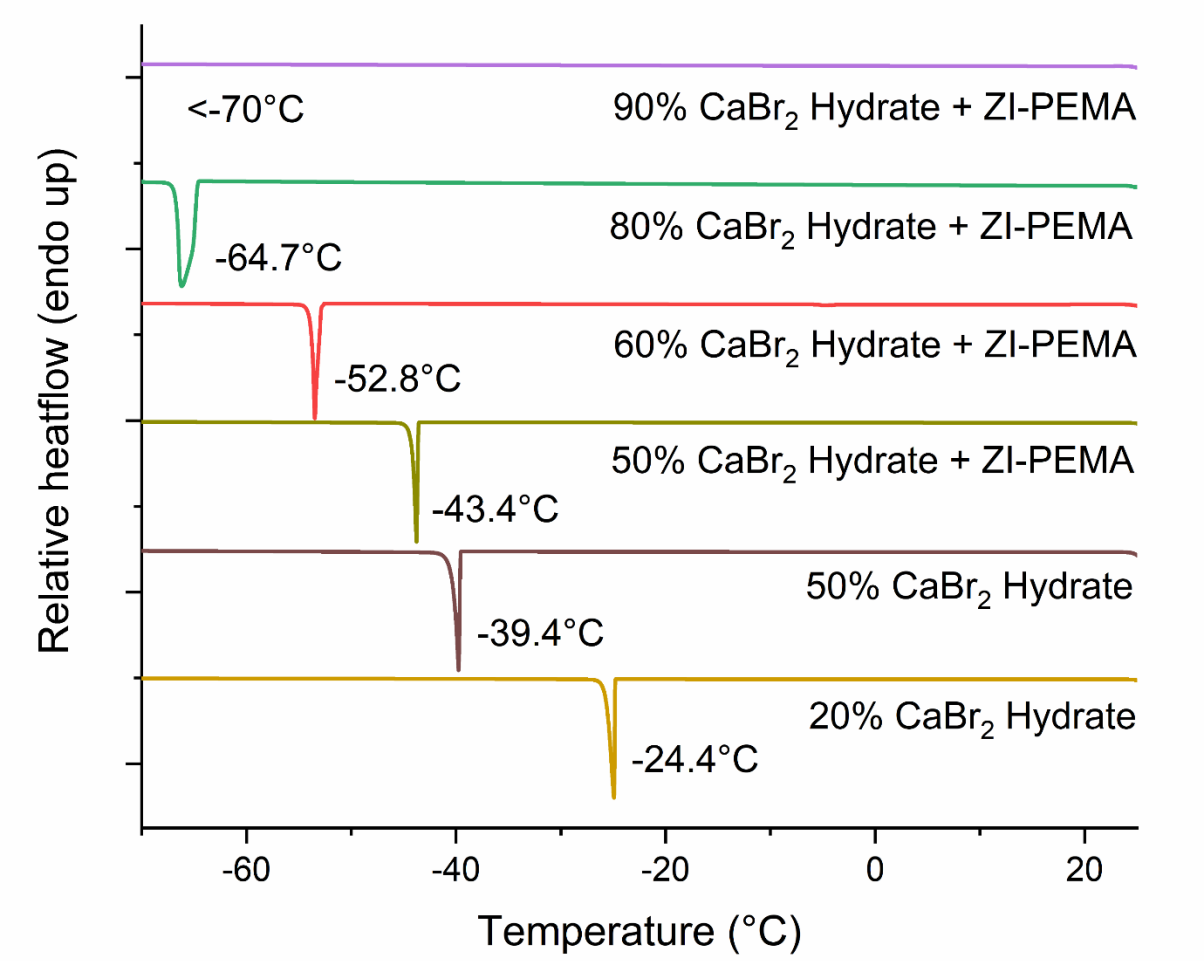


Figure 4. Low temperature differential scanning calorimetric analysis of calcium bromide solutions with and without ZI-PEMA (onset of transitions are indicated) (Note: Calcium bromide was dissolved in aqueous solution of 3 wt% ZI-PEMA in 1 wt% sodium chloride solution).

Table 2 shows the crystallization and melting temperature of aqueous calcium bromide solution as studied by low temperature differential scanning calorimetry.

Table 2. Crystallization and melting transitions of aqueous calcium bromide solutions.

Component	**Concentration of salt, wt%**	**T_{exo}, °C**	**T_{endo}, °C**
DI water	0	-13.27	2.61
$CaBr_2.xH_2O$	20	-19.73	-4.76
$CaBr_2.xH_2O$ with ZI-PEMA	20	-24.37	-5.90

$CaBr_2.xH_2O$	50	-36.81	-19.41
$CaBr_2.xH_2O$ with ZI-PEMA	50	-41.18	-21.10
$CaBr_2.xH_2O$ with ZI-PEMA	60	-52.79	-29.85
$CaBr_2.xH_2O$ with ZI-PEMA	80	-65.84	-37.17

T_{exo} – exothermic transition observed upon cooling from 20 °C to -70 °C in low temperature differential scanning calorimetric analysis at a rate of 2 °C/min.

T_{endo} – endothermic transition observed upon heating from -70 °C to 20 °C in low temperature differential scanning calorimetric analysis at a rate of 2 °C/min.

Unlike sodium chloride solution, in the case of hydrated calcium bromide solution, there was a clear trend that the addition of polymer not only enhanced the solubility limit of salt but also it uniformly lowered the crystallization temperature (T_{exo}). The melting transition (T_{endo}) also linearly decreased with increasing salt concentration. Thus, the difference between monovalent and divalent cations are apparent. The role of different anions involved namely chloride and bromide cannot be ruled out in the observed difference between the salts of mono and divalent cations.

3.2 Comparison with ZI-PIBMA

Previously ZI-PIBMA also showed good salt tolerance as indicated by the increasing viscosity with increasing salt concentration.[23] Hence, its ability to depress the freezing temperature of salt solutions were studied by low temperature DSC analysis. ZI-PIBMA did not increase the saturation limit of sodium chloride in water. Although ZI-PIBMA increased the dissolution of hydrated calcium bromide in water the depression of freezing point caused by it was lesser than that of ZI-PEMA as shown in Figure 5.

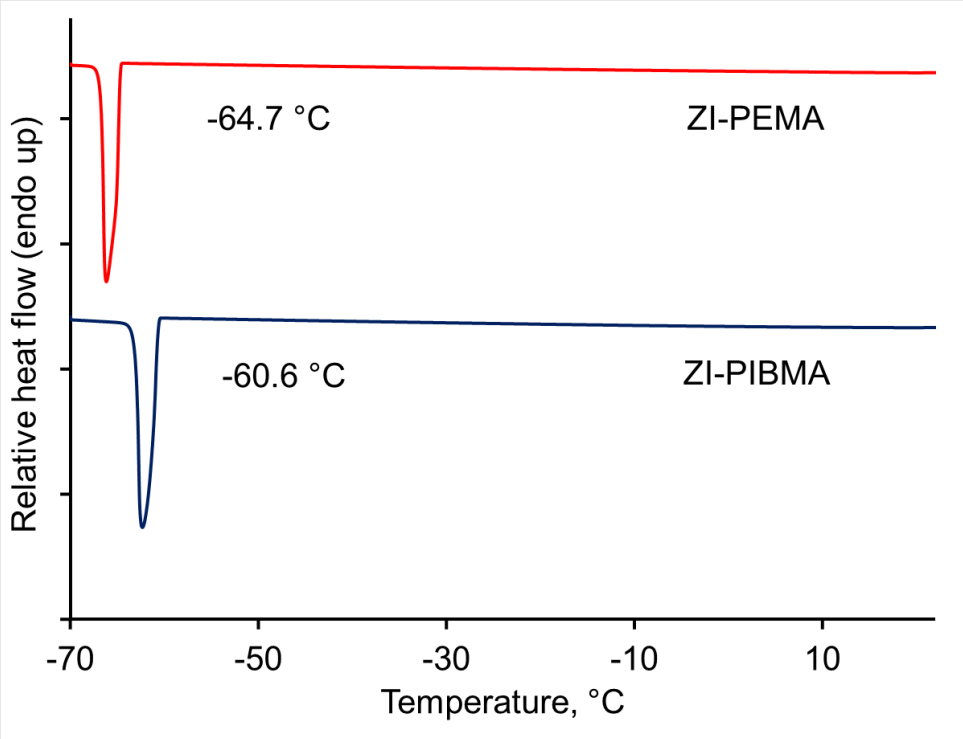


Figure 5. Low temperature differential scanning calorimetric analysis of 80% $CaBr_2.xH_2O$ solutions of ZI-PEMA and ZI-PIBMA (rate of cooling: 2 °C/min).

3.3 Role of substituent on salt tolerance in copolymaleimide sulfobetaines

Among the copolymaleimide based sulfobetaines studied, only ZI-PEMA showed the exceptional salt tolerance characteristics. This was further confirmed by the rheological studies of salt solutions of polymers. Figure 6 compares the change of viscosity of ZI-PEMA and ZI-PMVEMA with changing concentration of sodium chloride solution.

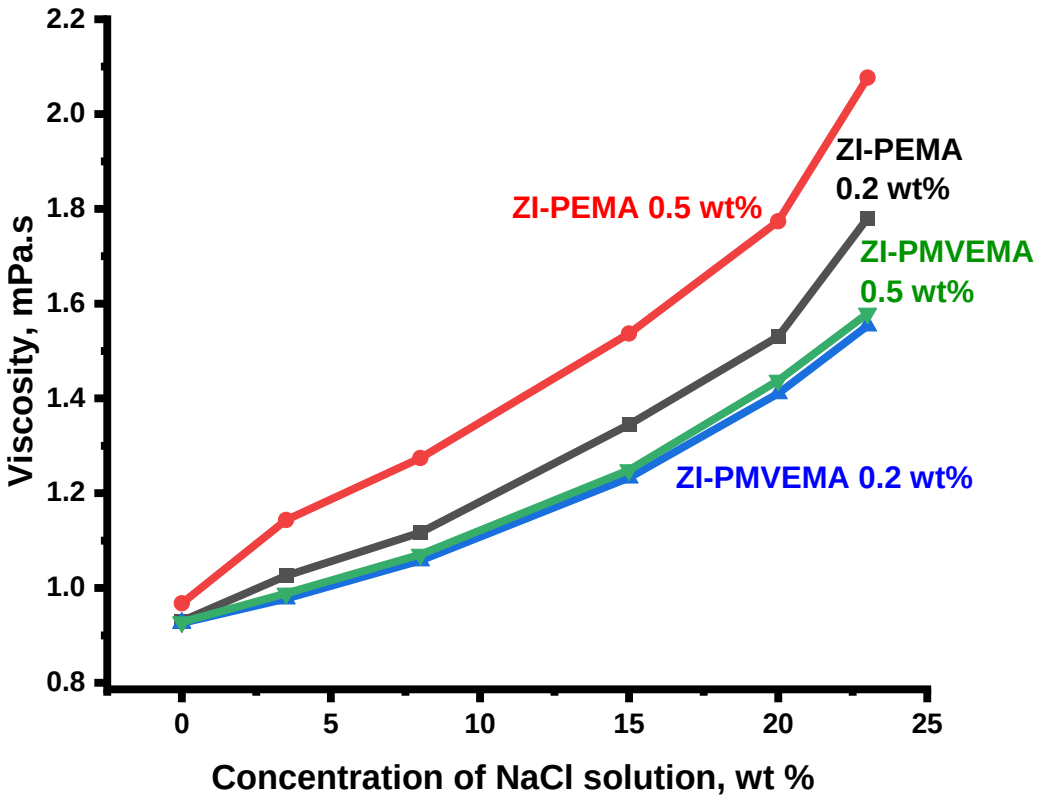


Figure 6. Comparing salt tolerance of ZI-PEMA and ZI-PMVEMA.

The viscosity increased with increasing salt concentration in both polymers. However, the rise in viscosity with increasing salt concentration was much higher in the case of ZI-PEMA confirming the importance of chain rigidity in dictating ionic interactions. With increasing chain rigidity, ionic interactions were regulated further, thereby enhancing the stacking of polymer chains and simultaneously expanding the globular structure. This in turn caused an increased drag between extended polymer chains leading to the rise in viscosity. The presence of substituents disturbed the formation of such expanded ordered structures. The rise in viscosity was even greater upon increasing the polymer concentration in the case of ZI-PEMA confirming the role of ordered ionic interactions that got extended with the presence of additional polymer chains. This is in contrast to what was observed in conventional zwitterionic poly(meth)acrylates and poly(meth)acrylamides. In conventional polymers, addition of salts like sodium chloride initially helps to expand the polymer chains leading to a rise in viscosity of aqueous solution. However, further addition of salt resulted in shrinkage of polymer chains thereby causing continued lowering of viscosity.[31] In ZI-PEMA, the underlying backbone rigidity of polymer chains limited the shrinkage of polymer chains upon adding more and more

salt. The polymer chain helped to regulate the nature of ionic clusters formed with increasing salt concentration. Unlike the salt concentration dependent solution conformation proposed for conventional zwitterionic polymers,[32] the solution conformation of ZI-PEMA remained expanded independent of salt concentration. Thus, any loss in entropy caused by the rigidity of polymer chain conformation is compensated by electrostatic interactions through the ordered ionic interactions induced by the polymer chain.[23]

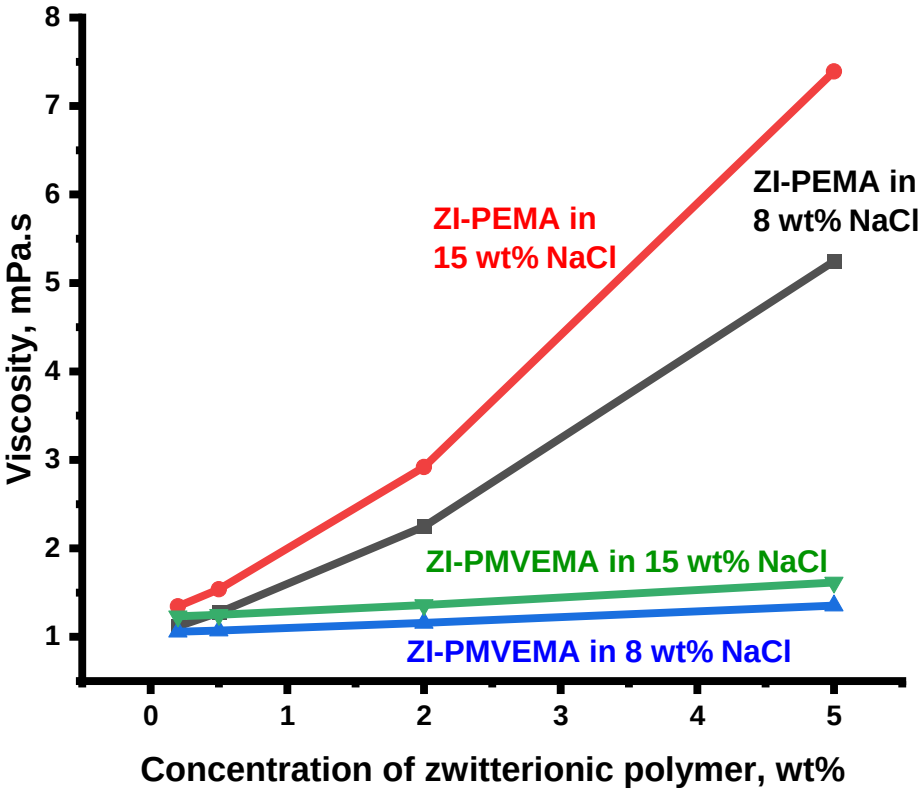
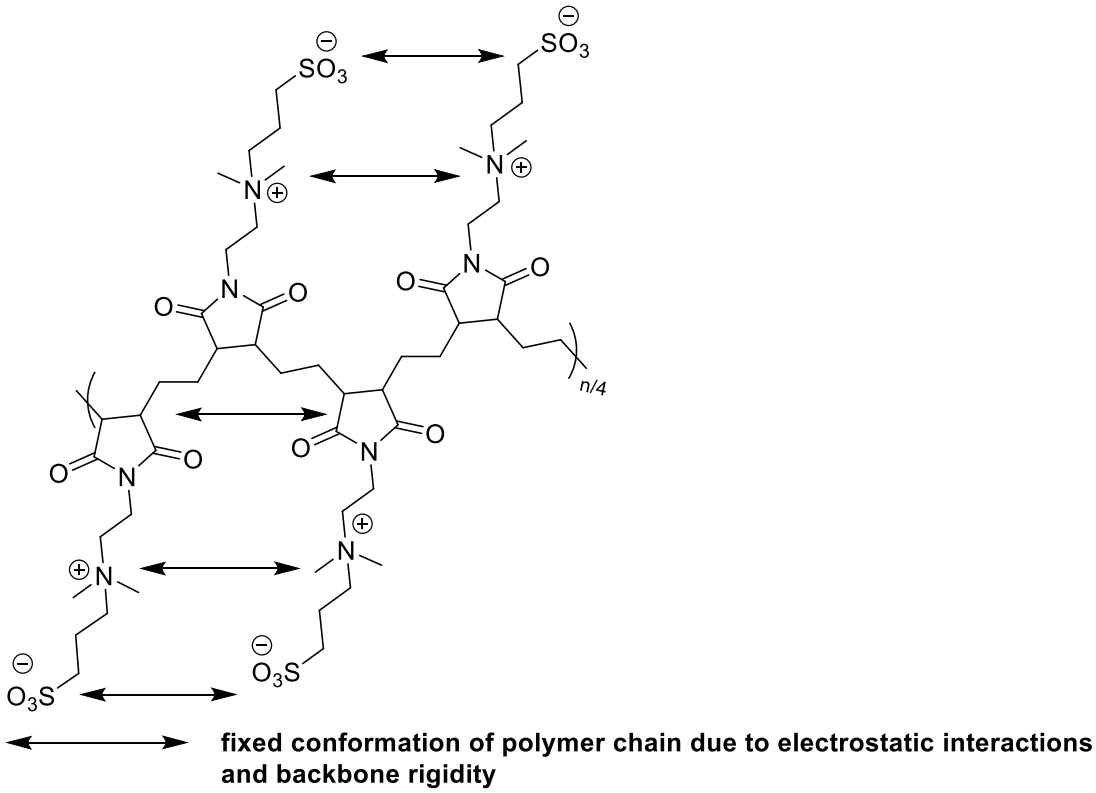


Figure 7. Change of viscosity with change in concentration of salt and polymer.

Figure 7 shows the change in viscosity with change in polymer concentration at various salt concentrations. Figure S7 shows the viscosity of 5 wt% ZI-PEMA in 15 wt% aqueous sodium chloride solution. As shown in Figure S8, negligible change in viscosity was noticed at very low shear rate (<1 /sec) and the viscosity remained steady in the range of 1 to 1000 /sec. Figure S8 shows the viscosity of 5 wt% ZI-PMVEMA in 15 wt% aqueous sodium chloride solution. The change in viscosity at low shear rate (<1 /sec) was considerably higher in the case of ZI-PMVEMA. But for this, the viscosity vs shear rate behavior was similar to that of ZI-PEMA in the shear rate range of 1 to 1000 /sec. In the case of ZI-PEMA, the viscosity of salt solution increased continuously with both increasing polymer concentration as well as concentration of salt. Apparently, the added salt induced the formation of more regular structures thus extending

the stacking of polymer chains. The comparison with ZI-PMVEMA confirms the importance of chain rigidity that is the driving force for regulating ionic structures.



Scheme 3. Proposed chemical structure of ZI-PEMA in one dimension with extended repeat units in a *trans* conformation showing alignment of polymer backbone as dictated by electrostatic interactions.

Interactions between counter ions is common and occur due to electrostatic attractions in aqueous medium. Under normal conditions, ionic clusters of various sizes prevail depending on the nature of conditions like salt concentration and temperature. However, in the presence of zwitterionic polymer with rigid backbone like ZI-PEMA, the interactions between counter ions are regulated to minimize repulsive interactions between similar charges. This fundamental ability to minimze repulsive interactions in turn helps in the formation of energetically favorable conformations that ultimately lead to higher ordered structures in salt solutions. As shown by the increasing viscosity with increasing salt concentration this ordered structure is capable of expanding itself with addition of more ions in the form of added salts. The formation of regulated, ordered structure further increases with addition of more rigid polymers. This becomes obvious by referring to the chemical structure of ZI-PEMA as shown in Scheme 3.

In majority of zwitterionic polysulfobetaines, the backbone rigidity is not high enough to regulate the structure. Even among copolymaleimide sulfobetaines, such rigidity is possible

only in ZI-PEMA since practically, two carbon atoms are the lowest possible connecting units linking two adjacent maleimide units unless it is possible to link two adjacent maleic anhydride derived units with methylene (-CH_2-) unit. Although comparable rigidity can be achieved with appropriate substitutions, e.g., ZI-PIBMA, the reactivity of vinyl comonomer with maleic anhydride would determine the molecular weight of polymer formed. Introduction of any other substituent disturbs the conformation of polymer chain in solution. It is interesting to note that the chemical structure of the polymer plays a dominant role in determining the viscosity of salt solutions in these polymers even more than the molecular weight of polymer. However, to achieve this a critical or threshold of molecular weight is required. Figure 8 confirms these observations.

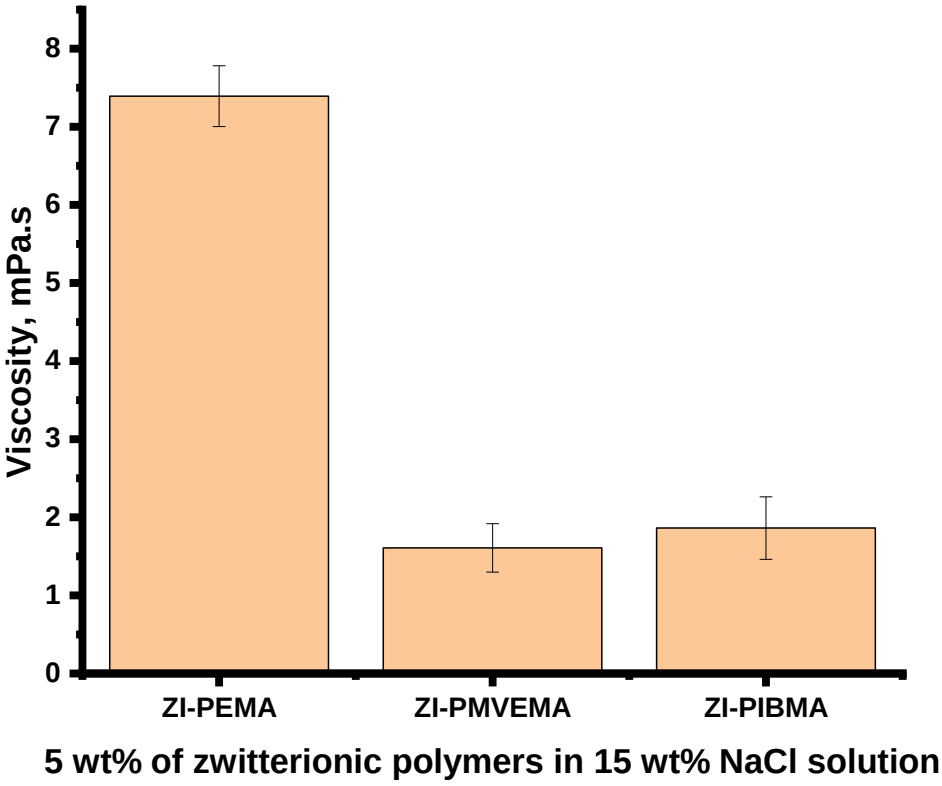


Figure 8. Viscosity of copolymaleimide sulfobetaines in 15 wt% NaCl solution.

The molecular weight of polymers decreased in the order: PMVEMA>PEMA>>>PIBMA. Even though the molecular weight of ZI-PIBMA is two orders of magnitude lower than ZI-PMVEMA, it showed higher viscosity in concentrated sodium chloride solution clearly signifying the effect of chemical structure and the resulting solution conformation in determining the viscosity of salt solutions.

3.4 Comparison of properties of zwitterionic copolymaleimides

Table 3. Aqueous solution characteristics of zwitterionic copolymaleimides.

Polymer	Appearance	Solubility in water	Solubility in brine	Influences saturation limit of NaCl in water	Enhancing viscosity of salt solutions
ZI-PEMA	Off-white	Insoluble	Soluble	Yes	Yes
ZI-PMVEMA	Dark	Soluble	Soluble	No	No
ZI-PIBMA[i]	Pale yellow	Soluble	Soluble	No	Limited
ZI-PSMA[ii]	White	Forms gel	Soluble	No	Limited
ZI-PAAmMA[iii]	Brownish white	Soluble	Soluble	No	Limited

[i]-reference [23].

[ii]-reference [22].

[iii]-reference [21].

Table 3 summarizes various properties of aqueous solutions of zwitterionic copolymaleimides reported until now including this article.[21-23]The appearance of zwitterionic copolymaleimides vary from white to dark in color. The dark color of ZI-PMVEMA may be derived from its precursor i.e., copolymer of methyl vinyl ether and maleic anhydride. This copolymer has been reported to be an organic luminescent material and this nature is derived from "clustering of locked carbonyl groups".[33] With the exception of ZI-PEMA and ZI-PSMA other zwitterionic polymers dissolved in water. The polydisperse particles formed by the insoluble ZI-PEMA in deionized water underwent reduction in size upon heating the dispersion (Figure S9). ZI-PSMA formed a gel in water. Only ZI-PEMA increased the saturation limit of salts in water and showed continuous rise in viscosity of salt solution with increasing concentration of salt. ZI-PAAmMA caused a rise in viscosity with increasing concentration of sodium chloride solution up to 4.5 M (26.3 wt%) concentration of sodium chloride in water after which the viscosity decreased. In the case of ZI-PIBMA the viscosity continued to rise with increasing salt concentration and the rise in viscosity was lower possibly because of its low molecular weight nature. In the case of ZI-PSMA, the solution viscosity remained constant in the range of 0.5 to 4 M (2.92 to 23.4 wt%) aqueous sodium chloride solution and marginal rise in viscosity was

noticed at 5 M (29.2 wt%) concentration of sodium chloride solution. As a cautionary note, while interpreting some of these characteristics it is important to bear in mind the differences in terms of molecular weight, degree of amine grafted to form the maleimide and the conditions under which viscosity was studied particularly for ZI-PAAmMA[21] and ZI-PSMA[22] which are taken from literature.

4. Conclusion

Zwitterioinc copolymaleimides that lacked any substituent in the polymer backbone such as ZI-PEMA showed exceptional salt tolerance. The rigidity of polymer backbone not only helped to keep the polymer in the expanded form in salt solutions but also helped to regulate the ionic interactions. Hence, the viscosity of salt solutions increased with increasing salt concentration as well as the concentration of polymer. This ultimately enhanced the saturation limit of both monovalent and divalent salts like sodium chloride and hydrated calcium bromide. The shift in saturation limit was confirmed by low temperature differential scanning calorimetry (DSC) analysis. DSC studies indicated that the freezing temperature lowered with increasing salt concentration and the depression of freezing point was greater than that of the saturated salt solution. The significance of absence of substituent in the polymer backbone or rather the importance of backbone rigidity was confirmed by comparing various zwitterionic copolymaleimides reported here as well as those reported previously by us and others. As a polymer class, zwitterionic copolymaleimides are not as thoroughly studied as those zwitterionic polymers derived from poly(meth)acrylates and poly(methacrylamides).

Until now zwitterionic polymers have been widely explored for antifouling applications as suitable replacements for poly(ethylene glycol) (PEG).[16,34-36] As shown here, in the case of zwitterionic copolymaleimides, the electrostatic interactions prevailing in zwitterionic polymers that are the source of its properties can also be influenced by fundamental polymer properties like backbone rigidity. These findings are significant in light of reports on unpredictability of properties of zwitterionic polymers based on its structure.[37] The ability to form hydration layers, the reason behind the antifouling behavior of zwitterionic polymers can also be influenced by modifying functionalities of zwitterionic moieties.[38] Salt tolerance in polymers is commonly enhanced by incorporating sulfonic acid containing monomers through copolymerization and hydrophobic association mechanisms.[39-42] Salt tolerance is an area where zwitterionic polymers could potentially gain traction and the zwitterionic copolymaleimides point to immense possibilities for applications requiring salt tolerance.

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Conflicts of interest

Agency for Science, Technology and Research (A*STAR) has filed a PCT application on this development with AP, SA, NJH and VAV as inventors.

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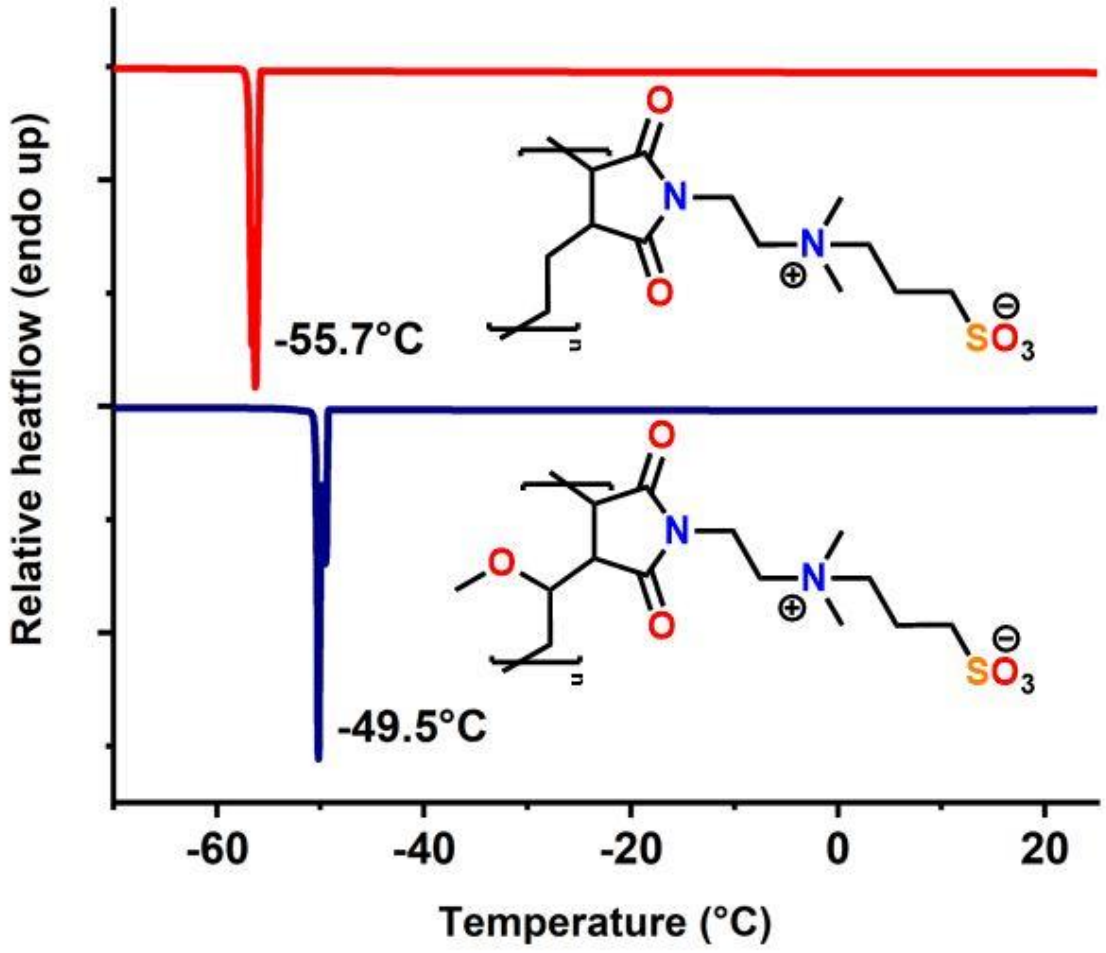
The table of contents entry

*Srinivasulu Aitipamula, Nanji J. Hadia, Vivek A. Vasantha and Anbanandam Parthiban**

An Exceptionally Salt Tolerant Copoly(maleimide sulfobetaine) – Structural Requirements for Ultra-salt Tolerance



Polysulfobetaine based zwitterionic copolymaleimides showed chemical structure dependent salt tolerant properties. Polysulfobetaine derived from poly(ethylene-co-maleimide) enhanced the solubility of metal salts in water well beyond normal saturation point. This increased solubility of metal salts is accompanied by the depression of freezing temperature of water well below than that occurred at normal saturation in the absence of zwitterionic polymer.