

Properties of Copolymers of Aspartic Acid and Aliphatic Dicarboxylic Acids Prepared by Reactive Extrusion

Randal L. Shogren,¹ J. L. Willett,¹ David Westmoreland,² Sergio O. Gonzalez,^{1*} Kenneth M. Doll,¹ Graham Swift²

¹Plant Polymer Unit, National Center for Agricultural Utilization Research, USDA/ARS, Peoria, Illinois

²Folia, Inc., Birmingham, Alabama

Received 30 April 2008; accepted 24 June 2008

DOI 10.1002/app.28944

Published online 10 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Aspartic acid is prepared chemically or by the fermentation of carbohydrates. Currently, low molecular weight polyaspartic acids are prepared commercially by heating aspartic acid at high temperatures (>220°C) for several hours in the solid state. In an effort to develop a more rapid, continuous, melt polymerization scheme, aspartic acid was copolymerized with adipic, azelaic, sebacic, and dodecanedioic acids using a vented twin-screw extruder. Copolymers having ratios of aspartic/diacid ≤ 16 and M_w up to 9100 were prepared at temperatures of 240–260°C and residence times of

only about 5 min. M_w generally increased with aspartic/diacid ratio but melt viscosities became very high and processing became difficult at ratios >16. Most of the copolymers exhibited inhibition of calcium carbonate precipitation at concentrations similar to that of pure polyaspartic acid and thus may find application as anti-scalants. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3348–3354, 2008

Key words: biodegradable; copolymerization; extrusion; polyamides

INTRODUCTION

Recently, the use of biobased products to replace those made from increasingly costly imported petroleum has gained momentum.^{1–4} For example, there is considerable interest in replacing polyacrylic acid, a petroleum-based, water soluble polymer, with a biobased alternative.^{5–9} Since polyacrylic acid is used as an antiscalant in water treatment and is not biodegradable, there is concern about possible accumulation in the environment and toxicity.⁶

Poly(aspartic acid) is being manufactured commercially and has begun to capture some of the market for water treatment polymers.¹⁰ The current process involves heating aspartic acid at high temperatures (220–270°C) for several hours to form polysuccinimide (PSI) followed by hydrolysis with NaOH solution to form Na polyaspartate.^{5,11,12} However, this process is rather slow and expensive due

to the high temperatures and long times required for such a solid state polyamidation.

To accelerate the reaction, a number of different solvents such as toluene, mesitylene, DMF, sulfolane, tetralin¹² and catalysts such as phosphoric acid, sulfuric acid, and salts thereof¹³ have been studied. The drawback of these methods is that the solvent and catalyst must usually be removed after reaction and this adds the cost of the product. An alternative method could involve adding a comonomer having a low melting temperature which would then transform the aspartic comonomer mixture into a melt. Reaction rates would be expected to be higher in the melt than solid state due to higher molecular mobility. There have been a number of previous studies of copolymerization of aspartic acid with other monomers such as 6-aminocaproic acid,¹⁴ 4-aminobenzoic acid,¹⁵ glutamic acid,¹⁶ lactide,^{17,18} and polyethylene glycol¹⁹ but these usually were conducted in the presence of solvent and catalyst. For this study, aliphatic diacids were chosen as comonomers because these have not been previously studied and diacids such as adipic and sebacic are readily available, inexpensive and biodegradable. Furthermore, molecular weights should be easily controlled by the ratio of diacid to aspartic acid.

The goal of this study was to prepare low molecular weight (1,000–5,000) copolymers of aspartic and aliphatic diacids via melt polymerization. This is the optimal molecular weight range for inhibiting precipitation of mineral salts by Na polyacrylate.²⁰ Reactive extrusion was chosen as the processing

The USDA neither guarantees nor warrants the standard of the product used in this study, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

*Present address: BASF Corporation, Freeport, Texas.

Correspondence to: R. L. Shogren (shogrerl@ncaur.usda.gov).

Contract grant sponsor: USDA/ARS, Folia, Inc. [Cooperative Research and Development Agreement (CRADA)], 58-3K95-3-0971.

Journal of Applied Polymer Science, Vol. 110, 3348–3354 (2008)
© 2008 Wiley Periodicals, Inc.

TABLE I
Source and Properties of Chemicals Used for Extrusion

| Name | Structure | Molecular weight | Melting temperature (°C) | Source |
|--------------------|---|------------------|--------------------------|--|
| L-Aspartic acid | HOOC—CH ₂ —CH(NH ₂)—COOH | 133.1 | >300 | Orsan, Amylum Group, Aalst, Belgium; SCOA, China |
| Adipic acid | HOOC—(CH ₂) ₄ —COOH | 146.1 | 152 | Aldrich, 99% |
| Azelaic acid | HOOC—(CH ₂) ₇ —COOH | 188.2 | 110 | Aldrich, 80% |
| Sebacic acid | HOOC—(CH ₂) ₈ —COOH | 202.3 | 135 | Aldrich, 99% |
| Dodecanedioic acid | HOOC—(CH ₂) ₁₀ —COOH | 230.3 | 128 | Aldrich, 99% |

method since twin-screw extruders can easily be configured to handle high viscosity melts, water of condensation can be vented off and the process is continuous. Experimental variables studied included extrusion temperature, ratio of aspartic to diacid and size of diacid (C6-C12). Samples were analyzed for molecular weight by GPC-MALLS and antiscalant activity by inhibition of calcium carbonate precipitation.

EXPERIMENTAL

Materials

Materials used for extrusion as well as source, structure, and melting temperatures are shown in Table I. Polyacrylic acid, sodium salt ($M_w = 5100$), and poly (α,β)-DL-aspartic acid, sodium salt ($M_w = 2100$), D₂O (99.96%D), and DMSO-d₆ (99.9%D) were from Sigma-Aldrich. Other chemicals were reagent grade.

Extrusion

A ZSK-30 twin-screw extruder (Coperion, Ramsey, NJ) was used with 30-mm diameter screws, L/D = 44 and 14 barrel sections. Barrel sections and screw elements were stainless steel to avoid corrosion and contamination of the products. The screw configuration consisted of four mixing sections located between barrel sections 4–5, 7–8, 10–11, and 13–14. The first mixing section had three kneading elements with 45° forward stagger angle and decreasing width. The three additional mixing sections each had two forwarding kneading elements (45° stagger), a neutral element (90° stagger) and a reverse element (45° stagger). The mixing sections were separated by vented barrel sections.

Aspartic acid and diacids were sieved then mixed and placed in a loss-in-weight feeder (Accurate, Whitewater, WI) over barrel section 1. Barrel sections 6, 9, and 12 were open (plugs removed) to allow evaporation of steam and suction trunks were placed over these. Feed rates were 0.11 lb/min and screw speeds were 100 rpm (except for aspartic/diacid = 16 where speed was increased to 150–180

rpm). The experimental design is shown in Table II. Samples were collected from the end of the extruder without a die, allowed to cool and then pulverized. Residence times were ~ 5 min as determined previously.⁸

Hydrolysis

Hydrolysis of the succinimide rings to the sodium salt form was conducted following the method of Mosig et al.²¹ Samples (1 g) were mixed with distilled water (30 g) and titrated with 1M NaOH using an autotitrator (Titronic Universal, Schott Instruments) in the pH stat mode at a pH of 9.5, temperature of 60°C for 1 h.

TABLE II
Experimental Design

| Sample no. | Diacid | Aspartic/diacid (mol/mol) | Temp (°C) |
|------------|---------------|---------------------------|-----------|
| 1 | Adipic | 4 | 260 |
| 2 | | 6 | 260 |
| 3 | | 8 | 260 |
| 4 | | 8 | 275 |
| 5 | | 8 | 260 |
| 6 | | 8 | 240 |
| 7 | | 8 | 220 |
| 8 | | 8 | 260 |
| 9 | | 10 | 260 |
| 10 | Azelaic | 10 | 260 |
| 11 | | 12 | 260 |
| 12 | | 12 | 260 |
| 13 | | 12 | 260 |
| 14 | | 14 | 260 |
| 15 | | Sebacic | 10 |
| 16 | 12 | | 260 |
| 17 | 14 | | 260 |
| 18 | 14 | | 260 |
| 19 | 14 | | 260 |
| 20 | 16 | | 260 |
| 22 | Dodecanedioic | 10 | 260 |
| 23 | | 12 | 260 |
| 24 | | 14 | 260 |
| 25 | | 16 | 260 |
| 26 | | 16 | 260 |
| 27 | | 16 | 260 |

FTIR

KBr pellets were made by grinding 1 mg sample with 200 mg anhydrous KBr in an agate mortar followed by compression in a Carver die and press at 10,000 psi for 2 min. FTIR spectra were obtained with a Thermo-Nicolet Avatar 370 FTIR.

NMR

Extruded samples (15 mg, PSI form) were dissolved in 0.7 mL DMSO- d_6 while hydrolyzed (sodium salt form) samples were dissolved in D_2O . 1H -NMR spectra were obtained at 25°C (60°C for PSI form in DMSO) on a Bruker Ultrashield 500 at 500 MHz.

Conversion

The amount of residual unreacted aspartic and diacids was estimated from the relative areas of the GPC refractometer peaks for the monomers and copolymer at 12.1–12.6 and 10–11 min, respectively. Weight percent of unreacted monomer was calculated as $100 A(\text{monomer}) / (A(\text{polymer}) + A(\text{monomer}))$.

GPC-MALLS

GPC-MALLS was carried out using a Waters 1525 HPLC system, a Waters 717 plus autosampler, a Waters 2414 refractive index detector and a Wyatt Technologies Dawn EOS light scattering detector. GPC analyzes were performed using a Polymer Labs aquagel-OH 30 column (300 \times 7.5 mm), an injection volume of 10 μ L of 1% solutions and a temperature of 30°C. The HPLC was set to an isocratic flow rate of 0.75 mL/min of a pH 7, 0.01M Na phosphate, 0.1M NaCl aqueous buffer solution. Values of refractive index increment (dn/dc) for the copolymers were determined to be 0.215 mL/g using the integrated signals from the refractive index detector and Wyatt Astra software. Weight and number average molecular weights were calculated using Wyatt Astra software.

Calcium carbonate crystallization inhibition assay

Stock solutions of 0.006M Na_2CO_3 and 0.006M $CaCl_2$ were filtered through 0.45- μ m nylon filters before use. These concentrations were chosen to mimic calcium carbonate concentrations usually encountered in clothes and dish washing (100–500 ppm).²⁰ Various amounts (0–0.1 mL) of 1% solutions of sample, pH 7, were added to 50 mL 0.006M Na_2CO_3 followed by immediate addition of 52 mL 0.006M $CaCl_2$. The mixtures were stirred with a magnetic stirrer for 10 min, aliquots added to 1-cm cuvettes and solution turbidities were assessed by measure-

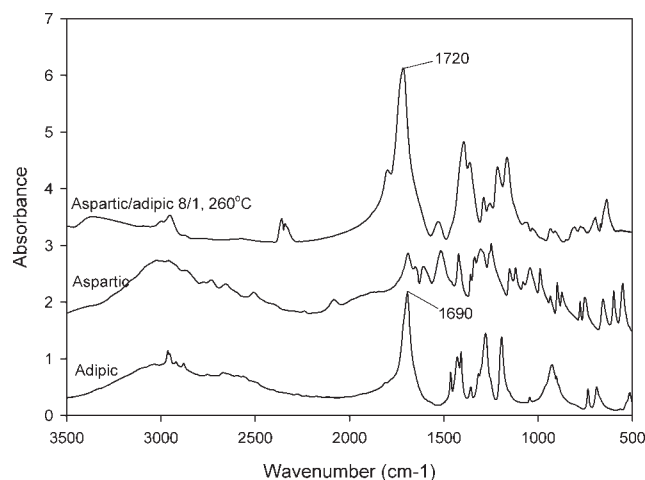


Figure 1 FTIR spectra of an aspartic/adipic acid copolymer extruded at 260°C, aspartic acid and adipic acid.

ment of absorbance at 400 nm. Plots of absorbance versus inhibitor concentration were used to determine at what concentration absorbance fell to 0.01 and this was designated the minimum inhibitory concentration (MIC).

RESULTS

The chemical structure of a copolymer made with aspartic acid/adipic acid 8/1 at 260°C was evaluated using FTIR and 1H -NMR. The FTIR spectrum of this sample (Fig. 1) as well as the rest of extruded samples (data not shown) had a large absorbance at 1720 cm^{-1} corresponding to carbonyl stretching in the succinimide residues.⁹ Ratios of 1H peaks at 4.6 and 4.4 ppm for the sodium salt of poly(aspartate-co-adipate) [Fig. 2(A)] which correspond to the methine proton for the alpha and beta forms indicated 22% alpha and 78% beta (see Fig. 3). This is close to the literature value of \sim 75% beta for thermal polyaspartates.²² Proton NMR spectra in DMSO [Fig. 2(B)] were similar to those published previously for polysuccinimide²³ with the addition of adipic CH_2 resonances at 1.5 and 2.1–2.2 ppm. A branch frequency of \sim 5 per hundred succinimide residues was estimated based on the areas of resonances at 4.6 and 8.5 ppm (CH and NH at branch points, respectively).²³

The effects of extrusion temperature on the conversion and properties of a copolymer made with aspartic acid/adipic acid 8/1 mol/mol are shown in Table III. Extrudates had the consistency of a thick, molten mass. Conversion, as measured by residual aspartic acid and adipic acid monomer, was rather low (59%) at 220°C then increased to >91% at 240–275°C. Molecular weights also increased significantly with temperature from 220 to 240°C then showed smaller increases above 240°C. On the basis of an

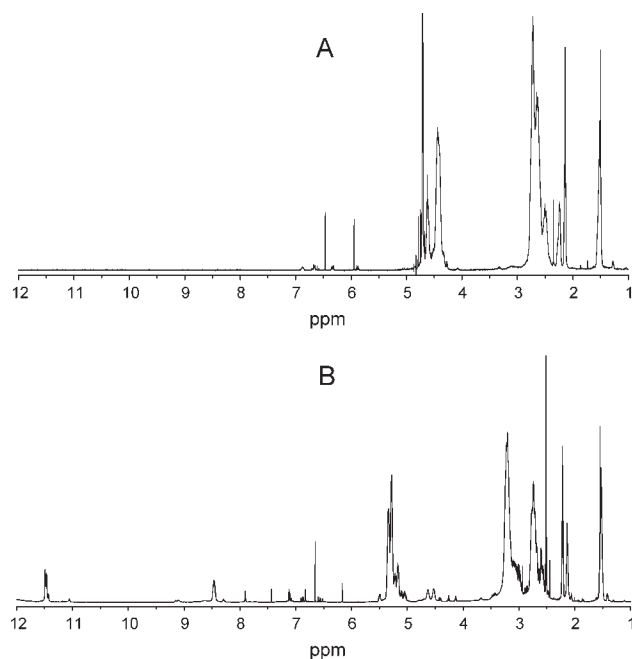


Figure 2 $^1\text{H-NMR}$ of aspartic/adipic 8/1 copolymer extruded at 260°C . (A) After hydrolysis (in D_2O), (B) Before hydrolysis (in DMSO-d_6 at 60°C).

idealized structure of one adipic acid and 8 aspartic acid residues (after hydrolysis of the succinimide residues to the sodium salt form, see Fig. 3), a molecular weight of 1294 can be calculated. This is rather close to the experimental value of M_n at 240°C (1560). Values of M_n for temperatures $\geq 260^\circ\text{C}$ (2200–2400) are somewhat larger, probably due to branching which is known to occur via the side chain carboxyl in uncatalyzed thermal aspartic polymerizations.²³ Titration results indicated a carboxyl content of 9.4–9.8 meq/g (PSI form). This is slightly lower than a value of 10.6 meq/g calculated for the idealized structure in Figure 1. Extruder motor torque values increased with temperature due to increases in molecular weight and hence melt viscos-

ity. Colors of the products darken significantly as temperature increased over 240°C , perhaps due to side reactions such as deamidation and decarboxylation. For example, previous NMR studies of thermal poly(succinimides) have demonstrated the presence of fumaramide and maleimide units resulting from deamination reactions and alanine residues resulting from decarboxylation.²³

The effect of monomer composition on extruder torque for extrusion temperatures of 260°C is shown in Figure 4. For adipic acid (C6), torque increased rapidly at monomer ratios of aspartic/adipic >10 so that it was not possible to extrude at higher ratios. Using azelaic acid (C9), compositions of aspartic/azelaic acid up to 14 could be extruded. Using sebacic and dodecanedioic acids (C10, C12), compositions having aspartic/diacid ratios up to 16 could be extruded. Thus, diacids with longer hydrocarbon chains facilitated a greater plasticization of aspartic-diacid copolymers and allowed the extrusion of copolymers with larger aspartic/diacid ratios and hence higher molecular weights (see below).

Weight percent of residual (unreacted) monomer (aspartic + diacid) as a function of starting composition are shown in Figure 5. The results are the inverse of those for extruder torque, i.e., residual monomer decreases as the aspartic/diacid ratio increases and as torque increases. This behavior may be due to localized heating of the melt above the set temperature due to mechanical energy input through the screw. Conversions greater than 96% were obtained at torque values of $>50\%$.

Weight and number average molecular weights for Na poly(aspartate-co-diacid) polymers are shown in Figure 6. As expected, both M_w and M_n increased with increasing aspartic/diacid ratio. There was, however, no significant dependence of molecular weight on type of diacid at a constant aspartic/diacid ratio. Values of M_w and M_n up to 9100 and 7200, respectively, were obtained for aspartic/

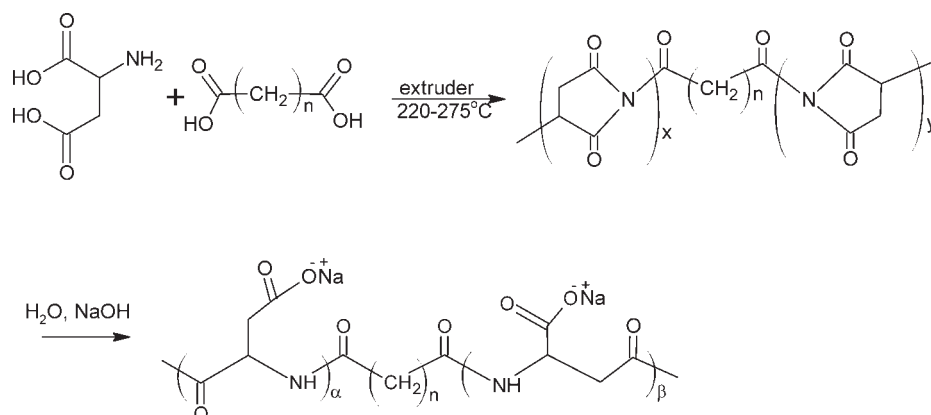


Figure 3 Idealized reactions for copolymerization of aspartic and dicarboxylic acids. For simplicity and clarity, branches were not included.

TABLE III
Effect of Extrusion Temperature on Conversion and Properties for Aspartic Acid/Adipic Acid 8/1 (mol/mol)

| Temperature (°C) | Torque (%) | Color ^a | Residual monomer (wt %) ^b | Titration (meq/g) | M_w | M_n |
|------------------|------------|--------------------|--------------------------------------|-------------------|------------|------------|
| 220 | 13 | Off-white | 41 | 10.65 | 1700 | 830 |
| 240 | 21 | Light tan | 8.1 | 9.76 | 2600 | 1560 |
| 260 | 26 ± 3 | Tan | 6.5 ± 0.3 | 9.41 ± 0.05 | 3400 ± 370 | 2300 ± 250 |
| 275 | 27 | Brown | 6.5 | 9.39 | 3500 | 2500 |

^a Color of extruded product before hydrolysis.

^b From GPC.

dodecanedioic acid copolymers. This is slightly higher than is usually obtained for conventional thermal, solid state polymerization of aspartic acid (1000–5000).⁵

Data for the minimum concentration of Na poly(aspartate-*co*-diacid) needed to inhibit precipitation of a supersaturated solution of CaCO₃ (300 ppm) (MIC) are shown in Figure 7. There was no significant dependence of MIC on either aspartic diacid ratio or type of diacid within experimental error. Combining all data for Na poly(aspartate-*co*-diacid) at 260°C, one obtains MIC = 2.4 ± 0.4 ppm. This compares to 1.7 ± 0.3 ppm for Na poly(acrylate) and 2.8 ± 0.2 ppm for Na poly(α,β)-DL-aspartate (presumably prepared by thermal, solid state polymerization). Thus, MIC for the sodium salts of polyaspartic acid prepared by heating of aspartic acid in the solid state and aspartic/diacid copolymers prepared by extrusion are similar within experimental error while MIC for sodium polyacrylate is significantly lower. One possible reason for the greater activity for Na polyacrylate is that it has a lower monomer molecu-

lar weight and hence a higher charge density, 10.6 meq/g compared to Na polyaspartate, 7.2 meq/g.

DISCUSSION

In summary, this study demonstrated that addition of small amounts of aliphatic dicarboxylic acid comonomer to aspartic acid transforms the polymerization from a solid state to a melt state reaction at temperatures of ≥220°C. Using a twin-screw extruder, reactions were complete within the approximate 5 min residence time at temperatures of ≥240°C. This is much faster than reaction times of several hours usually required for the solid state polymerization of aspartic acid alone and points to the importance of enhancing molecular mobility to increase polyamidation rate. Twin-screw extruders are well-suited to such melt reactions because water of condensation can easily escape from the thin layer of viscous reactants covering the screws. Although residence time in the extruder was not specifically studied, it is well-known that lower feed rates

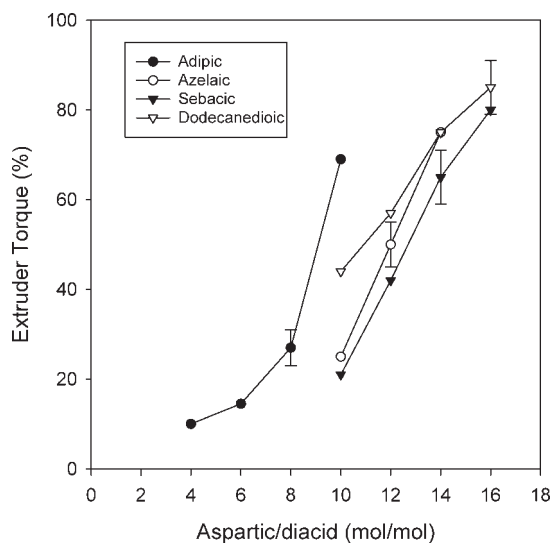


Figure 4 Effect of monomer composition on extruder torque.

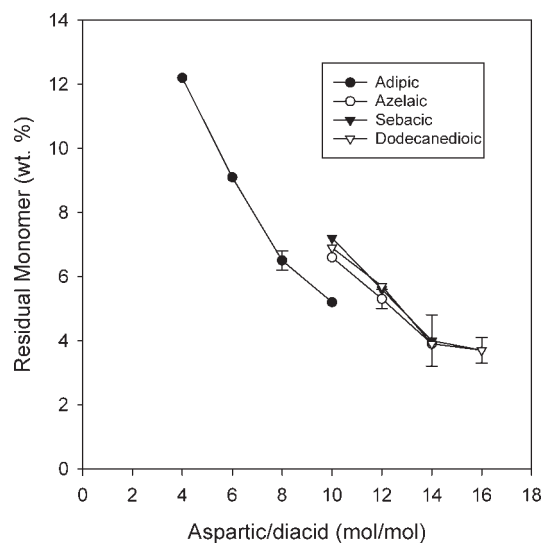


Figure 5 Effect of monomer feed composition on total residual monomer.

increase residence time thus increasing extent of reaction.⁸

Nakato et al.²⁴ have reported previously on the preparation of polyaspartic acid by twin screw extrusion of aspartic acid with 10 mol % phosphoric acid at 260°C. High conversion and molecular weights of 23,000 were obtained but extensive washing with water was necessary to remove phosphoric acid after reaction. Thus, the advantages of copolymerization of aspartic acid with dicarboxylic acids include no need to remove solvents or byproducts after reaction and control of molecular weight via aspartic/diacid ratio.

The presence of the dicarboxylic acid comonomer as well as molecular weight seemed to have little effect on the ability of the Na poly(aspartate-diacid) copolymer to inhibit precipitation of calcium carbonate in supersaturated aqueous solutions. It is thought that anionic polymers prevent mineral salt precipitation by binding to the surface of growing nanocrystals and disrupting further crystal growth.^{25,26} Whether the hydrophobic diacid residue actually binds to the CaCO₃ mineral surface is unknown. Hydrophobically modified polyaspartates have been prepared by reaction of polysuccinimide with hydrophobic amines followed by base hydrolysis.^{27,28} Such derivatives had better MnO₂ dispersing activity than pure polyaspartate²⁸ suggesting a tendency of the hydrophobic group to bind to the mineral surface. Further work could be done on the Na poly(aspartate-diacid) copolymers to determine if these also have soil dispersion or surfactant properties. Nakato et al.²⁴ found that pentamers of L-aspartic acid had similar calcium chelating ability as polyaspartic acid up to molecular weights of 80,000. Ross et al.²⁹ found that polyaspartates of molecular

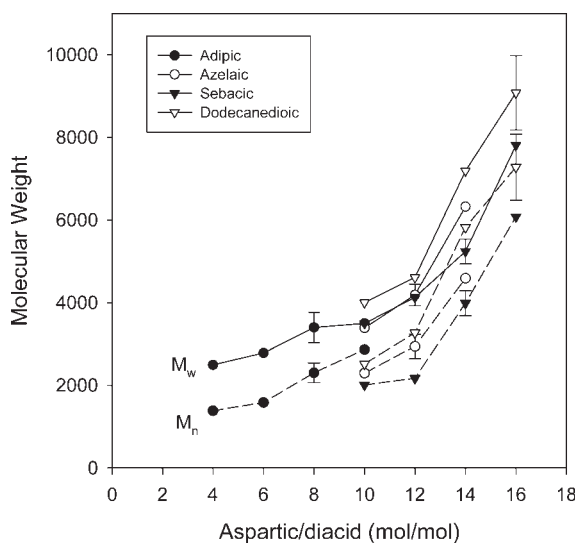


Figure 6 Effect of monomer composition on molecular weights.

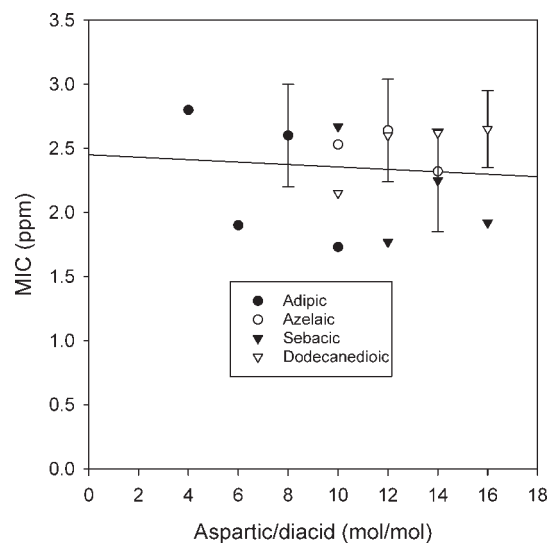


Figure 7 Effect of monomer composition on minimum concentration of Na Poly(aspartate-co-diacid) needed to inhibit precipitation of 300 ppm CaCO₃ (MIC).

weight 1000–4000 were most effective for inhibiting different mineral scales while Yang et al.³⁰ found that a molecular weight of 10,000 was best for CaCO₃. These data support our finding that molecular weight in the 1000–7000 range is not an important parameter in determining the ability of the Na poly(aspartate-diacid) copolymers to bind to CaCO₃ and prevent precipitation.

There are a number of other potential applications for Na polyaspartates and Na poly(aspartate-diacid) copolymers such as corrosion inhibitors,³¹ viscosity reducing aids for drilling fluids,³² hydrogels³³ and metalworking fluids³⁴ and these can be the subject of future studies. In addition, the biodegradability of aspartic copolymers can be the subject of future experimentation.

The technical assistance of Elizabeth Krietemeyer, Brian Jasberg, Gary Grose, Kelly Utt, and Kathy Hornback is gratefully acknowledged.

References

- Bastioli, C. *Starch/Stärke* 2001, 53, 351.
- Dale, B. E. *J Chem Technol Biotech* 2003, 78, 1093.
- Stewart, R. *Plast Eng* 2007, 63, 24.
- Gross, R. A.; Kalra, B. *Science* 2002, 297, 803.
- Low, K. C.; Wheeler, A. P.; Koskan, L. P. *ACS Sympos Ser* 1996, 248, 99.
- Swift, G.; In *Degradable Polymers*; Scott, G., Ed.; Academic: The Netherlands, 2002, p 379.
- Schwamborn, M. *Polym Degrad Stab* 1998, 59, 39.
- Shogren, R.; Gonzalez, S.; Willett, J. L.; Graiver, D.; Swift, G. *J Biobased Mater Bioenergy* 2007, 1, 229.
- Swift, G.; Westmoreland, D. G.; Willett, J. L.; Shogren, R. L.; Doll, K. M. U.S. Pat. 7,256,251 (2007).
- Reisch, M. S. *Chem Eng News* 2002, 80, 23.

11. Roweton, S.; Huang, S. J.; Swift, G. J *Environ Polym Degrad* 1997, 5, 175.
12. Thombre, S. M.; Sarwade, B. D. J.; *Macromol Sci Part A: Pure Appl Chem* 2005, 42, 1299.
13. Ross, R. J.; Batzel, D. A.; Meah, A. R.; Kneller, J. F. *Macromol Symp* 1997, 123, 235.
14. Kakuchi, T.; Minako, S.; Shigeyuki, M.; Takeshi, N.; Masayuki, T. *J Polym Sci Part A: Polym Chem* 1997, 35, 285.
15. Nakato, T.; Tomida, M.; Kusuno, A.; Shibata, M.; Kakuchi, T. *Polym Bull* 1998, 40, 647.
16. Rui, Z.; Tan, T. *J Appl Polym Sci* 2006, 100, 3626.
17. Arimura, H.; Ohya, Y.; Ouchi, T. *Biomacromol* 2005, 6, 720.
18. Shinoda, H.; Asou, Y.; Suetsugu, A.; Tanaka, K. *Macromol Biosci* 2003, 3, 34.
19. Sedlak, M.; Antonietti, M.; Colfen, H. *Macromol Chem Phys* 1998, 199, 247.
20. Zini, P. *Polymeric Additives for High Performing Detergents*; Technomic: Lancaster, PA, 1995; pp 1-65.
21. Mosig, J.; Gooding, C. H.; Wheeler, A. P. *Ind Eng Chem Res* 1997, 36, 2163.
22. Wolk, S. K.; Swift, G.; Paik, Y. H.; Yocom, K. M.; Smith, R. L.; Simon, E. S. *Macromolecules* 1994, 27, 7613.
23. Matsubara, K.; Nakato, T.; Tomida, M. *Macromolecules* 1997, 30, 2305.
24. Nakato, T.; Yoshitake, M.; Matsubara, K.; Tomida, M.; Kakuchi, T. *Macromolecules* 1998, 31, 2107.
25. Rieger, J. *Tenside Surfactants Detergents* 2002, 39, 221.
26. Dai, L.; Douglas, E. P.; Gower, L. B. *J Non-Cryst Solids* 2008, 17, 1845.
27. Kang, H. S.; Yang, S. R.; Kim, J.; Han, S.; Chang, I. *Langmuir* 2001, 17, 7501.
28. Nakato, T.; Tomida, M.; Suwa, M.; Morishima, Y.; Kusuno, A.; Kakuchi, T. *Polym Bull* 2000, 44, 385.
29. Ross, R. J.; Low, K. C.; Shannon, J. E. *Mater Perform* 1997, 36, 53.
30. Yang, S.; Huang, J.; Zhang, Y.; Tao, H. *Huagong Keji* 2003, 11, 24.
31. Zhou, B. *Corrosion Prot* 2006, 27, 26.
32. Leng, Y.; Huang, C.; Zhu, J.; Jiang, C.; Xu, L. *Specialty Petrochem* 2007, 24, 1.
33. Chang, C. J.; Swift, G. P. *J Macromol Sci Part A Pure Appl Chem* 1999, A36, 963.
34. Kalota, D. J.; Martin, D. A.; Silverman, D. C. *PCT Int. Appl. WO 9704052*, 1997.