

# Cationization of Cellulose Fabrics by Polyallylamine Binding

Min Wu, Shigenori Kuga

Department of Biomaterials Science, Graduate School of Agricultural and Life Sciences, The University of Tokyo, Yayoi 1-1-1, Bunkyo-ku, Tokyo, 113-8657 Japan

Received 23 March 2005; accepted 8 August 2005

DOI 10.1002/app.22895

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

**ABSTRACT:** Novel anion exchange materials was prepared from cellulose fabrics (cotton- and rayon-cloths) by binding polyallylamine to aldehyde groups introduced by partial oxidation of cellulose via sodium periodate treatment. Degree of oxidation (D.O.) was controlled to 2–8% by the amount of oxidant. Polyallylamine (MW: 60,000, 5000, and 1000) was bound to cellulose by reductive amidation via Schiff base formation. Amount of bound amino groups was determined by conductometric titration. With the same cellulose material and degree of oxidation, the level of cationization was strongly dependent on molecular weight of polyallylamine, its concentration, and the pH of reaction mixture. Influence of these factors could be interpreted based on the porous structure of cellulose and behavior of

polyallylamine in the solution. In summary, the level of cationization could be maximized by using high concentration of low-molecular weight polyallylamine under pH as high as possible. The maximum exchange capacity, ~2.5 meq/g, was obtained by a combination of rayon cloth, oxidation degree of 8%, polyallylamine (MW: 1000) concentration of 10% (w/w) in the reaction mixture, and at pH 11.6. The cationized cellulose showed an adsorption capacity of 1.5 g hemoglobin/g cellulose. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1668–1672, 2006

**Keywords:** cationic cellulose; cellulose fabrics; dialdehyde cellulose; polyallylamine; periodate oxidation

## INTRODUCTION

Cellulose can be derivatized in various ways by modifying its abundant hydroxyl groups. Apart from esterification and etherification for preparing organic-soluble derivatives, relatively low level of derivatization is also useful to manufacture ion-exchange materials retaining the original solid forms, such as regenerated gel beads or microcrystalline particles.<sup>1–4</sup> These materials are conventionally prepared by introducing ionic groups via etherification with carboxymethyl (CM) or diethylaminoethyl (DEAE) groups.<sup>5,6</sup> Preparation of these materials, however, involves activation of hydroxyls by strong alkali, laborious washing of product, and careful control of reaction for avoiding water-solubilization by excessive substitution.

One alternative for derivatization of cellulose is the use of partial oxidation with periodate. It cleaves the C2—C3 bond of anhydroglucose unit and gives two aldehyde groups per glucopyranose unit. The product, usually referred to as dialdehyde cellulose (DAC), serves as starting material for further derivatization

through reactivity of aldehyde groups, i.e., further oxidation to carboxyls, reduction to primary hydroxyls, and Schiff base (imine) formation with primary amines. Of these, the last one is particularly useful for introducing novel functionalities to cellulosic materials.

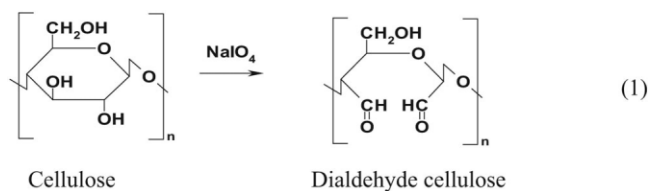
As such, a new type of cationic cellulose has been introduced by using binding of polyallylamine to partially oxidized cellulose gel of chromatography grade (Scheme 1).<sup>7,8</sup> To expand the type of cellulose material, we applied here the same procedure to native and regenerated cellulose fabrics. Such a process may lead to novel separation materials useful in industrial separation and waste water treatments.

## EXPERIMENTAL

### Materials

A commercial cotton cloth and a regenerated cellulose cloth (Bencot®, Asahi Chemical Industries, Japan) were used as starting materials, both of which are virtually pure cellulose. Polyallylamines (MW: 1000, 5000, and 60,000) were gifts of Nitto Boseki, Japan. Sodium periodate (NaIO<sub>4</sub>), sodium cyanotrihydroborate (NaBH<sub>3</sub>CN), hemoglobin (bovine blood) were used as received (Wako Pure Chemical Industries, Japan). Distilled water was used throughout the work.

Correspondence to: S. Kuga (Skuga@sbp.fp.a.u-tokyo.ac.jp).



**Scheme 1** Scheme of periodate oxidation of cellulose (1) and Schiff base reaction with polyallylamine (2) where cell is the other part of cellulose except for CH=O group  $124 \times 57 \text{ mm}^2$  ( $300 \times 300 \text{ DPI}$ ).

### Pore size analysis by nitrogen adsorption

Water-swollen cellulose material was subjected to solvent-exchange drying by ethanol and *t*-butyl alcohol. Nitrogen adsorption measurement of the dried sample was performed by a Quantachrome NOVA 4000 (Yuasa Ionics, Tokyo). Pore size distribution was obtained by capillary condensation analysis provided by the accompanying software.

### Preparation of dialdehyde cellulose

The cellulose cloth was cut into pieces of about  $60 \times 60 \text{ mm}^2$  ( $\sim 2 \text{ g}$ ). Each piece was treated with 100 mL of aqueous  $\text{NaIO}_4$  solution. The amount of  $\text{NaIO}_4$  added corresponded to the degree of oxidation (D.O.) of 2, 4, 5 or 8% if completely consumed by the cellulose specimen. The mixture was stirred gently at room temperature in the dark for 24–72 h, until absorption of  $\text{IO}_4^-$  at 280 nm (using a Shimadzu UV-1200 d spectrophotometer) decreased to near null. The D.O. was calculated from  $\text{IO}_4^-$  consumption.

### Polyallylamine binding by Schiff base reaction

Stock aqueous solution of polyallylamine (MW: 1000, 5000, or 60,000;  $\sim 15, 20$ , or 10% w/w) was adjusted to pH 2.6–11.7 by adding HCl solution and then diluted to concentrations (w/w) of 2, 6, and 11.2% for MW 1000 polyallylamine; 2, 6, 10, and 14% for MW 5000 polyallylamine; 6% for MW 60,000 polyallylamine by water. The oxidized cellulose sample was immersed in the PAA solution and stirred gently at room temperature for 4 h. The liquid ratio was 2 g cellulose/100 mL. Since the Schiff base reaction is reversible, the product was stabilized through reduction by  $\text{NaBH}_3\text{CN}$  (0.05 g in 100 mL distilled water) for about 4 h. The sample was washed with water to neutrality. The product is denoted as Cotton DAC-PAA and Rayon DAC-PAA in the following.

### Conductometric titration

The degree of cationization was determined by conductometric titration as follows: To the DAC-PAA sample immersed in 100 mL water, 0.1M HCl was added in 0.1 mL aliquots. The ion-exchange capacity was calculated from displacement in conductometric titration graph as exemplified by Figure 1.

### Hemoglobin adsorption

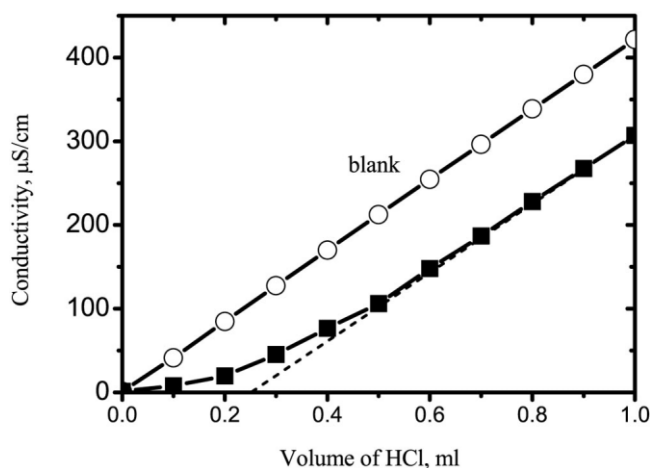
The DAC-PAA sample was immersed in 40 mL of hemoglobin solution in 0.02M phosphate buffer (pH 7.08), with hemoglobin concentration from 0.25 g/L (0.25g hemoglobin/1 L 0.02M phosphate buffer) to 14 g/L. The mixture was stirred at room temperature for 4 h, and the hemoglobin concentration in the supernatant was determined by absorption at 280 nm.

## RESULTS AND DISCUSSION

### Polyallylamine binding under various conditions

Table I shows the aldehyde and amino group contents of oxidized cotton and rayon cloths treated by polyallylamine (MW: 5000). Unexpectedly, the amount of introduced amino groups was generally lower than the amount of introduced aldehyde groups. For the cotton sample, the amino group content was not proportional to the D.O. and only slightly increased with the degree of oxidation. On the other hand, the rayon sample showed higher values, which roughly agrees with degree of oxidation. Still, these results are against expectation that the binding of polyamine would introduce extra amino groups via binding to weakly oxidized cellulose. The reason of this feature is considered here.

Various treatment conditions were examined regarding degree of oxidation, molecular weight of



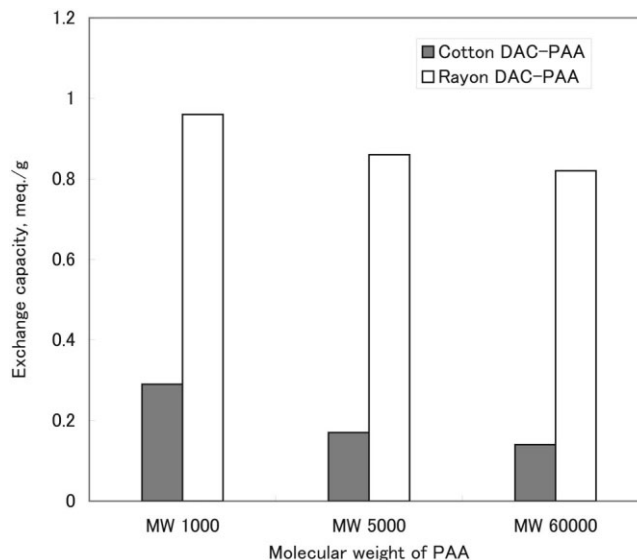
**Figure 1** Example of conductometric titration to determine amino group content.  $110 \times 79 \text{ mm}^2$  ( $300 \times 300 \text{ DPI}$ ).

**TABLE I**  
Aldehyde and Amino Group Contents in DAC and DAC-PAA

Degree of oxidation (%)	Aldehyde content (mmol/g)	Amino group (mmol/g)
Cotton DAC-PAA		
2.0	0.25	0.12
5.0	0.62	0.15
7.7	0.95	0.17
Rayon DAC-PAA		
4.0	0.49	0.47
8.0	0.99	0.86

PAA, MW: 5000; concentration, 6%; reaction, pH 5.

polyallylamine, its concentration, and reaction pH (Table II). Because polyallylamine has abundant amino groups, the ratio of amino group consumed by the reaction to surface aldehyde is expected to be low. Therefore, we expected that high-molecular weight PAA would give higher ion-exchange capacity. However, the results showed the opposite tendency as shown in Figure 2. The samples obtained from PAA 1000, PAA 5000, and PAA 60,000 had the exchange capacities of: cotton, 0.29, 0.17, and 0.14 meq/g; rayon, 0.96, 0.86, and 0.82. Thus, the PAA of lower molecular weight gives greater amount of bound amino groups. This behavior is considered to result from the molecular sieve effect of swollen cellulose, which has large

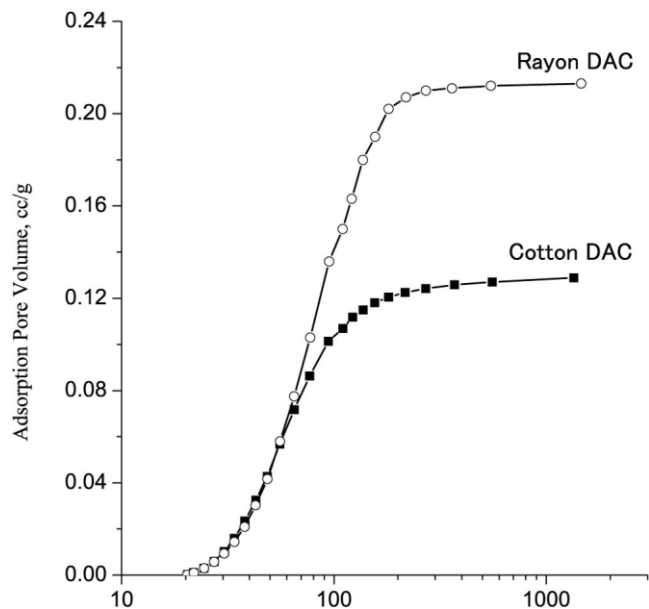


**Figure 2** Anion exchange capacity of PAA-modified cotton and rayon cloths. Influence of PAA fs molecular weight. 159 × 137 mm<sup>2</sup> (300 × 300 DPI).

internal surface area in micrometer–nanometer size pores. Figure 3 shows the pore size distribution of swollen rayon and cotton obtained by nitrogen adsorption measurement for the solvent-exchange dried samples from water-swollen state. The pore diameter ranged from 20 to 200 Å for both cotton and rayon samples, but the latter is apparently richer in large

**TABLE II**  
Preparation Conditions of the PAA-DAC Anion Exchange Materials

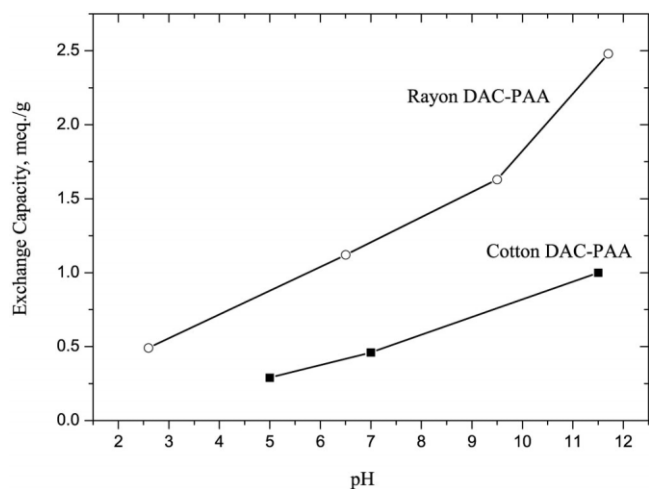
No.	D.O. (%)	PAA			Amino group (mmol/g)
		Molecular weight	Concentration (%)	pH	
Cotton DAC-PAA					
1	2.0	5,000	6	5.56	0.12
2	5.0	5,000	6	5.56	0.15
3	7.7	5,000	6	5.56	0.17
4	7.7	60,000	6	5.56	0.14
5	7.7	1,000	6	5.56	0.29
6	7.7	1,000	6	7.0	0.46
7	7.7	1,000	6	11.5	1.00
8	7.7	5,000	2	5.56	0.04
9	7.7	5,000	10	5.56	0.34
10	7.7	5,000	14	5.56	0.49
Rayon DAC-PAA					
11	4.0	1,000	11.2	6.5	0.83
13	6.1	1,000	11.2	6.5	1.09
14	8.0	1,000	11.2	6.5	1.12
15	8.0	1,000	6	6.5	0.96
16	8.0	5,000	6	6.5	0.86
17	8.0	60,000	6	6.5	0.82
18	8.0	1,000	11.2	2.6	0.49
19	8.0	1,000	11.2	9.5	1.63
20	8.0	1,000	11.2	11.7	2.48
21	8.0	1,000	2	6.5	0.57



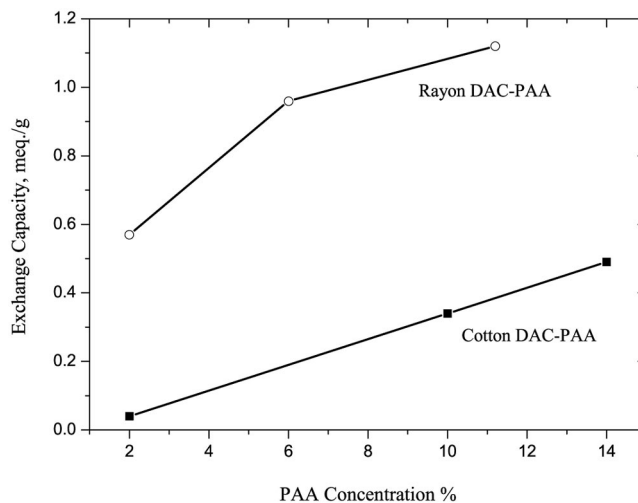
**Figure 3** Cumulative pore size distribution of solvent-exchange dried cotton DAC and rayon DAC.  $94 \times 88 \text{ mm}^2$  ( $300 \times 300 \text{ DPI}$ ).

pores. Therefore, the high-molecular weight PAA must have been excluded from the pores and cannot access the aldehyde groups.

Figure 4 shows the influence of reaction pH on exchange capacity. The Schiff base reaction is usually performed at pH 4–5, but Figure 4 shows that the higher pH is more favorable in binding PAA on to cellulose materials. This behavior seems to be caused by the change in the random coil size of PAA with pH change. Because lower pH causes protonation of amino groups, the chain molecule would expand because of the intramolecular repulsion, and the larger molecular size will cause more exclusion from the



**Figure 4** Influence of reaction pH on amount of bound PAA onto cellulose.  $102 \times 76 \text{ mm}^2$  ( $300 \times 300 \text{ DPI}$ ).



**Figure 5** Influence of PAA concentration on amount of bound PAA onto cellulose.  $101 \times 78 \text{ mm}^2$  ( $300 \times 300 \text{ DPI}$ ).

pores of the substrate. Also, the extended conformation of polyamine would tend to cause greater consumption of the aldehyde groups due to multiple binding for the polyamine molecules. For practical purpose, however, the reaction pH must be limited to below pH 7, since alkaline condition can result in significant chain scission of dialdehyde cellulose. In fact, those samples treated at above pH 7 were apparently fragile due to the rapid hydrolysis of cellulose.

Figure 5 shows the influence of PAA concentration in the Schiff base reaction on binding efficiency. For both cotton and rayon, higher PAA concentration resulted in higher exchange capacity. This feature can be attributed again to the possibility of multiple binding of PAA to cellulose; i.e., lower concentration of PAA would lead to higher probability of multiple bindings, because the free amino groups in a bound PAA will have greater chance to react with neighboring aldehyde groups. In contrast, higher concentration of PAA would result in competition of PAA molecules with each other, and give smaller number of linkage points per PAA molecule.

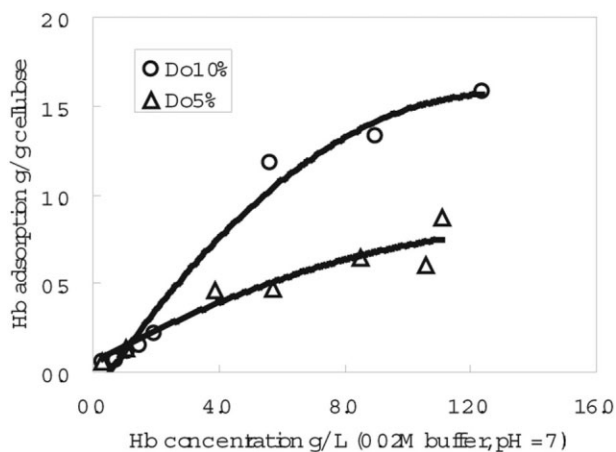
Thus, the highest degree of cationization could be achieved by a combination of the use of low-molecular weight PAA with high concentration, use of porous cellulose substrates, and under around pH 7. The highest values under these conditions were 0.46 mmol/g for cotton and 1.09 mmol/g for rayon (Table II). Figure 6 shows the adsorption isotherm for hemoglobin onto the Cotton DAC-PAA having a capacity of 0.25 and 0.21 mmol/g for D.O. 10% and D.O. 5%, respectively. It showed a saturation capacity of  $\sim 0.6 \text{ g}$  hemoglobin/gram dry substrate. These performances are comparable with those achieved by a highly porous cellulose gel for chromatography.<sup>7,8</sup>

### Stability of DAC-PAA in acid

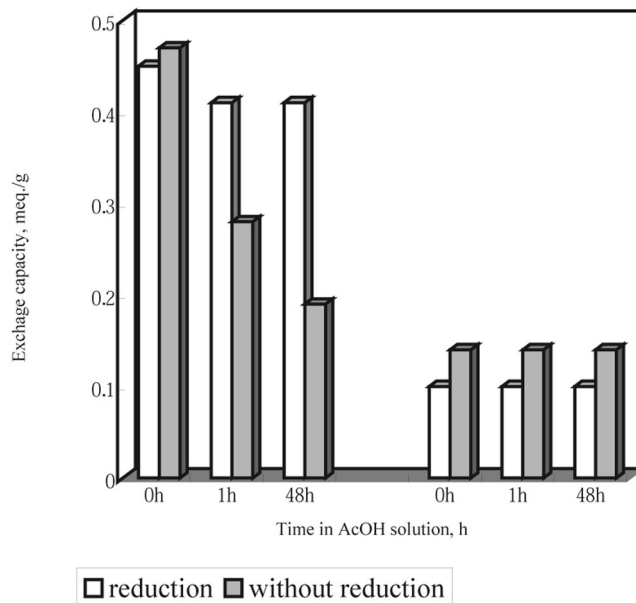
Because the Schiff base reaction is reversible, the product is usually stabilized through reduction by  $\text{NaBH}_3\text{CN}$ . Its effectiveness was examined by measuring the ion-exchange capacity after standing under acidic condition (1 wt % acetic acid). The DAC-PAA prepared by PAA of MW 1000 and hydroborate reduction was nearly stable (Fig. 7). However, the sample without reduction showed significant loss of capacity. This clearly shows the reversibility of Schiff base reaction. Interestingly, the DAC-PAA prepared from PAA of MW 60,000 did not show such decrease without reduction. This is probably because the long-chain molecule can form at multiple imine formation bindings to cellulose, which makes the probability of release very low.

### CONCLUSIONS

Common cellulose fibers could be cationized by periodate oxidation-polyallylamine treatment. Efficiency of binding was improved by using low-molecular weight polyallylamine in high-concentration, and under high pH. Influence of these factors could be inter-



**Figure 6** Adsorption of hemoglobin from aqueous solution onto Cotton DAC-PAA of 0.25 (for D.O. 10%) and 0.21 (for D.O. 5%) mmol/g exchange capacity. PAA, MW: 60,000.  $70 \times 51 \text{ mm}^2$  ( $300 \times 300 \text{ DPI}$ ).



**Figure 7** Stability of bound PAA under acidic condition. 1% acetic acid at room temperature.  $73 \times 69 \text{ mm}^2$  ( $300 \times 300 \text{ DPI}$ ).

preted by the behavior of polycation molecules in the solution. Under optimized conditions, the anion exchange capacity reached 1.0 mmol/g for cotton and 2.48 mmol/g for rayon, but practical values obtainable below pH 7 were 0.46 and 1.09 mmol/g, respectively.

The authors thank Nitto Boseki Co. for providing polyallylamine samples.

### References

1. Kuga, S. *J Chromatogr* 1980, 195, 221.
2. Kuga, S. *J Colloid Interface Sci* 1980, 77, 413.
3. Wu, P. C.; Huang, Y. B.; Lin, H. H.; Tsai, Y. H. *J Pharm* 1996, 145, 215.
4. Sutton, R. M. C.; Hill, S. J.; Jones, P. *J Chromatogr A* 1996, 793, 81.
5. Boeden, H. F.; Pommerening, K.; Becker, M.; Rupprich, C.; Holtzhauer, M.; Loth, F.; Müller, R.; Bertram, D. *J Chromatogr A* 1991, 552, 389.
6. Tishchenko, G. A.; Bleha, M.; Škvor, J.; Boštík, T. *J Chromatogr B* 1998, 706, 157.
7. Kim, U.-J.; Kuga, S. *J Chromatogr A* 2002, 946, 283.
8. Kim, U.-J.; Kuga, S. *J Chromatogr A* 2002, 955, 191.