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STRUCTURE AND PROPERTIES OF ISOTACTIC POLYACRYLIC ACID AND ITS SALTS*

Synthetic polyelectrolytes, owing to their ability, under the influence of relatively small perturbations, to undergo major structural and chemical changes, can model certain properties of biological polymers. This applies in particular to stereoregular synthetic polyelectrolytes, since, by analogy with other stereoregular polymers, it is precisely in this case that the variety and specificity of secondary structural formations, so characteristic of biological systems, should appear especially clearly.

In the present work we prepared a stereoregular polyelectrolyte—isotactic polyacrylic acid (PAA)—and studied the character of the secondary structures formed by the polyacid and its salts. To obtain isotactic PAA, previously synthesized isotactic polyisopropyl acrylate was subjected to alkaline hydrolysis. The degree of hydrolysis was monitored by potentiometric titration or by titration with phenolphthalein. Hydrolysis was brought to 100%. The resulting isotactic PAA precipitates from aqueous solutions in the form of a white crystalline powder upon addition of concentrated HCl (crystallization was demonstrated by the X-ray diffraction method). Thermogravimetric tests of crystalline isotactic PAA, carried out on analytical balances with continuous weighing, in combination with microanalysis data, showed that it crystallizes as a hydrate in which one molecule of water corresponds to two monomer units.

Electron-microscopic studies of the structure of isotactic PAA and its salts were carried out on a JEM-5Y electron microscope with a resolving power of 10 Å at a direct electron-optical magnification of 18,000–80,000×. The design of the microscope makes it possible to obtain electron micrographs of selected areas of the observed objects. Isotactic PAA specimens were thoroughly purified by electrodialysis. The objects were prepared by applying a drop of a dilute polymer solution to a collodion film support, followed by evaporation of the solvent.

Salts of isotactic PAA were obtained by potentiometric titration of its 1% aqueous solution with solutions of barium, sodium, and tetramethylammonium hydroxides. Potentiometric titration was performed using an LP-5 tube potentiometer with a glass electrode. Electron-microscopic study of isotactic PAA samples obtained from aqueous solutions with concentrations from 0.01 to 0.00001% showed that, depending on the concentration of the solution, the polymer forms either individual molecular globules or aggregates of such globules, analogous to those observed in work (2) for atactic PAA.

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* After completion of the present work, a brief communication appeared in the literature on the synthesis of isotactic polyacrylic acid by hydrolysis of poly-tert-butyl acrylate (1).

Electron micrographs obtained from such aggregates testify to their amorphous structure. Above we indicated that isotactic PAA crystallizes upon precipitation from an aqueous solution by concentrated hydrochloric acid. Specimens for studying crystalline PAA were prepared on a platinum grid from aqueous solutions of the polyacid heated to 100°, to which twice-distilled 6 N hydrochloric acid was added dropwise. Evaporation of the solvent was also carried out at 100°. In samples obtained from dilute solutions (0.00001–0.0001%), the formation of crystalline bundles (Fig. 1a), spiralized ribbons (Fig. 1b), and individual single crystals (Fig. 1c) was observed.

The crystalline structure of these formations was proved by the electron-diffraction method (Fig. 1d). The ability of isotactic PAA to crystallize readily in the presence of HCl is associated with complete suppression of the dissociation of the carboxyl groups and the elimination of chemical irregularity of the chains caused by the presence of COO^- groups in partially dissociated PAA. Thus, in an acidic medium isotactic PAA behaves as an ordinary stereoregular polymer.

For electron-microscopic study of the barium salt of PAA, samples were prepared from solutions with different degrees of neutralization: from pH 4.2 to pH 10.7. In parallel, viscosity measurements were carried out on solutions of the barium salt at different pH values.

In the electron-microscopic images, over the entire pH interval (Fig. 2a), compact dense formations consisting of globules were observed. The viscosity of barium polyacrylate solutions is lower than that of isotactic PAA solutions (at pH 5, η_{sp} PA Ba = 0.07; and η_{sp} PAA = 0.12), which indicates an even greater compaction of the spherical molecular coils.

A substantially different picture was observed in the study of the sodium salt of isotactic PAA, samples of which were prepared from PAA solutions titrated to various pH values (from 4.2 to 11.5). At low pH values (i.e., at low degrees of neutralization), formations of molecular globules could be seen in the electron-microscopic images, although they were less dense than in the case of

barium polyacrylate. At pH 6.75, unfolding of the molecular coils occurs in solution, caused by an increase in the dissociation of the carboxyl groups and by intramolecular electrostatic repulsion of the COO^- groups. In the corresponding electron-microscopic images one can see structures of bundle (fibrillar) type, built of parallel-packed, extended molecular chains (Fig. 2b). At pH 7.5, practically all the carboxyl groups of the polymer are dissociated. The molecular chains, as in the case of completely undissociated PAA, acquire chemical regularity. In the presence of a regular sequence of asymmetric atoms in the chains, this condition proves sufficient for intrabundle crystallization and the appearance of highly ordered structural forms, up to individual single crystals (Fig. 2c). In this same pH region, on the curve of the dependence of the reduced viscosity of the polyelectrolyte solution on pH, a maximum is observed, corresponding to the limiting unfolding of the molecular chains or their aggregates in solution. At higher pH values, excess low-molecular-weight ions screen the negative charges of the macromolecules, which leads to a decrease in intramolecular electrostatic repulsion. The chains assume the form of statistical coils, corresponding to the entropy maximum. In the electron-microscopic images, formations of the globular type are again observed.

The phenomena described for isotactic sodium polyacrylate are manifested still more strongly in the case of isotactic tetramethylammonium polyacrylate, for which, near the neutralization point, structures of the fibrillar type can be observed in electron-microscopic images, approaching in their perfection the structures of biopolymers. At

Fig. 1. Crystalline polyacrylic acid.
a –crystalline bundles ($C \approx 0.0001\%$), *b* –spiralized ribbons ($C \approx 0.0005\%$), *v* –separate single crystals ($C \approx 0.0001\%$), *g* –electron diffraction pattern of a PAA single crystal

Fig. 2. Salts of isotactic polyacrylic acid.
a –Ba salt, *b* –Na salt at pH 6.75, *v* –Na salt at pH 7.35

Fig. 3. Isotactic tetramethylammonium polyacrylate.
a –fibrillar-type structures, *b* –individual single crystals, *v* –electron diffraction pattern of a single crystal

Fig. 4. Microphotograph of a film of isotactic tetramethylammonium polyacrylate in polarized light.

Fig. 3a shows a transversely striated ribbon built up from individual bundles, and Fig. 3b shows individual single crystals of the polymer salt. The corresponding electron diffraction patterns of the samples display spot diffraction patterns, indicating a high degree of ordering of the structural elements in these formations (Fig. 3c). We were able to observe very interesting phenomena in studying films of tetramethylammonium polyacrylate with a polarization microscope. The samples were prepared by applying a drop of an aqueous polymer solution to a glass slide, followed by evaporation of the solvent at a temperature

of 100°. Observations were carried out at 40-60°, in order to avoid dissolution by atmospheric moisture in the hygroscopic polymer.

Figure 4 presents a microphotograph of a thin film of isotactic tetramethylammonium polyacrylate in polarized light. It is seen that the film consists entirely of large fused single crystals of rhombic form, whose dimensions reach 100 μ. The fine folded structure of the single crystals is clearly distinguishable. If the sample placed under the microscope is cooled to 20°, then, under the influence of atmospheric moisture, the crystal is destroyed. The destruction begins at the folds, which deepen and become increasingly wider. Soon the birefringence disappears completely: the intergrowth of single crystals turns into a swollen polymer film. However, if, without changing the position of the film under the microscope, it is heated again, the single crystals reappear, and their shape, dimensions, and mutual arrangement coincide completely with the original ones. This operation can be repeated several times. The phenomenon indicated can be explained only by assuming that in the swollen polyelectrolyte film (gel) a very strict mutual arrangement of the large structural formations is preserved.

From the potentiometric titration curves for isotactic polyacrylic acid, the dissociation constants and the constants ΔpK, which are determined by the conformations of the monomer units, were calculated.

It was found that, in titrating isotactic PAA with sodium hydroxide, $pK_{i_1} = 5.5$, and in titrating with tetramethylammonium hydroxide, $pK_{i_2} = 6.3$. Then, taking $K_0 = 10^{-4.86}$ (the ionization constant of an isolated carboxyl group), we obtain:

$$\Delta pK_1 = pK_{i_1} - pK_0 = 5.5 - 4.86 = 0.64;$$

$$\Delta pK_2 = pK_{i_2} - pK_0 = 6.3 - 4.86 = 1.44.$$

Thus, isotactic PAA and its salts are characterized by the same two basic types of structures that were previously established for atactic PAA: globular and fibrillar.

However, in the present case, owing to the presence of a regular sequence of configurations of the asymmetric atoms in the macromolecules, structures of the fibrillar type, under conditions in which the polyelectrolyte chains are chemically homogeneous, are characterized by considerably greater variety and perfection and, in their morphology, approach the regular structures of biopolymers.

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Note: Figure translations are in progress. See original paper for figures.