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NOVEL SOLUTION AND SOLID-STATE PROPERTIES OF AMPHOLYTIC 1/1
IONOMERS FROM ION-PAIR COMONOMERS(U) LOWELL UNIV MA
J C SALANONE 30 SEP 86 N00014-83-K-0674

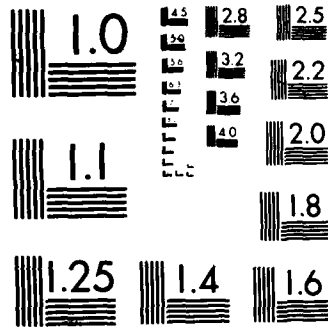
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XEROCOPY RESOLUTION TEST CHART

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<p>This investigation was concerned with the preparation of several types of ampholytic polymers for studies in drag reduction, water uptake, and apparent molecular weight as a function of added electrolyte. The polyampholytes studied have included an alternating copolymer of 4-vinyl-N-methylpyridinium methylsulfate and two random copolymers of 3-methacrylamidotrimethylammonium 2-acrylamido-2-methylpropanesulfonate and 2-methacryloyloxyethyltrimethylammonium 2-methacryloyloxyethanesulfonate. In general, as the salt concentration increased the apparent molecular weight decreased; however, the intrinsic viscosity usually increased while this effect occurred.</p> <p>Drag reduction studies showed that ampholytic ionomers based on polyacrylamide had very good drag reducing abilities, and were also highly shear stable.</p> <p>As part of this investigation, aqueous salt absorption studies of graft copolymers were also studied. The results revealed that the ampholytic graft materials were able to absorb more salt solution than deionized water, thus behaving similarly to their non-crosslinked analogs.</p>			
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FINAL REPORT

1. RESEARCH RESULTS

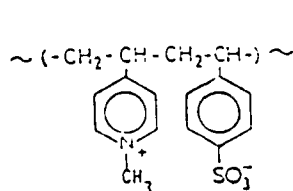
NOVEL SOLUTION AND SOLID-STATE PROPERTIES OF AMPHOLYTIC IONOMERS FROM ION-PAIR COMONOMERS

During the past few years, our research group has become interested in the synthesis and solution properties of various ampholytic polymers. These polyampholytes have been derived from sulfobetaines, in which the positive and negative charges are on one pendant group (1-3), or from the homopolymerization of an ion-pair comonomer, in which the positive and negative charges either alternate or exist in a random, pendant configuration (4-9). As reported previously, the ion-pair comonomers are a vinylic cation/vinylic anion salt, wherein no nonpolymerizable low molecular weight ions are present.

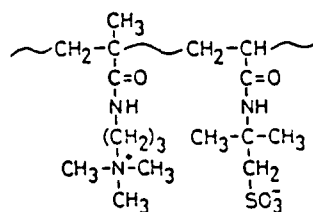
Previous studies on polyampholytes have demonstrated viscosity enhancement in the presence of increased salt concentration (3,9). Thus, the objectives of the present investigation were: to study the solution properties of an alternating polyampholyte of 4-vinyl-N-methylpyridinium p-styrenesulfonate, 4VMP/pSS (I), and two random polyampholytes of 3-methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulfonate (MPIMA/AMPS) 2-methacryloyloxyethantrimethylammonium 2-methacryloyloxyethanesulfonate, METMA/MES (III), and an ampholytic acrylamide ionomer with MPIMA/AMPS and METMA/MES.

The ion-pair comonomers MPMA/AMPS and METMA/MES were relatively stable and could be synthesized by several pathways; they were easily polymerized by free radical initiation.

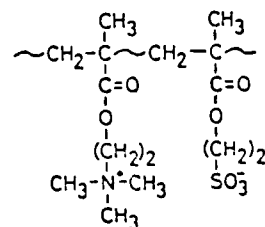
In general, the polyampholytes (I, II and III) were more soluble in salt solutions than they were in deionized water. Light scattering and dilute solution viscosity studies for all three polyampholytes in various salt solutions were conducted and the results are given in Table 1. It can be seen from Table 1 that the intrinsic viscosity, the radius of gyration and the second virial coefficient for all three cases did increase with increasing salt concentration. This unique behavior can be rationalized on the basis of chain expansion with increased solute-solvent interaction. A paper based on this study has been published [Proceedings of the ACS Division of Polymeric Materials: Science and Engineering; 55, 269 (1986)].



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TABLE 1

Effect of Salt Concentration on the Solution Properties of
Polyampholytes

[NaCl]	[n] dl/g	$\bar{M}_w \times 10^{-6}$ g/mol	$A_2 \times 10^6$ ml mol/g ²	R_{OG} A
Poly(MPTMA/AMPS)				
0.5	0.86	0.75	2.0	231
1.0	0.95	0.50	9.8	272
1.5	1.03	0.57	10.0	369
2.0	0.88	0.37	11.0	296
3.0	0.71	0.31	11.8	332
Poly(METMA/MES)				
1.0	1.77	2.37	5.5	700
3.0	2.05	2.20	8.0	717
5.0	2.14	2.00	11.0	812
Poly(4VMP/pSS)				
1.5	1.00	1.78	0.7	485
2.0	1.23	1.43	1.1	483
2.5	1.49	1.59	1.5	608
3.0	1.24	1.25	1.7	587

TABLE II

WATER ABSORBENCY OF GRAFT COPOLYMERS*

MPTMA/AMPS (mol%)	AM (mol%)	Graft Substrate (mol%)	Water Absorbency (g of water/g of polymer)		
			Delonized water	1.0 M NaCl	Simulated Urine
1) 8.56	27.30	64.14 (Starch)	9.83	17.54	16.21
2) 8.98	41.76	49.26 (Starch)	11.54	19.34	16.62
3) 15.01	64.96	20.03 (HEC)	14.11	38.60	29.45

*After 24H Exposure

In view of the above results and since there has been a considerable interest in grafted polysaccharides as viscosity modifiers in displacement fluids for enhanced oil recovery (10,11) as well as their ability to absorb large amounts of aqueous fluids (12,13), graft polymerization of MPTMA/AMPS coupled with neutral acrylamide (Am) monomer on to starch and hydroxyethyl cellulose (HEC) was attempted. Polymerization was carried out by two methods, (i) ceric initiation and (ii) cobalt-60 initiation, yielding either water soluble or insoluble polymers. The cobalt-60 irradiation procedure appeared to introduce higher percents of MPTMA/AMPS and Am on to starch or HEC than the Ce(iv) technique. Water absorbency of some of the insoluble grafted copolymers was measured and the results are given in Table II. There are two findings in these data. First, the water absorbency increased with the amount of MPTMA/AMPS in the grafted polymers, and second, the water absorbency followed the order 1.0 M NaCl > simulated urine > deionized water. This is in agreement with viscosity and light scattering studies. A paper on this topic has been published [Polymer, 26, 1234 (1985)].

Polymerization of MPTMA/AMPS and METMA/MES with neutral acrylamide monomer yielding ionomers IV and V of various ion contents. Light scattering studies on one of the terpolymers containing 1.45 mol % ion in the presence of various salt concentrations were conducted. The results are given in Table III. It is seen that despite the molecular weight decrease, the radius of gyration practically remained constant, while the second virial coefficient, A_2 , increased with increasing salt concentration. The decrease in molecular weight may be attributable to the breaking up of agglomerated structure, while individual chains expand which compensates the radius of gyration from being

reduced with decreasing molecular weight. The increase in the A_2 value with increasing salt concentration suggests that polymer-polymer interactions are reduced with a concomitant increase in polymer-solvent interaction.

It is evident from the light scattering studies that ampholytic ionomers can cause considerable aggregation in solution even at 1.0 M aqueous salt solution because of intermolecular and intramolecular ionic interaction. It was felt that these ampholytic ionomers might be more shear stable and could lead to a greater drag reduction. A comparative study was conducted for two samples of ionomer (1.46 mol % and 6.2 mol % ion contents) and for a neutral polyacrylamide and its hydrolyzed product. The study indeed showed that the ampholytic ionomer system was more shear stable with better drag reduction. A paper based on these results has been submitted for publication.

Based on the above results, a sample of ampholytic acrylamide ionomer containing 1.49 mol % ion (MPIMA/AMPS) was prepared in large quantity. This sample was tested by us and by NRL under various flow conditions. The results are given in Tables IV, V, VI. These results are consistent with our previous results. Thus, ampholytic acrylamide ionomer, particularly polymer IV, has demonstrated greater shear stability and salt tolerance with higher drag reduction.

TABLE III

Light Scattering of IV (1.45 mol % ion) as a Function
of [NaCl]

<u>[NaCl]</u> <u>M</u>	<u>M x10⁻⁶</u> <u>w</u>	<u>A₂x10⁸</u> <u>ml mol/g²</u>	<u>R_{OG}</u> <u>A</u>
1.0	14.97	0	2792
2.0	11.80	2.56	2827
3.0	11.70	5.50	2706
4.0	9.25	7.72	3074
5.0	5.07	10.98	2342

TABLE IV

A Comparative Data for Drag Reduction in Pipe-Flow System at
Various Reynolds Numbers

Sample	Molecular Parameters		% Drag Reduction*		
	$M_w \times 10^{-6}$	R_g	Re = 12,000	20,000	40,000
Ionomer	11×10^6	2109	52	62	65
PEOb	5.8×10^6	3035	46.7	--	--
PAm ^c	13.8×10^6	3369	42.6	45	51

*Drag reduction measured at 24 ppm polymer in deionized water.

- a) Mol. parameters were determined in presence of 3.0 M NaCl.
- b) Mol. parameters were determined in presence of 3.0 M NaCl.
- c) Mol. parameters were determined in presence of 0.5 M NaCl.

TABLE V

Drag Reduction Data (Pipe-Flow System) in Presence of Various NaCl Concentrations

Sample	Re = 20,000			% Drag Reduction*			Re = 40,000		
	H ₂ O	1M NaCl	2M NaCl	H ₂ O	1M NaCl	2M NaCl	H ₂ O	1M NaCl	2M NaCl
Ionomer	59	62	61	63	64	67			
PAM	37	37	32	40	40	38			

* Polymer concentration 12 ppm.

TABLE VI

Shear Stability in Pipe-Flow System Studied at 100 ppm Polymer Concentration in Deionized Water and at Re = 12,000.

Number of Passes	<u>Drag Reduction</u>		
	<u>Ionomer</u>	<u>PAM</u>	<u>PEO</u>
1	60	56	57
2	48	32	32
3	42	21	20
4	25	15	15

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