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Simultaneous Polymerization and Quaternization of 4-Vinyl Pyridine

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ABSTRACT: Quantitative polymerization of 4-vinyl pyridine (4-VP) and its quaternization has been done simultaneously for the first time in absence of organic solvents. 1, 4-dibromo-2-butene acts as quaternizing agent. The quaternized polymer has been characterized by chemical, thermal and spectral analysis. The mechanistic path involved in the polymerization and quaternization has been elucidated. Particle size, surface area, ion exchange capacity and metal ion binding property were determined. The polymer was found to have pH-dependent chromate ion binding capacity with high level of selectivity and good antibacterial activity. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Cationic polyelectrolytes, in general, have many potential applications in sludge dewatering,[1] design of new membrane,[2] phase transfer catalysis,[3] ion exchange separation[4] and stabilization of dispersion[5] (as lubricating agent, emulsifier, flocculating agents etc.). Most outstanding examples of cationic polyelectrolyte are quaternary ammonium polymers. Mainly, two synthetic routes are available for the preparation of quaternary ammonium polymers. These are polymerization of vinyl monomers with quaternary ammonium side group (Route 1) and quaternization of polymers having suitable nitrogen centre (Route 2). Diallyl dimetyl ammonium chloride,[6] methacryloxy ethyl trimethyl ammonium chloride,[7] and vinyl benzyl trimethyl ammonium chloride[8] are some commercially available quaternary ammonium monomers, which lead to quaternary ammonium polymers. Majority of quaternary ammonium monomers are hydrolytically unstable. As a result, the synthetic Route-1 becomes less effective. Quaternization of poly (vinyl pyridines) (Route-2) might be considered as an alternate choice to obtain quaternary ammonium polymers. Preparation of vinyl pyridinium monomers is difficult due to their spontaneous polymerization yielding pyridinium moieties in the main chain.[9] Many studies have carried out involving the quaternization of poly (4-vinyl pyridine)[10,11] and related compounds with aryl halides. Commercially available macro porous resin, Reillex^{TM} HPQ[12] is derived from poly(4-vinyl pyridine) by quaternization to the extent of 70% and is reported to offer much higher resistance to oxidation than conventional strong base polystyrene anion exchange resins[12] (Amberlite IRA-400). Typically, 65–70% quaternization is common with alkyl halides. Quantitative quaternization[10] of poly (4-vinyl pyridine) is an important goal to be achieved. Most of the quaternization reactions are carried out in polar organic solvants[10–14] such as tetrahydrofuran, dimethyl formamide, methanol, etc. Replacement of polar organic solvents by a greener solvent or no solvent during quaternization may lead to the synthetic Route-2 more popular. Simultaneous polymerization and quaternization in a quantitative fashion without using organic solvents is considered to be one of the new dimensions in the field of polymer synthesis.[15] Boucher and Mollett[16] studied the kinetic aspect of quaternization in details.

This study deals with simultaneous polymerization and quaternization of 4-vinyl pyridine with 1, 4-dibromo-2-butene in the absence of organic solvents quantitatively. The properties of the synthesized polymers have been studied in terms of ion-exchange capacity, metal ion binding property and antimicrobial activity for multiple uses.

EXPERIMENTAL

Materials

4-Vinyl pyridine (4-VP) (Sigma Aldrich, St.Louis), 1,4-dibromo-2-butene (Spectrochem, Mumbai, India) and 1,4-dibromo-2-butane (Spectrochem, Mumbai, India) were used as received. Potassium dichromate and Dimethyl sulfoxide (DMSO, E. Merck, Mumbai, India) was used for the preparation of stock solution (1000 mgL^{-1}). All the working solutions were prepared by proper dilution of stock solution with double distilled water. 1,5-Diphenyl carbazide used for the colorimetric estimation[17] of Cr(VI) was of analytical grade (Merck, Mumbai, India).

Table I. Composition of the Polymerization System

Polymers	4-Vinyl pyridine (mL)	1,4-Dibromo butene (g)	1,4-Dibromo butane (g)	Solvent	Yield (g)
QP-1	2.56	1.3		–	3.7
QP-2	2.56	1.3		DMF(8 mL)	3.1
QP-3	2.56	1.3		Methanol (8 mL)	3.6
QP-4	2.56	1.3		n-Hexane (8 mL)	3.4
QP-5	5.12	1.3			4.5
QP-6	2.56	2.6			3.5
QP-7	2.56	-	1.3		2.1

Methylene blue stain (Merck, Mumbai, India) was used to determine specific surface area[7] of the quaternized poly 4-vinyl pyridine (P4-VP). Nutrient Agar Media (Himedia, Mumbai, India) was used as received.

Instruments

The FTIR spectrum was recorded using KBr pellets by Shimadzu-8400S. TGA and DTA were made using a Perkin Elmer thermal analyzer (STA-6000) in nitrogen atmosphere at a heating rate of 10 °C/min. The chromium (VI) was estimated by UV-VIS-NIR spectrometer (Shimadzu UV-PC). The pH of the solution was measured by Elico (L1120) pH meter. Sonicator (Branson, 1510) was used to produce ultrasound.

Simultaneous Polymerization and Quaternization

Simultaneous polymerization and quaternization were carried out in a three necked flask with the help of ultrasound using a sonicator (Branson 1510). 4-Vinyl pyridine monomer of requisite quantity was taken in the flask and nitrogen gas was passed through the monomer for half-an-hour. The quaternizing agent 1, 4-dibromo-2-butene was then mixed with the monomer both in presence and absence of the solvent (Table I). The controlled ultrasound (40 kHz) was then applied for simultaneous polymerization and quaternization at ambient temperature. The quantitative polymerization was achieved within 10 minutes. The products were washed several times with acetone and water sequentially. The quaternized products were then dried in open air to a constant weight.

Ion-Exchange Capacity

The quaternized polymer was taken into 10 mL 1.5(N) HNO_3. An excess of 0.1 (N) $AgNO_3$ (10 mL) was added. The mixture was shaken thoroughly and the residual silver nitrate was determined with standard 0.1(N) ammonium thiocyanate using ferric alum as indicator (Volhard's method).[17] The exchangeable bromide ion was measured using the relationship [eq. (1)]

$$1.0\,\mathrm{mL}\,(\mathrm{N})\,\mathrm{AgNO_3} \equiv 0.07992\,\mathrm{g\ exchanged\ Br^-} \tag{1}$$

Swelling Experiments

Preweighted dry sample were immersed in distilled water at room temperature until they swelled till equilibrium. The swelling ratio was calculated as a function of time as follows[18] [eq. (1)]

$$\text{Swelling ratio}\,(Q) = (W_s - W_d)/W_d \tag{2}$$

where W_s and W_d are weights of swollen and dry gel, respectively.

Network Studies

One of the important parameters characterizing cross links is M_c, the average molar mass between cross links, which is directly related to cross link density. The magnitude of M_c greatly affects the physical and mechanical properties of cross-linked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine M_c. Early research by Flory and Rehner laid the foundation for analysis of equilibrium swelling. According to the theory of Flory and Rehner,[19] for a network

$$M_c = \frac{-V_1 d_p\left(V_s^{1/3} - V_s/2\right)}{\mathrm{In}(1 - V_s) + V_s + \chi V_s^2} \tag{3}$$

where M_c is the number average molar mass of the chain between crosslinks; V_1 is the molar volume of water; d_p is the polymer density; V_s is the volume fraction polymer in the swollen gel; and χ is the Flory-Huggins interaction parameter between solvent and polymer.[20]

The swelling ratio (Q) is equal to $1/V_s$. Here, the crosslink density, q, is defined as follow[18] [eq. (4)].

$$q = M_o/M_c \tag{4}$$

where M_o is the molar mass of the repeating unit. M_0 can be calculated using the following equation[18] [eq. (5)].

$$M_o = (n_{\mathrm{monomers}} \times \mathrm{it's\ mol.\ wt} + n_{\mathrm{crosslink}} \times \mathrm{it's\ mol.\ Wt})/(n_{\mathrm{monomers}} + n_{\mathrm{crosslink}}) \tag{5}$$

Sorption and Desorption Experiment

Sorption experiments were carried out by Batch method. To determine the amount of chromate absorbed, 0.2 g quaternized product was taken into a 100-mL beaker with 25-mL chromate solution (70 ppm). The pH (1–9) of the reaction medium was maintained as per standard method[21] using sodium acetate–acetic acid buffer. The amount of chromium (VI) adsorbed was calculated using the relationship[21] [eq. (6)]

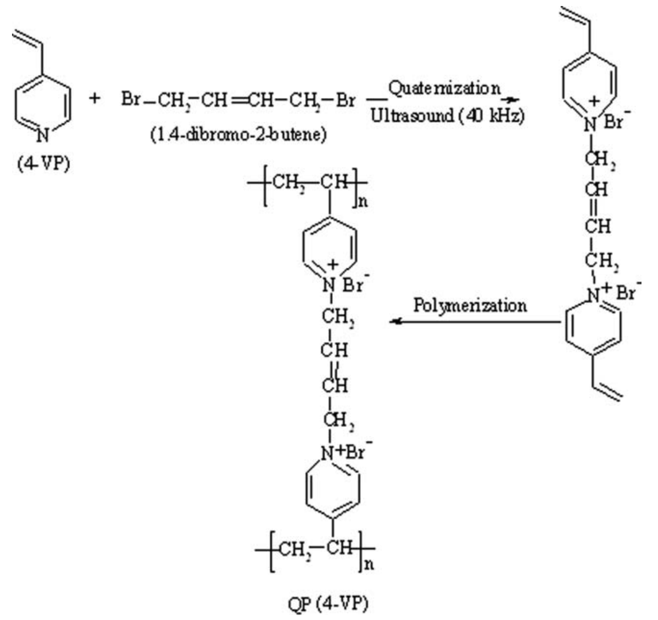
$$q_t = (W_i - W_f)/m \tag{6}$$

where q_t is the Cr(VI) adsorbed per unit mass of the polymer (q_t is popularly known as sorption capacity, expressed in mg/g), W_i and W_f are the initial and residual amount of Cr(VI) respectively, and m represents the mass of the polymer expressed in g.

For desorption study, 0.2 g polymer was taken in a 100 mL beaker with 25 mL of Cr(VI) solution (70 ppm) and kept for 1 h at room temperature. The adsorbed Cr(VI) was then subjected to 0.1 (N) NaOH, NaCl, Na_2CO_3, and Na_2SO_4 to desorb chromate.

Antimicrobial Activity Test

Antibacterial sensitivity of the compound was determined by Agar Cup Assay.[22] The sample was dispersed in DMSO at the concentration 500, 250, 125, and 62.5 μg/mL. In this test



Scheme 1. Simultaneous polymerization and quaternization.

nutrient broth suspension of 24 h old *Salmonella typhi* (10^6 CFU/mL) were poured in nutrient agar plates, spread uniformly and allowed to solidify. Desired number of wells were made using a sterile cork borer and filled with the control (100 μL). The plates were then incubated at 37°C for 24 h. Plates were observed for inhibition zone around the cups after the incubation.

RESULT AND DISCUSSION

Synthesis of Quaternized Polymer

The quaternized polymers (QP-1- QP-7) were synthesized sonochemically (Table I). The yield of the product was almost quantitative in absence of organic solvent (QP-1, 97.36%). The use of organic solvents (QP-2, QP-3, and QP-4) did not increase the yield. The probable mechanistic path is suggested as below (Scheme 1). Here 1, 4-dibromo 2-butene acts both as quaternizing and crosslinking agents and ultrasound produces requisite free radicals for polymerization. The production of free radicals by ultrasound was reported by several researchers.[21] The yield of the products was varied with the weight ratio of monomer and quaternizing agent. The yield was not quantitative with decreasing (QP-6) or increasing (QP-5) ratio from 2.56: 1.33 (QP-1). The 1,4 di-bromo butane was found to be far less active than 1,4 di bromo butene with respect to yield (QP-1 vs. QP-7) (Table I).

Physico-Chemical Characteristic of the Quaternized Product

The size, surface area, and anion (bromide) exchange capacity of the quaternized product (QP-1) was found to be within 0.25–0.50 mm, 38–40 m^2/g, 5.3 meq/g, respectively. The exchange capacity indicates that the polymer contains 0.0053 mole/g exchangeable bromide. The nitrogen content of the product was found to be 0.0062 mole/g by chemical analysis (Kjeldhal's method).[21] Thus, it may be concluded that about 85.48% quaternization took place. These parameters are much improved than commercially available widely used anion exchangers such as Amberlite-400 and Reillex^{TM} HPQ. The polymer was insoluble in water, methanol, acetone, dimethyl formamide, tetrahydron furan, carbon tetrachloride, acid, and base. The insolubility of the synthesized polymer may be explained by quaternization through crosslinking (Scheme 1). The crosslinking density of the product was within 9 to 10%. The average molar mass of the chain between crosslinks was found to be 1188.

FTIR Analysis

The FTIR spectrum (Figure 1) of the quaternized product (QP-1) shows the characteristic peaks at 3484, 3227, 1639, 1454, and 1172 cm^{-1}. The peaks at 3416, 3043, 1640, 1468 and 1165 cm^{-1} may be assigned to O—H stretching[23] (due to adsorbed water), aromatic C—H stretching,[23] quaternary ammonium group,[13] C=C stretching[23] and C—N stretching,[23] respectively. The spectral features support the structure of quaternized product. The absorption of moisture is also reflected in the TGA traces. The test of unsaturation (bromine water test)[24] confirm the presence of unsaturation in the product, QP-1. The FTIR spectrum thus confirms the simultaneous polymerization and quaternization as suggested by the Scheme 1.

TGA Analysis

The TGA trace (Figure 2) of the quaternized product (QP-1) shows that there is four stages weight loss. The first stage (40–100°C, 10.74%) is due to the loss of absorbed moisture. The presence of moisture is also indicated by FTIR analysis of the sample (Figure 1). The second (100–200°C, ≈ 6.45%) and the third one (250–300°C, ≈ 6.50%) seems to be due to evolution of bromine. The elemental analysis of the sample also indicates that the bromine content of the sample is in the order of 11.62%. The degradation pattern reveals that the polymer contains two different types of bromide. The fourth step (300–425°C, ≈ 59.94%) suggests the degradation of the polymer by depolymerization. The IPDT[25] (Integral procedure decomposition temperature) value for the quaternized product was found to be 360°C. Such higher IPDT value indicates good thermal stability of the product.

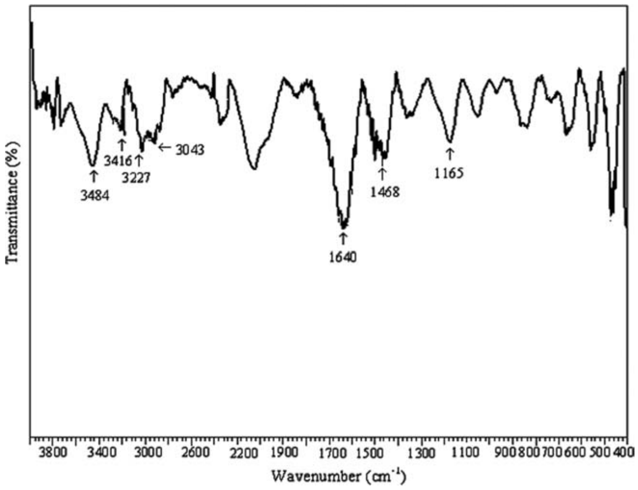


Figure 1. The FTIR spectrum of the quaternized product (QP-1).

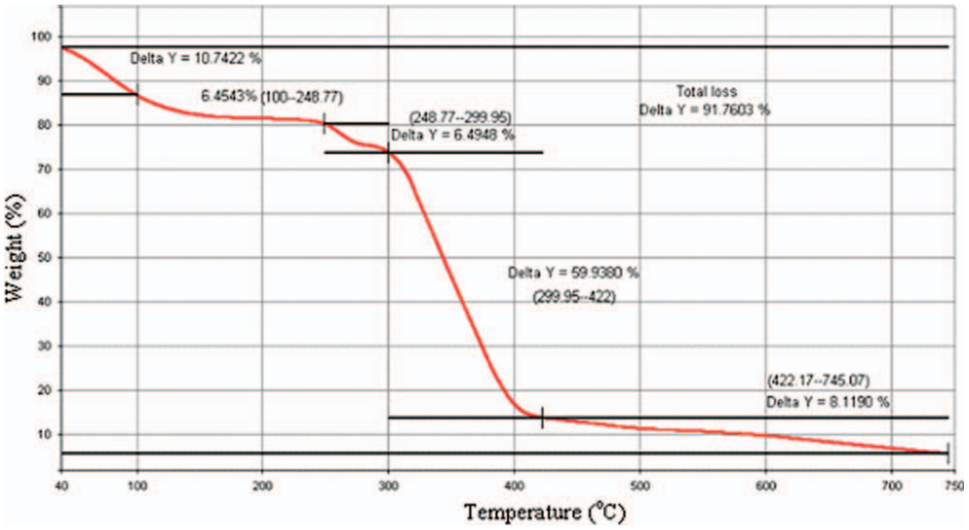


Figure 2. The TGA trace of the quaternized product (QP-1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Chromate Ion Binding Capacity

Sorption of chromium was studied at various pH values to determine the optimum pH range for its removal and the results are presented in Figure 3. The pH was adjusted with the additions of diluted sodium acetate and acetic acid. The sorption of Cr(VI) was fruitful($\approx$ 350 mg/g) at pH values between 3.0 and 8.0. It is noteworthy to mention here that most of the anion exchange resin functions well between 3.0 and 5.0 (acidic medium) and becomes inactive in the basic medium. The favorable wide pH range (both acidic and basic) may be attributed to quaternized structure of the polymeric sorbent. The quaternized structure of the polymer does not change with the pH of the medium. At very low pH (<2), the Cr(VI) remains mainly as nonionic form (H_2CrO_4), which accounts for its low sorption. At pH>8, the hydroxyl ion competes with chromate ion and results in low chromium sorption. The chromate ion binding capacity was found to be higher than that of commercially available resin Relliex^{TM} HPQ and Amberlite-400.

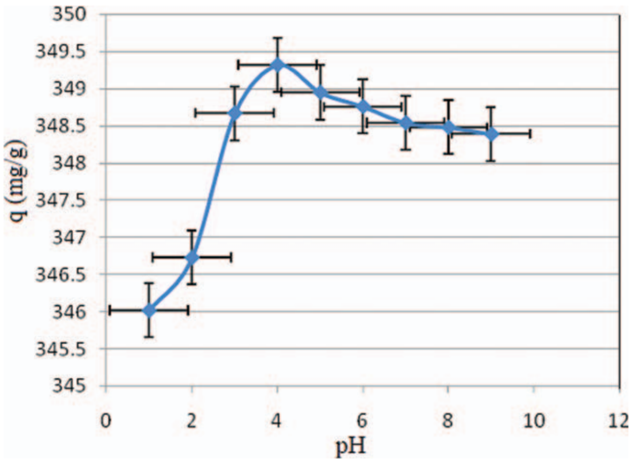


Figure 3. Variation of sorption capacity with pH (Sorbent: 8 g/L, sorbate: 70 ppm, time: 2 h, temperature: 25°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The pH dependent sorption mainly took place through ion exchange process [eq. (7)]. It was supported by the elution studies, discussed later.

$$(\equiv\overset{+}{N}\text{—}R)_2\,Cr_2O_7^{=}(S) + 2X^{-} \rightleftharpoons \equiv\overset{+}{N}\text{—}RX^{-}(S) + Cr_2O_7^{=} \quad (7)$$

Ion Exchange Property

The ion exchange property of the quaternized product was studied in the light of elution profile and measuring ion exchange capacity. About 2.025 g of chromate bound polymer (1.23% chromate) was taken in a 100 mL conical flask. The polymer was then treated with various 0.1 (N) eluents such as NaOH, NaCl, Na_2CO_3, and Na_2SO_4. The elution result is shown in Table II. The result indicates that the bound chromate was desorbed nicely by NaOH (73.70–87.25% elution). The high elution power of the hydroxyl ion is probably due structural change of Cr(VI) in basic medium. In basic medium, Cr(VI) remains as chromate. Desorption took place mainly through ion exchange process [eq. (7)]. The high ion exchange capacity (5.3 meq/g) also support the ion exchange mechanism of desorption. The eluents chloride and sulfate have low desorption power probably due to their less affinity toward sorbents. The less affinity was further elucidated by selectivity test, discussed later.

Table II. Elution Data

Eluent (0.1N)	Chromate taken (mg)	Chromate eluted (mg)	Elution (%)	RSD (%)
NaOH	1.75	1.53	87.42	0.94
Na_2CO_3	1.75	1.28	73.14	1.35
NaCl	1.75	0.26	14.85	6.37
Na_2SO_4	1.75	0.11	6.28	7.39

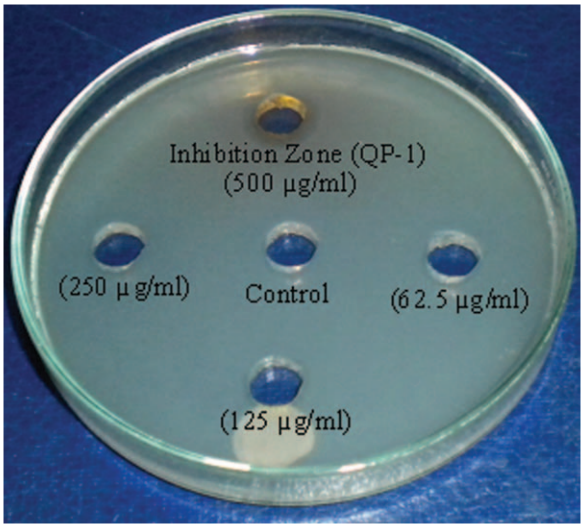


Figure 4. Antibacterial activity of quaternized product (QP-1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Selectivity Test

To measure the selectivity, equilibrium chromate sorption was measured in the presence of 200-fold molar excess of SO$_4^{2-}$ and 400-fold molar excess of Cl$^-$ at different levels of pH of the aqueous medium. The selectivity (S)[12] defined as:

$$S = \{\mathrm{Cr(VI)\ sorption\ in\ presence\ of\ SO_4^{2-}/Cl^-}\} / \{\mathrm{Cr(VI)\ sorption\ in\ absence\ of\ SO_4^{2-}/Cl^-}\}.$$

The selectivity value was found to be greater than 0.5 over the pH range 3–8, which suggests the preference of chromate over both sulfate and chloride. It is well-known that the selectivity order for the common anions of the commercially available styrene anion exchanger[26] is: SO$_4^{2-}$>CrO$_4^{2-}$>Cl$^-$. In our case, the synthesized resin has a reversal selectivity namely CrO$_4^{2}$> Cl$^-$> SO$_4^{2-}$.

It is reported[12] that at high concentration of bisulfate (pK_2 = 2.1) and chloride, hydrochromate (HCrO$_4^-$) may form mononuclear complexes [eqs. (8) and (9)] at acidic medium.

$$\mathrm{HSO_4^- + HCrO_4^- = CrSO_4^{2-} + H_2O} \qquad (8)$$

$$\mathrm{HCrO_4^- + H^+ + Cl^- = CrO_3Cl^- + H_2O} \qquad (9)$$

These mononuclear complexes contribute significant Cr(VI) sorption against high salt background. The reason for chromium selectivity over sulfate anion is due to the formation of π-type sandwich arrangement between transition metal anion and pyridine ring. Negu[27] reported similar type of observation.

Antimicrobial Activity

The bacterial growth occurred uniformly around the control and 250, 125 and 62.5 μg/mL of quaternized product (QP-1). However, the QP-1 showed a good antibacterial property against the gram negative bacteria *Salmonella typhi* with the inhibition zone 10 mm at 500 μg/mL (Figure 4).

CONCLUSION

Quantitative polymerization of 4-Vinyl pyridine and its quaternization has been done simultaneously for the first time in absence of organic solvents. 1, 4-dibromo-2-butene acts as efficient quaternizing agent. Quaternization of poly(4-Vinyl pyridine) by 1, 4-dibromo-2-butene leads to better thermal stability (IPDT = 360°C), higher chromate binding capacity($\approx$ 350 mg/g) at wide pH range (3–8), superior ion exchange property($\approx$ 5.3 meq/g Cl$^-$), improved selectivity (CrO$_4^{2-}$>Cl$^-$ >SO$_4^{2-}$) and significant antimicrobial activity in the polymer systems. The quaternized product shows a good antibacterial property against the gram negative bacteria *Salmonella typhi* with the inhibition zone 10 mm. The quaternized product may be used in the field of analytical chemistry as well as biochemistry.

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REFERENCES

1. Kulicke, W. M.; Lenk, S.; Detzmer, H. D.; Weiss, T. *Chem. Ing. Tech.* **1993,** *65*, 541.
2. Reineke, C. E.; Jagodzinski, J. A.; Denslow, K. R. *J. Membr. Sci.* **1987,** *32*, 207.
3. Toral, M. I.; Navarrete, J. G.; Leiva, A.; Rios, H. E.; Urzua, M. D. *Eur. Polym. J.* **2009,** *45*, 730.
4. Sengupta, A. K.; Roy, T. In Ion exchange for Industry; Streat, M., Ed.; Ellis Horwood: Chickester, **1988.**
5. Urzua, M. D.; Rios, H. E. *Polym. Int.* **2003,** *52*, 783.
6. Wandrey, C.; Jaeger, W. *Acta Polym.* **1985,** *36*, 100.
7. Chowdhury, P.; Roy, K.; Mondal, P. *Polym. Bull.* **2010,** *64*, 351.
8. Bon, S. A. F.; Vanbeek, H.; Piet, P.; German, A. L. *J. Appl. Polym. Sci.* **1995,** *58*, 19.
9. Chovino, C.; Gramain, P. *Macromolecules* **1998,** *31*, 7111.
10. Bicak, N.; Gazi, M. *J Macromol. Sci. Part A-Pure Appl. Chem.* **2003,** *40*, 585.
11. Kawaguchi, D.; Satoh, M. *Macromolecules* **1999,** *32*, 7828.
12. Chanda, M.; Rempel, G. L. *React Polym.* **1993,** *21*, 77.
13. Sahiner, N. A. *Turk J. Chem.* **2009,** *33*, 23.
14. Sonmez, H. B.; Bicak, N. *React Funct. Polym.* **2002,** *51*, 55.
15. Rembaum, A.; Calif A. Cationic vinyl pyridine copolymers and products thereof, United States Patent O Ce. 3,754,055, Aug 21, **1973.**
16. Boucher E. A.; Mollett, C. C. *J. Polym. Sci. Polym. Phys. Ed.* **1977,** *15*, 283.
17. Vogel, A. I. Quantitative Inorganic Analysis, 3rd ed.; Longmans: Great Britain, **1961.**
18. Shukla, S.; Bajpai, A. K. *J. Appl. Polym. Sci.* **2006,** *102*, 84.
19. Flory P. J.; Rehner, J. Jr. *J. Chem. Phys.* **1943,** *11*, 521.
20. Gedeman, L. A.; Pappas, N. A. *J. Appl. Polym. Sci.* **1995,** *55*, 919.

21. Mondal, P.; Roy, K.; Bayen, S. P.; Chowdhury, P. *Talanta* **2011,** *83*, 1482.
22. Norrel, S. A.; Messley, K. E. Microbiology Laboratory Manual Principles and Application; Printice Hall: Upper Saddle River, New Jersy, **1977.**
23. Pavia, D. L.; Lampman, G. M.; Kriz, G. S. Introduction to Spectroscopy, 3rd ed.; Saunders College Publishing; USA, **2001.**
24. Solomons, T. W. G.; Fryhle, C. B. Organic Chemistry, 8th ed.; Wiley: India, **2007.**
25. Chowdhury, P.; Singha, B.; Mukherjee, A. *Ind. J. Chem.* **2011,** *50A*, 1730.
26. Mondal, P.; Saha, S. K.; Roy, K.; Bayen, S. P.; Chowdhury, P. *Sept. Sci. Technol.*, DOI: 10.1080/01496395.2012.686422.
27. Negu, V. *J. Hazard. Mat.* **2009,** *171*, 410.