Ordered polyelectrolyte complex formation from amorphous polyions*

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The preparations of three types of polyelectrolyte complexes formed between poly(vinylbenzyltrimethylammonium chloride) and poly(methacrylic acid) are reported in this work. These types include unusual needle-like structures, radially extended 'fuzzy spheres', and an amorphous powder; each type being produced under different conditions.

INTRODUCTION

In recent years, polyelectrolyte complexes have received considerable attention due to their interesting and unique properties and their similarity to certain biological systems[1–8]. Significantly, whereas these polyelectrolyte complexes are normally amorphous 1:1 compositions of polycations and polyanions, Kabanov *et al.*, Tsuchida *et al.* and Blumstein *et al.* have shown that crystalline materials can be obtained under a variety of conditions[9–16].

During the course of our investigations on ampholytic polymers, we have observed the formation of a new, highly ordered, crystalline polyelectrolyte complex which is discussed in this work.

EXPERIMENTAL

The polycation that was used for the preparation of all the polyelectrolyte complexes discussed in this work was poly(vinylbenzyltrimethylammonium chloride), Dow Chemical Co., ECR-34 $[\eta] = 0.114$ dl g^{-1} in 0.1 N NaBr at 25°C. Based on CHN analyses and chloride ion determinations by titration, the composition of the polycation mixture was deduced to be approximately 77% quaternized polymer, 19% unquaternized polymer, and 4% NaCl.

Anal. Calcd. for $C_{12}H_{18}NCl$: C, 68.05%; H, 8.51%; N, 6.62%; Cl, 16.75%

Found: C, 62.63%; H, 7.96%; N, 5.08%; 15.33%.

Poly(methacrylic acid)

Poly(methacrylic acid) which had been recovered from spontaneously polymerized monomer and purified twice by precipitation in methanol was obtained from Dr E. Ellis of the University of Lowell. The viscosity average molecular weight, $\bar{M}_v$, was estimated to be 3.6×10^4 g/mol based on the equation

$$[\eta] = 66 \times 10^{-5}\, M^{0.5}$$

in 0.002 MHCl at 30°C[17].

Anal. Calc. for $C_4H_6O_2$: C, 55.81%; H, 7.03%.

Found: C, 55.48%; H, 7.20%.

Polyelectrolyte complexes

To 125 ml of 4 day old poly(vinylbenzyltrimethylammonium chloride) solution (0.13 M) was added 75 ml of poly(methacrylic acid) solution (0.28 M). A rapid increase in the viscosity of the mixture was observed as it apparently gelled. In addition, some small particles were seen to be suspended in the viscous gel. The mixture was transferred to a 1 l erlenmeyer flask and agitated overnight by continuous shaking. The viscosity of the mixture was significantly reduced and the homogeneity increased. To this solution was added 0.479 g of poly(vinylbenzyltrimethylammonium chloride) dissolved in distilled water. Continuously stirring, 0.50505 g of poly(methacrylic acid) dissolved in water was also added. The total volume of the resulting mixture was 300–400 ml. Within 15 min. small particles were visible in the solution. Once again, the solution was stirred overnight. When the agitation was stopped, needle-like particles were observed. Allowing an additional 3 h for settling, the supernatant liquid was partially decanted and a portion of the needles was crudely washed and filtered on a sintered glass funnel. The remaining supernatant liquid and needles were dialysed against distilled water and lyophilized. The needle-like particles were found to have an elemental CHN composition which is compatible with 1 mole of poly(vinylbenzyl trimethylammonium ion) to 5.5 moles of poly(methacrylic acid).

Equivalent and non-equivalent polyelectrolyte complexes were prepared by dissolving the required amount of each of the homopolymers in water and adding freshly prepared poly(methacrylic acid) to the freshly prepared polycation solution. The resulting gelled solution was agitated as before and when inspected, appeared homogenous. After 5 days, small particles were visible in the system, and after 2 weeks, 'fuzzy spheres' or radially extending fibres, ranging in size from 2mm to 10 mm in diameter (in solution), were apparent. The 'fuzzy spheres' increased in number and size with time.

An amorphous polyelectrolyte complex was prepared by adding 0.0269 mol of poly(methacrylic acid) in *ca.* 130 ml of water to 0.0180 ml of poly(vinylbenzyltrimethylammo-

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nium chloride) in 175 ml. water. Prolonged stirring, as before, followed by dialysis and lyophilization yielding a complex which had a CHN composition which was compatible with 1 mole of poly(vinylbenzyltrimethylammonium ion) to 1.4 mole of poly(methacrylic acid).

Anal. Calcd. for $C_{16}H_{23}NO_2$: C, 73.5%; H, 8.89%; N, 5.35%.

Found (amorphous): C, 60.59%; H, 8.85%; N, 3.26%.

Found (needlelike); C, 55.44%; H, 7.94%; N, 1.16%

Thermal studies

Thermogravimetric studies of the complexes were conducted utilizing a Perkin–Elmer TGS-1 Thermobalance with a UU-1 Temperature Program Controller.

Differential scanning calorimetry studies were conducted on each complex and homopolymer using a Perkin–Elmer DSC 1B.

X-ray studies

The X-ray beam was produced by a Norelco Generator with a Cu tube and Ni filter, $\lambda = 1.54$ Å. A Warhus camera having an adjustable sample to film distance of either 4.97 cm or 5.35 cm was used.

RESULTS AND DISCUSSION

In this investigation of the interactions of commercially available poly(vinylbenzyltrimethylammonium chloride) with low molecular weight poly(methacrylic acid), three types of polyelectrolyte complexes were obtained, *viz.*, needle-like particles, fuzzy spheres, and an amorphous powder. The amorphous polyelectrolyte complex could be obtained in nonstoichiometric proportions depending upon the method of preparation and purification employed. At the concentration of homopolymers used, Tsuchida reported that a precipitate should form upon mixing[12]. However, it is believed that the presence of NaCl in the commercial polycation may have hindered precipitation by reducing polymer-polymer interactions. This was supported by an experiment in which a dialysed sample of poly(vinylbenzylammonium chloride) with no NaCl present resulted in the formation of a precipitate with poly(methacrylic acid) when used at the described concentration.

Since the nonstoichiometric complex was in gel form, exhaustive dialysis concentrated the polymer components while removing microsolutes. After lyophilization, the nonstoichiometric complex had a theoretical composition of 1:1.5 poly(vinylbenzyltrimethylammonium ion) to poly(methacrylic acid), whereas the composition based on N elemental analysis indicated a composition of 1:1.4.

In contrast to the amorphous complex, the needle-like particles and the fuzzy spheres were obtained as a result of time dependent processes: the needles when aged solutions were used; and the fuzzy spheres when the polymer complex gel was left undisturbed for a period of two weeks. The composition of the crystalline needles was determined to be, surprisingly, the 1:5.5 poly(vinylbenzyltrimethylammonium ion) to poly(methacrylic acid). The yield of this highly crystalline complex was found to be approximately 9% of that of theoretical 1:1 complex. Interestingly, the formation of the needle-like complex was observed under three conditions. The first of these was when the homopolymer solutions were aged at least 3 to 4 days. No needles were observed if freshly prepared solutions were used, even if the rest of the procedure described was followed exactly. The second condition was that the impure polycation containing NaCl was used. An experiment using a 3 day old solution of dialysed polycation resulted in a large amount of white precipitate forming immediately upon addition of the poly(methacrylic acid) solution, whereas a 3 day old solution of the impure polycation resulted in needle formation. The relative proportion of poly(methacrylic acid) to poly(vinylbenzyltrimethylammonium chloride) did not seem to be critical, with needles being observed when both equivalent and nonequivalent amounts of homopolymers were used.

Needles were observed using a less complicated procedure than that described in the Experimental section, although the yield was much smaller (less than 1% of that of a theoretical 1:1 yield). If the gel obtained by adding the aged polyacid solution to the aged polycation solution was agitated overnight and then allowed to settle, needles were observed on the bottom of the vessel and could be recovered. If the solution was placed on a magnetic stirrer for an additional day, the yield of needles increased. It is not understood how the addition of homopolymer solutions to the day old gel solution as previously described affects needle formation or yield.

The third condition that shows influence on the process is the molecular weight of the polyanions. Preliminary experiments with a high molecular weight poly(methacrylic acid), ($\bar{M}_v = 820\,000$), which was aged for 5 days, and impure poly(vinylbenzyltrimethylammonium chloride) gave a rapid precipitation with no needle formation. The solubility properties of highly ordered complex were also interesting and were quite different than those of other polyelectrolyte complexes. It was found that the needle-like complex was soluble only in basic media and not in any of the following solvent systems: methanol; acetone; DMSO; 25 and 50% H_2SO_4; 25 and 50% H_3PO_4; 10, 20, 30 and 40% (w/w) $NaBr/H_2O$; and the ternary solvents of NaBr, acetone and H_2O in the proportions of 35, 15 and 50%; 25, 10, and 65%; 15, 25, and 60%; and 30, 10 and 60%. In contrast, the 1:1.4 complex was soluble in 10% (w/w) $NaBr/H_2O$ as well as in base.

That the needle-like structures were indeed crystalline was supported by polarizing microscopy and by X-ray studies. A powder diffraction X-ray analysis showed a highly ordered structure with 5 diffraction lines. The *d* spacing, and relative intensities are listed in *Table 1*. It appears that d_1 is an integrated multiple of d_5, with $n = 2$ in the Bragg equation. Under similar conditions, the 1:1.4 complex failed to give a diffraction pattern and showed instead only a typical amorphous halo. In addition, a d.s.c. study of the amorphous complex gave an exothermic transition at 435 K which may have been due to crystallization. However, a pellet of the amorphous complex was heated on the d.s.c. to 480 K and then cooled at 20°/min to room temperature.

Table 1 Spacings of 1:5.5 Needle-Like Complex

Ring	Intensity	d, Å
1	strong	4.59
2	medium	3.23
3	weak	2.68
4	weak	2.56
5	medium	2.28

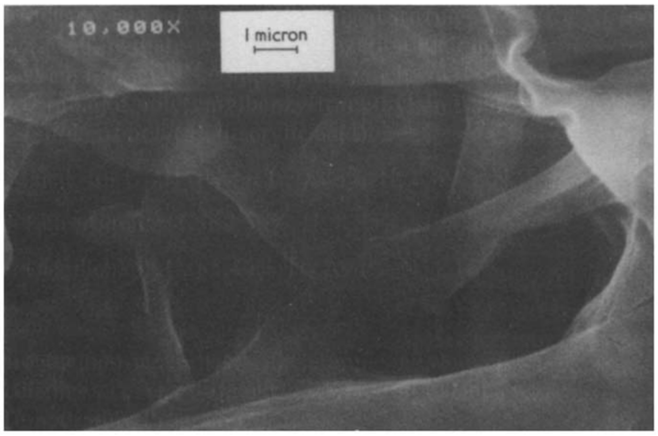

Figure 1 Scanning electron micrograph of the network structure of a 'fuzzy sphere' polyelectrolyte complex

Again, the X-ray analysis showed no diffraction pattern, and it would appear that the 435 K transition in the amorphous complex is not due to crystallization.

In order to ascertain the crystallinity behaviour of the individual homopolymers, X-ray studies of purified and unpurified poly(vinylbenzyltrimethylammonium chloride) were undertaken, as well as that of the low molecular weight sample of poly(methacrylic acid) used. The X-ray analysis of the unpurified polycation showed a halo, a very sharp line at 2.81 Å, which is not typical of polymers but is typical of a low molecular weight compound, and dots, indicating the pressure of salt. Since the reported spacing of the 2,0,0 plan of NaCl is 2.82 Å and because of the elemental analysis obtained, it was therefore concluded that the unpurified polycation was amorphous and was contaminated with NaCl. This was confirmed when a sample of the dialysed polycation was shown to be amorphous by X-ray analysis. Similarly, the poly(methacrylic acid) used was also shown to be amorphous. It would thus appear that the crystallinity of the needles is not related to homopolymer morphology but is instead related to the nature of the polycation-polyanion interaction.

To obtain more information on the needles and 'fuzzy spheres', scanning electron microscopy was performed. *Figure 1* is a micrograph showing the detail in the network formation of a 'fuzzy sphere' of poly[(vinylbenzyltrimethylammonium)poly(methacrylate)]. It is similar to related polyelectrolyte complexes described by Tsuchida[11], although he does not describe his networks as spherically shaped such as observed in this case. The formation of a network was also observed when the purified polycation with no NaCl present was used, and appeared similar to the 'fuzzy sphere' type network when observed under the polarizing microscope.

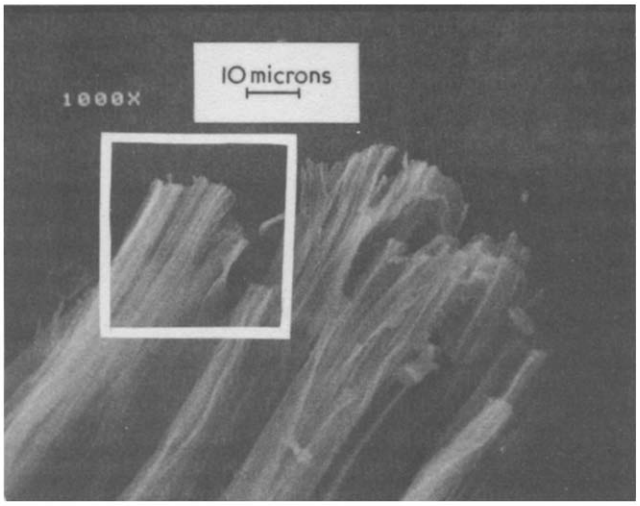

Figure 2 Scanning electron micrograph of the needle-like polyelectrolyte complex

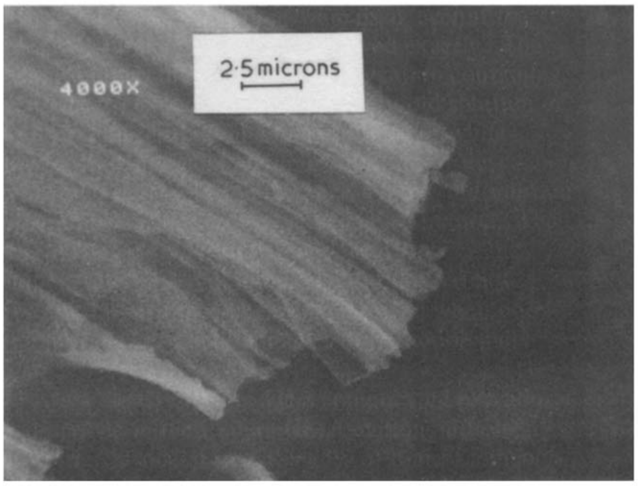

Figure 3 Scanning electron micrograph enlargement of the boxed area of Figure 2

In *Figures 2* and *3* are shown the scanning electron micrographs of the needle-like, 1:5.5 polyelectrolyte complex. The largest of the needle-like structures obtained were 2 mm long and 0.1 to 0.2 mm wide. *Figure 2* is a section of a needle and the boxed area in this figure is shown in more detail in *Figure 3*. X-ray analysis of a single needle-like structure showed the same diffraction pattern as a powder sample, suggesting no orientation within the needle. Instead of arcs indicating orientation, complete rings were observed.

As the order shown in *Figures 2* and *3* is highly unexpected for the formation of a polyelectrolyte complex from amorphous polyions, preliminary C^{13} spectra have been undertaken in order to determine if there was stereoregular enhancement in the complex. For the poly(methacrylic acid) homopolymer in D_2O using the peak assignments of Klesper *et al.* and standard curve resolving techniques, it was determined that the polymethacrylic acid used was atactic. Similarly, the polycation homopolymer in D_2O, based on the quaternary carbon peak of poly(vinylbenzyltrimethylammonium chloride) was also determined to be atactic based on peak assignments for polystyrene. For the 1:5.5 needle-like complex in 10% NaOD in D_2O, a 10–20% syndiotactic enrichment of the poly(methacrylic acid) moiety appears to be present, whereas for the amorphous 1:1.4 complex this is not the case.

It is apparent that considerable work remains in order to characterize this unusual new form of polyelectrolyte complex, and we hope to report on these studies in the near future.

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