

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### POLY(ASPARTIC ACID) HYDROGEL

C. J. Chang<sup>a</sup>; G. Swift<sup>a</sup>

<sup>a</sup> Rohm and Haas Company, Research Laboratory, Spring House, PA

**To cite this Article** Chang, C. J. and Swift, G.(1999) 'POLY(ASPARTIC ACID) HYDROGEL', Journal of Macromolecular Science, Part A, 36: 7, 963 – 970

**To link to this Article: DOI:** 10.1080/10601329908951192

**URL:** <http://dx.doi.org/10.1080/10601329908951192>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## POLY(ASPARTIC ACID) HYDROGEL

C. J. CHANG and G. SWIFT\*

Rohm and Haas Company  
Research Laboratory  
Spring House, PA 19477

Key Words: Poly(aspartic acid), Hydrogel, Superabsorbent Polymers, pH and Salt Responsive, Polyamino acid, Biodegradable

### ABSTRACT

Stimuli-responsive hydrogels have attracted much interest recently [1]. In this paper, we report a pH- and electrolyte-responsive hydrogel based on a crosslinked poly(aspartic acid). The lightly crosslinked, high molecular weight sodium polyaspartate impart extremely high water absorbency and can be used as a superabsorbent [2]. It is derived from a naturally occurring non-toxic amino acid, L-aspartic acid. A hydrogel based on poly(aspartic acid) possesses most of the features of poly(acrylic acid) hydrogels plus improved biodegradability. We expect it to be useful in a variety of applications including personal care and biomedical areas.

### INTRODUCTION

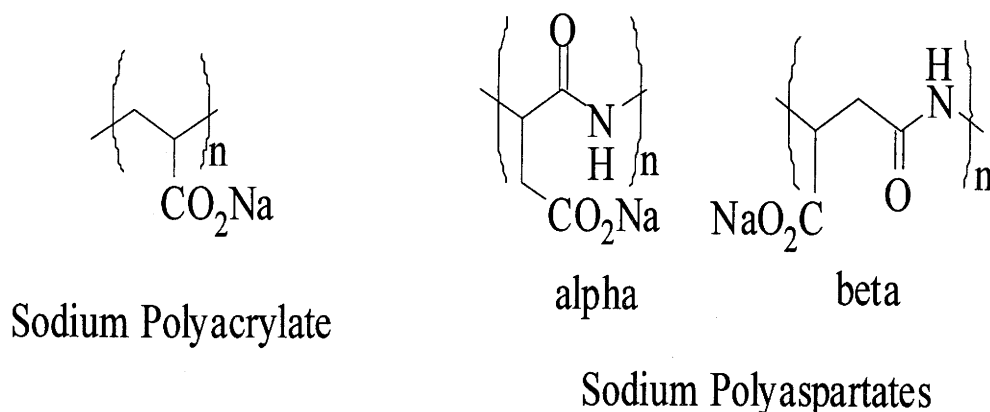
Superabsorbent polymers have enjoyed an enormous commercial success for the last 15 years. Their major application is for baby diapers. Today, just about all the disposal diapers on the market contain superabsorbent polymers. The most common superabsorbent polymer is based on the partially neu-

---

\* Author to whom correspondence should be addressed.

tralized and lightly crosslinked poly(acrylic acid) hydrogel [3]. One major deficiency of the poly(acrylic acid) based superabsorbent hydrogel is its very poor biodegradability, which causes a waste disposal problem and poses an environmental concern.

We believe a poly(aspartic acid) superabsorbent hydrogel can solve this problem without compromising the performance. Being a polyamino acid, it was not surprising that poly(aspartic acid) was found to be biodegradable. Poly(aspartic acid), like poly(acrylic acid), is a polyelectrolyte. It is expected to give high absorbency in water and body fluid when neutralized and crosslinked and is also expected to be pH- and electrolyte-sensitive [4, 5]. The structures of sodium salts of poly(acrylic acid) and poly(aspartic acid) are shown below:



## EXPERIMENTAL

### Synthesis of Polysuccinimide (PSI)

A solution-like mixture was obtained by heating two parts of L-aspartic acid with one part of 85% phosphoric acid under the reflux temperature of 145°C. The mixture was then poured into a Teflon pan and placed in an oven at 180°C for one hour. The mixture was allowed to cool and the solid condensate was ground to powder. The powder was subjected to further condensation at 160° to 180°C for 2 to 16 hours. It was identified as polysuccinimide by NMR spectroscopy with a Mw of 30,000 to 40,000 measured by aqueous GPC using Rohm and Haas company poly(acrylic acid) standard. Further increase in Mw was achieved by coupling washed PSI with dicyclohexyl carbodiimide in DMF (6) to give PSI of Mw 70,000 to 80,000.

### Synthesis of Sodium Polyaspartate

After repeated washing of PSI powder with water, the PSI was hydrolyzed with NaOH to give sodium polyaspartate following the method reported previously [7].

### Synthesis of Crosslinked Sodium Polyaspartate

We added 10.0 g of an aqueous solution of 10% sodium polyaspartate at pH 5-6.5 to 1-ounce vials containing a magnetic stirring bar. Each of the vials was then treated with 0.02 to 0.10 g of 50% aqueous solution of ethylene glycol diglycidylether (Aldrich) while stirring the mixture. The contents of each vial were transferred to a freeze-drying vial and the samples were frozen using an acetone-dry ice mixture. The samples were then freeze dried in LabConco Freeze Dry System. The samples were ground to powders, heat treated for 30 minutes at 180°C, allowed to cool under vacuum or inert (nitrogen) atmosphere.

### Absorbency Measurement

The absorbency was measured by the teabag method. 0.2 gram of sample is placed in a teabag-like pouch (2" by 2") of nonwoven fabric and heat sealed. The teabag is subjected to 15 second immersion in 0.9% saline solution, one minute drip dry, and weighing, followed by a 2 minute, 45 second immersion, a one minute drip dry, and weighing, and then an additional 7 minute immersion, a one minute drip dry, and weighing. The absorbencies for 15 seconds, 3 minutes, and 10 minutes are calculated according to the following equation:

$$\text{Absorbency in g/g} = (\text{weight of the teabag with treated sample} - \text{weight of a wet teabag}) / \text{weight of sample}$$

## RESULTS AND DISCUSSION

To be a superabsorbent polymer, the polymer has to have a very high swell ratio in water or body fluid. From the polymer network swelling theory, the swell ratio can be expressed according to the following equation:

$$\text{Swell Ratio} \sim (A_2 M_c)^{0.6}$$

$A_2$  is the free energy of the mixing parameter

$M_c$  is the molecular weight between crosslinks

To be a superabsorbent polymer, one must have high  $A_2$  and  $M_c$ . For a polyelectrolyte such as the neutralized poly(acrylic acid) or poly(aspartic acid),  $A_2$  is very large. To have a high  $M_c$ , one must start with a high primary molecular weight polymer.

For poly(acrylic acid), prepared by the free radical polymerization, to obtain high MW is easily achievable. However, for poly(aspartic acid), prepared by the condensation reaction, to obtain high MW requires special conditions. In addition to high MW, optimum crosslinking is essential in preparing a superabsorbent polymer. On one hand, the less crosslinking you have, the higher swell ratio you get. On the other hand, if the crosslinking is insufficient, it will result in a water soluble polymer or a large fraction of water soluble polymer, which not only contribute very little, if any, to the absorbency, but also can have detrimental effects on the other performance properties such as stickiness and irritation to the skin.

The key to producing a poly(aspartic acid) hydrogel with a high water absorbency is to employ a proper crosslinking chemistry on a high MW poly(aspartic acid). The high MW polysuccinimide (PSI), the precursor of poly(aspartic acid), was prepared by the modifying the procedures of Neri [6] as described in the Experimental section. The obtained Mw of up to 80,000 is still significantly lower than the Mw of a typical high MW poly(acrylic acid), which can be as high as one million or higher.

Unlike the previously reported poly(aspartic acid) superabsorbent preparations[8, 9], our method of crosslinking reaction did not involve the handling of a highly swollen hydrogel. This was accomplished by freeze drying an aqueous mixture of sodium polyaspartate and ethylene glycol diglycidyl ether at pH 5-6.5, followed by the crosslinking reaction in the solid state at 180°C for 30 minutes.

The crosslinking is a acid catalyzed nucleophilic attack of the carboxylate anion on the epoxide ring, resulting in a ring opening and ester formation. The pH is very critical. If the pH is below 4, the concentration of carboxylate anion will be low and the hydrolysis of epoxide will be significant. On the other hand, if the pH is greater than 7, the epoxide ring is not protonated or activated and the reaction will be slow.

TABLE 1. Effects of MW, pH, and Crosslinker Level on Absorbency

Sample	Mw of pAsp	Crosslinking Reaction			Absorbency. g/g in 0.9% NaCl		
		% Neut.	pH	% EGDGE	15 sec.	3 min.	10 minm
1	33,000	93	6.5	1	<1	<1	<1
2	33,000	93	6.5	5	<1	<1	<1
3	33,000	87	6.0	1	2	9	20
4	33,000	87	6.0	5	12	22	24
5	33,000	76	5.5	1	1	3	7
6	33,000	76	5.5	5	11	18	22
7	33,000	63	5.0	1	1	8	15
8	33,000	63	5.0	5	15	20	21
9	69,800	76	5.5	1	11	15	16
10	69,800	76	5.5	2	44	48	49
11	69,800	76	5.5	5	15	18	20

Table 1 summarizes the absorbency and the rate of absorption of the prepared hydrogel in 0.9% NaCl solution. We were surprised that in spite of its relative low MW of the sodium polyaspartate, the absorbency of the crosslinked polymers are comparable to those of commercial SAPs based on poly(acrylic acid). One explanation of the high swelling of the relatively low MW poly(aspartic acid) hydrogel is the contribution of the amide functionality to the hydration and thus higher  $A_2$  than poly(acrylic acid) hydrogel.

Being a polyelectrolyte, the absorbency of the sodium polyaspartate hydrogel is very sensitive to the electrolyte concentration as shown in Figure 1. Being a weak acid sodium salt, its swelling is also very sensitive to the pH changes. Its absorbency is drastically reduced as the pH drops below 5 or the degree of neutralization is less than 60% (Figure 2). The swelling was reversible.

The crosslinked, swellable poly(aspartic acid) can be irreversibly converted back to uncrosslinked, soluble poly(aspartic acid). This is carried out by treating the swollen hydrogel at  $\text{pH} \geq 11$ . The hydrogel was destroyed in minutes when it was treated at  $\text{pH} \geq 12$  at ambient temperature or at  $\text{pH} \geq 11$  at an elevated temperature (Figure 3).

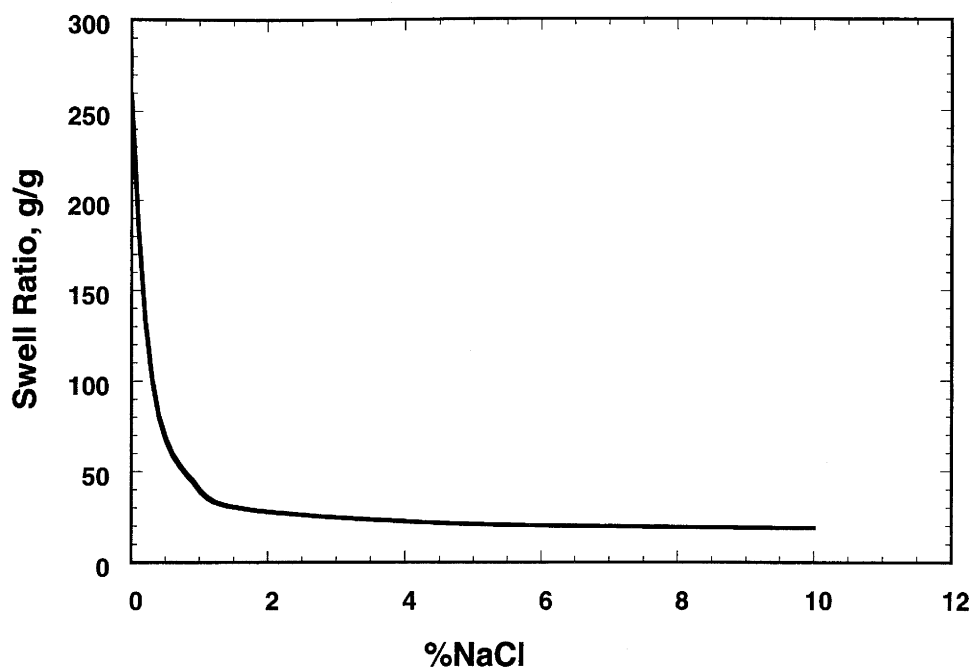


Figure 1. Salt effect on swell ratio.

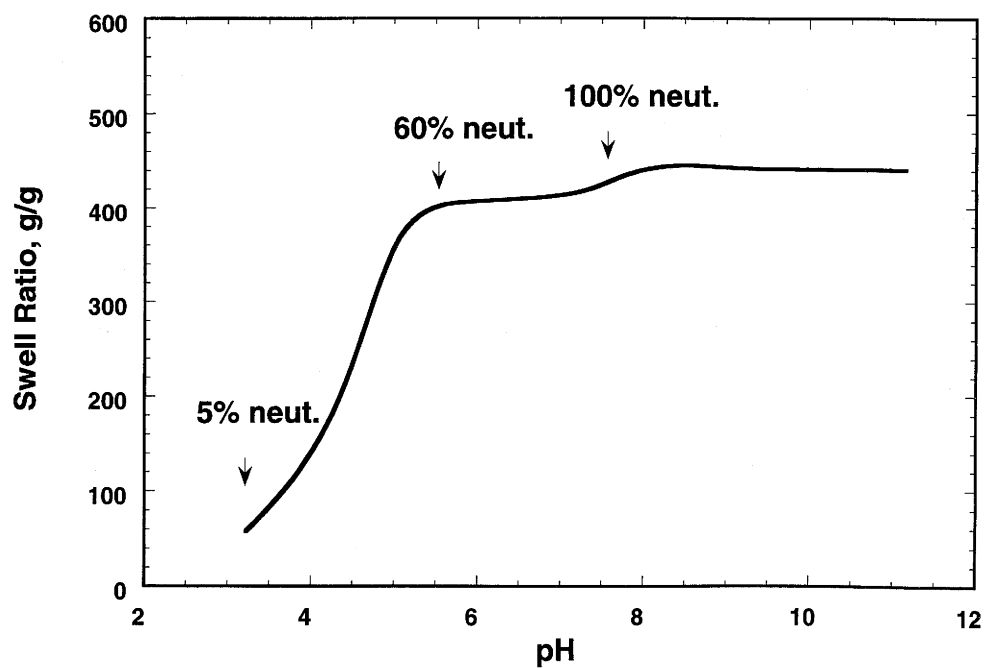


Figure 2. pH effect on swell ratio in deionized water.

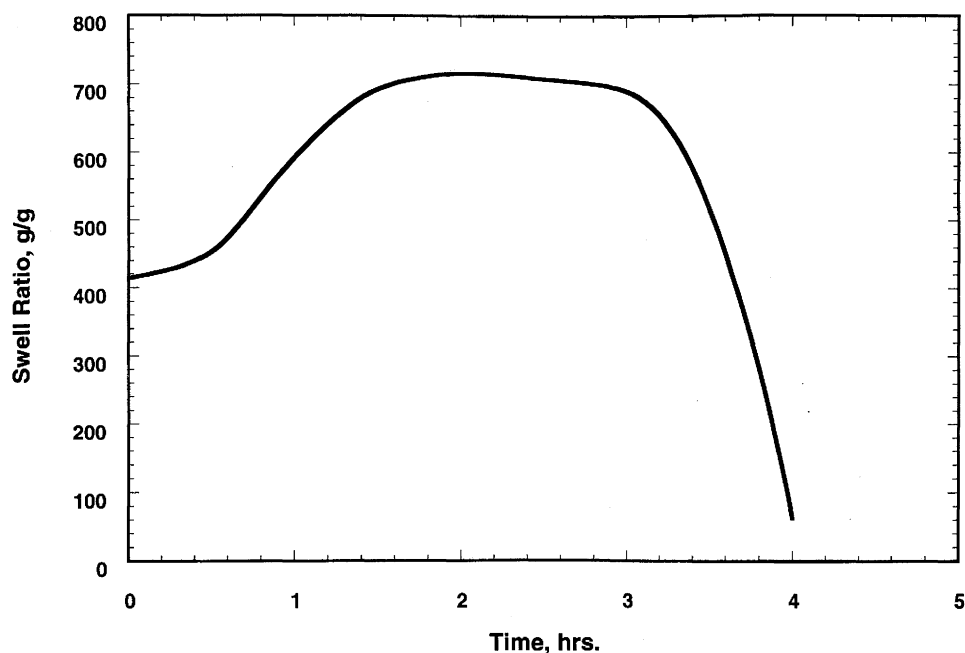


Figure 3. Swell ratio/time profile at pH 11.

### CONCLUSION

We have synthesized a novel crosslinked poly(aspartic acid), which is a pH- and electrolyte-responsive hydrogel. It can impart extremely high swelling and the swelling is reversible but can be rendered irreversible. We expect it to have good biodegradability and to be useful in a variety of applications including personal care and biomedical areas.

### REFERENCES

- [1] H. Park and K. Park, in *Hydrogels and Biodegradable Polymers for Bioapplications*; R. M. Ottenbrite, S. J. Huang, and K. Park, Eds., ACS Symposium Series 627, ACS, Washington, D.C., 1996, pp. 2-10.
- [2] L. Brannon-Peppas and N. A. Peppas, *Chem. Eng. Sci.*, **46**, 715-722 (1991).
- [3] I. Ohmine and T. Tanaka, *J. Chem. Phys.*, **77**, 5725-5729 (1982).
- [4] F. L. Buchholz, in *Superabsorbent Polymers*, F. L. Buchholz and N. A.



- Peppas, Eds., ACS Symposium Series 573, ACS, Washington, D.C., 1994, pp. 27-38.
- [5] Rohm and Haas Patent Application, filed on 5/29/97.
- [6] P. Neri, G. Antoni, F. Benvenuti, F. Cocola, and G. Gazzei, *J. Med. Chem.*, *16*, 893-897 (1973).
- [7] S. Wolk, G. Swift, Y. Paik, K. Yocom, R. Smith, and E. Simon, *Macromolecules*, *27*, 7613-7620 (1994).
- [8] J. Donachy and C. S. Sikes, U.S. Patent 5,284, 936, 1994.
- [9] A. Nagatomo, H. Tamatani, M. Ajioka, and A. Yamaguchi, U.S. Patent 5,525,682, 1996.