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SYNTHESIS AND PROPERTIES OF HYDROXYETHYLCELLULOSE GRAFT COPOLYMERS AS SUPER WATER-ABSORBENTS*By Namiko Miyata*¹ and Isao Sakata*²*

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ABSTRACT: Graft copolymers of hydroxyethylcellulose (HEC) and other polysaccharides (PS) [e.g., mannan, alginic acid, agar, pectin and starch] containing partially hydrolyzed polyacrylamide (P-Hyd-PAM) or poly(methyl acrylate) (P-Hyd-PMA), poly(2-dimethyl aminoethyl methacrylate) (PDM) and poly(sodium acrylate) (PAA-Na) were synthesized as super water-absorbents. The absorbency of HEC-P-Hyd-PAM was greater than that of other polysaccharides and HEC graft copolymers containing the other types of branch polymers. The HEC-P-Hyd-PAM graft copolymers absorbed deionized water and a physiological saline solution up to 1000 - 3000 g/g and 100 - 300 g/g of absorbent, respectively. These values were 3 - 5 times greater than those of commercially available super water-absorbents. The HEC and the monomers were converted to the trunk and branch polymers of the HEC graft copolymers in the yields of about 30 - 60% and 20 - 80%, respectively. With an increase in grafting, the absorbencies of water and saline solutions of HEC-P-Hyd-PAM increased and reached maxima at 150 - 300% grafting, while those of HEC-PDM and the compressive strength of both gels increased monotonously. The gels of HEC-P-Hyd-PAM showed a discrete volume change at certain CH₃OH-H₂O compositions. The absorbencies of water and saline solutions of the graft copolymers of HEC and the other polysaccharides depended on the viscosity of the trunk polymers.

1. INTRODUCTION

Since starch-acrylonitrile graft copolymers named "Super-Rubbers" were synthesized by Fanta *et al.*[1], super water-absorbents have received considerable attention, and are now used as sanitary materials, agricultural and gardening agents, industrial dehydration agents, sensors and drying preventives, *etc.* Three kinds of super water-absorbents, starchy, cellulosic and synthetic polymeric materials are currently known. However, the water absorbencies of the cellulosic super water-absorbents prepared from carboxymethylcellulose (CMC) and other cellulosic materials[2,3] are smaller than those of starchy and synthetic water-absorbents. The main disadvantage of most super water-absorbents is the difficulty in the absorption of ionized water such as a physiological saline solution (0.85% NaCl solution) and urine[2].

In this study, an attempt was made to synthesize

graft copolymers of HEC and other polysaccharides as super water-absorbents, which do not have the above mentioned disadvantage and are able to absorb much more ionized water. Some of their properties were investigated in comparison with those of commercial products. Some parts of this study were reported in a previous paper[4], and this paper describes further details of the study.

2. EXPERIMENTAL

2.1 Materials

Hydroxyethylcelluloses (HEC) with the molar substitution (MS) of 1.2 - 4.0 were reagent grade and used as received from Tokyo Chemical Industry Co., Ltd. and Daicel Chemical Industries, Ltd. Other polysaccharides (konjac mannan, alginic acid, agar, starch and pectin) and *N,N'*-methylenebisacrylamide were reagent grade and used as purchased from Tokyo Chemical Industry Co., Ltd. Acrylamide (AM), methyl acrylate (MA), acrylic acid (AA), 2-dimethylamino

ethyl methacrylate (DM) and other chemicals were reagent grade and purified by conventional methods. Commercial super water-absorbents, i.e., Sanwet-IM1000 (starch-PAA), Sumika-gel NP-1010 [poly (vinyl alcohol) (PVA)-PAA] and GP-03 (PVA-maleic acid ester) were obtained from Sanyo Chemical Industries, Ltd., Sumitomo Chemical Industries, Ltd., and Nippon Synthetic Chemical Industry

Co., Ltd., respectively, and used without further purification.

2.2 Synthesis

Grafting of AM and other monomers onto HEC and other polysaccharides was carried out in the presence of *N,N'*-methylenebisacrylamide as a bridging agent using ceric ammonium nitrate ($\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$: 8.3×10^{-4} mol/l) as an initiator[5] in a 0.06 N

Table 1 Super Water-absorbents from HEC

Materials	Monomer conc. (%)	Trunk polymer conc. (%)	Bridging agent conc. (%)	Grafting time (h)	Degree of grafting (%)	Hydrolysis time (min)	Degree of hydrolysis (%)	Trunk polymer/ HEC (%)	Branch polymer/ monomer (%)
HEC-P-Hyd-PAM 1	2.5	2.5	0.3	2.0	98.0	20	89.3	—	—
HEC-P-Hyd-PAM 2	15.0	5.0	0.3	1.0	141.4	20	49.8	46.3	21.8
HEC-P-Hyd-PAM 3	5.0	2.5	0.3	5.0	161.7	84	52.9	38.3	30.8
HEC-P-Hyd-PAM 4	5.0	2.5	0.3	2.8	281.8	40	60.8	28.0	39.7
HEC-P-Hyd-PAM 5	15.0	5.0	0.3	2.0	424.8	20	63.9	37.5	53.1
HEC-P-Hyd-PAM 6	5.0	2.5	0.3	2.0	507.1	20	65.9	30.5	77.3
HEC-P-Hyd-PAM 7	12.5	2.5	0.3	2.0	615.8	5	41.4	—	—
HEC-P-Hyd-PAM 7	12.5	2.5	0.3	2.0	615.8	10	66.0	—	—
HEC-P-Hyd-PAM 7	12.5	2.5	0.3	2.0	615.8	20	74.6	—	—
HEC-P-Hyd-PAM 7	12.5	2.5	0.3	2.0	615.8	25	88.1	—	—
HEC-P-Hyd-PAM 8	15.0	5.0	0.1	3.5	373.2	20	57.2	38.8	48.2
HEC-P-Hyd-PAM 9	5.0	2.5	0.6	2.3	312.7	25	58.1	48.3	75.8
HEC-P-Hyd-PAM10	5.0	2.5	0.9	1.8	309.9	20	54.3	42.3	82.2
HEC-P-Hyd-PAM11	5.0	2.5	1.5	1.1	590.1	20	58.4	8.7	25.7
HEC-PDM 1	12.5	2.5	1.3	19.0	30.9	—	—	61.0	9.0
HEC-PDM 2	12.5	2.5	0.3	18.5	388.8	—	—	—	—
HEC-PDM 3	12.5	2.5	0.6	17.5	407.5	—	—	—	—
HEC-PDM 4	5.0	2.5	1.0	21.2	449.1	—	—	—	—
HEC-PDM 5	12.5	2.5	1.0	21.7	613.1	—	—	59.0	72.2
HEC-P-Hyd-PMA	12.5	2.5	0.3	0.8	—	60	75.6	—	—
HEC-AA	5.0	2.5	0	16.2	73.0	—	—	—	—
HEC-PAANa	5.0	2.5	0	2.8	392.5	30	—	—	—

Table 2 Super Water-absorbents from Other Polysaccharides

Materials	Monomer conc. (%)	Trunk polymer conc. (%)	Bridging agent conc. (%)	Grafting time (h)	Degree of grafting (%)	Hydrolysis time (min)	Degree of hydrolysis (%)	Trunk polymer/ PS (%)	Branch polymer/ monomer (%)
Mannan-P-Hyd-PAM	12.5	2.5	0.3	2.8	392.5	30	57.3	—	—
Alginate-P-Hyd-PAM	12.5	2.5	0.3	16.0	219.8	30	55.1	—	—
Starch-P-Hyd-PAM	12.5	2.5	0.3	1.5	184.3	20	68.2	78.1	36.7
Agar-P-Hyd-PAM	12.5	2.5	0.3	4.8	169.4	20	55.3	50.7	17.2
Pectin-P-Hyd-PAM	12.5	2.5	0.3	17.7	281.7	20	46.3	95.0	73.1
Sodium Arginate-P-Hyd-PAM	12.5	2.5	0.3	21.5	253.5	20	57.7	—	—

HNO_3 solution under nitrogen stream at 40 °C for a prescribed time. After grafting, homopolymers (PAM, PAA and PDM) and unreacted trunk polymers were removed by extraction with water for 1 - 2 days, and PMA was removed by extraction with acetone for 1 day. Polyacrylamide and the other branch polymers which could not be removed by the extraction were supposed to be graft copolymerized.

The degree of grafting was determined as follows; the contents of PAM and PDM in the HEC graft copolymers were calculated from the nitrogen contents determined by the Kjeldahl method, and the contents of PAA in HEC-PAA and HEC-PAA-Na were measured by a calcium acetate method.

The branch polymers, *i.e.*, PAM and PMA in the graft copolymers of the HEC and the other polysaccharides were partially hydrolyzed with 0.5 N-NaOH solutions at 100 °C for 20 - 100 min. The products (HEC-P-Hyd-PAM and others) were neutralized with HCl solutions and precipitated with methanol. They were then dissolved in a diluted NaOH solution, precipitated again with methanol and dried in a vacuum for 48 h at 40 °C. The degree of hydrolysis of HEC-P-Hyd-PAM was determined from the nitrogen content, and the carboxyl groups content of HEC-P-Hyd-PMA was determined by the calcium acetate method. Tables 1 and 2 show the super water-absorbents obtained from the HEC and the other polysaccharides, respectively.

2.3 Fluid Absorbency Test

About 0.1 g of each water-absorbent was put into 100 - 200 ml of deionized water, 50 ml of 0.85% NaCl solution or 100 ml of an aqueous methanol solution. After 16 h, the swollen water-absorbents were separated from an unabsorbed solution by screening through an 80 mesh sieve. The unabsorbed solutions were then weighed, and the fluid absorbency was calculated as grams of absorbed solution per gram of absorbent.

The pH of the solutions was adjusted with HCl and NaOH.

2.4 Viscosity Determination

The viscosities of the trunk polymers were measured with a rotating viscometer (Tokyo Keiki Co.) at 20 °C.

2.5 Compressive Strength Determination

Compressive strengths of the gels of the water-absorbents were determined with a Tom-200 type Universal Testing Machine at 20 °C. The samples in the form of a cylinder, 29 mm in diameter, were compressed between flat parallel plates at a crosshead speed of 50 mm/min.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Fluid Absorbency

Table 1 shows that HEC was converted to the trunk polymer in 30 - 60% yield, and the monomers were converted into the branch polymers in the HEC graft copolymers in 20 - 80% yield. The conversions of the monomers (AM and DM) to the branch polymers increased with an increase in the degree of grafting. However, the conversion of HEC to the trunk polymer was almost constant as shown in Fig. 1. These results suggest that in HEC the number of sites for grafting were limited and the monomers were polymerized on the grafting sites. They were converted to the branch polymers and only the degree of the polymerization increased. Fig. 1 shows that the HEC and the monomers were converted to the trunk polymer and the branch polymers in 40 - 50% and 75 - 82% yields, respectively, in the presence of 0.3 - 0.9% of the bridging agent. The yields were lower on 0.1% and 1.5% addition of the bridging agent.

Figs. 2 and 3 show the effects of the kinds of trunk

Fig. 1. Trunk polymer/HEC (%) and branch polymer/monomer (%) versus bridging agent concentration and the degree of grafting of HEC-P-Hyd-PAM. Trunk polymer/HEC: ○, bridging agent, ●, degree of grafting. Branch polymer/Monomer: △, bridging agent, ▲, degree of grafting.

Fig. 2. Effects of the trunk polymers of the graft copolymers containing P-Hyd-PAM on the absorbencies of water and 0.85% NaCl solution in comparison with commercial super water-absorbents. a, HEC; b, mannan; c, algaic acid; d, starch; e, agar; f, pectin; g, sodium alginate; h, Sanwet; i, Sumika-gel; and j, GP.

Fig. 3. Effects of the branch polymers of the HEC graft copolymers on the absorbencies of water and 0.85% NaCl solution in comparison with commercial super water-absorbents. a, P-Hyd-PAM; b, P-Hyd-PMA; c, PAA-Na; d, PDM; e, PAA; f, PAM; g, PMA; h, Sanwet; i, Sumika-gel; and j, GP.

and branch polymers on the absorbencies of distilled water and 0.85% NaCl solution. The absorbencies of water and 0.85% NaCl solution of the HEC graft copolymers were about three times as much as those of the graft copolymers of other polysaccharides and the commercial water-absorbents, and HEC-P-Hyd-PAM could absorb NaCl solution and water up to 325 g/g and 3000 g/g of absorbent, respectively. The absorbencies of water and 0.85% NaCl solution decreased in the order, HEC > konjac mannan, alginic acid > starch > agar > pectin, and partially hydrolyzed PAM > partially hydrolyzed PMA > PAA-Na > PDM > PAA > PAM, that is to say, partially hyd-

Fig. 4. Absorbencies of water and 0.85% NaCl solution of the graft copolymers versus the viscosities of the trunk polymers. H₂O: ○, HEC; ⊙, mannan; ●, starch; ⊕, alginic acid; ⊖, pectin; and ⊗, sodium alginate. NaCl soln.: △, HEC; ⊠, mannan; ▲, starch; and ⊡, alginic acid; ⊢, pectin; and ⊣, sodium alginate.

rolyzed > ionic and hydrophilic > hydrophilic > hydrophobic, as shown in Figs. 2 and 3.

Fig. 4 shows that the viscosity of HEC was high and the HEC graft copolymers could absorb a lot of water. However, those of sodium alginate, pectin and alginic acid were low and their graft copolymers were unable to absorb a large quantity of water. It is concluded therefore that absorbencies of water and NaCl solution of the graft copolymers of HEC and other polysaccharides depended on the viscosity of the trunk polymer.

3.2 Effects of Bridging Agent and Degree of Grafting

The mechanism of water absorption of super water-absorbents is different from that of cottons or sponges which is based on capillary action, and can be accounted based on the theory of the ionization of the polymer network(6,7). The forces for the absorption of pure water and saline solution are attributed to the osmotic pressure based on the movable counter ions (e.g., Na⁺), the polymer-solvent affinity and the rubber elasticity which relates to the bridging density of the super water-absorbents. The water absorbencies of super water-absorbents are determined by the balance of these forces. The water absorbencies and the strength of super water-absorbents can be expressed by Eq. 1 Flory's equation(6) and Eq. 2(8), respectively.

$$Q^{3/5} = [(i/2 \cdot V_u S^*)^{1/2}]^2 + (1/2 - X_1)/V_1 / (\nu_e/V_0) \quad (1)$$

$$G = RT \cdot \nu_e/V_0 \quad (2)$$

where Q is degree of swelling, i/V_u is charge density of polymer, S^* is ionic strength of solution, $(1/2 - X_1)/V_1$ is polymer-solvent affinity, ν_e/V_0 is bridging density and G is rigidity.

Their water absorbencies, therefore, increase with an increase in the number of hydrophilic and ionic functional groups, and with a decrease in the bridging density of the polymer network and in the concentration of ionic solvents (NaCl solution, urine *etc.*).

We reported in the previous paper[4] that as the degree of hydrolysis of branch PAM increased, the water absorbency of HEC-P-Hyd-PAM increased while the compressive strength decreased.

Fig. 5 shows that as the amount of bridging agents increased, the absorbencies of water and NaCl solutions of HEC-P-Hyd-PAM decreased and those of HEC-PDM increased, while, the compressive strengths of the gels of HEC-P-Hyd-PAM and HEC-PDM also increased.

The absorbencies of water and NaCl solutions of HEC-P-Hyd-PAM were in good agreement with Eq. 1,

Fig. 5. Effects of bridging agent concentration on the compressive strength and absorbencies of water and 0.85% NaCl solution of HEC-P-Hyd-PAM and HEC-PDM. HEC-P-Hyd-PAM: ○, water absorbency; △, NaCl absorbency; and □, compressive strength. HEC-PDM: ●, water absorbency; ▲, NaCl absorbency; and ■, compressive strength.

Fig. 6. Effects of the degree of grafting on absorbencies of water and 0.85% NaCl solution and the compressive strength of HEC-P-Hyd-PAM and HEC-PDM. The symbols are the same as shown in Fig. 5.

while, those of HEC-PDM were in poor agreement. The compressive strength of HEC-P-Hyd-PAM and HEC-PDM agreed with Eq. 2 because their rigidity decreased as their bridging density increased.

Fig. 6 shows the effects of the degree of grafting on the absorbencies of water and NaCl solutions and the compressive strength. With an increase in the degree of grafting, the absorbencies of water and NaCl solutions of HEC-P-Hyd-PAM increased, reached maxima at 150 - 300% grafting and then gradually decreased. However, those of HEC-PDM increased monotonously with grafting. It is reported[3] that water and saline retention values (WRV and SRV) of the hydrolyzed polyacrylonitrile grafted cotton fibers increased with grafting and then leveled off at about 35 g/g and 15 g/g, respectively, as the degree of grafting reached about 120 - 140%. However, WRV of the DM-grafted fibers increased with grafting and was 7.0 g/g at 110% grafting. Though the behavior is similar to that of HEC water-absorbents, these WRV and SRV values are much lower than those of HEC water-absorbents.

The compressive strength of the gels of the HEC-P-Hyd-PAM and HEC-PDM graft copolymers increased with an increase in the degree of grafting, and the absorbency and the compressive strength of the former was greater than those of the later as shown in Fig. 6. These results led to the conclusions that their water absorbencies increase with an increase in the number of hydrophilic and ionic func-

Fig. 7. Water absorbency versus the compressive strength of the graft copolymers of HEC and the other polysaccharides. ○, HEC-P-Hyd-PAM; ⊙, HEC-P-Hyd-MA; ⊗, HEC-PAA-Na; ●, HEC-P-DM; △, alginic acid-P-Hyd-PAM; ▲, mannan-P-Hyd-PAM; ⊠, sodium alginate-P-Hyd-PAM; ▴, agar-P-Hyd-PAM; ▴, starch-P-Hyd-PAM; ■, commercial water-absorbent (Sanwet).

tional groups and in the osmotic pressure as mentioned above, and with a decrease in the bridging density.

Fig. 7 shows that the compressive strength of the HEC graft copolymers containing various branch polymers were close to each other from 110 g to 190 g, although their water absorbencies were very different from 380 g/g to 3000 g/g. However, the graft copolymers of various polysaccharides containing P-Hyd-PAM had a wide range of compressive strength and the water absorbencies from 40 g to 210 g and 390 g/g to 3000 g/g, respectively. These results suggest that the water absorbency and the compressive strength of the graft copolymers of HEC and the other polysaccharides especially depend on the kinds of branch and trunk polymers.

3.3 Effects of pH, Temperature and Aqueous Solvent Composition on Absorbency

Fig. 8 shows that the water absorbency of the HEC graft copolymers and a commercial super water-absorbent varied with pH. A sharp maximum appeared at pH 7, and beyond this pH, the water absorbency decreased and reached a low value at pH 13. When the pH is reduced, some of the ionized carboxyl groups on the HEC graft copolymers recombine

Fig. 8. Water absorbency versus pH. ○, HEC-P-Hyd-PAM (grafting 507.1%; hydrolysis 65.9%); ▲, HEC-P-Hyd-PMA (hydrolysis 75.6%); ■, Commercial water-absorbent (Sanwet).

with super-abundant hydrogen ions. As a result, the water absorbency is reduced at acidic pH. When the pH is raised, the concentrations of sodium and hydroxide ions increase in the solution, and then the osmotic pressure and the polymer-solvent affinity decrease. Therefore, the water absorbency is reduced. It is known that the super water-absorbents with carboxyl groups have a weakpoint in the pH dependence of water absorbency[2]. The HEC graft copolymers as super water-absorbents could not overcome this weakpoint.

It is reported[7] that partially hydrolyzed PAM gels absorb a lot of water, and they swell at temperatures higher than room temperature and shrink below

Fig. 9. Effect of temperature on the liquid absorbency of HEC-P-Hyd-PAM (grafting 507.1%; hydrolysis 65.9%). Liquid: ○, water; △, water: methanol (60:40); and ●, water: methanol (40:60).

Fig. 10. Effects of the degree of hydrolysis and the composition of aqueous methanol solution on the liquid absorbency of HEC-P-Hyd-PAM (grafting 615.8%). Degree of hydrolysis: ○, 88.1%; △, 74.6%; □, 66.0%; and ●, 41.4%.

room temperature. However, the liquid absorbency of HEC-P-Hyd-PAM was independent of the temperature in the range from -20°C to 70°C , as shown in Fig. 9.

Fig. 10 shows the effect of the composition of aqueous methanol solutions on the liquid absorbency of HEC-P-Hyd-PAM. The liquid absorbency was high at low methanol concentrations, and as the methanol concentration increased, it gradually decreased. The liquid absorbency steeply decreased by a factor of 40 at about 55–70% methanol concentration, and remained low at higher concentrations of methanol. Partially hydrolyzed PAM gels are found[9] to undergo discrete volume transitions upon changes in solvent composition, pH, salt concentration of the solution or in temperature. It was found that

HEC-P-Hyd-PAM underwent also similar discrete volume transitions upon changing the $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ composition. These steep changes in the fluid absorbency of HEC-P-Hyd-PAM due to the change in the solvent composition are based on three forces; the osmotic pressure which is associated with the ionization of the absorbent network, the polymer-solvent affinity, and the rubber elasticity based on the resistance of the individual polymer chains to stretching or compression. The total force acting on the HEC water-absorbents is the sum of the above mentioned forces. The competition among the three forces changes, the fluid absorbency of HEC-P-Hyd-PAM.

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