A Study of Pyridinium-Type Functional Polymers. III. Preparation and Characterization of Insoluble Pyridinium-Type Polymers

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ABSTRACT: The copolymers of 4-vinylpyridine (4VP), styrene (St) and divinylbenzene (DVB) with varied compositions, P(4VP-St-DVB), were synthesized by suspension polymerization using 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The insoluble (crosslinked) pyridinium-type polymers in benzyl–pyridinium bromide form, which possess various macromolecular chain compositions, were prepared by the reaction of each P(4VP-St-DVB) with benzyl bromide (BzBr), respectively. By using different halohydrocarbon RX in the quaternization of P(4VP-St-DVB), the insoluble pyridinium-type polymers with various pyridinium group structures were obtained. The structures of P(4VP-St-DVB) and its quaternized product Q-P(4VP-St-DVB) were identified by FTIR. The 4VP content in each copolymer P(4VP-St-DVB) was measured by nonaqueous titration; and the pyridinium group content (C_q) in each Q-P(4VP-St-DVB) sample was determined by means of the back titration manner in argentometry and/or the elemental analysis method, respectively. In addition, the particle structure and the surface morphology of the thus-prepared polymer were observed using SEM. According to a series of experimental results, the preparation and characterization of insoluble pyridinium-type polymers are analyzed and discussed. This work can prepare the ground for a study on the antibacterial activity of insoluble pyridinium-type polymers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 668–675, 2000

Key words: 4-vinylpyridine; insoluble pyridinium-type polymer; functional polymer; preparation; characterization

INTRODUCTION

As a type of cationic polymers containing both hydrophilic cationic groups (i.e., pyridinuim groups) and hydrophobic (nonpolar) segments in the macromolecular chains, pyridinium-type polymers may be a homopolymer containing almost one charge per monomer unit, such as a polyelectrolyte, or a copolymer of one monomer containing a charge and another containing no charge. In the latter case, they possess lower charge density than conventional polyelectrolytes. However, they can show some characteristic of polyelectrolytes. Soluble (linear) pyridinium-type polymers whose backbone chains contain 4-vinylpyridine (4VP) units and styrene (St) units can exhibit a typical polyelectrolyte solution behavior, that the reduced viscosity of the polymer/polar solvent system increases with dilution.[1] This fact implies that ion-containing polymers, whether their charge density is high or low, possess the common characteristic of being able to interact strongly with opposite charges. Thus, in-

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soluble (crosslinked) ion-containing polymers also have the same characteristic although their three-dimensional network will restrict the activity of segments, causing the mode of interaction of macromolecules with negatively charged species to differ from that of the corresponding soluble polymers. It is because of the interaction between the positive charges along the polymer chains and the substances bearing negative charges that the soluble and the insoluble pyridinium-type polymers are endowed many unique properties in coagulation of microbial cells,[2] capture or isolation of bacteria and viruses,[3–8] water disinfection, and removal of organic pollutants from water.[9–12] Therefore, they have exhibited the broad developing and applying prospects in the fields of bioengineering, water treatment, polymeric disinfectants, and environment protection. Japanese professor N. Kawabata and his colleagues have investigated the many unique properties of pyridinium-type polymers and made remarkable achievements in this research field.

In recent years, we have been making a systematic research into the antibacterial activity of this new type of functional polymers against bacteria in sterilized distilled water, not in sterilized physiological saline, which is the suspension medium of bacteria used in the studies by N. Kawabata et al. We have studied the preparation and characterization of soluble pyridinium-type polymers[1] and reported their antibacterial activity.[13] Based on these studies, we attempted to investigate the antibacterial activity of the corresponding polymers with three-dimentional network structure. For this purpose, insoluble pyridinium-type polymers with various compositions of macromolecular backbone chain and structures of pyridinium groups were prepared first. The preparation and characterization of these polymers are analyzed and discussed in this paper. This work will prepare the ground for a study on the antibacterial activity of insoluble pyridinium-type polymers.

EXPERIMENTAL

Materials

Comonomers 4-vinylpyridine (4VP), styrene (St), and commercial product of divinylbenzene (DVB), which contains 45% of DVB, were purified by distillation under reduced pressure before polymerization. As an initiator of polymerization, 2,2′-azobisisobutyronitrile (AIBN) was refined by recrystallization twice. Benzyl bromide (BzBr), various halohydrocarbons (RX), other chemicals and solvents were used without further purification.

Preparation of Polymer Samples

Synthesis of the Copolymers Containing Pyridine Rings

The copolymerization reaction of 4VP, St, and DVB was carried out in a four-necked, round-bottom flask equipped with a thermometer, a mechanical stirrer, a nitrogen inlet, and a reflux condenser. A series of the copolymers P(4VP-St-DVB) of varying composition was synthesized by suspension polymerization using AIBN as an initiator and polyvinyl alcohol as a dispersing agent at 75–80°C for 7 h under a nitrogen atmosphere. The synthesized copolymer was collected by filtration, washed with ethanol followed by washing thoroughly with distilled water, and dried at 60–75°C under vacuum to constant weight.

Preparation of Insoluble Pyridinium-Type Polymers

The copolymers containing pyridine rings, P(4VP-St-DVB), are the precursor copolymers of insoluble pyridinium-type polymers. The pyridine rings of P(4VP-St-DVB) were converted to pyridinium groups by quaternization with an excess of halohydrocarbons (RX) in ethanol at 75–80°C under nitrogen atmosphere. The quaternization reaction was also carried out in a four-necked, round-bottom flask equipped with a thermometer, a mechanical stirrer, a nitrogen inlet, and a reflux condenser. After 6 h, the product was collected by filtration, washed with ethanol followed by washing thoroughly with distilled water, and dried under vacuum to constant weight. By using different halohydrocarbons in the quaternization of P(4VP-St-DVB), a series of insoluble pyridinium-type polymers with various structures of pyridinium groups was prepared. These polymers may be designated as Q-P(4VP-St-DVB) and Q-P(4VP-St-DVB)-RX, respectively, when the used quaternizing agent RX is benzyl bromide (BzBr) or other halohydrocarbons. Each sample was purified by Soxhlet extraction using ethanol as an extractant for 24 h in order to remove thoroughly oligomers and other impurities from it.

Polymer Characterization

Nonaqueous Titration

The 4VP content in each P(4VP-St-DVB) sample was determined by nonaqueous titration on the

Table I   Synthesis and Composition Analysis of the P(4VP-St-DVB) Samples

Sample No.	Monomer Ratio (mol %)			4VP Content in the Feed (mmol/g)	4VP Content in the Copolymer (mmol/g)	Yield (%)
	4VP	St	DVB			
C0	60.00	40.00	0.00	5.73	6.02	89.09
C1	60.99	37.61	1.40	5.80	5.56	97.09
C2	61.67	35.98	2.35	5.86	5.53	96.18
C3	63.44	31.72	4.84	5.98	5.45	96.98
C4	69.14	17.35	13.23	6.41	5.27	96.01
C5	76.63	0.00	23.37	6.90	4.94	92.52
D3	30.84	66.81	2.35	2.94	2.69	94.42
D4	41.12	56.53	2.35	3.91	3.74	92.26
D5	51.39	46.25	2.35	4.88	4.59	90.36
D6	61.67	35.98	2.35	5.86	5.41	96.09
D7	71.95	25.70	2.35	6.82	6.53	96.78
D8	82.23	15.42	2.35	7.79	7.25	97.11
D9	97.65	0.00	2.35	9.24	8.60	98.47
D10	100.00	0.00	0.00	9.51	9.06	78.65

basis of a procedure previously developed by Burleigh et al.[14] with minor modifications.

Argentometry

The pyridinium group content C_q (i.e., the content of quaternized 4-vinylpyridine ring) in each Q-P(4VP-St-DVB) or Q-P(4VP-St-DVB)-RX sample was measured by the method of back titration in argentometry using ferric ammonium sulfate as an indicator.

Elemental Analysis

In order to examine the reliability of the data obtained by argentometry, elemental analysis of some representative insoluble pyridinium-type polymer samples was also carried out using Heraeus elemental analyzer.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the copolymers P(4VP-St-DVB) and their quaternized products Q-P(4VP-St) were recorded in KBr pellets using Analect RFX-65 spectrophotometer.

Scanning Electron Microscopy Observation

The particle structure and the surface morphology of an insoluble pyridinium-type polymer were observed with a scanning microscope (model JSM—T300, JEOL Ltd.).

RESULTS AND DISCUSSION

Effects of the Monomer Ratio on the Copolymer Composition

The monomer ratio in synthesizing two groups of copolymers (Group C and Group D) and their composition and yield are listed in Table I. The results show that when the mole fraction of 4VP and the total mole fraction of St and DVB in the feed are basically constant, the 4VP content in the copolymer will be lower than that in the feed and decrease with an increase in the mole fraction of DVB in the feed. It is due to the fact that DVB molecule contains two functional groups with reactivity. The participation of DVB in the copolymerization decreases the relative probability that 4VP molecules participate in the copolymerization reaction and are combined into the macromolecular chains of P(4VP-St-DVB). The higher the mole fraction of DVB in the feed, the more remarkable this tendency will be. However, in the sample C0 containing no DVB, the 4VP content in the copolymer is higher than that in the feed, which is consistent with the measured results for P(4VP-St) copolymer samples synthesized by a solution polymerization.[1] It shows that the reactivity of 4VP is stronger than that of St.

In the 4VP homopolymer D10 prepared by the same method, the measured 4VP content is 9.06 mmol/g, which is lower than the theoretical value 9.51 mmol/g. It is due to the fact that the synthesized 4VP homopolymer sample unavoidably con-
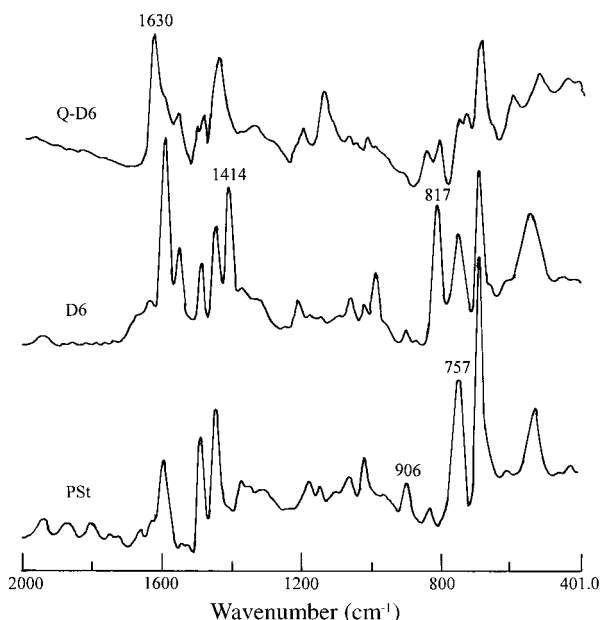
Figure 1 FTIR spectra of PSt, D6, and Q-D6.

tains some remained dispersing agent and initiator end groups.

It can be found by analyzing the yield of copolymerization in Table I that the existence of DVB can increase the conversion of copolymerization under the same conditions of a suspension polymerization. Thus, these experimental results suggest that DVB possesses the highest reactivity among three comonomers 4VP, St, and DVB.

Identification of P(4VP-St-DVB) and Its Quaternized Product

A series of insoluble pyridinium-type polymers, Q-C0, Q-C1, . . . Q-C5, and Q-D3, Q-D4, . . . Q-D10, were obtained by quaternizing the P(4VP-St-DVB) copolymers C0, C1, . . . C5 and D3, D4, . . . D10 with BzBr, respectively. A series of insoluble pyridinium-type polymers Q-D6-RX were obtained by the quaterization of P(4VP-St-DVB) sample D6 using different halohydrocarbons RX as quaternizing agents, respectively. Therefore, the pyridinium-type polymers in Groups Q-C and Q-D possess different macromolecular main chain compositions and the same pyridinium group structure while the polymers in Group Q-D6-RX possess the same macromolecular main-chain compositions and different pyridinium group structure.

FTIR was used to identify the prepared P(4VP-St-DVB) and its quaternized product Q-P(4VP-St-DVB). Figure 1 shows the FTIR spectra of PSt

(the homopolymer of St), P(4VP-St-DVB) sample D6 and its quaternized product Q-D6.

In Figure 1, the FTIR spectrum of D6 exhibits the characteristic absorption peaks of St located at 757 cm^{-1} and 906 cm^{-1},[15] and those of 4VP located at 1414 cm^{-1} and 817 cm^{-1}, which are respectively attributable to the symmetric C—N stretching vibration[16–18] and the C—H out-of-plane bending vibration[15,18] of pyridine ring in 4VP chain units. This suggests that the sample D6 contains both the chain units of 4VP and St. On the other hand, the qualitative examination into the solubility of D6, the other P(4VP-St-DVB) copolymers and their quaternized products in organic solvents has testified that they can be only swelled and not dissolved in glacial acetic acid, anhydrous ethanol, tetrahydrofuran, and dimethylformamide, in which PSt is insoluble while the linear copolymers P(4VP-St) and their quaternized products can be completely dissolved. Thus, P(4VP-St-DVB) copolymer samples synthesized in our experiment indeed contain the chain units of DVB and there does not exist the possibility of containing the homopolymer of St and the long St blocks in these samples. In other words, the copolymerization of 4VP with St and DVB is random and the resultant P(4VP-St-DVB) copolymers are random copolymers.

In the spectrum of Q-D6, a peak at 1414 cm^{-1} disappeared and a new peak at 1630 cm^{-1}, assigned to the absorbance of quaternized pyridine ring,[19] appeared. It proves that the 4VP chain units in Q-D6 had been completely quaternized.[16,17]

The FTIR spectra of Q-D3 and Q-D9 are shown in Figure 2. The content of 4VP chain units in Q-D3 and Q-D9 are respectively lower and higher than that of Q-D6, and Q-D9 contains no St. It can be seen from the spectra of Q-D3 and Q-D9 that the characteristic absorption peak of 4VP at 1414 cm^{-1} did not appear and the peak at 1630 cm^{-1} assigned to the absorbance of quaternized pyridine ring appeared. This indicates that the prepared insoluble pyridinium-type polymers P(4VP-St-DVB) have very high degree of quaternization.

The spectra shown in Figures 1 and 2 also indicate that the method of preparing insoluble pyridinium-type polymers used in our experiment is feasible and by this method the expected products can be prepared.

However, it was found that when C_4H_9Cl was used as a quaternizing agent, the increased weight of the quaternized product Q-D6-C_4H_9Cl was much lower than the theoretically expected increase in weight. In the light of FTIR spectrum
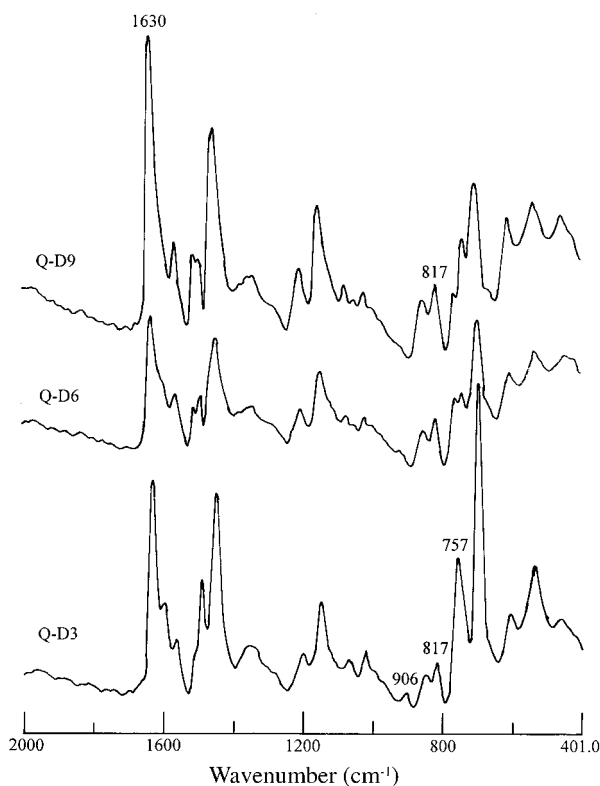
Figure 2 FTIR spectra of Q-D3, Q-D6, and Q-D9.

of Q-D6-C_4H_9Cl as shown in Figure 3, the characteristic absorption peak of 4VP at 1414 cm^{-1} did not disappear and that of quaternized pyridine ring at 1630 cm^{-1} also appeared. Therefore, only a part of 4VP units in Q-D6-C_4H_9Cl sample were quaternized and the degree of quaternization of the sample was relatively low. Since the conditions of quaternizing reaction for each sample are basically the same, this result also suggests that the quaternizing reaction of a copolymer D6 with C_4H_9Cl is more difficult than with the other quaternizing agent such as BzBr.

Analysis of Pyridinium Group Content (C_q) in Insoluble Pyridinium-Type Polymers

The C_q values of insoluble pyridinium-type polymers determined by the argentometry technique are listed in Table II, and the C_q values of a few representative samples, which are listed in Table III, were determined by the elemental analysis. By comparing the C_q values obtained by both the methods, it is found that for the sample Q-D6 containing a crosslinking agent DVB, the C_q obtained by the elemental analysis and the degree of quaternization (DQ) of pyridine rings calcu-

lated from C_q are greater than those by the argentometry, and the difference between the corresponding values obtained by the both methods cannot be attributed to experimental error. It should be noted that the result obtained by the elemental analysis is basically identical with the analysis of FTIR spectrum of Q-D6 showed in Figure 1. But for the samples Q-C0 and Q-D10 containing no DVB, the values of C_q and DQ obtained by the both methods are basically in concordance. This has been also proved by the analysis results of C_q in soluble pyridinium-type polymers determined by use of both argentometry and elemental analysis.[1] It seems to suggest that a small portion of pyridinium groups in the sample Q-D6 cannot react chemically with a titrant in the whole titrating process. The reason for it, we think, is that the sample Q-D6 possessing three-dimensional network structure can be only swelled and not dissolved in the titrating medium so as to restrain the reactivity of a portion of pyridinium groups to some extent and finally make them difficult to react with a titrant.

Besides, in the sample Q-C0-$C_4H_8Br_2$, which was prepared by quaternization of the DVB-free copolymer P(4VP-St) sample C0 with $C_4H_8Br_2$, C_q and DQ obtained by the elemental analysis are also greater than those by the argentometry and cannot be attributed to experimental system error. It is considered that the precursor copolymer C0 can react with a quaternizing agent $C_4H_8Br_2$ in two manners:[20] one reacting manner is that one molecule of $C_4H_8Br_2$ reacts simultaneously with two pyridine rings to produce two pyridinium groups linked with —C_4H_8—, leading to the crosslinking of the polymer backbone; another reacting manner is that one molecule of $C_4H_8Br_2$ reacts only with one pyridine ring to produce one pyridinium group, leading to the monofunctionalization of pyridine rings. In the former case with
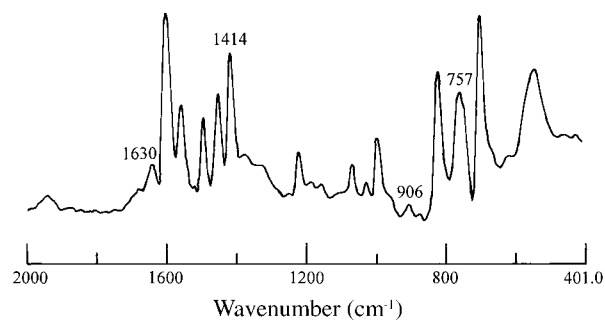

Figure 3 FTIR spectrum of Q-D6-C_4H_9Cl.

Table II Composition Analysis of the Insoluble Pyridinium-Type Polymers

Sample No.	C_q (mmol/g)	DQ (%)	Sample No.	C_q (mmol/g)	DQ (%)
Q-C0	2.94	98.47	Q-D8	2.99	84.59
Q-C1	2.56	81.61	Q-D9	3.19	81.46
Q-C2	2.56	82.46	Q-D10	3.52	97.72
Q-C3	2.52	81.42	Q-D6-BzCl	2.78	79.26
Q-C4	2.58	88.29	Q-D6-C_2H_5Br	2.55	65.29
Q-C5	2.14	68.18	Q-D6-C_2H_5I	2.70	86.28
Q-D3	1.76	93.73	Q-D6-C_4H_9Cl	0.075	1.40
Q-D4	2.15	90.75	Q-D6-C_4H_9Br	2.48	69.60
Q-D5	2.30	82.40	Q-D6-C_4H_9I	2.54	88.44
Q-D6	2.47	78.82	Q-D6-$C_8H_{17}Br$	1.89	55.01
Q-D7	2.87	86.55	Q-C0-$C_4H_8Br_2$	1.99	42.02

no monofunctionalization, all the bromine contained in the pyridinium group structure will be found in the ionic state, while only half of the total bromine bonded will appear in the ionic form and another half of the bromine bonded will appear in the covalent form when only monofunctionalization occurs. However, there is likely to be competition between the two processes, resulting in the polymer network structure as shown in Figure 4. The study of solubility of Q-C0 and Q-C0-$C_4H_8Br_2$ in organic solvents, which were quaternized with monofunctional BzBr and difunctional $C_4H_8Br_2$, respectively, shows that Q-C0 is soluble in glacial acetic acid, anhydrous ethanol, tetrahydrofuran, and dimethylformamide, while Q-C0-$C_4H_8Br_2$ is insoluble but swellable in these solvents. This testifies that the sample Q-C0-$C_4H_8Br_2$ indeed possesses the crosslinking structure, that is, there certainly exists the above-mentioned first reacting manner during the course of reaction of C0 with $C_4H_8Br_2$. Sample Q-C0-$C_4H_8Br_2$ contains not only ionically bonded bromine existing in the pyridinium form, but also covalently bonded bromine unreacting with a pyridine ring. According to the basic principles of the both analysis meth-

ods, the elemental analysis can determine the total bromine in the sample while the argentometry can only determine the ionically bonded bromine, which causes the bromine content determined by the elemental analysis is greater than that by the argentometry, so as to bring about the difference between the corresponding results calculated from the bromine content as listed in Table II and Table III. It is thus considered that the reaction of a precursor copolymer C0 with $C_4H_8Br_2$ can occur in the above-mentioned two manners.

By comparing the C_q and DQ values of Q-D6-C_4H_9Cl in Table II with the corresponding values in Table III, it is found that the C_q and DQ values of Q-D6-C_4H_9Cl obtained by the argentometry are identical with those obtained by the elemental analysis method on the whole. It is also identical with the result reflected in the FTIR spectrum of Q-D6-C_4H_9Cl as showed in Figure 3. It can be safely said that the quaternizing reaction of a copolymer D6 with C_4H_9Cl is very difficult.

From the above discussion it can be concluded that the C_q values of crosslinked pyridinium-type polymers determined by the argentometry are generally lower than those determined by the elemen-

Table III Elemental Analysis of the Insoluble Pyridinium-Type Polymers

Sample No.	N (%)	Br or Cl (%)	C_q (mmol/g)	DQ (%)
Q-C0	3.91	22.07	2.75	98.57
Q-D6	3.90	21.48	2.69	96.76
Q-D10	4.98	28.47	3.56	100.00
Q-C0-$C_4H_8Br_2$	5.73	17.69	2.21	54.03
Q-D6-C_4H_9Cl	7.87	0.27	0.08	1.42
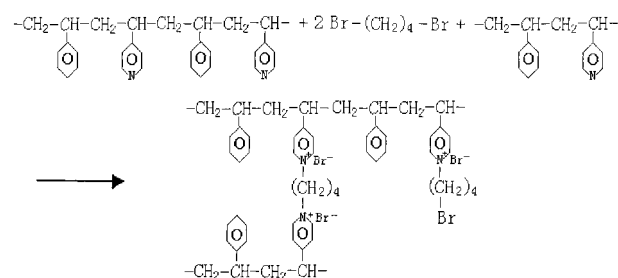
Figure 4 Scheme of reaction of the sample C0 with $C_4H_8Br_2$.

tal analysis, but the C_q values of linear pyridinium-type polymers determined by the both methods are basically the same. The reason for it can be found by carefully analyzing the principles and the procedures of argentometry. Seeing that a titration of the polymer samples is likely to be affected by macromolecular conformation in medium so that the titrating reaction could not be completed instantaneously, the manner of back titration in argentometry was selected to determine the pyridinium group content C_q in each Q-P(4VP-St-DVB) sample. It mainly includes following three steps: (1) the Q-P(4VP-St-DVB) sample reacts with an excess of concentrated nitric acid (HNO_3) using 50% acetic acid solution as the titrating medium to convert the pyridinium salts in halogen form into the pyridinium salts in nitrate form and to form free X^-; (2) a proper excess of 0.1N $AgNO_3$ standard solution is added to the above titrating system with producing AgX sediment; and (3) the unreacted $AgNO_3$ in the system is titrated by 0.01N NaSCN standard solution using ferric ammonium sulfate as an indicator. When a very small amount of excess NaSCN standard solution reacts with Fe^{3+} and the stable red color of $Fe(SCN)_3$ appears, the titration reaches an end point. In the titrating process, the reaction of pyridinium groups attached to macromolecular chains with HNO_3, that is, Step 1, is of crucial importance. It is obvious that the accuracy of titration depends on whether the reaction in Step 1 is fully conducted. In order to carry out the reaction to completion, the reaction has to continue for 2–3 h prior to implementing Step 3. When the determined sample is soluble in the titrating medium, the reaction can be carried out completely. This has been proved by the analysis result of C_q in soluble pyridinium-type polymers determined by use of both the argentometry and the elemental analysis.[1] However, when the determined sample is insoluble in the titrating medium but swellable, the reaction of pyridinium groups bonded onto its macromolecular chain with HNO_3 can not be carried out to completion since a portion of the pyridinium groups involved in the polymer network may not participate in the reaction. In this case, the halogen content determined by the back titration with NaSCN standard solution is on the low side so as to obtain slightly lower C_q and DQ values. The above analysis of the back titration procedure can explain the experimental result that the C_q and DQ values in the sample Q-D6 obtained by the argentometry are lower than those by the elemental analysis. In the meantime, it implies that the C_q value of an insoluble pyridinium-type polymer measured by the

argentometry is not its overall pyridinium group content, but rather reflects the content of the pyridinium groups which can participate in the titrating reaction in the process of measurement. So this C_q value is lower than the actual content of the sample and then the DQ value calculated from it is lower than the actual DQ value.

It should be pointed out that since a very small portion of pyridinium functional groups can not participate in the titration reaction in argentometry, they will similarly not be effective for interaction occurring between an insoluble pyridinium-type polymer and bacterial cells. Therefore, as for a study on the interaction between an insoluble pyridinium-type polymer and bacterial cells, it is not only reasonable but also more suitable to actual circumstances to use the data on C_q obtained by the argentometry as the standard of measuring the pyridinium group content in the polymer.

The Particle Structure and Surface Morphology of an Insoluble Pyridinium-Type Polymer

The particle structure and surface morphology of an insoluble pyridinium-type polymer are sure to have an effect upon the interaction between the polymer and bacterial cells. The SEM photographs shown in Figure 5 reflects the particle structure and surface morphology of the polymer.

It can be observed from the photographs that the polymer particles are formed by the gathering of smaller granules, which are uneven in size and whose surfaces are full of bumps and holes. Many very tiny holes exist on the surfaces of these granules, exhibiting porous morphology. The size of many tiny holes is less than 1 μ. The granule surface possesses very complicated fine structure.

CONCLUSIONS

The copolymers of 4-vinylpyridine (4VP), styrene (St), and divinylbenzene (DVB) with varied compositions, P(4VP-St-DVB), were synthesized and their compositions were analyzed. Among the comonomers 4VP, St, and DVB, DVB possesses the strongest reactivity. For this reason, when the mole fraction of 4VP and the total mole fraction of St and DVB in the monomer ratio were basically constant, the 4VP content in the copolymer P(4VP-St-DVB) was lower than that in the feed and decrease with an increase in the mole fraction of DVB in the feed. The existence of DVB resulted
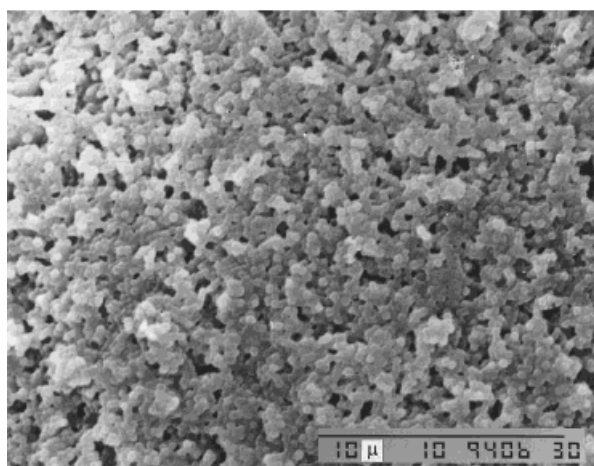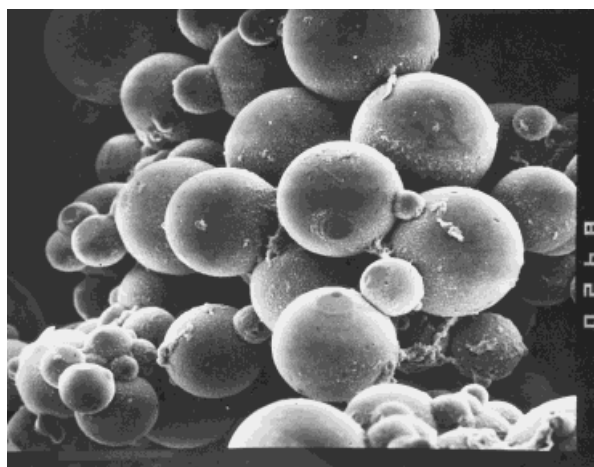
Figure 5 SEM photographs of the particle structure and the surface structure of an insoluble pyridinium-type polymer.

in an increase of the conversion of copolymerization under the same polymerization conditions.

The synthesized copolymers P(4VP-St-DVB) were quaternized with benzyl bromide (BzBr) or different halohydrocarbon (RX) as a quaternizing agent, respectively, thus producing the insoluble pyridinium-type polymers in the benzyl–pyridinium bromide form and in the alkyl–pyridinium halide form, that is, Q-P(4VP-St-DVB) and Q-P(4VP-St-DVB)-RX. The results of polymer characterization indicate that the pyridinium group content, C_q, in an insoluble (crosslinked) pyridinium-type polymer determined by the argentometry is generally lower than that determined by the elemental analysis, but the C_q values in a soluble (linear) pyridinium-type polymer

determined by the both methods are basically the same. The reason for it is that the insoluble polymer possessing three-dimensional network structure can be only swelled and not dissolved in the titrating medium so as to restrain the reactivity of a portion of pyridinium groups involved in its network to some extent, thus making them difficult to react with a titrant. It seems to suggest that the effect of a polymer network structure on a titrating reaction should be taken into consideration in view of specific conditions and requirements.

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