

Preparation and Physical Properties of *N*-Defunctionalized Derivatives of Poly(aspartic acid)

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ABSTRACT: A number of *N*-substituted poly(aspartic acid)s was prepared under mild conditions using the silylation–alkylation technique. Their physical properties were studied. Free swelling capacity (FSC) tests were performed for polymers obtained by crosslinking the parent poly(aspartic acid) as well as its defunctionalized derivatives. The hypothesis that H-bonding is critical in superabsorbency was demonstrated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 85–90, 2001

Key words: poly(aspartic acid); defunctionalization; silylation; absorbency

INTRODUCTION

The development of biodegradable polymers is now highly urgent from the standpoint of environmental preservation. During the last 20 years, many biodegradable polymers have been reported.^{1–9} Biodegradable poly(aspartic acid) (PAA) based polymers are currently being investigated for many possible applications including use as scale inhibitors and dispersants,¹⁰ coatings, resin modifiers,^{11,12} drug carriers,^{13–17} chelating agents, fertilizers, and detergents,¹⁸ hair conditioners and fixatives,^{19–21} corrosion inhibitors,²² metal-working fluids,²³ and, especially, superabsorbent materials.^{7–9,24–26}

Currently, the major product used in the superabsorbent field is a polyacrylate-based material which is not biodegradable. Biodegradable PAA-based superabsorbent polymer (SAP) materials produced from relatively low molecular weight PAA (MW = 30,000–200,000) provide

higher absorbency. It seemed likely that hydrogen bonding in the PAA polymer plays a significant role in absorbency. In the present work, the N–H bond of PAA was defunctionalized in an attempt to help to understand the manner in which hydrogen bonding in PAA polymers affects the absorbency of SAP materials. Defunctionalized and undefunctionalized PAA were crosslinked to make SAP materials. As is shown later, none of the defunctionalized polymers gave significant improvements in absorbency. These findings support our theory that H-bonding in PAA-based polymers plays an important role in absorbency. Relatively low molecular weight polymers of PAA could give absorbency comparable with higher molecular weight polyacrylate-based SAP.

EXPERIMENTAL

Materials

L-Aspartic acid was obtained from Solutia Inc. (St. Louis, MO). Sodium hydroxide and hydrochloric acid were purchased from Fisher (Pittsburg, PA).

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Table I Characteristic NMR Signals for *N*-Defunctionalized PAA Derivatives 4a–c

Compound	R	NMR Signals of the R Substituent	
		¹ H-NMR (δ)	¹³ C-NMR (δ)
4a	Me	3.60 (3.44 ^a) (s, 3H, N—CH ₃)	41.2 (39.8 ^a) (N—CH ₃)
4b	—CH ₂ COOCH ₂ CH ₃	1.19 (t, <i>J</i> = 6.5 Hz, 3H, CH ₃)	13.9 (CH ₃), 47.3 (N—CH ₂)
		3.10–3.40 (m, 2H, N—CH ₂)	61.0 (O—CH ₂)
		4.10–4.16 (m, 2H, O—CH ₂)	
4c	—CH ₂ Ph	4.50 (s, 2H, N—CH ₂)	62.0 (CH ₂), 127.0, 128.1, 129.0, 139.0 (Ph)
		7.18–7.50 (m, 5H, Ph)	

^a NMR spectra were recorded in D₂O.

Phosphoric acid was purchased from Mallinkrodt Baker (Phillipsburg, NY). *N,N*-Dimethylformamide (DMF) was purchased from EM Science (Gibbstown, NJ). All other chemicals were purchased from Aldrich (Milwaukee, WI). All materials were used as received.

Preparation of PAA-based Polymers

L-Aspartic Acid Polycondensation

L-Aspartic acid, 133.4 g, and 126.4 g of 86.4% phosphoric acid were charged into a 2-L round-bottom flask. The flask containing the above mixture was attached to a rotary evaporator. The polycondensation reaction was carried out at 180°C in a silicon oil bath for 24 h under high vacuum. The solid polymer was dissolved into 700 mL DMF, and the polymer DMF solution was precipitated into 2 L water. The polymer was then milled by a blender and washed to pH 7.0, finally washed with DI water, and dried to constant weight to give 88 g polysuccinimide (yield: 78%).

SAP Powder Preparation

Into a round-bottom flask was added 2 g (20.6 mmol) of the polymer from step 1 [MW = 97,000 daltons by gel permeation size-exclusion chromatography (GPC)] and 60 g of water. The mixture was heated to 50°C. Added to the above mixture was 8.25 mL (20.6 mmol) of a 10% (by w/v) NaOH solution and the mixture was heated for another 1 h. After the reaction mixture was cooled to room temperature, 2.20 mL (3.62 mmol) of 5.83% (w/w) HCl was slowly added to the reaction mixture to pH 5.5. The reaction mixture was stirred at room temperature for another 2 h. The undissolved particles were removed by filtration. The filtrate was concentrated and the resulting thick solution

(about 50% solid) was admixed with 0.30 g (0.86 mmol) of a 50% ethylene glycol diglycidyl ether solution (in water). The solution was stirred at room temperature overnight. A thin film of the above mixture was dried under nitrogen gas and heated in an oven at about 140°C for 30 min to complete the crosslinking. Samples of the final product were taken for the standard tea bag test for absorbency in water and a saline solution.

Preparation of *N*-Alkylated Derivatives of PAA

A mixture of PAA (1.0 g, 8.7 mmol) and freshly distilled hexamethyldisilazane (2.0 g, 22.6 mmol) in DMSO (5 mL) was heated at 100°C for 48 h. After cooling to room temperature, an electrophile (21 mmol) and a fluoride anion donor (15 mmol) were added to the reaction mixture. The resulting mixture was stirred at room temperature for 72 h; then, water (50 mL) was added. The solution was transferred to a dialysis bag and subjected to dialysis at room temperature for 48 h. Water was then removed to afford the product as a light-brown solid.

Characteristic NMR data for *N*-alkylated PAAs 4a–c are presented in Table I. ¹H- and ¹³C-NMR spectra were recorded on a Gemini 300 MHz spectrometer (300 and 75 MHz, respectively) in DMSO-*d*₆ as a solvent (unless stated otherwise) and with TMS or a solvent, respectively, as an internal standard.

Preparation of SAP Powder Based on *N*-Alkylated Derivatives of PAA

The procedure was the same as that for making PAA-based SAP powder. Samples of the final product were taken for the standard tea bag test for absorbency in water and a saline solution.

Table II Reactions of Silylated PAA with Electrophiles

Product	R	X	Promoter	T (°C)	Yield (%)
3	Me	I	Bu ₄ NF	25	20
4a	Me	I	—	25	15
4a	Me	I	KF	25	50
4b	—CH ₂ CO ₂ C ₂ H ₅	Br	KF	60	41
4b	—CH ₂ CO ₂ C ₂ H ₅	Br	CsF	30	40
4c	C ₆ H ₅ CH ₂ —	Br	CsF	60	30
4d	—CH ₂ CH ₂ CH(CO ₂ C ₂ H ₅) ₂	I	KF	25	50

Analytical**GPC**

Molecular weight (MW) and the molecular weight distribution (MW_d) of sodium polyaspartate samples were determined from GPC experiments using TosoHaas TSK Gel G2500 PW 7.8 mm × 30 cm and TosoHaas TSK Gel G4000 PW 7.8 mm × 30 cm columns with 0.05M sodium phosphate (pH 7) as the carrier solvent. A Waters Differential (refractive index detector) or a SpectraPhysics SP8480XR (UV detector) 210 nm was used as a detector. Sodium polyaspartate samples were prepared by diluting about 0.06 g (28% polymer content) in a 10-mL mobile phase. PAA (MW ~ 40,000) was used as an external calibration standard. For a comprehensive examination of the procedure used in this analysis, refer to the Analytical and Measurement Technology (AMT) Standard Analytical Methods (SAM) AMT-SAM-001 and AMT-SAM-002 dated July 12, 1995.

Thermogravimetric Analysis (TGA)

T_g and T_m were determined by the TGA method using a DuPont 951 thermogravimetric analyzer at a heating rate of 20°C/min and in 1% oxygen in nitrogen with a flow rate of 50 mL/min.

Free Swelling Capacity (FSC) Test

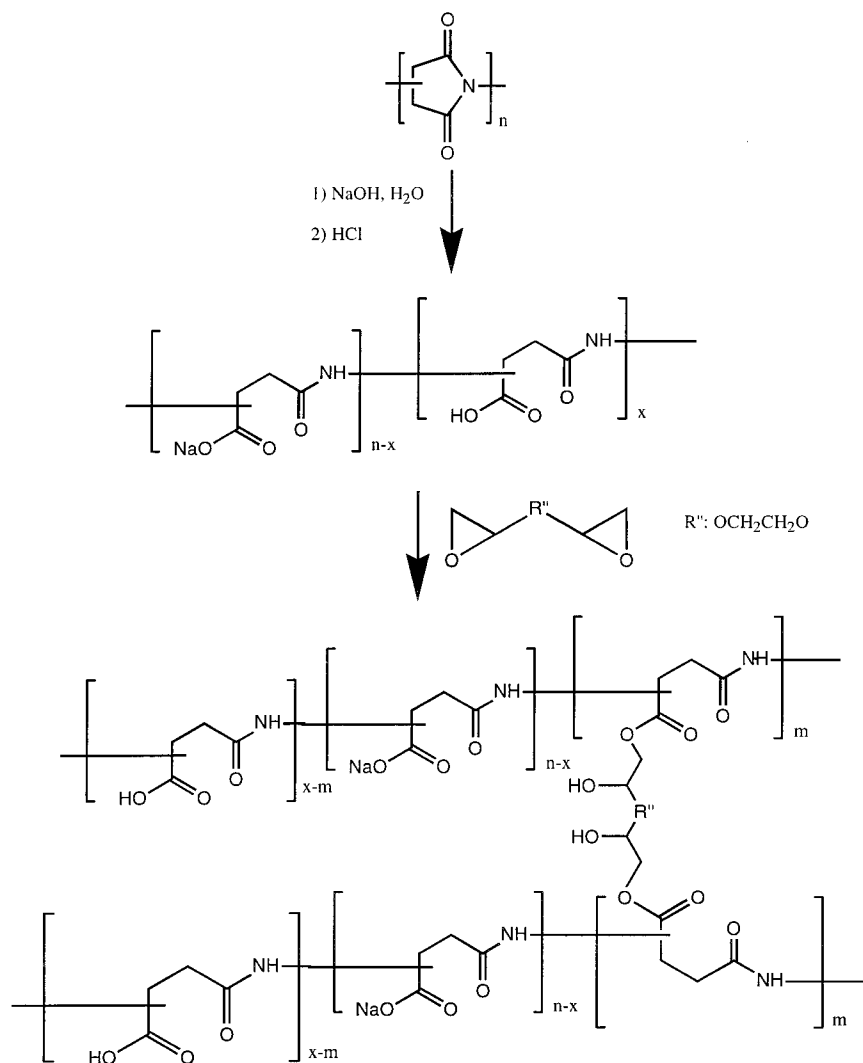
The tea bag test for measuring superabsorbence referred to above is conducted as follows: About 0.2 g of the SAP sample is placed in a tea bag-like pouch (2 in. × 2 in.) of nonwoven fabric and stapled. The tea bag is subjected to a 15-s immersion in a 0.9% saline solution or DI water, 1-min drip dry and weighing, followed by a 2-min 45-s immersion, 1-min drip dry and weighing, and then an additional 7-min immersion, 1-min drip dry, and weighing. The absorbencies for 15 s, 3 min, and 10 min are calculated according to the follow-

ing equation and the 10-min value reported as the superabsorbing performance:

$$\left[\begin{array}{l} \text{Absorbency (g/g)} \\ \\ = \frac{\text{weight of the treated sample} \\ - \text{weight of the SAP sample}}{\text{weight of the SAP sample}} \end{array} \right]$$

RESULTS AND DISCUSSION**Preparation and Chemistry of PAA-based SAP Powder**

PAA is prepared by thermal polycondensation of L-aspartic acid.²⁷ PAA-based polymers are very brittle and do not have a T_g or T_m . Scheme 1 shows the method used for the preparation of SAP powder utilizing diepoxide as a crosslinker. The resulting polymers were reacted with sodium hydroxide to give hydrolyzed polymers, which were partially acidified to pH 5.5 with a hydrochloric acid solution. The undissolved particles were removed by filtration. The filtrate was concentrated and the resulting thick solution (about 50% solids) was admixed with 50% ethylene glycol diglycidyl ether (EGDE) (Scheme 1). To make powders, a thin film of the above polymer mixture was dried by nitrogen gas and heated in an oven at about 140°C for 30 min to complete the crosslinking. Samples of the final product were taken for the standard tea bag test for absorbency in water and a saline solution.⁷ One gram of this SAP powder absorbs 101 g of water and about 36 g of the saline solution in 10 min.



Scheme 1 Preparation of PAA-based SAP powder.

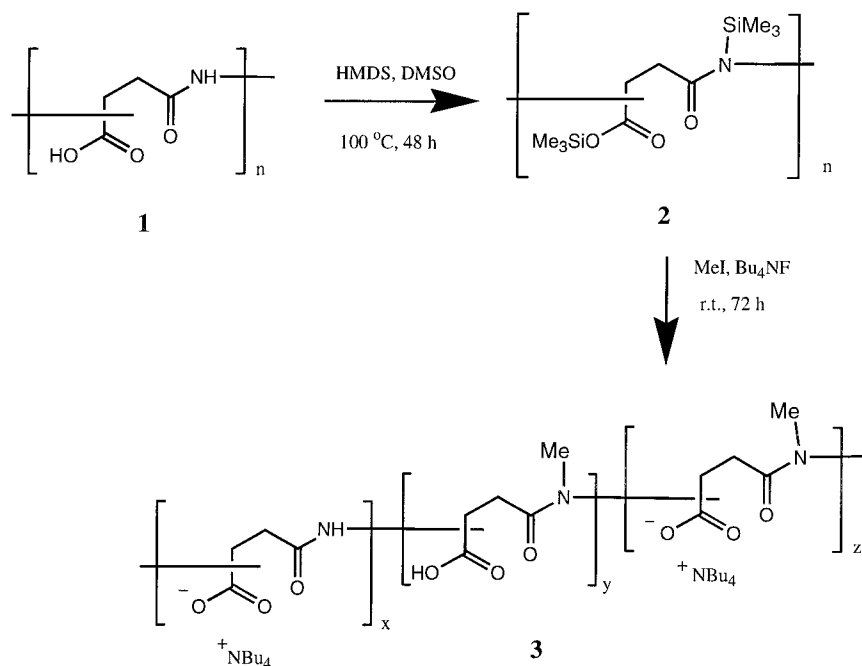
Defunctionalization of N—H Bond of PAA Using Silylation Technique

A possible method to introduce functional groups into PAA would be to utilize the nucleophilicity of the amide group in PAA. However, the intrinsic low nucleophilicity of the amide nitrogen is expected to be further reduced in polymeric PAA due to steric factors. Nucleophilicity is much increased in an amide anion compared to a neutral amide²⁸; however, attempts to react PAA and alkyl halides under basic conditions gave polysuccinimide as a major side-reaction product.

A general method for the activation of an amino or amido group for further transformations is based on treatment of the N—H functionality with an appropriate silylation reagent, such as hexamethyldisilazane (HMDS). Nitrogen anions

generated *in situ* from such *N*-silylated intermediates by treatment with a fluoride anion donor (Bu_4NF , KF , CsF , etc.) readily react with electrophiles.^{29–32} Although various types of amides and amines have been modified by this procedure, to our knowledge, no previous application of this method to polyamides has been reported.

The PAA used in the subsequent defunctionalization reactions was prepared by the hydrolysis of polysuccinimide (PSI) under basic conditions according to the literature procedure.²⁷ Silylation of PAA **1** using hexamethyldisilazane (HMDS) in DMSO at 100°C gave the corresponding trimethylsilyl derivative **2** (Scheme 2). Subsequent alkylation of **2** *in situ* with MeI in the presence of Bu_4NF under mild conditions afforded **3** with $x:(y:z) = 5:1$ as was confirmed by ^1H - and ^{13}C -

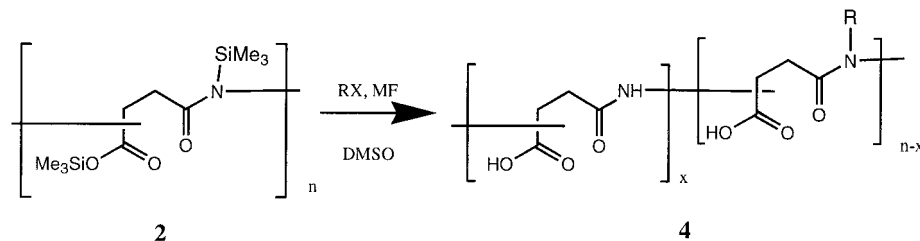


Scheme 2 Preparation of *N*-methylated PAA **3**.

NMR spectra [for *N*-Me group, δ_{H} 3.44 ppm and δ_{C} 41.2 ppm (in DMSO- d_6) (see Experimental section)]. However, $^1\text{H-NMR}$ also indicated the presence of the *n*-butyl group (presumably as a constituent of the tetrabutylammonium cation) in the spectrum of product **3** (Scheme 2). Carrying out this reaction without any fluoride anion donor gave *N*-methylated polymer **4a** in 15% yield. The attempts to vary the solvent by replacing DMSO with DMF were unsuccessful: after dialysis of the reaction mixture, only the starting materials were recovered. In a similar reaction of **2** with ethyl bromoacetate in DMSO, no formation of the product **4b** was observed. This prompted us to investigate the possibility of applying other potential fluoride anion donors, which would allow us to increase the yield of an *N*-alkylated PAA, altogether avoiding the formation of the quaternary salts. We found that inorganic fluorides KF

and CsF can be used successfully for the alkylation of **2** with various electrophiles (Scheme 3, Table II). For example, alkylation of **2** with methyl iodide in the presence of KF afforded **4a** with 50% degree of alkylation. The effect of the nature of a cation in an inorganic fluoride is negligible: Alkylation of **2** with ethyl bromoacetate in DMSO in the presence of KF or CsF gave similar results (see Table II).

Although the yields of the products **4** (Table II) range from low to moderate, the silylation-alkylation technique of the defunctionalization of PAA has some definite advantages: (i) the formation of a trimethylsilyl ester prevents possible side reactions on the carboxylic group, and this trimethylsilyl protection can be removed easily during the dialysis; (ii) activation of the amide group, protection of the carboxylic group, and alkylation could be carried out in one pot; and (iii) reactions of the



Scheme 3 Alkylation of *N*-silylated PAA.

silylated PAA with electrophiles occur under mild conditions.

Physical Properties of Defunctionalized Aspartic Acid Derivatives

Thermal properties of defunctionalized derivatives **4a–d** of PAA were tested; however, it was found that none of these compounds has a T_g or T_m . Crosslinking of these derivatives was also performed, but none of the materials thus produced gave any absorbency in standard testing. These findings confirm that the H-bonding of PAA-based polymers plays an important role for absorbency.

In summary, we have extended the silylation–alkylation procedure, previously applied exclusively to monomeric amines and amides, for *N*-alkylation of polyamides and prepared a number of defunctionalized derivatives of PAA including those with additional ester functional groups. The physical properties of the polymers obtained and their cross-linked derivatives were investigated and the important role of H-bonding for absorbency of PAA-based materials was confirmed.

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