Water-Soluble Copolymers. I. Biodegradability and Functionality of Poly[(sodium acrylate)-*co*-(4-vinylpyridine)]

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ABSTRACT: As a biodegradable functional polymer, poly[(sodium acrylate)-*co*-(4-vi-nylpyridine)] [P(SA-*co*-4VP)] containing a small amounts of 4-vinylpyridine groups were prepared and their biodegradability, dispersity, and complex performance were analyzed. The polymers can be useful as detergent builders and dispersants. It was found that the biodegradation of P(SA-*co*-4VP) was more conspicuous when content of the 4-vinylpyridine in the copolymer was larger. This indicates that the 4-vinylpyridine, which acts as biodegradable segments, should be incorporated into the polymer main chain in such a manner that they are digested by activated sludge. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1953–1957, 1999

Key words: poly[(sodium acrylate)-*co*-(4-vinylpyridine)]; biodegradability; functionality

INTRODUCTION

Water-soluble polymers have become increasingly important in industrial applications over the past several decades. In particular, polyelectrolytes are commonly utilized in commercial processes as detergent builders and dispersants.^{1,2} A widely used polymer-type detergent builder or dispersant is synthetic poly(sodium carboxylate),³ in which the polymer chains contain carboxylic acid only. However, high-molecular-weight synthetic poly(sodium carboxylate) is generally highly resistant to biodegradation.^{4,5} On the other hand, nonbiodegradable water-soluble used polycarboxylate, especially as detergent builder, will be a new environmental polluter to rivers and near seas. Therefore, it is necessary that the synthetic poly(sodium carboxylate) should have good biodegradability with fine functionality. The introduction of biodegradable segments into the main chain of the synthetic polymer is one way to design a biodegradable polymer because these segments are cleaved by the degrading enzymes of environmental microbes to produce low-molecular-weight fractions, which are further assimilated by the microbes.^{6–12}

In this work, the copolymers of acrylic acid (AA) with a small amounts of 4-vinylpyridine (4VP) in the backbone as biodegradable segments were prepared by radical polymerization and subsequent neutralization with sodium hydroxide (NaOH). The relationship between the 4-vinylpyridine content in the copolymers main chain and the biodegradability as well as functionality was studied.

EXPERIMENTAL

Materials and Measurements

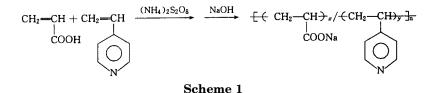
All materials were of the highest available purity and used as purchased. Fourier transform infra-

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Contract grant sponsors: Natural Science Foundations of the Guangdong Advanced Educational Department and the South China University of Technology.

Journal of Applied Polymer Science, Vol. 71, 1953-1957 (1999)

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red (FTIR) spectra were measured using a Analect RFX-65 Fourier Transform Infrared Spectrometer. Viscosity-average molecular weight (\bar{M}_{η}) was measured by viscosimeter. The molecular weights of P(SA-*co*-4VP) were estimated by gel permeation chromatography (GPC; column, shimpack DIOL-300; eluant, 0.01*M* phosphate buffer + 1.0*M* sodium chloride, pH 7.0; poly(vinyl alcohol) standard).

Preparation of Poly[(sodium acrylate)-*co*-(4-vinylpyridine)]s

Poly[(sodium acrylate)-co-(4-vinylpyridine)] [P(SAco-4VP)] was prepared by radical copolymerization of AA with 4VP and subsequent neutralization with NaOH, as shown in Scheme 1. Composition of the polymer, as well as the amount of the pyridine group contained in the polymer were ascertained based on the content of nitrogen determined by elemental analysis of the polymer.

Biodegradation Test

The biochemical oxygen demand (BOD) was determined by the oxygen consumption method, basically according to the ISO 5815-1983(E) at 20°C using activated sludge, which comes from Datansha Sewage Works in Guangzhou. The concentration of the polymer in the incubation media was 25 ppm. The residual polymers present in the culture media before and after the biodegradation test (BOD test) were analyzed directly by GPC after ultrasonic treatment with a small amount of a nonionic surfactant to avoid any adsorption loss of the polymer onto the microbial cell.⁸

Dispersive Power Test

The dispersive power was determined by KMnO_4 method at a total polymer concentration of 500 ppm and 1 g MnO_2 (chemical powder) after mixing and statically placing for 4 h at 25°C.⁷ The dispersive power was expressed as the amount of MnO_2 in mg in 100 mL of the suspension.

Calcium Sequestration Capacity

The calcium sequestration capacity⁸ was determined using a calcium ion electrode (Model PCa-1, Electric-light Appliance Works, Shanghai) at a total polymer concentration of 2.0×10^{-2} wt %, a total calcium concentration of $1.0 \times 10^{-3}M$ and an ionic strength (μ) of 0. 08*M* KCI was maintained with KCI at 25°C. The calcium sequestration capacity was expressed as the amount of calcium ions in grams sequestered by 100 g of the polymer.

RESULTS AND DISCUSSION

P(SA-*co*-4VP) was prepared by radical copolymerization of acrylic acid with 4VP in order to incorporate 4VP into the polymer main chain with subsequent neutralization (Scheme 1).

Table I shows the synthesis and composition analytical data of P(SA-co-4VP). By varying the content of 4VP in monomer mixture, the 4VP content in the copolymer varied from 0.6 to 8.7 mol %, but these polymers kept a approached \bar{M}_{η} . In addition, by varying the polymerization conditions, such as the concentration of initiator, the chain transfer agent, and the reaction temperature, the different \bar{M}_{η} polymers maintained with 3.3 mol % 4VP in the copolymers were obtained.

To characterize P(SA-co-4VP), the FTIR spectra of the polymers were measured. Figure 1 shows the spectra of A-5 and A-1. The homopolymer of sodium acrylate (A-1) exhibit three bands characteristic absorption peaks of —COOH located 3425 (O—H stretching) and 1700 cm⁻¹ (C=O stretching), and —COO⁻ located 1400–1600 cm⁻¹.¹⁴ These spectral features were similar to those in A-5. However, the spectrum of A-5 gave a new peak at 2362 cm⁻¹, as signed to the absorbance of quaternized pyridine ring (C=NH[⊕]). The above analyzed results show that carboxyl and pyridyl groups in P(SA-co-4VP) could contain partially ionic interaction.¹⁴⁻¹⁶

Figure 2 shows the relationship between biodegradability (BOD_5/TOD) after 5 days of incubation calculated by the BOD value and the theoretical oxygen demand (TOD), and the 4-vinylpyridine content in the polymer. It was found that the biodegradability was dependent on the content of 4VP group in the polymer main chain,

Polymer	4VP Content in Monomer Mixture (mol %)	4VP Content in Copolymer (mol %)	${ar M}_\eta \ (imes 10^4)^{ m a}$	Neutralized Extent of —COOH in Theory (mol %)	Chain Transfer Agent
A-1	0.00	0.0	1.40	90	H_3PO_2
A-2	0.68	0.6	1.46	90	$H_{3}PO_{2}$
A-3	1.36	1.6	1.28	90	$H_{3}PO_{2}$
A-4	2.04	2.5	1.23	90	$H_{3}PO_{2}$
A-5	3.41	3.4	1.52	90	$H_{3}PO_{2}$
A-6	6.81	5.6	1.79	90	H_3PO_2
A-7	13.62	8.7	1.43	90	H ₃ PO ₂
B-1	3.31	3.3	3.20	90	HSCH ₂ CH ₂ OH
B-2	3.31	3.3	7.36	90	HSCH ₂ CH ₂ OH
B-3	3.31	3.3	12.52	90	HSCH ₂ CH ₂ OH
B-4	3.31	3.3	18.20	90	HSCH ₂ CH ₂ OH
B-5	3.31	3.3	28.05	90	

Table I Synthesis and Composition Analysis of P(SA-co-4VP)

^a The results based on $[\eta] = 1.55 \times 10^{-5} \bar{M}_n^{0.9}$ (Hanabusami¹³).

and the biodegradation of P(SA-co-4VP) was more conspicuous when content of the 4VP in the copolymer was larger. Because the neutralized extent of —COOH in the copolymer was 90 mol % (see Table I), and carboxyl and pyridyl groups in P(SA-co-4VP) contain partially ionic interaction, the content of quaternized pyridine (pyridinium) group in the copolymer was larger when content of 4VP was larger. The presence of pyridinium group in the copolymer enhances copolymer's affinity with cells of microorganisms; therefore, this

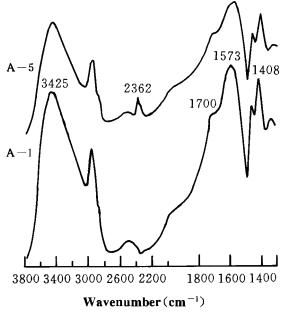


Figure 1 FTIR spectra of A-5 and A-1.

biodegradability of the polymer was more significant when content of the pyridinium group was larger.¹⁰ Based on these reasons, it is suggested that the decisive factor for the biodegradation by activated sludge is the 4VP content in the copolymer.

Figure 3 shows the correlation between BOD₅/ TOD and \bar{M}_{η} . It was confirmed that low \bar{M}_{η} P(SAco-4VP) was more easily degraded than was the high \bar{M}_{η} P(SA-co-4VP).

The GPC curves of A-5 are given in Figure 4. The biodegradation test was performed according to the closed bottle test. The polymer was gradually reduced, and after 14 days of incubation, the

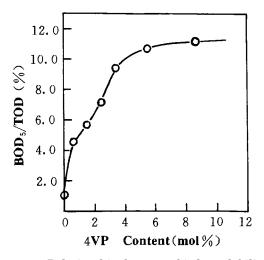


Figure 2 Relationship between biodegradability of P(SA-co-4VP) (BOD₅/TOD) and the 4VP content of A series.

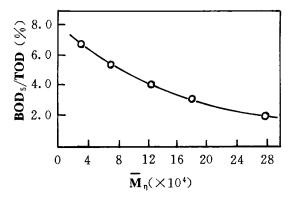


Figure 3 Relationship between biodegradability of P(SA-co-4VP) (BOD₅/TOD) and the M_n of B series.

original polymer was degraded to great extent. From these results, P(SA-co-4VP) was biodegraded by the activated sludge. It suggest that these polymers are environmentally biodegradable.

It was reported that high-molecular-weight poly(sodium carboxylate)s containing carboncarbon backbones exhibit an excellent builder performance in heavy duty detergent formulations as a substitute for sodium triphosphate (STPP) builder.^{17,18} However, these polymeric polycarboxylates are extremely resistant to biodegradation, which is an important criterion for environmentally acceptable compounds. In this report, the detergency builder performance of P(SA-co-4VP) was evaluated on an equal weight

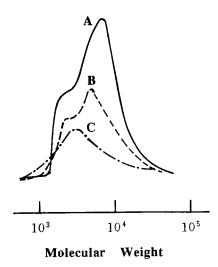


Figure 4 GPC profiles of A-5 before and after the biodegradation by activated sludge in the closed bottle. (A) 0, (B) 5, and (C) 14 days.

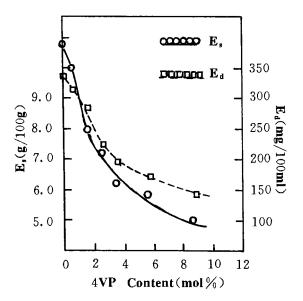


Figure 5 The calcium sequestration capacity (E_s) and dispersive power (E_d) expressed as a function of the 4VP content of the A series.

basis by the calcium sequestration capacity. The target is shown as a function of the 4VP content in Figure 5. It was found that calcium sequestration capacity is dependent on the content of the acrylate fractions in the polymer. The polymers with high acrylate contents have high calcium sequestration capacity, which is most indispensable for a detergent builder. In an aqueous polymer solution, the calcium ion is sequestered into the anionic domain, which is created by the neighboring carboxylate groups in the copolymer chain. Therefore, the calcium sequestration capacity is dependent on the amount of carboxylate groups in the copolymer chain when compared on an equal weight basis.

The sodium polyacrylate in which the polymer chains contain acrylic acid only is a widely used polymer-type dispersant. If other components, such as 4VP, are introduced into the polymer, the second component will influence the adsorption of the polymer, the charge density of the particles adsorbed by it, and, consequently, the dispersing ability of that polymer.^{19,20} The relation of dispersive power versus the 4VP content of P(SA-*co*-4VP) is shown in Figure 5. It was found that the dispersive power is dependent on the content of the acrylate fractions in the polymer as well as the calcium sequestration capacity. The polymers with high acrylate contents show a better dispersity.

Figure 6 shows the calcium sequestration capacity and dispersive power as a function of the

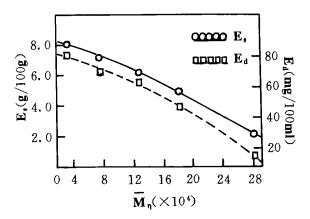


Figure 6 The calcium sequestration capacity (E_s) and dispersive power (E_d) expressed as a function of the \bar{M}_{η} of the B series.

 M_{η} of B series. The sequestrating and dispersing ability of P(SA-co-4VP) with the same composition decrease with increasing \bar{M}_{η} in the range studied. It is very clearly that too high-molecularweight P(SA-co-4VP)s are not appropriate for detergent builders and dispersants because their calcium sequestration capacity and dispersive power are all lower.

Biodegradability and functionality as builder and dispersant show inverse tendencies against the 4VP content. However, the low-molecularweight P(SA-*co*-4VP)s containing small amounts of 4VP, such as A-2, have good dispersing properties and biodegradability.

The authors thank both natural science foundations of the Guangdong Advanced Educational Department and the South China University of Technology for support of this research.

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