

Synthesis and Flocculation Properties of *N*-Oxide Polymers

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ABSTRACT: *N*-oxide polymers possess strong zwitterionic character, high solubility in water, and high chelating properties with various cations. In this work, *N*-oxide polymers were synthesized following various routes and their solution properties were determined. Molecular properties of the polymers (molecular weight, square root of the mean-squared radius, and virial coefficients) were related to their chain expansion in solution by determining the intrinsic viscosity as a function of pH. Viscosity results were corre-

lated with the flocculation ability of the polymers for suspending solids removal. These polymers exhibit dramatic conformational changes as the solution pH is varied, especially at low pH values. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2693–2700, 2002

Key words: *N*-oxide polymers; flocculation; solution viscosity–pH relationship

INTRODUCTION

Zwitterionic polymers possess unique properties in solution, such as the so-called anti-polyelectrolyte behavior, strong binding capability, and high solvation of their polymeric matrices in salts of widely different lattice energies.^{1–6} These interesting properties are due to the high dipole moment and ionic character of the polymers. Some of their applications include their use as flocculants, ion-exchange resins, and electrolytes for solid batteries.

Galín et al.⁴ examined the solution properties of poly(sulfopropylbetaines) and *N*-oxide polymers. Cardoso and coworkers^{1,7} also reported solution and solid-state properties of zwitterionic polymers and copolymers. These polymers possess high dipolar moment ($\mu > 4$ D) and high-chelating properties with a variety of metal cations. Moreover, *N*-oxide polymers have shown a strong zwitterionic character (where the

$\begin{array}{c} | \\ -\text{N}^+-\text{O}^- \\ | \end{array}$ group is the major mesomeric form) and

high solubility in water.⁴ In fact, they are considered among the best hydrogen-bond acceptors.^{4,7} Orta de Velázquez et al.⁸ examined the potential use of these polymers as flocculants in water-treatment operations. High efficiencies were obtained in polymer-treated waters (around 87% of turbidity removal) and in contaminated waters treated with the polymer and coag-

ulant aids (around 95% of turbidity removal was obtained).

In this work, the synthesis, characterization, and flocculation properties of aliphatic *N*-oxide polymers are reported. Conformational changes of the polymer as a function of pH are related to the flocculation of suspended solids in water-treatment operations.

EXPERIMENTAL

Polymer preparation

The synthesis of the polymers was carried out according to the modified technique reported by Holt et al.⁹ An aliphatic amine, *N,N*-dimethyl aminoethyl methacrylate (Aldrich) was polymerized in bulk by using AIBN as initiator, at 70°C for 20 h, in nitrogen atmosphere with stirring. Oxidation of the resulting precursor polymer, a poly(amine), was carried out in glacial acetic acid with aqueous hydrogen peroxide (30%) by using a stoichiometric ratio of $[\text{H}_2\text{O}_2] : [\text{amine}]$ 1 : 1 at 70°C, under nitrogen atmosphere with stirring. After 3 h of reaction time, an excess of 30% of H_2O_2 was added, rendering a total stoichiometric ratio of $[\text{H}_2\text{O}_2] : [\text{amine}]$ 1.3 : 1. The reaction proceeded at the same temperature for another 18 h. The solvent was removed by continuous evaporation, and subsequently, the residue was dissolved in water. Additional acetic acid was eliminated by azeotropic distillation at reduced pressure (room temperature and 40 mmHg). Additional water was added and the solution was distilled once more, up to a pH of 4. The acidic solution was separated in two parts. The first one was dissolved in water, and the remaining acetic acid was removed by elution in a strongly basic ion-exchange

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resin, Merck-III.⁴ The product was labeled ZW-IV. The second part of acidic solution was neutralized with a 0.1M NaOH aqueous solution up to a pH of 6. In this case, the polymer was labeled ZW-II. The polymer was recovered by precipitation in chilled acetone. The polymers were dried under vacuum at 30°C for 24 h. ZW-III was synthesized and neutralized under the same procedure as in ZW-II, but the resulting polymer had a lower molecular weight.

Characterization of polymers

The structure of the polymeric materials was verified by FTIR by using polymeric films. ¹H- and ¹³C-NMR were effected on a 5–10 wt % solution of NaCl-D₂O with 3-(trimethylsilyl)-1-propane sulfonic acid sodium salt as internal reference, and δ (ppm) units were recorded. Elemental analysis verified the chemical composition of the polymers. The sodium percentage was determined by atomic absorption. Light-scattering experiments were performed at room temperature in a Dawn-F (Wyatt Technologies) apparatus ($\lambda = 632$ nm) by using a 0.1M NaCl aqueous solution. The refractive index increments dn/dc were measured at 298 K by using a Brice Phoenix 2000 differential refractometer fitted with a neon laser beam using the same solvent at a fixed wavelength ($\lambda = 632$ nm). The thermal behavior of the polymers was determined by a 951 TA-Thermogravimetric module linked to a Thermal Analyzer 2100 microprocessor, at a heating rate of 10°C/min under flowing nitrogen or air (flow rate = 50 mL/min). TGA with flowing air was also used to determine the sodium percentage of the samples.

Viscosity measurements

Viscosity measurements were carried out in a modified Ubbelohde viscometer. A temperature-controlled bath (Neslab, RTE-220) kept the temperature of the viscometer within $\pm 0.01^\circ\text{C}$. The solution contained deionized water, wherein the polymer is wholly soluble. Viscosity was determined as a function of pH, within the 2–8 range.

Flocculation measurements

The flocculation properties of the polymers were determined by measuring the decrease in turbidity of wastewater as the polymer is added, using a jar-testing device and following the ASTM-D2035 procedure. A controlled experiment (with blank) was set up to properly account for the removal of suspended solids from the solution. Experimental parameters include the initial turbidity, stirrer speed, flocculant dosage, solution pH, temperature, and sedimentation time. For these tests, wastewater from the University treatment plant was used. The mean properties of the

effluent are as follows: turbidity (NTU, nephelometric turbidity units) 18–63, pH 8.2 ± 0.3 , chemical oxygen demand (COD) 333 ± 99 mg/L, and volatile suspended solids (VSS) 40 mg/L. Turbidity measurements were effected in a 2100P portable turbidimeter (Hach) with an accuracy of $\pm 2\%$. Appropriate statistical analyses were applied to all data sets.

Zeta-potential determinations

Zeta potentials were determined by using a NICOMP 370 ZLS apparatus. The polymer aqueous solutions were prepared by using deionized water at a 1×10^{-3} g/L concentration. These were filtered through an 8- μm -size porous disk (Millipore), keeping the sample temperature at 23°C. Particle size was measured by using an AccuSizer Model 770 (Particle Sizing Systems, Inc.) with a laser wavelength of 635 nm. Particle-size measurements as a function of time determine the aggregation of the zwitterionic polymers in water. The solutions' pH was fixed at 6, 6, and 8 for ZW-II, ZW-III, and ZW-IV, respectively.

RESULTS AND DISCUSSION

The infrared spectra of the precursor polymer and that of the two *N*-oxide polymers are shown in Figure 1. Peaks of the ester group, C=O (1736 cm^{-1}) and C—O ($1138\text{--}1126\text{ cm}^{-1}$), methyl, and methylene groups ($2980\text{--}2770\text{ cm}^{-1}$) are shown. The N—O band in the infrared spectrum (955 cm^{-1}) demonstrates the presence of this functional group. *N*-oxide polymers present a new peak at 1567 cm^{-1} related to the —COO[−] group. Its intensity is higher in the NaOH-neutralized polymers than in those purified with the ion-exchange resin. This provides evidence of the presence of reaction-remaining acetate groups interacting with the quaternary nitrogen.

Figure 2 depicts the structure of the precursor and *N*-oxide polymers, and Figure 3 shows the ¹H-NMR spectra for both compounds. The proposed structure was confirmed, inasmuch as it contains the signals of methyl and methylene groups joined to the nitrogen atom, which are displaced to low field by the presence of the oxygen atom.

Elemental analysis results of the synthesized polymers are shown in Table I. There is good agreement between experimental and calculated values of the products, if we consider a specific sodium acetate content and a proportion of three, three, and two molecules of water per monomeric unit of ZW-II, ZW-III, and ZW-IV, respectively (see TGA data). These results added further evidence to the proposed structures shown in Figure 2.

TGA measurements confirm the hygroscopicity of the precursor polymer, with water content around $3 \pm 1\%$. Furthermore, they show two main stages of

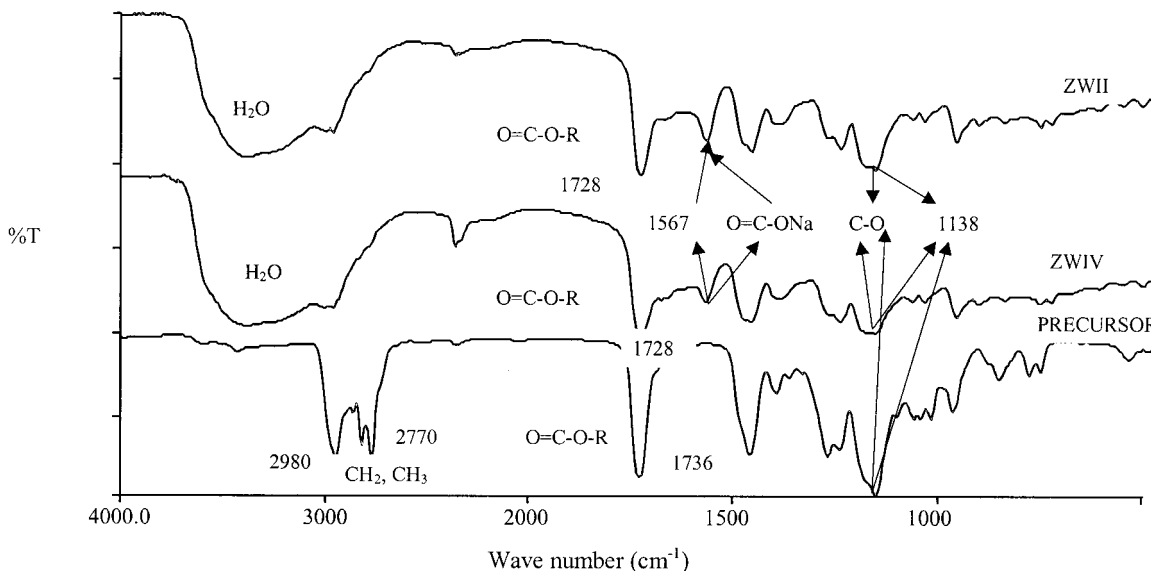
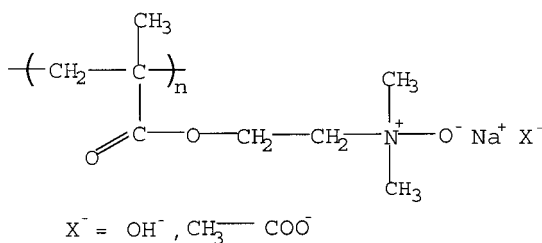
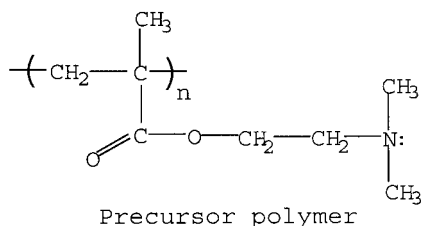


Figure 1 Infrared spectra of the precursor, ZW-II, and ZW-IV polymers.

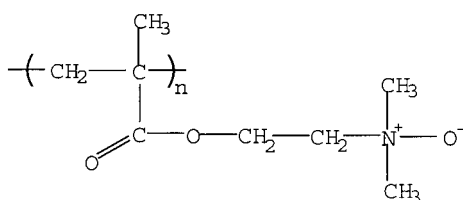
decomposition by heating under nitrogen. The first one, which starts at 270°C and ends at 340°C, was attributed to the elimination of dimethylvinylamine leading to a polymethacrylic-like chain. Thereafter, in the second stage (350–450°C), the decarboxylation

process is suggested, followed by the onset for scission of the main chain. Finally, a carbonlike residue is left at around 570°C with $8 \pm 1\%$ of residual mass.

N-oxide polymers show a different decomposition pattern. They are quite hygroscopic and the evolved



ZW-II and ZW III structures



ZW-IV structure

Figure 2 Structure of synthesized polymers.

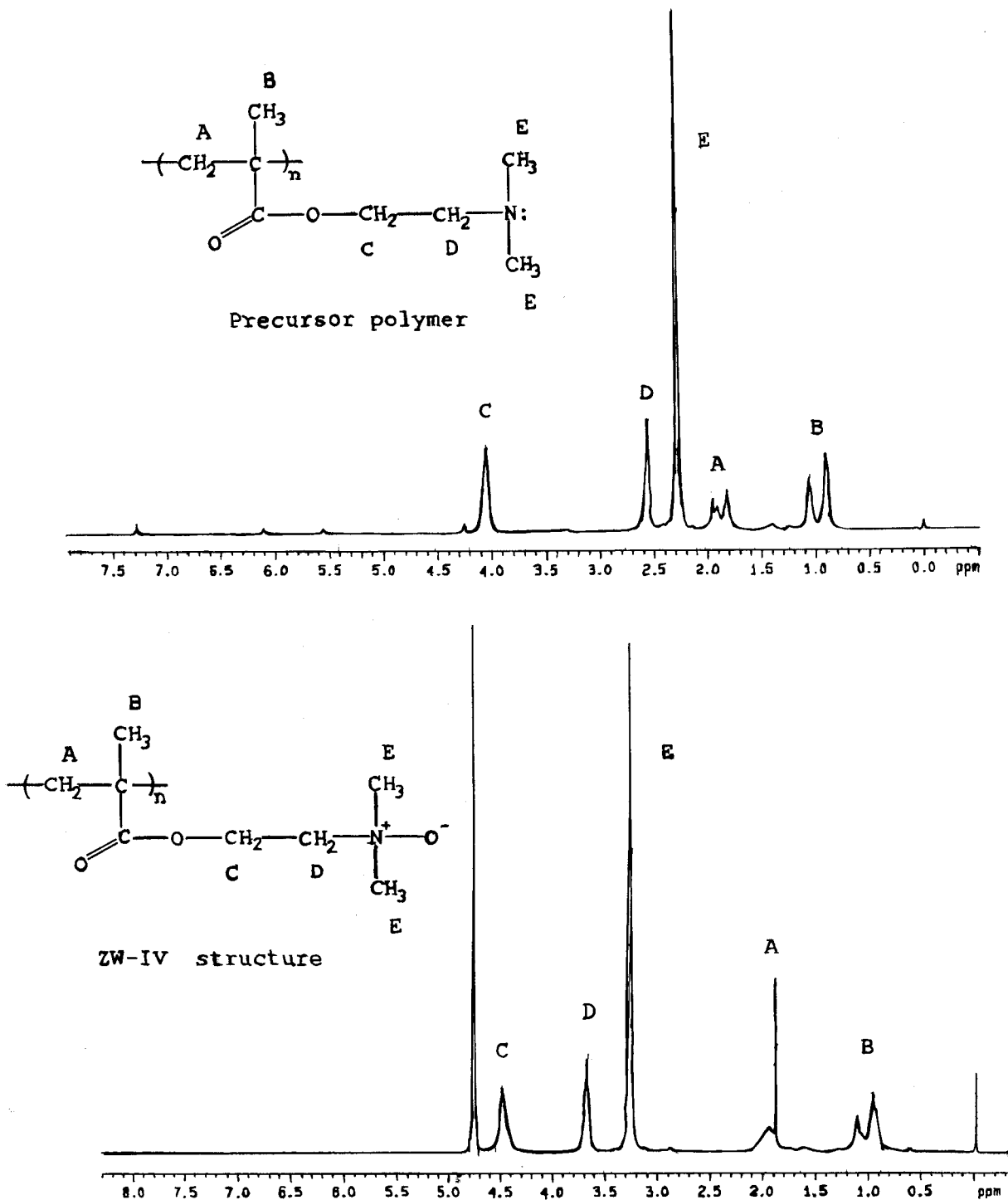


Figure 3 $^1\text{H-NMR}$ spectra of the precursor and the ZW-IV polymer.

water, as they are heated up to 150°C , is 12–21% for ZW-II and ZW-IV. Further heating of the polymers does not provide indication of the end of one stage and the beginning of the next stage. In this respect, we assume similar decomposition behavior as in the precursor polymer. ZW-II and ZW-III show sodium acetate decomposition around 400°C , when they are heated under nitrogen atmosphere. In the experiments

TABLE I
Elemental Analysis of *N*-Oxide Polymers

| Polymer | C (%) | | H (%) | | N (%) | |
|---------|--------|-------|--------|------|--------|------|
| | Theor. | Exp. | Theor. | Exp. | Theor. | Exp. |
| ZW-II | 42.29 | 42.91 | 9.25 | 9.28 | 6.17 | 6.13 |
| ZW-III | 42.29 | 41.29 | 9.25 | 9.24 | 6.17 | 5.96 |
| ZW-IV | 45.93 | 46.24 | 9.09 | 9.42 | 6.70 | 7.69 |

TABLE II
Sodium Percentage in Weight of Polymers

| Polymer | Na (%) (by AA) | Na (%) (by TGA) | CH ₃ COONa/ monomeric unit |
|---------|-------------------|--------------------|--|
| ZW-II | 0.84 | 1.0 | 0.12 |
| ZW-III | 0.79 | 0.9 | 0.11 |

under air atmosphere, the thermal stability of the sample decreased, as expected, although they show almost the same thermal decomposition pattern. When the sample is heated under air atmosphere, the residual product at 700°C for ZW-II and ZW-III is mainly Na₂CO₃, a decomposition product from sodium acetate. This result was confirmed when sodium acetate alone was analyzed by TGA under similar conditions applied to the ZW polymers. This leads to the possibility of determining the sodium percentage by TGA. Results of this analysis are presented in Table II, and they are compared with the atomic absorption (AA) results.

The refractive index increments dn/dc were measured for each polymer at $\lambda = 632$ nm: dn/dc (mL/g): -0.0526 for the precursor polymer in CHCl₃, and 0.1015 and 0.156 for ZW-II and ZW-IV in 0.1M NaCl, respectively. When the precursor polymer is dissolved in methanol, dn/dc is 0.157, as reported by Monroy-Soto and Galin.³ Monroy-Soto and Galin⁴ also reported a dn/dc value of 0.119 mL/g for a polymer with the same structure of ZW-IV (labeled PDMAEMAO in the former article). According to our results, it is apparent that acetic acid elimination is not straightforward nor easy in these systems. When five successive elutions are made in the basic ion-exchange resin, Merck-III, the infrared spectra of the recovered products, contains a band around 1567 cm⁻¹ (see Fig. 1), corresponding to a carboxylic group from the acetic acid. The discrepancy in the refractive index increment may be ascribed to the amount of residual acetic acid embedded in the polymers. Similarly, when *N*-oxide polymers are neutralized with NaOH, sodium acetate was produced and the refractive index increment reflects the sodium acetate concentration. In general, when the sodium acetate concentration in the polymer increases, dn/dc decreases.

Light scattering measurements were used to determine the molecular weights and solution properties of the precursor and the three *N*-oxide polymers. Results obtained from the classical Zimm plots are shown in Table III. According to these values, zwitterionic polymers present degradation during the oxidation reaction to a relatively high extent (around 67%), in agreement with Monroy-Soto and Galin results.⁴ The square root of the mean-squared radius of a coiled polymer chain (root mean square radius) and the second virial coefficient (A_2) are also shown. As is well

known, A_2 reflects polymer-solvent interactions and is dependent on several factors (i.e., the molecular weight, molecular weight distribution, and molecular shape of the macroions). The high values of A_2 for *N*-oxide samples show that NaCl solution is a good solvent for the zwitterionic polymers, in agreement with published results.⁴ Despite the fact that ZW-II and ZW-IV are produced following the same synthesis procedure, however, they present different molecular weights. The reason is that in the former polymer, sodium acetate molecules interact very strongly with the *N*-oxide group, forming an integrated structure.

The fivefold difference in the molecular weight between ZW-II and ZW-IV provides an indication that around 0.1 sodium acetate molecules attach to each *N*-oxide group in ZW-II, as further confirmed by elemental analysis. On the other hand, ZW-III presents the lowest molecular weight but the highest value of A_2 . Root mean square for ZW-III was not obtained because its determination exceeds the apparatus range.

Flocculation measurements

Figure 4 shows the solids removal efficiency (%) as a function of pH at 1 mg/L polymer concentration. The highest efficiency (about 65%) belongs to ZW-II when the solution pH is 2. This result confirms that flocculation increases in the more expanded coils. On the other hand, the removal efficiency decreases as pH increases for all polymers. ZW-III shows a lower removal efficiency for a wide range of pH. Certainly, this is associated with its lower molecular weight. Furthermore, ZW-IV presents the lowest removal efficiency because of the coil compactness.

Figure 5 illustrates the removal efficiency (%) as a function of polymer concentration when the solution pH is 2 and with an initial turbidity of 53 NTU. Removal is almost independent of the dosage in the three polymers. According to results shown in Figures 4 and 5, in domestic wastewater, the optimum values for pH and polymer dosage are 2.5 and 1 ppm, respectively.

Orta de Velázquez et al.⁸ have examined the flocculation properties of zwitterionic polymers by using a

TABLE III
Characterization of Zwitterionic Polymers

| Polymer | M_w (Da) | RMS (nm) | A_2 (mol ml/g) |
|------------------------|--------------------|----------|-----------------------|
| Precursor ^a | 2.09×10^5 | 50.1 | 7.01×10^{-4} |
| ZWII ^b | 1.90×10^5 | 126 | 1.87×10^{-3} |
| ZWIV ^b | 3.95×10^4 | 40 | 3.33×10^{-3} |
| Precursor ^c | 2.38×10^5 | 36.2 | 3.04×10^{-4} |
| ZWIII ^b | 7.35×10^3 | — | 1.56×10^{-2} |

^a In methanol.

^b In 0.1 NaCl.

^c In chloroform.

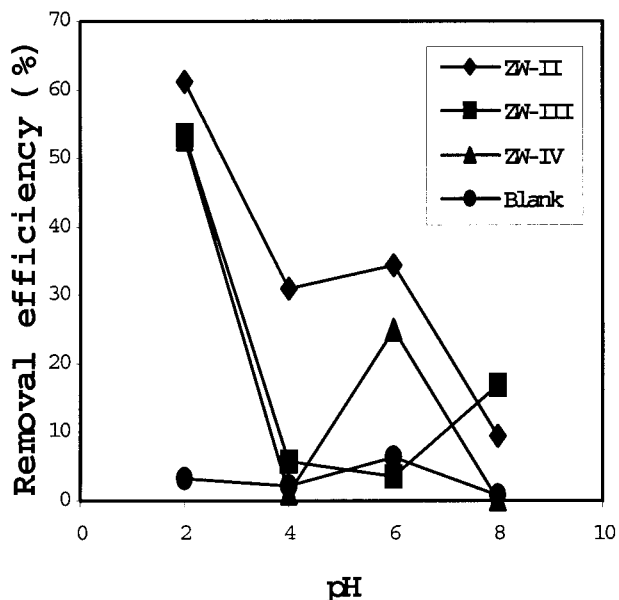


Figure 4 Removal efficiency (%) as a function of pH for a polymer concentration of 1 mg/L and with initial turbidity of 53 NTU.

variety of wastewaters in water-treatment operations. Up to 87% of turbidity removal was obtained with cationic and anionic polymers. Zwitterionic polymers presented considerable chain expansion in the presence of high ionic strengths or high salinity, in contrast to the behavior exhibited by polyelectrolytes.⁶ In the following section, viscosity measurements are carried out to confirm conformational changes in the polymers and to relate them with the removal efficiency.

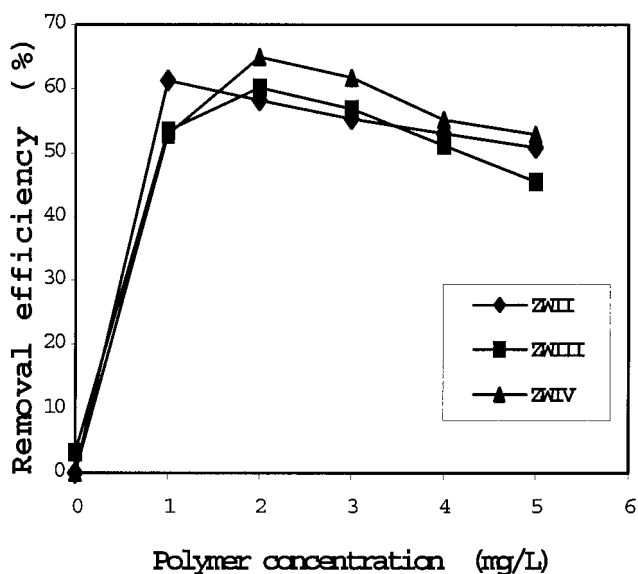


Figure 5 Removal efficiency (%) as a function of polymer concentration at pH = 2.

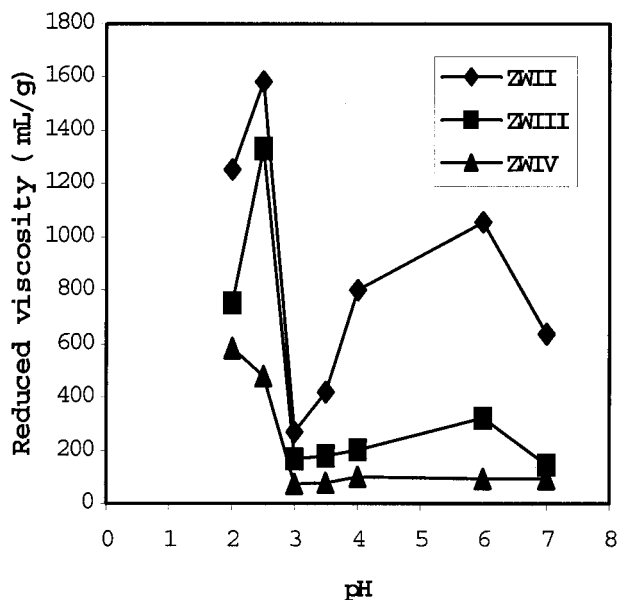


Figure 6 Reduced viscosity profiles of the three zwitterionic polymers as a function of pH.

Viscosity measurements

In Figure 6, the reduced viscosity is plotted with solution pH for the three zwitterionic polymers dissolved in deionized water. All polymers exhibit a minimum in the reduced viscosity at a pH of 3–4 as a result of undergoing a polyanion \rightarrow polyzwitterion \rightarrow polycation transition. Initially, at a pH = 8, the polyanion structure presents a high viscosity in ZW-II, due to repulsion between negative charged groups. ZW-IV shows a lower expansion because extraction of counterions by the resin has been made. As the pH of the solution is lowered by the addition of HCl, the *N*-oxide group becomes progressively protonated, reducing the repulsion among charged groups. Due to the zwitterionic nature of the N^+-O^- group, the charge ratio between anionic and cationic atoms approaches unity, which leads to a reduction in the hydrodynamic volume and a minimum in the reduced viscosity. This is observed at the isoelectric point. Further lowering of pH beyond this point results in protonation of the oxygen in the N^+-O^- group. The drastic increase in viscosity at low pH (ca. 2) is attributed to the increase in the ionic strength of the solution due to the presence of hydronium and chloride ions as well as residual acetic acid from the reaction. The polymer acquires an overall cationic charge placed on the quaternary ammonium moieties. Repulsion between these groups causes an extension of the polymer coil. The effect on the viscosity is similar to that observed in proteins and in some synthetic copolymers and terpolymers.¹⁰ The suggested structural transitions of the *N*-oxide polymer as a function of pH are shown in Figure 7. The existence of an amine oxide

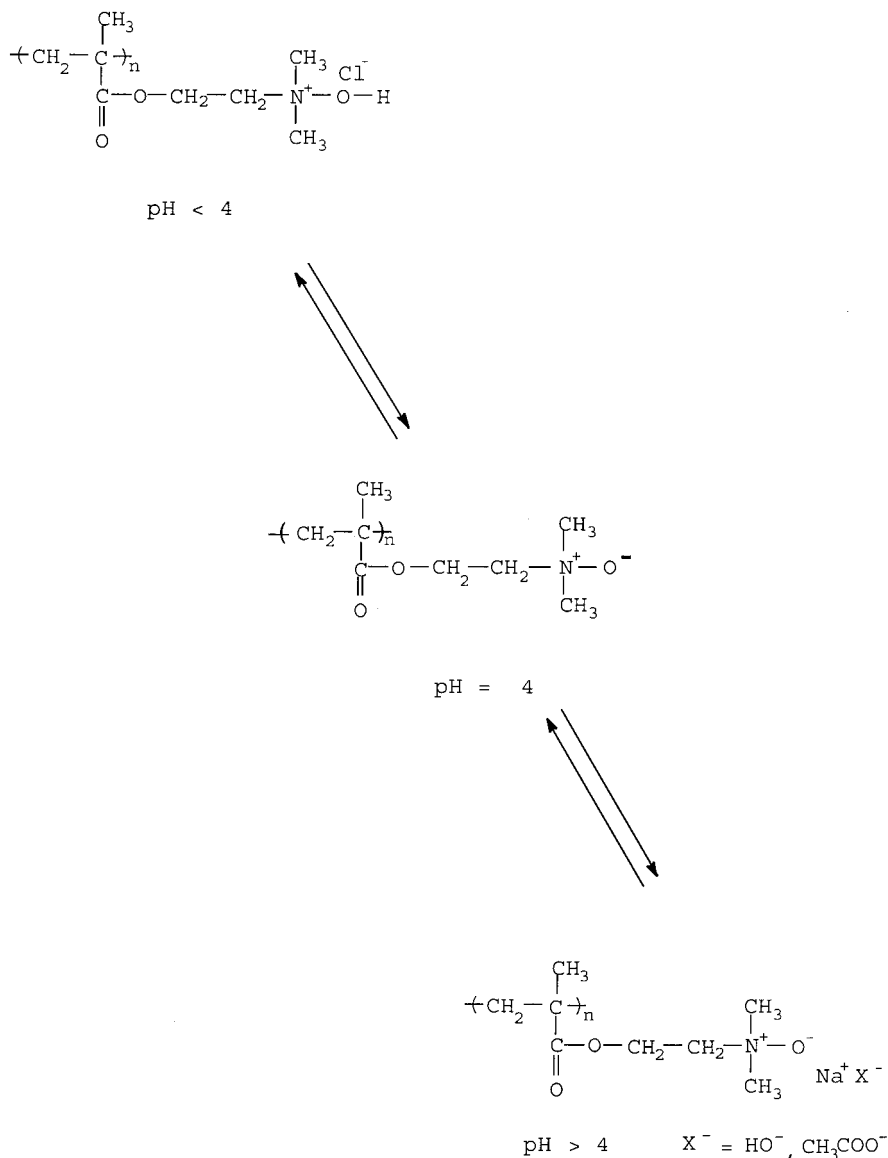


Figure 7 Structural changes in the polyanion \rightarrow polyzwitterion \rightarrow polycation transition.

polyanion at high pH can be explained to occur because of an excess of OH^- groups that lead to a neutralizing action on the positive nitrogen of the quaternary amine group. In addition, preliminary experimental evidences have shown that the z-potential has a change in sign at high pH values, depending on acetate group concentration in the sample. This study is currently under attention.

NMR studies of these polymers in deuterated aqueous solutions illustrate the structural changes when the solution pH is changed. For instance, the proton-NMR signal of the methyl groups joined to the nitrogen atom changes from 3.3 to 3.7 ppm when solution pH is changed from 6 to 2, in the ZW-II polymer. This change is associated with the increase in ionic strength of the solution due to transition polyzwitterion \rightarrow polycation when the hydronium and chloride ions are added.

In Figure 6, ZW-II exhibits a higher reduced viscosity throughout the pH range. This enhancement results from repulsion among charged groups, as mentioned before. However, it is very interesting that the contraction observed at the isoelectric point is the same independent counterion type and molecular weight of the polymers.

The close relationship existing between the removal efficiency and the reduced viscosity as a function of pH is remarkable. Holt and Tamami¹¹ have shown conformational changes due to variations in pH in vinylpyridine oxide copolymers. Two major viscosity changes of a different nature were observed: the first one located at intermediate pH values⁷⁻⁸ was ascribed to intermolecular interactions, and another one, at low pH,²⁻⁴ was assigned to electrostatic repulsion. This behavior is very similar to that shown by synthetic

polyampholytes having different basic and acid groups. According to these results, it seems that variations of the chain expansion with pH play an important role in the flocculation process. This behavior is in close agreement with Orta de Velázquez et al. results.⁸

Finally, zeta-potential determinations were made to measure the aggregation degree of the polymers. Electrokinetic phenomena and more specifically, zeta-potential measurements, have long been used to probe interfacial phenomena and the stability of colloidal systems according to results by Nicoli et al.¹² The net charge in colloidal particles is strongly influenced by pH, and therefore, pH controls their stability, preventing aggregation. Zeta-potential (ζ) determinations may provide a good representation of the electrical potential on the particles surface, and its magnitude is important to establish whether the repulsive electrostatic potential barrier between neighboring particles of suspended solids and polymers is high enough to preclude their agglomeration.

Results of ζ and particle sizes (number-weight mean) for filtered ZW-II, not filtered ZW-II, ZW-III, and ZW-IV, are 9.11, 16.53, -5.62, and 14.98 MV and 0.67 ± 0.59 , 0.71 ± 0.59 , 0.71 ± 0.65 , and 0.79 ± 0.65 μm , respectively. It is apparent that the zwitterionic polymers agglomerate in a similar degree. With the exception of ZW-III, they show similar ζ -values of the positive electrical potential at the surface of the particles. The higher ζ -value for ZW-II (not filtered) is due to the higher concentration of sodium acetate groups, which induces agglomeration. In fact, filtration of ZW-II was difficult because aggregation begins at low polymer concentrations. Additional studies on zeta-potential determinations as a function of pH in these materials are in progress.

CONCLUSION

Results presented in this work show that coil expansion in zwitterionic *N*-oxide polymers is closely related to their flocculation ability to remove suspending solids in water-treatment operations. Molecular properties of the polymers, including the molecular weights, were associated with chain expansion as determined by the variation of the reduced viscosity with solution pH. Conformational changes of the *N*-oxide polymers prepared by various synthetic routes strongly influence the flocculation process for suspending solids removal.

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