

Polyacids from Polyacrylonitrile. Viscosimetry in Pure Aqueous Solution

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The viscometric behaviour of polyelectrolytes, obtained by alkaline saponification of polyacrylonitrile, has been compared with that of polyacrylic acid, prepared directly from the monomer by redox polymerization in aqueous solution. It is apparent that differences exist, but their qualitative significance may be interpreted in terms of the Flory theory on general frictional properties of macromolecules.

When a suspension of polyacrylonitrile is heated to 75—80° C in strong (10—30 %) sodium hydroxide solution, a saponification of the nitrile groups takes place, finally resulting in a viscous solution of sodium polyacrylate. The base should be present in a great excess. The polymer formed shows a limiting nitrogen content of 1.5—2.0 % after purification, but solubility in water occurs much earlier than that value has been reached. A complete removal of the nitrile groups has not been successful in the present investigation, and it is doubtful if this can be carried out in the present way. From analytical specifications¹ it is known that only 94—95 % of the nitrile groups in the polymer are accessible to alkaline saponification in aqueous media.

Two reaction steps before dissolution can be identified by the appearance of distinct colours. The first one is a change to "carotene" colour, accompanied by a low degree of swelling. Simultaneously the polymer loses its property of being soluble in dimethyl formamide. As the reaction proceeds, a gel state is obtained and the colour changes into that of *lycopene*. Most of the ammonia gas is liberated during this step. When the gel gradually dissolves, the colour turns into a faint yellow one.

The purification and isolation of the polyelectrolyte is comparatively intricate. The large excess of sodium hydroxide, indispensable for a proper handling of the reacting polymer, makes precipitation with sulfuric acid rather unattractive. Moreover, this method has to be combined with a dialysis, preferably amplified with a reprecipitation². We have noticed, however, that only a minor amount of methanol, added to the alkaline solution, is sufficient for the separation of the polymer as a white curd. A further washing with pure

methanol reduces the plasticity, thus gives a more rigid structure, but does not remove the free base. It seems questionable if the alcohol penetrates the polymer phase as syneresis takes place when the water is extracted. According to our present experience the simplest way for a further purification is adding pure water to the centrifuged specimen and decant after some hours. A moderate swelling of the polymer takes place, but only a minor fraction dissolves. The operation can be repeated carefully, until a stage is reached where swelling and dissolution is rapid. This behaviour seems to be an analogy to the increase of the thickness of the Debye-Hückel ionic atmosphere around (the) *polyions* at increasing dilution. The successive removal of sodium hydroxide by "dialysis" in water reduces the compressive forces, acting on the polyions, even in the gel state. An increase in swelling is therefore expected, but also a gradual diffusion of the *counter* ions from their original position into the regions previously occupied by pure solvent. But this will cause an increase of the net charge of the polyanions (intramolecular Coulomb repulsion), finally ending in complete dissolution. The point of view is equivalent in meaning of that presented by Fuoss and Strauss³, valid for the reverse case, *i. e.* screening of a polyelectrolyte by addition of inorganic electrolytes. — Of course the presence of methanol in the precipitated polymer must have some influence on the rate of swelling, but not on the efficiency of the operation as a whole. If desirable the main fraction of the alcohol can be removed *in vacuo* before the final purification, but no tenable reason could be found for this more tedious operation.

Solutions of sodium polyacrylate, obtained in this way, may still show a slight excess of base, but a final purification can be carried out by adding a controlled amount of hydrogen-saturated cation exchanger to the aqueous system as a finely divided suspension. An excess of ion exchanger reduces the pH value rapidly, reaching the limiting value of 5.1 within a few minutes. After filtering or decanting the solution can be used directly for viscometry.

The viscometric behaviour of polyelectrolytes is extensively discussed in the fundamental papers of Fuoss and Strauss^{3,4}, and Kern⁵. A study on polyacrylic acid, prepared by reduction activation of acrylic acid in aqueous solution, has been carried out by Markowitz and Kimball². In most cases a rapid increase of the numerical value of the viscosity number (η_{sp}/c) has been observed at increasing dilution, provided no inorganic electrolytes are present. Recent investigations^{5,6,10}, however, indicate deviations from this rule at exceedingly dilute systems, and our present study on saponified polyacrylonitrile seems to confirm these observations. Obvious difficulties in measuring viscosities at very high dilutions still makes it uncertain to draw any conclusion of general validity, but it seems clear that not all experimental data can be handled satisfactorily according to the empirical Fuoss-Strauss equation⁴

$$\eta_{sp}/c = A/(1 + B \cdot c^{1/2}),$$

where η_{sp}/c is the viscosity number, c concentration of the polyion in monomer units per unit of volume, A and B constants. In other formulation, a plot of $(\eta_{sp}/c)^{-1}$ against $c^{1/2}$ would indicate a straight line.

The present study was carried out in order to compare the viscometric behaviour of the polyacids, obtained by saponification of polyacrylonitrile, with the corresponding polymer from pure polyacrylic acid. The main difference in structure is believed to be the presence of unsaponified nitrile groups in the former compound; a linear structure is thus tacitly assumed in both chain molecules. On account of this the first type should be considered as a random copolymer of acrylic acid and acrylonitrile. The last mer unit decreases the solubility in water (the entrapment of solvent in the Huggins⁸ theory), why a change of the numerical value of the expansion factor α in the Flory⁹ treatment of the frictional properties of polyelectrolytes should be expected.

Special attention was devoted to the preparation of the polymers in order to maintain most similar polymerization conditions and a high degree of purity (see experimental part). Here should be mentioned only the principal details. The acrylonitrile was a commercial grade, prepared from ethylene oxide and substantially free from bifunctional impurities. The acrylic acid was obtained from the same monomer by hydration with strong sulfuric acid in the presence of copper powder and hydroquinone, followed by distillation *in vacuo* over copper wire and repeated crystallization of the main fraction. Polymerization was initiated in homogenous system (aqueous solution) by identical activators in all cases. The polyacrylonitrile was reprecipitated from ethylene carbonate by dilution with water. The polymer from acrylic acid was neutralized with sodium hydroxide, precipitated in methanol and purified with ion exchanger as described above.

EXPERIMENTAL

Preparation of polyacrylonitrile and saponification to sodium polyacrylate (random copolymer). The freshly distilled monomer was mixed with water at 50° C (40 g acrylonitrile in 1 000 ml water) in a flask with three necks, equipped with agitator, thermometer, reflux condenser and inlet for nitrogen gas. On slow agitation the activator system was added as separate solutions of 0.20 g ammonia persulphate and 0.30 g sodium pyrosulphite in small amounts of water. The initiation of polymerization was very rapid and within five minutes a thick slurry of finely divided polymer was obtained. It was collected on a Pyrex G3 glass filter, washed with distilled water at 50° C, with acetone at 20° C and with tepid distilled water again. The wet cake was used directly for saponification after determination of dry content at 110° C on a small sample. The specimen was dispersed in water and a filtered aqueous solution of sodium hydroxide (45 % by weight) was added to give a reaction mixture, approximately containing 5 % polymer in 20 % sodium hydroxide solution. This dispersion was heated on a water bath to 70° C for several hours (62 hours for polymer I, 40 hours for polymer II, and 36 hours for polymer III). After cooling to room temperature, methanol (250 ml, distilled over sodium hydroxide flakes) was added to precipitate the polymer. The soft putty, immediately obtained, was soaked in pure methanol, repeatedly in distilled water until a rapid swelling was observed, diluted to a large volume (solid content about 1 %) and purified with ion exchanger (Amberlite IR-120, hydrogen saturated) as mentioned above.

Preparation of sodium polyacrylate from acrylic acid. Crystals of glacial acrylic acid were dissolved in distilled water to give a 4 % solution (40 g monomer in 1 000 ml water) and heated to 50° C before the addition of the activator system, being identical with that previously applied for acrylonitrile. The reaction showed a long period of induction and the expected increase in viscosity, originating from polymer formation, did not appear before at least 20 minutes had elapsed. After three hours a viscous dope had been formed. Viscosity still increased on neutralization with sodium hydroxide, but rapidly drops when the base finally is in excess. Also in this case the polymer was precipitated with methanol, soaked in water, diluted and purified with cation exchanger. The procedure was repeated to remove a possible residue of monomer (sodium acrylate).

Table 1a. Polymer I (sodium polyacrylate from polyacrylonitrile). Nitrogen content of polymer, dried at 110° C: 1.91 %. Measurements of viscosity number (η_{sp}/c) of aqueous solutions at pH 7.0. Measuring temperature 20.02°. Viscometer: Type Ubbelohde, calibration constant $K = 0.010$. Viscosity of water = 102.1 sec = 1.021 cst. (uncorrected value).

Solid content (c) (g/100 ml) $\times 10^3$	Viscosity, sec.	Red. viscosity, η_{sp}/c
225	1 500.6	61
113	991.3	77
56.3	670.6	100
28.2	446.5	119
14.1	282.9	125
7.05	192.5	126
3.53	142.0	111
1.77	120.4	102
0.89	111.4	102

Table 1b. Polymer I (sodium polyacrylate from polyacrylonitrile), deionised with an excess of hydrogen saturated cation exchanger (Amberlite IR-120). Initial pH of solution: 5.1. Measurements of viscosity number at 20.02° C in Ubbelohde viscometer.

Solid content (c) (g/100 ml) $\times 10^3$	Viscosity, sec.	Red. viscosity, η_{sp}/c
500	1 204.4	21.5
250	868.1	29.9
125	639.1	42.0
62.5	469.7	57.5
31.3	333.8	72.5
15.6	231.5	81.0
7.8	167.7	82.1
3.9	130.5	70.7
2.0	117.3	75.3

Table 2. Polymer II. Nitrogen content 2.16 %. Measurements of viscosity number at pH 7.0, temperature 20.02° C, in Ubbelohde viscometer.

Solid content (c) (g/100 ml) $\times 10^3$	Viscosity, sec.	Red. viscosity, η_{sp}/c
375.0	1 362.5	32.9
187.5	905.0	41.8
93.75	642.3	56.3
46.88	423.0	66.9
23.44	228.0	52.3
11.72	178.2	63.7
5.86	140.4	64.0
2.93	120.8	62.5
1.47	111.6	63.2
0.74	106.2	56.2

Table 3a. *Polymer III. Nitrogen content 2.09 %. Measurements of viscosity number at pH 7.0, temperature 20.02° C, in Ubbelohde viscometer.*

Solid content (c) (g/100 ml) × 10 ³	Viscosity, sec.	Red. viscosity, η_{sp}/c
605.0	3 077.7	48.1
302.5	1 979.8	60.7
151.3	1 245.2	74.0
75.6	852.3	97.1
37.8	523.0	108.8
18.9	300.0	102.3
9.5	197.0	98.0
4.7	137.8	73.6
2.4	119.4	71.1
1.2	110.4	67.8

Table 3b. *Polymer III, deionised with an excess of hydrogen saturated cation exchanger (Amberlite IR-120). Initial pH of solution: 5.1. Measurements of viscosity number at 20.02° C in Ubbelohde viscometer.*

Solid content (c) (g/100 ml) × 10 ³	Viscosity, sec.	Red. viscosity, η_{sp}/c
605.0	666.0	9.1
302.5	494.4	12.6
151.3	370.2	17.2
75.6	281.2	23.0
37.8	214.1	28.7
18.9	167.7	33.1
9.5	135.3	33.9
4.7	117.8	32.0
2.4	108.8	27.1
1.2	105.4	26.3

Table 4a. *Polymer IV (sodium polyacrylate, prepared by redox polymerization of acrylic acid). Measurements of reduced viscosity number at pH 7.0, temperature 20.02° C, in Ubbelohde viscometer.*

Solid content (c) (g/100 ml) × 10 ³	Viscosity, sec.	Red. viscosity, η_{sp}/c
312.4	3 850.5	117.3
156.2	2 099.6	125.2
78.1	1 073.5	121.8
39.0	534.4	108.4
19.5	282.5	90.4
9.8	171.0	69.0
4.9	134.5	64.8
2.5	119.2	68.2
1.2	110.7	68.2

Table 4b. Polymer IV, deionised with an excess of cation exchanger (Amberlite IR-120). Measurements of viscosity number at 20.02° C in Ubbelohde viscometer. Initial pH of solution: 5.1.

Solid content (c) (g/100 ml) $\times 10^3$	Viscosity, sec.	Red. viscosity, η_{sp}/c
625.0	1 888.4	27.9
312.5	1 282.1	36.9
156.3	902.3	50.1
78.1	636.9	66.9
39.1	424.0	81.0
19.5	286.0	92.0
9.8	209.3	107.4
4.9	154.7	105.2
2.5	128.4	106.6
1.2	115.5	109.1

SOME COMMENTS

The change in solid content, taking place on adding ion exchanger to solutions of sodium polyacrylate has been left unconsidered, as the number of macromolecules in solution is unchanged. The ratio of the two units sodium acrylate and acrylic acid (1.3) might be included in the expressions for viscosity number, but the physical significance of this calculation is doubtful, as the polymers studied do not show identical building sequences. The general feature of the viscosity changes on dilution can, anyhow, be deduced from the semi-logarithmic diagrams in Figs. 1 and 2. Distinct maxima are apparent on all curves, representing highly ionised polymers (sodium polyacrylates Ia, II,

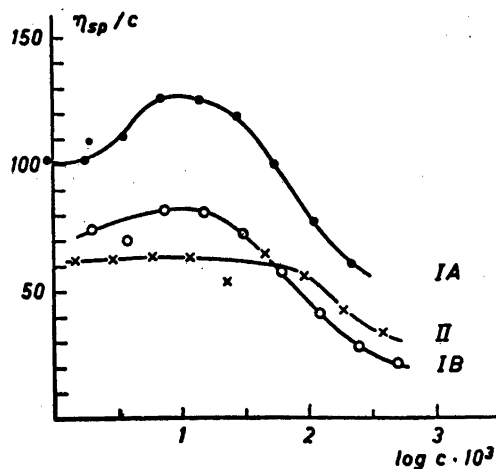


Fig. 1. Reduced viscosity of two polymers (Tab. 1 and 2), obtained by alkaline saponification of polyacrylonitrile.

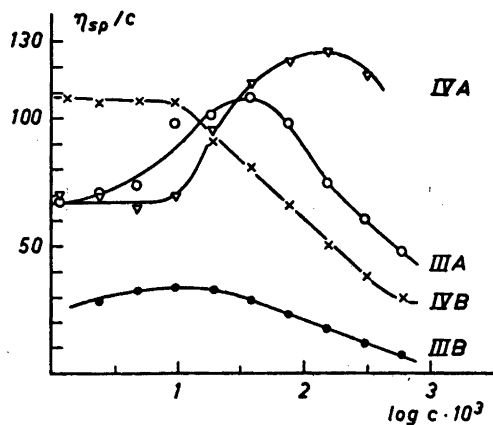


Fig. 2. Reduced viscosity behaviour of a polymer (Tab. 3), obtained by alkaline saponification of polyacrylonitrile, compared with that of a polymer, directly obtained from acrylic acid (Tab. 4).

IIIa and IVa). An asymptotic approach to the vertical axis has not been detected for any polymer, a circumstance that clearly points out the non-validity of the Fuoss-Strauss relation in the present case. The polyacids (Ib, IIIb and IVb) show maximum viscosity numbers at an average concentration of 10^{-3} g/100 ml. The straight acrylic acid polymer (IVb) keeps its (maximum) viscosity number unchanged at further dilution, but the polyacids, containing hydrophobic mer units (acrylonitrile), show a gradually decreasing value of the reduced viscosity. One is inclined to interpret this screening effect of the molecules as a return to a more coiled shape, possible when the overlap forces between separate polyions are gradually reduced. Along the separate chains the Coulomb field, arising from charged side groups is of course perturbed by the presence of the second mer unit in a random fashion, with the possible consequence that coiling takes place more readily than in the case of pure polyacrylic acid. This is explicitly formulated by saying that the volume expansion factors are not identical, or, that the two types of polyacids show different *Flory* temperatures.

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Received June 20, 1955.