

Aqueous salt absorption by ampholytic polysaccharides

J. C. Salamone, E. L. Rodriguez, K. C. Lin, L. Quach, A. C. Watterson and I. Ahmed

Polymer Science Program, Department of Chemistry, University of Lowell, Lowell, Massachusetts 01854, USA

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Studies of the solution properties of polyampholytes have revealed that these polymers are capable of undergoing viscosity increases in the presence of increasing salt concentration. Employing this unique characteristic, we have prepared graft copolymers of the ampholytic ion pair comonomer 3-methacrylamido-propyltrimethylammonium 2-acrylamido-2-methylpropanesulphonate with acrylamide onto starch and hydroxyethyl cellulose by both ceric ion and cobalt-60 irradiation. The deionized water and aqueous salt absorbing properties of these materials are reported.

(Keywords: ampholytic polysaccharides; ampholytic ion pair comonomer; graft copolymer; ceric iron; cobalt 60 irradiation; aqueous salt absorption)

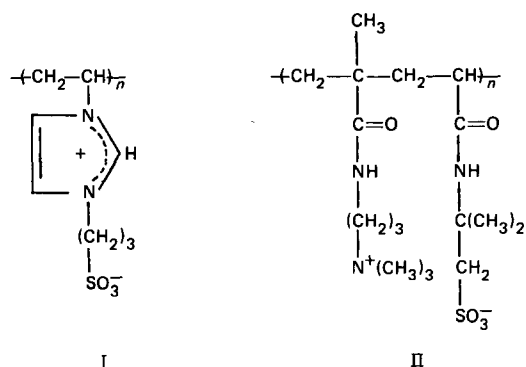
INTRODUCTION

The grafting of vinyl monomers onto polysaccharides has been the subject of extensive investigation using tetravalent cerium¹⁻¹⁰ and cobalt-60 radiation¹¹⁻¹⁶ as initiators. The possibility of using water soluble grafted polysaccharides as viscosity modifiers in displacement fluids for enhanced oil recovery^{8,9} and the ability of some hydrophilic saccharide graft copolymers to absorb large amounts of aqueous fluids^{13,14} have generated considerable interest in both academic and industrial research. These products may have many different applications and hold industrial promise for the future.

The synthesis and characterization of saccharide graft copolymers from a mixed monomer system is a potentially promising area of new materials. A cationic monomer or an anionic monomer coupled with a neutral monomer and grafted onto starch or dextran has been investigated in several instances to reveal unusual properties. Thus, the co-grafting of monomer pairs onto various polysaccharides using cerium (IV) initiation has been reported for acrylonitrile/acrylamide², acrylonitrile/*t*-butylaminoethyl methacrylate¹⁷, acrylonitrile/isoprene¹⁸ and acrylamide/sodium-2-acrylamido-2-methylpropanesulphonate¹⁹. Cobalt-60 radiation was also used to graft the monomer pairs acrylamide/2-methacryloyloxyethyltrimethylammonium methylsulphate¹² and acrylamide/2-acrylamido-2-methylpropanesulphonic acid¹⁵ onto polysaccharides.

As part of our research programme on ionic polymers, our group has been engaged in an investigation of the solution properties of ampholytic polymers²⁰⁻²⁵. These polymers have either been of the form of poly(1-vinyl-3-sulphopropylimidazolium hydroxide inner salt), I, a sulphobetaine where the positive and negative charges are on one pendant group, or of the form of copoly(3-methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulphonate), II, a polyampholyte derived from an ion-pair comonomer in which the positive and negative charges are on different pendant groups. For each of these systems, the intrinsic viscosities of the polymers increased markedly as the concentration of salt increased and as the site binding ability of cation or the anion of the added electrolyte increased. Such polyampholytes were also quite stable in the presence of multivalent cations. It is also interesting to note that when a covalently crosslinked gel of I was prepared, it was found to imbibe 91% of 1 M NaCl, while in the presence of deionized water, the gel absorbed only 46%²⁰.

Because of the large interest in polysaccharide graft copolymers and related to our studies of the synthesis, characterization and solution properties of water soluble copolymers of acrylamide and 3-methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulphonate, MPTMA-AMPS, it was decided to prepare graft copolymers of this ion-pair comonomer and acrylamide onto starch and onto hydroxyethyl cellulose. Water absorbency studies were then conducted to assess the effects of copolymer structure and ionic strength on the swelling properties of the grafted copolymers.



EXPERIMENTAL

Materials

A 50% aqueous solution of 3-methacrylamidopropyltrimethylammonium chloride was purchased from the Jefferson Chemical Company. It was decolorized twice with activated carbon and diluted with an equal volume of distilled water prior to use. From Lubrizol Corporation was obtained 2-acrylamido-2-methyl-

propanesulphonic acid (refined grade) which was recrystallized twice from chloroform. The cationic anionic monomer pair, 3-methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulphonate (II) was prepared as reported previously²⁶. Soluble starch was obtained from Fisher Scientific Company and hydroxyethyl cellulose (cellosize HEC WP-09) was obtained from Union Carbide Co. Both polysaccharides were used as received. Cerium ammonium nitrate, from Aldrich Chemical Company, was also used as received.

Graft polymerizations

Ceric initiation: Reactions were carried out in 100 ml glass ampoules. A homogeneous solution of soluble starch or hydroxyethyl cellulose in deionized water was prepared in the ampoules by heating the solution to 60°C. A mixture of MPTMA·AMPS and acrylamide monomer in 10 ml of deionized water was added to the above solution and agitated until completely dissolved. The paste was evacuated to 10⁻¹ mmHg and degassed by a freezing and thawing technique using isopropanol-dry ice as a cooling bath. This evacuation and melting procedure was repeated three times to displace dissolved oxygen. A solution of 0.005 N cerium ammonium nitrate in 2 ml 0.05 N nitric acid was added to the frozen paste with a syringe. The ampoule was then sealed *in vacuo*. The mixture was allowed to melt and then placed into a water bath at 25°C. The polymerization continued for three hours while shaking. The reaction product was then transferred to a dialysis bag and dialysed against distilled water for approximately four days. The purified polymer was obtained by freeze-drying. The polymers were dried in a vacuum oven at 60°C for a period of 4 h.

Cobalt-60 initiation: The cobalt-60 gamma ray source was a Gammacell 200 unit from Atomic Energy of Canada Ltd. The dose rate at the centre of the chamber was 0.113 Mrad h⁻¹ as calculated from the initial dosimetry data provided by the manufacturer and the decay rate of cobalt-60. The preparation process for the reactive mixture was the same as for the ceric initiation. The reaction was then irradiated with the gamma ray source for 1 to 10 h (0.1 to 1.0 Mrad), yielding either soluble or insoluble polymers. For the resulting tough-rubbery polymers, these were cut into small pieces and reduced to granular solids by high-shear blending with isopropanol. The solids were then washed thoroughly with isopropanol to remove unreacted monomer. The water soluble polymers were further purified by dialysis and freeze-drying, although they were not studied in this work. The water insoluble materials were dried *in vacuo* at 60°C for 4 h.

Structural characterization

Carbon, hydrogen, nitrogen and sulphur were analysed by Atlantic Microlab, Inc. of Atlanta, Georgia. The starch graft copolymer compositions expressed in mol fraction of starch, acrylamide (AM) and MPTMA·AMPS were calculated using equations (1)–(3) based on sulphur and nitrogen analysis.

$$S\% = \frac{32.064 F_{(MPTMA \cdot AMPS)}}{229.39 F_{(MPTMA \cdot AMPS)} - 91.06 F_{(AM)} + 162.14} \times 100 \quad (1)$$

$$N\% = \frac{42.021 F_{(MPTMA \cdot AMPS)} + 14.007 F_{(AM)}}{229.39 F_{(MPTMA \cdot AMPS)} - 91.06 F_{(AM)} + 162.14} \times 100 \quad (2)$$

$$F_{(starch)} = 1.00 - F_{(AM)} - F_{(MPTMA \cdot AMPS)} \quad (3)$$

The hydroxyethyl cellulose graft copolymer compositions expressed in mol fraction of hydroxyethyl cellulose, acrylamide and MPTMA·AMPS, were calculated using equations (4)–(6) based on sulphur and nitrogen analysis.

$$S\% = \frac{32.064 F_{(MPTMA \cdot AMPS)}}{573.53 - 182.00 F_{(MPTMA \cdot AMPS)} - 502.45 F_{(AM)}} \times 100 \quad (4)$$

$$N\% = \frac{42.021 F_{(MPTMA \cdot AMPS)} + 14.007 F_{(AM)}}{573.53 - 182.00 F_{(MPTMA \cdot AMPS)} - 502.45 F_{(AM)}} \times 100 \quad (5)$$

$$F_{(hydroxyethyl\ cellulose)} = 1.00 - F_{(AM)} - F_{(MPTMA \cdot AMPS)} \quad (6)$$

Measurement of water absorbency¹⁵

An accurately weighed 100.0 mg sample of polymer was allowed to stand one day in 10.0 ml of solvent at room temperature. The swollen polymer was separated from unabsorbed solvent by screening through a tared 230-mesh sieve that measured 4.8 cm in diameter. The polymer in the sieve was weighed to determine the weight of solvent-swollen gel. Absorbency was calculated in grams of solvent per gram of dry polymer taking into account the initial moisture content of the polymer (approximately 10%). Deionized water, 1.0 M NaCl and simulated urine (0.64 g CaCl₂, 1.14 g MgSO₄·7H₂O, 8.20 g NaCl, 20.0 g urea, 1000 g deionized water)¹³ were used as solvents.

RESULTS AND DISCUSSION

Graft copolymers

Graft polymerization was carried out by first preparing a blend of pregelatinized starch or hydroxyethyl cellulose with a water solution of acrylamide and MPTMA·AMPS and polymerizing the resulting mixture with Ce(IV) or cobalt-60 irradiation. Pregelatinized starch or hydroxyethyl cellulose is the paste obtained after heating the initial polysaccharide in water to the gelatinization temperature (60°C–70°C), at which point the materials undergo a rapid irreversible swelling accompanied by a loss of birefringence²⁸. High grafting efficiency, under conditions similar to these, was obtained with different monomer systems^{12,15}. The water soluble graft copolymers obtained in our case were exhaustively dialysed with distilled water using a membrane with a 12 000–14 000 molecular weight cut-off. The water insoluble rubber-like materials were dewatered by blending them with isopropanol. These two procedures served to remove any unreacted monomer.

In the first series of experiments, Ce(IV) was used to induce the graft copolymerization of starch or hydroxyethyl cellulose with MPTMA·AMPS and acrylamide. The concentration of cerium ammonium nitrate was adjusted to achieve a good degree of grafting². The conversion of monomer to polymer was higher for starch than for hydroxyethyl cellulose as is illustrated by the per cent yield in Table 1. The compositions of the graft copolymer obtained from the elemental analysis, based on the per cents of sulphur and nitrogen, clearly shows that acrylamide and MPTMA·AMPS are more easily grafted onto starch than onto hydroxyethyl cellulose, as illustrated in Table 2.

In our second series of reactions (Table 3), starch or hydroxyethyl cellulose, MPTMA·AMPS and acrylamide

water blends were prepared and irradiated to different total doses in Mrad. In each reaction the weight proportion of polysaccharide/acrylamide/MPTMA·AMPS was maintained at 2/1/1. The conversion of monomer to graft polymer was nearly quantitative as seen from the per cent yield (Table 3). Both starch and hydroxyethyl cellulose were found to produce similar results in per cent yield as is shown in Table 3. From the compositions of the graft copolymers (Table 4), the amount of acrylamide-MPTMA·AMPS in the starch and hydroxyethyl cellulose products were significantly greater. Thus, judging from this, and the per cent yield, the cobalt-60 irradiation procedure appears to introduce higher percentages of acrylamide and MPTMA·AMPS on to starch or hydroxyethyl cellulose than the Ce(IV) technique. In addition, the cobalt-60 procedure leads to graft copolymers that are tough and rubber-like, probably caused by a considerable degree of crosslinking that causes the insolubility in water of these materials. The Ce(IV) technique apparently did not produce crosslinking, and the graft copolymers remained water soluble.

Water absorbency

Water absorbency was next determined for some of the graft copolymers. It was found that all of the copolymers obtained using the Ce(IV) procedure were soluble. Mostly all of them were partially soluble after $\frac{1}{2}$ h and completely soluble after one day's exposure in the different aqueous solutions. The opposite situation was found for the graft copolymers obtained using the cobalt-60 procedure. The majority of these grafted materials were non-water soluble. For these cases, selected samples (numbers 7, 8 and 12) were measured for absorbency in deionized water, 1.0 M NaCl and simulated urine (Table 5). It was found that for sample 7, where 8.56% of MPTMA·AMPS and 27.30% of acrylamide were grafted onto starch, the deionized water absorbency measured was 9.83 g H₂O/g of polymer. This water absorbency is slightly lower than for sample 8, where the incorporation of 8.98% of MPTMA·AMPS and 41.76% of acrylamide onto starch resulted in a value of 11.54 g H₂O/g polymer. For run 12, 15.01% of MPTMA·AMPS and 64.96% acrylamide were grafted onto hydroxyethyl cellulose to produce a water

Table 1 Conditions for Ce(IV) induced graft copolymerization

Sample	Polysaccharide (g)	MPTMA·AMPS (g)	AM (g)	Ce(IV) (mmole)	Total volume (ml)	Time (h)	Temp. (°C)	Yield (%)
Starch								
1	2.0	1.0	1.0	0.5	22.0	3.0	25.0	62.5
2	2.0	1.0	1.0	0.5	22.0	3.0	25.0	62.5
3	2.0	1.0	1.0	0.5	11.0	3.0	25.0	32.5
Hydroxyethyl cellulose								
4	10.0	5.0	5.0	0.5	22.0	3.0	25.0	30.2
5	2.0	1.0	1.0	0.5	11.0	3.0	25.0	25.3

Table 2 Elemental analysis and compositions of the graft copolymers obtained by Ce(IV)

Sample	C%	H%	N%	S%	MPTMA·AMPS (mol%)	AM (mol%)	Graft substrate (mol%)
Starch							
1	43.79	7.10	5.80	1.91	8.96	35.41	55.63
2	43.83	7.11	5.79	1.90	8.91	35.42	55.67
3	43.99	7.50	5.51	2.03	9.87	31.72	58.41
Hydroxyethyl cellulose							
4	46.20	7.49	0.68	0.18	2.75	15.55	81.70
5	45.91	7.35	0.24	0.10	1.71	4.27	94.02

Table 3 Conditions for cobalt-60 induced graft copolymerizations

Sample	Polysaccharide (g)	MPTMA·AMPS (g)	AM (g)	Total volume (ml)	Dose (Mrad)	Time (h)	Temp. (°C)	Yield (%)
Starch								
6	2.0	1.0	1.0	20.0	1.0	8.0	25.0	90.0
7	2.0	1.0	1.0	20.0	1.0	8.0	25.0	85.5
8	10.0	5.0	5.0	200.0	1.3	11.0	25.0	90.5
9	10.0	5.0	5.0	200.0	0.1	1.0	25.0	88.7
10	10.0	5.0	5.0	200.0	0.1	1.0	25.0	86.1
Hydroxyethyl cellulose								
11	2.0	1.0	1.0	20.0	1.0	8.0	25.0	99.8
12	10.0	5.0	5.0	200.0	1.3	11.0	25.0	93.3
13	10.0	5.0	5.0	200.0	0.1	1.0	25.0	99.5
14	10.0	5.0	5.0	200.0	0.1	1.0	25.0	93.5
15	10.0	5.0	5.0	200.0	0.1	1.0	25.0	94.0

Table 4 Elemental analysis and compositions of the graft copolymers obtained by cobalt-60

Sample	C%	H%	N%	S%	MPTMA·AMPS (mol%)	AM (mol%)	Graft substrate (mol%)
6	46.61	7.91	6.76	1.82	7.97	43.87	Starch 48.16
7	41.92	7.16	4.73	1.75	8.56	27.30	64.14
8	46.06	8.15	6.65	1.99	8.98	41.76	49.26
9	45.07	7.87	7.11	2.30	10.56	43.03	46.41
10	40.73	6.20	2.91	1.05	5.18	17.32	77.50
11	46.67	7.68	7.55	1.86	11.32	71.21	Hydroxyethyl cellulose 17.47
12	46.45	8.17	7.01	2.19	15.01	64.96	20.03
13	46.28	8.06	6.23	1.82	13.11	63.41	23.48
14	46.96	7.54	6.29	1.83	13.09	63.74	23.17
15	46.35	7.44	6.54	1.85	12.82	65.28	21.90

Table 5 Weight of water absorbency of graft copolymers* (g of water/g of polymer)

Sample	Deionized water	1.0 M NaCl	Simulated urine
7	9.83	17.54	16.21
8	11.54	19.34	16.62
12	14.11	38.60	29.45

* After 1 day exposure

absorbency of 14.11 g H₂O/g polymer in deionized water. These results indicate that the water absorbency increases with the amount of MPTMA·AMPS incorporated into starch or hydroxyethyl cellulose. For all the samples, however, it is interesting to note that the water absorbency follows the order 1.0 M NaCl > simulated urine > deionized water. Visual observation confirmed the above in terms of swelling power. Thus, the presence of both positive and negative charges in the polymer chain incorporated onto the starch or hydroxyethyl cellulose is responsible for the water affinity in salt solutions. This is relatively in agreement with our findings in that polyampholytes usually show greater affinity for salt solutions than for pure water^{26,27}. Additionally, 1.0 M NaCl solution has a greater ionic strength than the simulated urine (0.20 M) solution. This explains the fact that the grafted copolymers showed a greater water absorbency with increasing ionic strength, even though simulated urine contains divalent cations which do not particularly affect polyampholytes. Again, this is attributed to the presence of the ion comonomer MPTMA·AMPS in the graft copolymers.

Taylor *et al.*¹³ prepared hydrolysed starch-g-polyacrylonitrile and measured the water absorbency of the graft copolymers in pure water and simulated urine. They reported that the water absorbency for the graft copolymer with 48% of added acrylonitrile dropped from 270 g H₂O/g polymer in pure water to 28 g H₂O/g polymer in simulated urine. In the above case, the hydrolysed starch-g-polyacrylonitrile copolymers behaved more like a typical polyanion, resulting in chain contraction in salt solution, particularly when divalent cations are present.

The graft copolymerization of the anionic monomer 2-acrylamido-2-methylpropanesulphonate and acrylonitrile onto starch has been reported²⁹. Saponification of these products (containing up to 10 mole per cent of 2-acrylamido-2-methylpropanesulphonic acid) with hot alkali to convert the nitrile substituents to carboxamide

gave highly absorbent polymers (about 1000 g of deionized water/g polymer). In a related case of the Co-60 gamma ray initiated graft copolymerization of 2-acrylamido-2-methylpropanesulphonic acid and acrylamide onto starch¹⁵, the resulting product showed absorbency properties comparable to the acrylonitrile saponified products (about 750 g H₂O/g polymer). However, the acidity of the sulphonic acid containing system caused some starch hydrolysis, which apparently contributed to the observed high percentages of water solubility and absorbency. Neutralization of 2-acrylamido-2-methylpropanesulphonic acid with NaOH drastically reduced both the water solubility and absorbency of the final products. It is unfortunate that this system was not investigated for absorption in aqueous salt where the absorbency would have been expected to be lower than in deionized water because of contraction of the polyanion segments.

In our system, since MPTMA·AMPS is a neutral monomer pair (where the positively charged group is compensated by a negatively charged group), the grafting of the ion-pair comonomer and acrylamide onto starch resulted in a neutral polymer with less water absorbency, but with the result that such systems can be greatly expanded in aqueous solutions containing high concentrations of salt. Indeed, the acrylamide and ion pair comonomer grafts onto polysaccharides, in conjunction with our early data on a crosslinked poly(vinylimidazolium sulphobetaine)^{20,22}, appear to support the belief that insolubilized polyampholytes can be highly effective in absorbing aqueous salt solutions in much the same fashion as the soluble derivatives of these polyampholytes are more compatible in aqueous salt solutions than they are in deionized water^{22,26,27}.

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