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Aqueous Solution Properties of Cationic Naphthalene-labeled Poly(hydrochloride quaternized 2-norbornene-5-methylamine)

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SUMMARY: Naphthalene-labeled cationic poly(hydrochloride quaternized 2-norbornene-5-methylamine), poly(HCQNBMA)/NA, has been prepared by living ring-opening metathesis polymerization (ROMP), using $\{RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2\}$ as catalyst in methylene chloride, followed by hydrogenation, hydrolysis and quaternization. The aqueous solution properties of poly(HCQNBMA)/NA are examined in terms of fluorescence, viscosity, degree of binding, and flocculation studies. As the naphthalene label was introduced into the poly(hydrochloride quaternized 2-norbornene-5-methylamine), the behavior of the solution properties of the poly(HCQNBMA)/NA could be clearly defined in term of fluorescence analysis. The intensity decreases with an increasing $CuCl_2$ concentration. Quenching efficiency of $CuCl_2$ was reduced with increasing KCl concentration arising from compacted conformation of polymer chains. An increase in NaCl concentration caused the reduced viscosity to decrease at the same poly(HCQNBMA)/NA concentration. In the presence of KCl, the polyelectrolyte has a lower degree of binding, indicating that the proton ion (H^+) has difficulty binding to Cl^- in poly(HCQNBMA)/NA solution. Optimum flocculation of bentonite suspensions, corresponding to the complete removal of turbidity from the supernatant, is achieved. Models are proposed to account for quenching.

INTRODUCTION

The synthesis of water-soluble polymers that contain ionic pendant groups has been the goal of academic and industrial laboratories for the past several years.$^{1)}$ Many workers have focused on fluorescently labeled water-soluble polymers to correlate the microscopic, photophysical response with a macroscopic event.$^{2-4)}$ Photophysical analysis of the fluorescently labeled polyelectrolytes has demonstrated that salt-dependent intermolecular and intramolecular interactions are both macroscopic and microscopic in nature.

Living or controlled / “ living ” polymerization techniques provide the synthesis of well-defined polymers with controlled molecular weight, polydispersities and terminal functionalities.$^{5)}$ These techniques can proceed by anionic,$^{6)}$ cationic,$^{7)}$ group transfer,$^{8)}$ metathesis,$^{9)}$ Ziegler-Natta,$^{10)}$ or radical mechanism.$^{11)}$ Increasing interest in ring-opening metathesis polymerization (ROMP) of norbornene derivative has developed over recent years to provide polymer structure with functional substituents which display interesting properties.$^{12)}$ Recently, norbornene derivatives have been polymerized by at least two research groups using classical, nonliving olefin metathesis catalysts such as $RuCl_3$ and $RuCl_2(PPh_3)$.$^{13)}$ The resulting copolymer was reported to exhibit interesting properties, but control over the molecular weight and molecular distribution was poor.

Previously, the synthesis, viscosimetric, and fluorescence properties of these water-soluble naphthalene-labeled acrylamide-based copolymers have been reported.$^{14)}$ The behavior of

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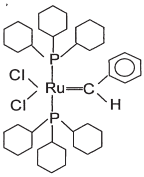
the dilute aqueous solution properties of the water-soluble acrylamide-based copolymer can be clearly defined from their viscosimetric and photophysical studies. Moreover, in recent years attention has focused on the aqueous solution properties, photochemistry, and practical applications of the water-soluble copolymers containing hydrophobic residues and charged units. The content of the residues is adjusted to 50 mol % to secure the formation of the microphase structure consisting of the styrene aggregates. These phenomena are different from the corresponding acrylamide-based copolymer without a hydrophobic group.14) Low-polydispersity copolymer of a norbornene derivative, naphthalene-labeled cationic poly(hydrochloride quaternized 2-norbornene-5-methyl amine), poly(HCQNBMA)/NA, was prepared by the living ring-opening metathesis polymerization (ROMP) with the ruthenium complex. In this study, the aqueous solution properties of poly(HCQNBMA)/NA having a hydrophobic polynorbornene backbone are examined particularly the behavior of fluorescence quenching, viscosity, degree of binding, and flocculation.



EXPERIMENTAL

Monomers and Polymerization

The synthesis of 2-norbornene-5-methyl amine (NBMA) and 2-norbornene-5-methyl bromide (NBMB) were reported previously.15) 2-Norbornene-5-methylphthalimide (NBMPI) was prepared by azotropic removal of water from an equimolar solution of NBMA and phthalic anhydride in xylene.15) 2-Norbornene-5-methoxylnaphthalene (NBMNA) was prepared by adding naphthalene methanol in anhydrous DMF dropwise to a stirred suspension of sodium hydride in DMF over a period of 30 min. After 2hr, NBMB was added dropwise in 30 min, then stirred for 6hr at 130^{0}C. Colorless oil was obtained by vacuum distillation (160^{0}C /2mmHg). [endo/exo=3:2, ^{1}H NMR ($CDCl_3$): δ (ppm)=6.11 (m, =CH, endo), 6.85 (m, =CH, endo), 6.85 (m, =CH, exo), 7.43~8.51 (m, 7H, aromatic)].

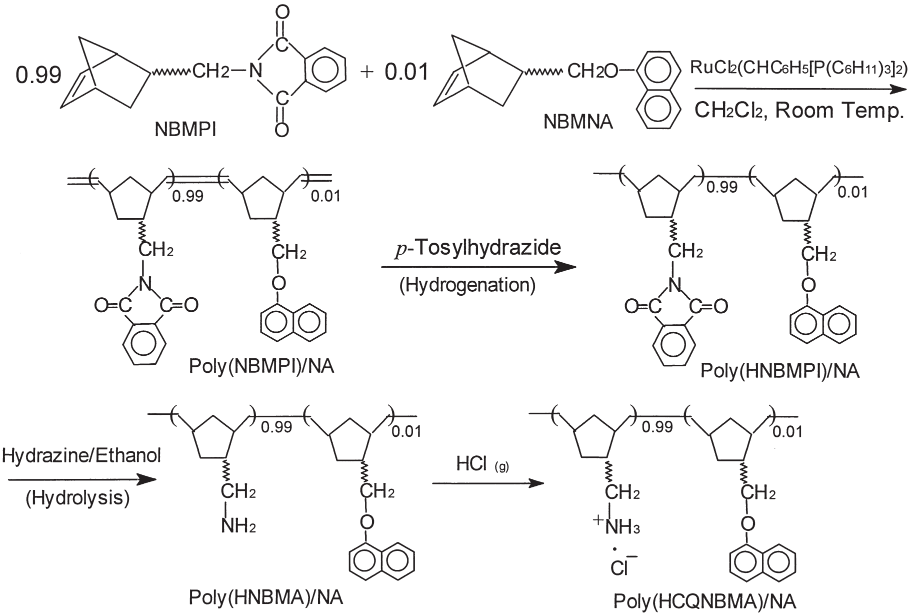
The polymerization reaction is shown in Scheme I. Before hydrogenation, there were olefinic resonance of poly(NBMPI)/NA between 5.0 and 5.6 ppm; while after hydrogenation, the resonances completely disappeared. The aromatic resonances of the poly(HNBMPI)/NA between 7.1 and 8.0 ppm, still appeared, indicating that the phthalimide group was remained. After the hydrolysis and quaternization, the NMR spectra of poly(HCQNBMA)/NA showed the peak of NH_3^+ is between 2.0 and 2.2 ppm. The molecular weight of poly(NBMPI)/NA was measured to be Mn=506,000 by GPC. ([(NBMPI)/NA]/[Initiator]=2000 and PDI=1.18)

Characterization methods

Fluorescence spectra were recorded on Shimadzu RF-5031 spectrophotometer. The diluted polymer and quencher solutions were mixed together in a predetermined ratio. All the fluorescence measurements were performed at room temperature by excitation at the 290 nm wavelength in polymer at a concentration of 0.1 g/dL. According to the Stern-Volmer polt, the Ksv was evaluated by the following correlation, **Io** / **I**= 1+Ksv [Q] (eqn.1), where Ksv is the Stern-Volmer quenching constant. **Io** is the emission intensity in the absence of quencher, **I** is the emission intensity in the presence of quencher, and [Q] is the quencher concentration.

Viscosimetric measurements were taken with Ubbelohde viscometer (the viscometer had a flow time of 67.20 s in pure water) at 30 ± 0.01^{0}C. The polymer samples were dissolved in the salt concentration to yield a stock solution of solvent.

The pH measurements were obtained with a KYOTO ELECTRONICS AT-210 instrument with a Mallinckrodt standard buffer solution (pH 7.00±0.01 and 4.01±0.01 at 25℃). The instrument's sensitivity was 0.01 pH units. Experiments were performed with solutions containing either monomer or polymer 0.1g in 100mL.



Scheme I

RESULTS AND DISCUSSION

Fluorescence quenching

Naphthalene-labeled poly(HCQNBMA)/NA excimer emission was investigated by fluorescence measurement to elucidate the solution's behavior. The fluorescence spectrum of cationic naphthalene-labeled in aqueous salt-free solution was measured. A peak at 330 nm resulting from the fluorescence emission of isolated naphthalenes (monomer emission) was observed. When salt was added, the fluorescent spectra pattern would change. Fig. 1 shows the fluorescence spectra of the cationic poly(HCQNBMA)/NA in the presence of varying concentrations of quencher [$CuCl_2$] in 0.1M KCl solutions. The intensity of fluorescence emission decreases with an increase in the quencher [$CuCl_2$] concentrations, particularly at 330nm. The quenching of poly(HCQNBMA)/NA in different concentrations of KCl was measured using the quencher $CuCl_2$. This quencher was selected on the basis of its expected interactions with poly(HCQNBMA)/NA. Stern-Volmer plots of **Io/I** versus various quencher concentration ([$CuCl_2$]) for poly(HCQNBMA)/NA in different concentration of KCl solutions are depicted in Fig. 2.

The Ksv values derived from Stern-Volmer plots (Fig. 2) and eqn.1 could indicate that conformational or environmental changes of the fluorescent labels reside in a various hydrated environment (0.1 M and 0.3 M $KCl_{(aq)}$). The Ksv values in 0.1 M and 0.3 M $KCl_{(aq)}$ are 127.6 (M^{-1}) and 67.1 (M^{-1}), respectively. Upon addition of KCl, the quenching is considerably reduced. In the other aspect, the added KCl will shield the positive charge of cationic group at poly(HCQNBMA)/NA side chain, which disrupts the expanded conformation of polymer chain. The compacted conformation of poly(HCQNBMA)/NA was formed by Coulombic interaction of hydrophobic polynorbornene backbone. The quencher $CuCl_2$ would have difficulty traversing the naphthalene labels of poly(HCQNBMA)/NA having hydrophobic polynorbornene backbone for quenching. Therefore, the quenching efficiency of $CuCl_2$ was reduced with increasing KCl salt concentration. (Fig. 3)

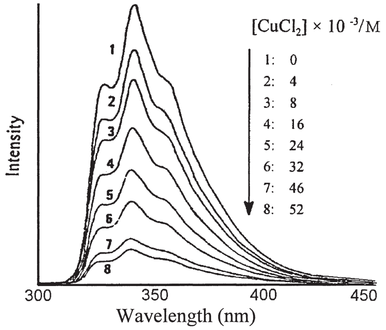


Fig.1. Fluorescence spectra of poly(HCQNBMA)/NA salt solution (0.1 M KCl) in the presence of varying concentration of $CuCl_2$

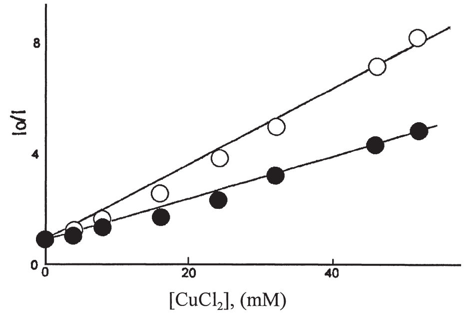
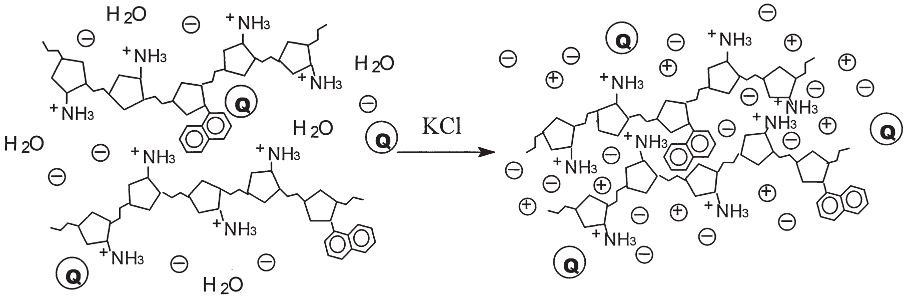


Fig. 2. Stern-Volmer plot for the fluorescence and salt quenching by $CuCl_2$ in water aqueous solution.
(○) 0.1M KCl; (●) 0.3M KCl



- Expanded conformation
- Quencher is easily traveled to close to naphthalene label for quenching reaction
- Quenching efficiency ↑

- Compacted conformation
- Quencher is difficultly traveled to close to naphthalene label for quenching reaction
- Quenching efficiency ↓

Fig. 3. Proposed model for effect of KCl salt addition on poly(HCQNBMA)/NA solution (Q : quencher, ⊕: K^+, ⊖: Cl^-)

Viscosity of poly(HCQNBMA)/NA

The reduced viscosities of NaCl solutions of different concentrations containing poly(HCQNBMA)/NA were determined, with the results shown in Fig. 4. The reduced viscosity decreases with increasing polymer concentration, i. e., as more salt was added, lower viscosities were obtained. These phenomena might be due to the fact that the addition of salt can loosen the poly(HCQNBMA)/NA structure in aqueous solution as a result of the inter- and intra- ionic repulsive forces; thus, the polymer can behave more freely in the salt solution. In other words, the higher the salt concentration, the lower the electrostatic repulsive forces; and thus, the lower the viscosity.

Degree of binding

The potentiometric titration of the cationic polyelectrolyte with hydrochloric acid in aqueous solution was carried out in the presence and absence of NaCl salt. The results are shown in Fig. 5 for the poly(HCQNBMA)/NA. From Fig. 5, it is seen that polymer in the presence of salt has a lower pH value at the same amount of added HCl solution. This means that poly(HCQNBMA)/NA has a certain degree of site binding with NaCl. The salt NaCl hinders the binding ability of the cationic poly(HCQNBMA)/NA with HCl solution. Consequently, the concentration of free HCl solution increases, resulting in the lower pH value in the presence of NaCl salt. The pKa can be calculated from a modified Henderson-Hasselbach equation: $pH=pKa+ n\log(1-\alpha)/\alpha$ (eqn.2), where α is the degree of binding for the cationic polyelectrolyte with HCl solution and Ka is the constant of binding. From Figure 5 and eqn.2, the relationship between pH and α can be calculated. It is clear that the polyelectrolyte in the presence of NaCl has a lower degree of binding at the same pH value in comparison to that in the absence of NaCl. These phenomena could be explained by the argument that it is relatively difficult for the proton ion (H^+) to bind to the Cl^- at the polymer end, thus resulting in the lower degree of binding in the presence of NaCl. From the plot of pH vs. $\log(1-\alpha)/\alpha$, the pKa could be calculated; that is, the pKa is equal to the pH as α is equal to 0.5. Poly(HCQNBMA)/NA in the absence of NaCl has the Ka value (2.57×10^{-3}), which slightly increases with addition of NaCl (2.63×10^{-3}).

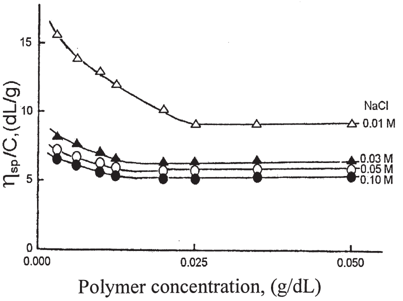


Fig. 4. Variation of the reduced viscosities with poly(HCQNBMA)/NA concentration in various concentrations of $NaCl_{(aq)}$.

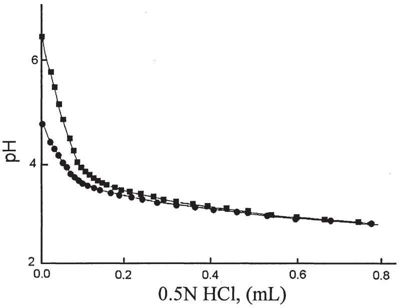


Fig. 5. Relationships of pH vs 0.5N HCl for. poly(HCQNBMA)/NA (■) non-salt; (●) 0.1M NaCl

Flocculation

Residual turbidity would be plotted as functions of the cationic polymer concentration. The polymer-bentonite system showed flocculation characteristics similar to those reported for other polymers in inorganic suspensions. Residual turbidity decreases with increasing polymer concentration below the saturation level of adsorption. Optimum flocculation, corresponding to the complete removal of turbidity in the supernatant, is then achieved (2-10% based on bentonite). Beyond the optimum flocculation, high polymer dosages redisperse the bentonite suspensions (>10% based on bentonite). These results indicate that poly(HCQNBMA)/NA is an efficient flocculant for bentonite suspension. The equivalency of the cationic poly(HCQNBMA)/NA on a charge-for-charge basis and the coincidence of the optimum flocculation point with neutralization of the particle charge indicate that flocculation in these systems is due entirely to a charge neutralization mechanism.

CONCLUSIONS

Poly(HCQNBMA)/NA has been successfully prepared by living ring-opening metathesis polymerization (ROMP), using $\{RuCl_2\ (CHC_6H_5)[P(C_6H_{11})_3]_2\}$ as catalyst, followed by hydrogenation, hydrolysis and quaternization. The aqueous solution properties of cationic poly(HCQNBMA)/NA are examined in terms of fluorescence, viscosity, degree of binding, and flocculation studies. Quenching efficiency of $CuCl_2$ was reduced with increasing salt concentration, as a result of the enhanced compacted conformation of polymer chains. An increase in NaCl concentration caused the reduced viscosity to decrease at the same poly(HCQNBMA)/NA concentration. Poly(HCQNBMA)/NA in the absence of NaCl has the Ka value (2.57×10^{-3}), which slightly increases with addition of NaCl (2.63×10^{-3}). Optimum flocculation, corresponding to the complete removal of turbidity in the supernatant, is then achieved (2-10% based on bentonite). Beyond the optimum flocculation, high polymer dosages redisperse the bentonite suspensions (>10% based on bentonite).

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