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Note

A new transmission electron microscopic (TEM) method to determine differences between cationic polymers in solution

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Summary

The physical structures of two types of cationic polymers (Polymers JR 125, 400, 30M, and Gafquat copolymers 734, 755N) in aqueous solution were determined by a new transmission electron microscopic method. Differences occurred between the coiling tendency of the two types and between the polymers individually. The molecular weight and molecular structure of a polymer play an important role in the coiling tendency of the polymer in solution and may influence the diffusion of substances from the polymer coil.

The solution process of a polymeric solute is quite different from that of a simple monomeric substance. Initially, the polymer imbibes the solvent and becomes a swollen gel which may ultimately undergo disintegration and dispersion to yield a solution of uniform composition. Polymers vary greatly in their solubility in different solvents and their solutions do not, in general, exhibit the simple saturation phenomena characteristic of monomeric solutes (Richards, 1972).

For a given polymer-solvent system, solubility decreases with increasing molecular weight (Allen, 1968). Polymers are, in general, not stretched out threads or rods but exist as randomly organized coils. In solution these coils are more or less completely solvated and extended when dissolved in the solvent. The size and degree of extension of the molecular coil depend on the polymer-solvent interaction forces. In a good solvent extended coils exist and in a poor solvent the reverse may be the case (Billmeyer, 1971; Vollmert, 1973).

The aim of this study was to determine the physical structure of two types of cationic polymers in an aqueous solution.

The materials were used as received from the suppliers: Polymers JR 125, 400 and 30M (Union Carbide) with average molecular weights of 250000, 400000 and 600000 respectively (supplied as white powders); Gafquat copolymer 734 (GAF) with a molecular weight of 100000 supplied as a 50% viscous alcoholic solution; Gafquat copolymer 755N with a molecular weight of 1×10^6, supplied as a 20% viscous aqueous solution.

Solutions of 1% (w/v) in normal saline of each of the polymers were freshly made up. The poly-

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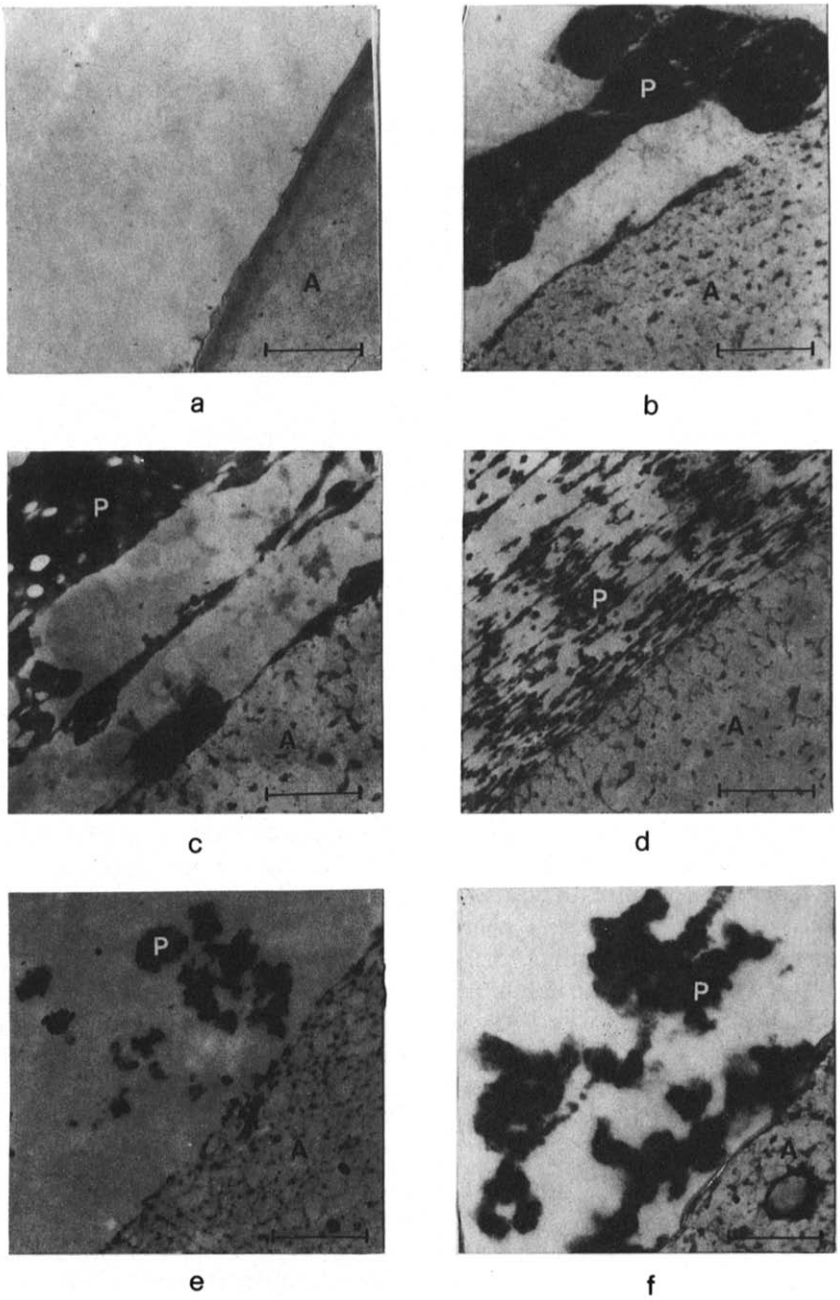
mer solutions were prepared for transmission electron microscopy (TEM) by combining and adapting methods used by Du Plessis et al. (1986) and Van der Merwe (1986).

Preparation of agar capsules: The needle of a syringe (0.5 mm in diameter) was dipped into a hot agar solution (3% in water). After removal the needle was covered with a thin layer of agar. The



layer was allowed to solidify. A scalpel blade was used to cut the agar into segments (5 mm in length). The polymer solution was slowly injected into each segment while sliding the segment off the needle. The ends of the segments were sealed by dripping hot agar solution onto them. A control capsule was prepared by injecting normal saline solution, without the polymer, into the segment. Finally, the agar capsules were placed into polytops and fixed for 5 days in a 2% (w/v) osmium tetroxide solution. The osmium tetroxide was stained black with plant proteins (a piece of leaf) to enhance the staining of the agar capsules. This procedure was repeated for each polymer solution.

Preparation of capsules for TEM: After being washed with distilled water for 5 min the capsules were dehydrated in a graded acetone series 50, 75, 95, 100% (v/v) for 15 min in each case. After dehydration the capsules were placed in a 1:1 mixture of Spurr's resin in Teflon frames and left at 70 °C for 24 h to set. Sections of 120 nm thickness were cut on an ultramicrotome with glass knives and lifted onto 400-mesh grids. The sections were stained with 2% (w/v) uranyl acetate and lead citrate (Reynolds, 1963) and thereafter viewed with a transmission electron microscope. Micrographs were taken by means of the electron microscope camera.

The micrographs taken (Fig. 1a–f) reflect cross-sections of the control capsule and the capsules filled with the polymer solutions. The micrographs were taken along the solution agar interface. All the micrographs were taken at an enlargement of ×11 500. The bar on each micrograph represents 1 μm.

The micrographs show a close resemblance to those taken during gel permeation chromatography of a polystyrene gel by Vollmert (1973). The fixation process used during TEM preparations included the dehydration of the agar capsules and replacement of the normal saline with resin. With the extraction of the normal saline the dissolved polymer coils moved towards the solution/agar interface. The molecular size of the polymers prevented them from moving across the solution/agar interface. Agar is a natural polymer and forms pores within its matrix (Tiedt, 1985). This characteristic allowed some penetration of the polymers into the agar. The individual polymers penetrated the agar to a varying extent. This can be seen by comparing Fig. 1a (control) with the rest (polymers). This phenomenon may be the result of differences in the interaction forces between individual polymer chains (Tompa, 1956; Vollmert, 1973), in that smaller coils or individual chains penetrate the agar better. The coil density of the polymers may have increased during the dehydration process. The fixation process was, however, the same for all the polymers and it can be concluded that the polymers have different coil structures as shown in the micrographs.

The micrographs have shown that differences occurred between the coiling tendency of the JR and the Gafquat polymers, and between the polymers individually. This provides substantial evidence that the molecular weight and the molecular structure of a polymer play an important role in

Fig. 1. Transmission electron micrographs of different polymer solutions. (a) The control capsule without any polymer – polymer coils are absent and the agar is clear. (b) The capsule with normal saline and polymer 125. The polymer tends to form large and densely packed coils (P). The three-dimensional structure of the polymer coil is visible. Pores (white spots) formed by these coils can be seen clearly. The polymer formed a layer on the surface of the agar and penetration of the polymer into the agar (A) is indicated by the black spots. (c) The capsule with normal saline and polymer JR 400. The polymer coils are as densely packed as the coils of JR 125 but do not tend to associate as strongly. The pores are much larger and a thicker layer is formed on the agar surface. There was a high penetration of the polymer into the agar. (d) The capsule with normal saline and polymer JR 30M. Smaller and more loosely packed coils are formed. The structure of the coils is different from the previous two polymers, forming layers rather than spheres. The layer formed on the solution/agar interface is less continuous than the previous two polymers. The penetration into the agar was the same as that of the previous two polymers. (e) The capsule with normal saline and the Gafquat 734 polymer. The overall structure of the coils is different from the polymers of the JR range. The coils are less numerous and much smaller. The individual coils are as densely structured as polymer JR 400 and 125, but do not form the continuous layer on the solution/agar interface. A higher penetration into the agar occurred. (f) The capsule with normal saline and the Gafquat 755N polymer. The three-dimensional structures of the polymer coils are clearly visible. Larger and more compact coils are formed, the pores are better defined and a lower penetration into the agar occurred than with Gafquat 734.

the coiling tendency of the polymer in solution and may influence the diffusion of substances from these polymer coils.

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