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Complex formation between poly(sodium phosphate) and poly(4-vinylpyridinium chloride) in aqueous solution

Nermin Acar[a], Malcolm B. Huglin[a,*], Tülay Tulun[b]

[a]Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK
[b]Department of Chemistry, Technical University of Istanbul, 180626, Maslak–Istanbul, Turkey

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Abstract

Insoluble polyelectrolyte complexes were produced by admixture of (0.2 M) aq. solutions of poly(sodium phosphate) (PSP) and poly(4-vinylpyridinium chloride) (P4VPC) over the whole range of composition. Independent of the order of addition, the weights of isolated complex were approximately equal to those calculated on the basis of reaction stoichiometry. Stoichiometry was also confirmed by analysis of the supernatant liquid in conjunction with the weights of initial components and complex. Dissolution of the complex required a certain minimum hydrogen ion concentration obtained by using either a strong acid/base or a weak acid. Analysis showed that the starting materials were thereby regenerated. In dilute (1×10^{-4} M) aq. solutions, the complex did not precipitate, but UV spectroscopy demonstrated its presence and its change of shape with time. © 1999 Elsevier Science Ltd. All rights reserved.

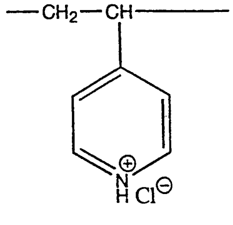
Keywords: Poly(sodium phosphate); Poly(4-vinylpyridinium chloride); Polyelectrolyte complex

1. Introduction

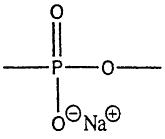
Polyelectrolyte complexes (PEC) are materials produced by coulombic interactions between polymers bearing groups, which may be in the main chain (integral type) or in the side chain (pendant type) [1]. The conditions whereby the PEC forms as species of colloidal dimensions or precipitates immediately from solution have been discussed elsewhere [2]. PEC are also produced in matrix polymer reactions [3]. Significant differences exist between the chemical, thermal and mechanical properties of PEC with respect to those of their components due in part to the cross-linked nature of PEC [4,5]. Limited swellability in water and organic liquid obtains, yielding the analogue of hydrogels and organogels respectively known in chemically crosslinked polymers.

Previous studies cognate to the present investigation have focused considerably on precursors of the pendant type for example poly(4-vinylpyridinium chloride) (P4VPC) and poly(sodium 2-methyl-2-acrylamido propane sulphonate) (PSAMPS), using the measurement of conductivity and pH to follow the PEC formation of up to the equivalence point [6]. Poly(sodium phosphate) (PSP) is interesting because it is not an organic polymer and is, rather unusually, one of the few anionic polymers of the integral type. It has been used as a template in the matrix polymerisation of 4-vinylpyridine (4VP) [7,8] and determination of the end point in its reaction with P4VPC has been reported previously [9].

The present article is a more detailed continuation of the work on the interaction between P4VPC and PSP the repeat units of which have the following structures:



P4VPC



PSP

2. Experimental

2.1. Materials

Unquaternised P4VP was obtained from Reilly Industries Inc. as a 25% w/w solution in methanol from which the solid was obtained by evaporation of solvent. The measured value

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* Corresponding author. Tel.: + 44-161-295-3509; fax: + 44-161-295-5111.

E-mail address: m.b.huglin@chemistry.salford.ac.uk (M.B. Huglin)

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of the limiting viscosity number in ethanol at 298 K (19.3 $dm^3\,kg^{-1}$), in conjunction with the Mark Houwink constants [10], yielded a molecular weight of 17.6 × 10^3 $g\,mol^{-1}$. Conversion to the polysalt P4VPC was effected by the addition of the stoichiometric quantity of standardised aq. HCl followed by evaporation and final drying in a vacuum oven at 314 K. The degree of quaternization of 97% was yielded both by a gravimetric method [11], and by a volumetric procedure [11].

PSP was purchased from Aldrich Chemical Co. The measured value of the limiting viscosity number in 0.415 M aq. NaBr at 298 K (2.6 $dm^3\,kg^{-1}$), in conjunction with the Mark–Houwink constants [12], gave a molecular weight of 2.77 × 10^3 $g\,mol^{-1}$. The GPC analysis (courtesy of Mr S.K. Nixon, University of Manchester) in 0.5 M aq. $NaNO_3$ based on poly(ethylene glycol) calibration afforded $M_w = 2.10 \times 10^3\ g\,mol^{-1}$ and $M_w/M_n = 1.14$. Measurements on solutions of P4PVC under similar conditions proved unsatisfactory probably on account of the cationic nature of both the polymer and the column.

The number average degree of polymerisation of PSP was also obtained by end group analysis [13]. Orthophosphate is the monomer of polyphosphates. The chain phosphates have one strongly ionised hydrogen for each phosphorus atom and have one weakly ionised hydrogen at each end of the chain. By titrating this weak hydrogen it is possible to determine the number of end groups present in the chains.

A sample of PSP was dissolved in water and the pH was lowered to ca. 3 with HCl in order to convert polyphosphate to polyphosphoric acid. Potentiometric titration vs. aq. NaOH was conducted through the first (ca. pH 4.5) and second (ca. pH 9) end points between which the number of moles of base consumed (A) corresponds to the weak hydrogen of polyphosphoric acid.

To determine the total phosphorus content, polyphosphate was degraded by hydrolysis to orthophosphate by boiling the solution containing a known mass of sample, in 1 N HNO_3 for 1 h. The pH was lowered to ca. 3 with HCl in order to convert orthophosphate to orthophosphoric acid. Potentiometric titration vs. NaOH was then conducted through end points near pH 4.5 and 9. The number of moles of base consumed (A_h) corresponds to the total phosphorus in the sample.

The fraction of the total phosphorus present as end group is given by:

$$\text{Fraction of total } P_2O_5 \text{ as end groups} = \frac{A}{A_h}. \quad (1)$$

As every chain is limited by two end groups, it follows that in a sample containing only chain phosphates, the number average chain length ($\bar{X}_n$) of the phosphate is given by:

$$P_2O_5\ (\text{total})/P_2O_5\ (\text{end}) = \bar{X}_n/2. \quad (2)$$

All other materials were of AnalaR grade. Deionised water was obtained from a Millipore-Milli-U10 purification unit.

3. Methods

3.1. Formation and separation of PEC

Two series of PEC were prepared by mixing 0.2 M PSP and P4VPC solutions, where molarity M is in moles of monomer units per dm^3. The mole fractions of 4VPC units in the feed (X_{4VPC}) were 0.1, 0.3, 0.5, 0.7, 0.9. In series 1, P4VPC was added dropwise to PSP; in series 2, the order of addition was reversed. Before mixing, the individual solutions were clear but, upon mixing, precipitates formed immediately. After isolation of precipitates by centrifugation, they were washed repeatedly with deionised water and dried to a constant mass in vacuo at 343 K.

3.2. UV analysis of supernatant liquids

The supernatant liquids associated with each PEC from series 1 and series 2 were analysed by UV spectrophotometry using a Hewlett–Packard 8452 spectrophotometer. P4VPC has an absorbance peak at 260 nm (λ_{max} = 260 nm), at which wavelength PSP does not absorb. The absorbance of standard solutions of P4VPC, having concentrations between 10^{-4} and 10^{-6} M was measured at this wavelength and found to obey the Lambert–Beer law, the extinction coefficient having a derived value of 268 $m^2\,mol^{-1}$.

Formation of a yellow precipitate on reaction of phosphate with molybdate in acidic solution was utilised to determine colorimetrically the phosphorus content of the supernatant liquid [14].

After drying at 378 K for 1 h a 0.02 wt.% solution of monopotassium phosphate was prepared. A 3.76 wt.% solution of ammonium molybdate was prepared by initial dissolution in water followed by an addition of concentrated H_2SO_4 and finally dilution to a fixed volume with water. To 2 ml ammonium molybdate was added separately 1, 2, 3, 4, 5 and 6 ml of the monopotassium phosphate solution, 10 ml acetone and sufficient water to yield a final volume of 25 ml.

The absorbance of these standard solutions was measured at 338 nm using a blank that had been prepared from 2 ml ammonium molybdate solution, 10 ml acetone and final dilution to 25 ml water. The derived value of the extinction coefficient was 1.58 $m^2\,g^{-1}$.

The supernatant liquid and washings from each solution were collected and made up to a known volume with deionised water. Concentrations, and thereby, the total mass of unreacted P4VPC and PSP in the supernatant liquids, were determined from the measured absorbances at 260 and 338 nm, respectively. NaCl is produced in PEC formation. To examine its possible effect on the absorbance of the individual polyanions, absorbance was measured on

Table 1
Comparison of the actual weights of precipitates (w_a) with the weights calculated on a stoichiometric basis (w_c). (Here, as well as in the later Tables 2, 4 and 5, error limits were estimated using standard deviations with the statistical parameter *t* according to the procedure of Skoog et al. [16])

X_{4VP^+} in feed	w_c (g)	w_a (g)	w_a/w_c
Series 1 PSP as titrant			
0.1	0.074	0.058 ± 0.002	0.78 ± 0.02
0.3	0.222	0.191 ± 0.015	0.86 ± 0.07
0.5	0.370	0.344 ± 0.018	0.93 ± 0.05
0.7	0.222	0.191 ± 0.014	0.86 ± 0.06
0.9	0.074	0.056 ± 0.003	0.76 ± 0.04
Series 2 P4VPC as titrant			
0.1	0.074	0.055 ± 0.002	0.74 ± 0.03
0.3	0.222	0.192 ± 0.012	0.86 ± 0.05
0.5	0.370	0.352 ± 0.019	0.95 ± 0.05
0.7	0.222	0.230 ± 0.006	1.03 ± 0.03
0.9	0.074	0.056 ± 0.003	0.77 ± 0.04

solutions containing a constant amount of polyion and different concentrations of NaCl.

3.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were made with a Mettler TA-3000 instrument. Indium and zinc standards were used to calibrate the temperature and the thermal scale. The measurements to determine glass transition temperatures (T_g) were carried out in a N_2 atmosphere at a heating rate of 10° min^{-1} and the middle point criterion was used. In order to avoid differences in thermal history, all the samples were subjected to the same thermal treatment.

3.4. Optical density

PEC formation leading to precipitation was effected on 0.2 M solutions. Measurements of optical density were used to investigate the situation prevailing in very dilute (ca. 1×10^{-4} M) solution. The product of the admixture was stirred for at least 24 h and transferred to a 1 cm path length cell maintained at 298 ± 0.1 K. Optical density between 300 and 630 nm was scanned at 2 nm intervals. Scans were also made after additional periods of time [6].

3.5. Breakdown of PEC

To a fixed mass of dried PEC was added a fixed volume of strong acid and a weak acid of various molarities and breakdown accompanied by dissolution after 48 h at room temperature was assessed visually. When dissolution did occur, the breakdown products were determined analytically.

3.6. Polyelectrolyte complex in dilute solution

PEC formation in dilute solution was examined spectrophotometrically. Between 200 and 1000 nm PSP does not show any absorbance, whereas P4VPC has a maximum absorbance at 255 nm. While mixing dilute solutions of polyions, no precipitation was observed. None of the mixtures was turbid. To 1 ml of 1×10^{-3} M P4VPC were added separately 1, 2, 4 and 9 ml of 1×10^{-3} M PSP. Finally, all the solutions were diluted to 25 ml and the spectra were measured.

3.7. Suppression of PEC formation

To a fixed volume of standard aq. P4VPC were included various volumes of standard aq. NaCl solution in order to assess visually whether the PEC precipitate was produced or not by subsequent addition of standard PSP.

4. Results and discussion

4.1. End groups in PSP

In the potentiometric titrations the values of A and A_h were 0.047 mol and 0.54 mol, respectively. Hence via Eqs. (1) and (2) the values of the fraction of total phosphorus present as an end group and the number of average chain are calculated to be 0.087 and 23, respectively. The corresponding molecular weight is thus $23 \times 102 = 2.35 \times 10^{-3}$ g mol^{-1}, which is similar to the values yielded by viscosity and GPC.

4.2. Mass and composition of PEC

The precipitate compositions were calculated by assuming that complete stoichiometric reaction and total counterion release occurred [15]. Reaction stoichiometry may be described by comparing the actual weights of precipitates (w_a) with the weights calculated on a stoichiometric basis (w_c).

In Table 1, where X_{4VP^+} denotes the mole fraction of 4-vinyl pyridinium units in the feed, it is seen that

(a) Generally actual weights are somewhat smaller than the calculated ones.
(b) The order of addition does not affect the actual weights.

Finding (a) may have two possible causes. First, the p*K*a of P4VP at 298 K is 4.2 [17]. Complete protonation of P4VP by strong acid, HCl, is difficult to achieve (degree of quaternization was 97%, as indicated in Section 2) and unprotonated groups cannot participate in the formation of the complex. Second, the PSP is of a rather low molecular weight. Hence (via Eq. (1)) the experimentally determined content of the end groups is significant (8.7%) and a reaction involving an end group is less effective in building up a complex than one involving a main chain unit.

4.3. Mass and composition of supernatant liquids

PEC compositions calculated from UV analysis of supernatant liquids in series 1 and series 2 are presented in Table 2. Each PEC composition was obtained from the concentration of unreacted polyions detected in the supernatant. As indicated in Table 2, estimated experimental errors ranging from ±0.024 to ca. twice this amount apply to the mole fractions of P4VPC in PEC. Table 2 shows that

(a) Composition of PEC is independent of the order of addition.

(b) For all feed mixtures, reaction stoichiometry is very close to 1:1.

The slight departures from 1:1 stoichiometry are probably due to errors associated with transference losses. In the review of their work on PEC from mixing a wide range of polyelectrolytes, Philipp et al. [1] suggested that 1:1 PEC should be considered to encompass precipitates containing a molar ratio of anionic to cationic groups between 0.9 and 1.1, as deviations from 1:1 stoichiometry within the range may be apportioned to limitations in reproducibility of preparation and characterisation of PEC. In the present work, the average value of the ratio of cationic to anionic groups in the complex is 1.04.

4.4. Breakdown and suppression of PEC formation

To assess the stability of the PEC, various solutions were added to a fixed mass (0.0163 g) of dried PEC, as noted in Section 2. The findings are summarised in Table 3. It is seen that very dilute solutions of the strong acid HCl were ineffective in breaking down the complex and that a concentration $[H^+] = 10^{-2}$ mol dm^{-3} was necessary. The same results hold for another strong acid, HNO_3. Using the value of $K_a = 1.78 \times 10^{-5}$ as the acid dissociation constant for the weak acid, acetic acid, a value of $[H^+] = 10^{-2}$ mol dm^{-3} is yielded at a molarity of 5.56. As indicated in Table 3, dissolution does indeed occur at this concentration. Finally, as $[H^+] = 10^{-2}$ mol dm^{-3} is equivalent to $[OH^-] = 10^{-12}$ mol dm^{-3}, it was demonstrated experimentally that the PEC breaks down at this concentration of strong base.

After breakdown, the resultant solution was neutralised with NaOH to yield a precipitate, which was isolated by centrifugation and dissolved in ethanol. The UV spectrum of this solution was identical with that of the original P4VP in ethanol.

After the previous precipitation, ammonium molybdate in acidic solution was added to the supernatant liquid. The immediate formation of a yellow precipitate verified the presence of phosphate. The breakdown products having been identified qualitatively, their contents were analysed quantitatively by UV as detailed previously in Section 2. Expressed as percentage by weight of the initial PEC, the contents of phosphate and of $P4VP^+$ were 41.0 and 55.3%, respectively. These values compare favourably with the corresponding ones of 42.7 and 57.3%, respectively calculated from the composition of the initial PEC. Breakdown of a PEC often requires a more complex (often ternary) solvent. The present system is unusual in the respect that one of the components (polyphosphate) is irreversibly hydrolysed by acid to orthophosphate.

With regard to suppression of PEC formation, the solutions each comprised 2 ml of 0.2 M aq. precursor. The concentration of the aq. NaCl contained within the aq. P4VPC was 5 M and the volumes (V) of NaCl solution used were 2.0, 2.4, 2.5, 2.6 and 3.0 ml. PEC formation, i.e. precipitation, was observed, when $V = 2.0$ ml. Turbidity was evident when $V = 2.4$ and 2.5 ml. Suppression of PEC formation, i.e. complete clarity, was obtained only at the higher two salt concentrations afforded by $V = 2.6$ and 3.0 ml. Hence the lower of these two values represents the minimum critical concentration of the salt necessary. This concentration corresponds to a high value of 33 for the ratio of number of moles of salt/number of moles of ionic precursor.

In PEC formation NaCl is eliminated and the role of added NaCl is to suppress PEC formation by the common ion effect. Additionally, although the precursors are dissociated, masking of their charges by NaCl reduces the ionic interaction between the polyelectrolytes. It is interesting to note by way of comparison that masking of charges in aq. poly(2-methyl-2-acarylamidopropane sulfonic acid), which is a very strong acid cf. polyphosphoric acid, requires incorporation of a very high concentration of NaCl. Within the relevant range of concentration of polymer, where the effect was examined viscometrically [18] (1–10 g dm^{-3}), the ratio of number of moles of salt/number of moles of monomer unit is considerably in excess of 33, the value lying within the range 84–840.

4.5. Polyelectrolyte complex in dilute solution

The effect of the addition of PSP on UV spectrum of P4VPC under the dilute conditions described in Section 2 is shown in Fig. 1 relating to (a) P4VPC and four mixtures (b)–(e). The values of X_{P4VP^+} are 1.0, 0.50, 0.34, 0.20 and 0.10 in (a)–(e), respectively. The PSP component does not have any absorbance between 200 and 1000 nm and the peak at 255 nm in all the curves is due to the pyridine ring. Although the mole fractions differ, the mass and the concentration of P4VPC was fixed at a constant value for all the systems. Hence, in the absence of any interactions, the absorbances at 255 nm would also be expected to remain constant. In fact for the mixtures, this absorbance is seen to increase with the increase in X_{P4VP^+}. In the mixtures an additional peak or shoulder appears at 220 nm, its absorbance following a similar sequence to that exhibited at 255 nm (at the lowest X_{P4VP^+} the absorbance at 220 nm is only barely detectable). The hyperchromic effect at 255 nm and new peak formation at 220 nm are probably due to the

Table 2
PEC composition calculated from UV analysis of supernatant liquids (A = calculated from UV analysis; D = C − B; F = E − D; I = G/(G + H))

X_{4VP^+} in feed	A $10^4 \times$ moles of $4VP^+$ in washing	B $4VP^+$ in washing (g)	C Weight $4VP^+$ in feed (g)	D Weight $4VP^+$ in complex (g)	E w_a (g)	F Weight phosphate in complex (g)	G $10^4 \times$ moles of $4VP^+$ in complex	H $10^4 \times$ moles of phosphate ion in complex	I X_{4VP^+} in complex
Series 1, P4VPC as titrant									
0.1	0.550 ± 0.03	0.006	0.042	0.036	0.055 ± 0.020	0.019	3.39	2.41	0.585 ± 0.026
0.3	1.27 ± 0.01	0.013	0.127	0.114	0.192 ± 0.012	0.078	10.7	9.87	0.521 ± 0.038
0.5	2.89 ± 0.02	0.031	0.212	0.181	0.352 ± 0.019	0.171	17.1	21.7	0.441 ± 0.027
0.7	15.3 ± 0.01	0.162	0.297	0.135	0.230 ± 0.016	0.095	12.7	12.0	0.514 ± 0.042
0.9	33.5 ± 0.01	0.356	0.387	0.031	0.057 ± 0.003	0.026	2.92	3.29	0.470 ± 0.030
Series 2, PSP as titrant									
0.1	0.427 ± 0.01	0.005	0.042	0.037	0.057 ± 0.002	0.020	3.49	2.53	0.579 ± 0.024
0.3	1.09 ± 0.01	0.012	0.127	0.115	0.191 ± 0.015	0.076	10.8	9.62	0.530 ± 0.049
0.5	2.92 ± 0.02	0.031	0.212	0.181	0.344 ± 0.018	0.161	17.2	20.4	0.457 ± 0.027
0.7	17.9 ± 0.01	0.190	0.297	0.107	0.191 ± 0.014	0.084	10.1	10.6	0.487 ± 0.041
0.9	33.6 ± 0.02	0.357	0.387	0.030	0.056 ± 0.003	0.026	2.83	3.29	0.462 ± 0.029

Table 3
Effect of acidic and basic aq. solutions on the stability of PEC. ((+) dissolved; (−) did not dissolve)

	Concentration (mol dm^{-3})				
	10^{-12}	10^{-4}	10^{-3}	10^{-2}	5.56
HCl		−	−	+	
HNO_3		−	−	+	
CH_3COOH					+
NaOH	+				

formation of ionic bonds between the phosphate and pyridinium groups by analogy with the observations and interpretations of Inai and co-workers [19,20] on complexation of P4VP with poly(methacrylic acid). The latter polymer has a p*K*a ~ 6.9 [21], which is higher than the p*K*a values (ca. 2.95 and 4.5) of the two main dissociations of poly(phosphoric acid) and hence pyridine–phosphate interaction is even more favourable.

4.6. Turbidity

To supplement the findings via UV analysis on complex formation in 10^{-3} M solution, measurements of turbidity, (τ) were made on dilute (10^{-4} M) solutions, as described previously in order to evaluate the shape parameter β in Eq. (3), where λ denotes the wavelength in vacuo:

$$\tau \propto \lambda^{\beta-4}. \tag{3}$$

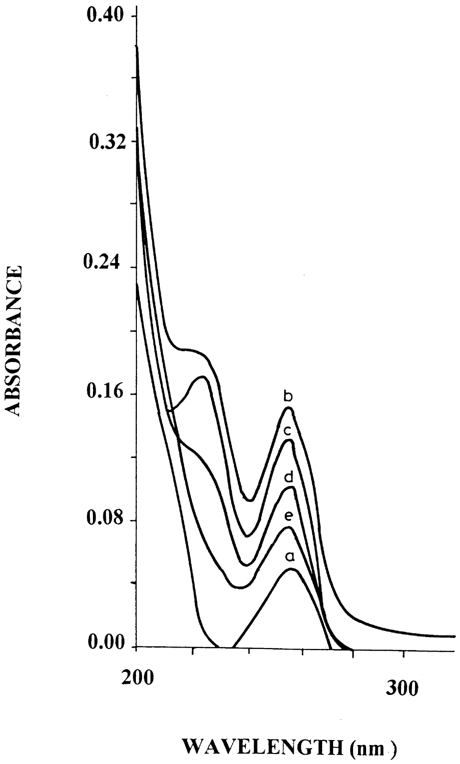

Fig. 1. Effect of addition of PSP solution on absorbance of P4VPC. For explanation of (a)–(e) see text.

Table 4
Effect of time on the shape of PEC produced in very dilute solution

Time (days)	β	Time (days)	β
Series 1, PSP as titrant		*Series 2, P4VPC as titrant*	
1	1 ± 0.08	1	2.3 ± 0.02
2	1 ± 0.02	2	2.2 ± 0.01
3	1 ± 0.01	3	1.9 ± 0.03
4	1 ± 0.03	4	1.8 ± 0.05
5	1.6 ± 0.04	5	[a]
6	1.7 ± 0.02	6	[a]
7	2 ± 0.01	7	[a]
8	2 ± 0.05	8	[a]

[a] Although values of β were recorded, full reliance is not made on them because of slight separation of bacterial growth.

Optical density was taken as the measurement of turbidity and from the accurately linear plots of log τ vs. log λ encompassing 150 values of λ (not reproduced here), the slope ($\beta - 4$) yielded the values of β (see Table 4). These values were ca. 1 initially, but thereafter increased with time up to a value of ca. 2 when PSP was titrant, whereas for the opposite order of addition the values of β did not differ significantly from 2. Values of 1 and 2 for β correspond to scattering by particles that are rod-like and spherical, respectively.

4.7. Glass transition temperatures

The DSC measurements on the precipitated PEC each displayed only one T_g. The results are shown in Table 5. Among these findings there are some that are unusual enough to merit reporting, despite the fact that we have been unable to explain them satisfactorily.

(a) The order of addition in producing a complex has no effect on T_g.
(b) The complexes, as opposed to the feed mixtures, all have approximately the same composition.
(c) With regard to item (b), all the values of T_g would therefore be expected to be the same.

Table 5
Glass transition temperatures (K) of complexes of P4VPC with PSP

X_{P4VPC} in feed	T_g	X_{P4VPC} in complex
PSP as titrant		
0.1	401	0.57 ± 0.02
0.3	425	0.53 ± 0.05
0.5	414	0.46 ± 0.03
0.7	394	0.49 ± 0.04
0.9	392	0.46 ± 0.03
P4VPC as titrant		
0.1	405	0.59 ± 0.03
0.3	425	0.52 ± 0.04
0.5	411	0.44 ± 0.03
0.7	393	0.52 ± 0.04
0.9	391	0.46 ± 0.03

(d) However, even within the maximum experimental uncertainty of ±2 K, there is a definite departure from constancy among the values.

(e) The measured values of T_g for the precursors P4VPC and PSP, which are not included within Table 5, were 401 and 540 K, respectively. The value of T_g, that can be calculated on the basis of the Fox equation for copolymers or blends, must lie in the interval 401–504 K. To this value should be added an increment due to the crosslinking. However, in the Table it is seen that for two of the complexes the value of T_g is actually less than 401 K.

(f) Although the precursors P4VPC and PSP are in their salt forms, the resultant PEC contains the moieties P4VP and poly(phosphoric acid). Hence it may well be more appropriate to make the calculation in item (e) on the basis of these components.

The measured value for the P4VP sample was 394 K and Eisenberg et al. [22] have obtained a value of 263 K for poly(phosphoric acid). The latter appears satisfactory in view of their reported value of 553 K for PSP, cf. our value of 540 K for the present PSP of very low molecular weight. On the basis of P4VP and poly(phosphoric acid) as components of the PEC the T_g should lie in the lower interval of 263–394 K with some augmentation for the crosslinking. Hence, in contrast to the situation in which the salt form are regarded as precursors, the observed T_g values now become too high (instead of too low).

The majority of T_g values of PEC relate to systems in which there are specific interactions such as hydrogen bonding between the precursors not in their salt form; the values of T_g are greater than the calculated ones. In one exception reported by Wang et al. [23] the lower T_g values cf. those calculated were attributed to the plasticising effect of the residual, high boiling solvent used in casting the blends from the solution. This possible explanation is not relevant to the present situation. With regard to PEC from the precursors in their salt forms, most emphasis has been placed on formation and stoichiometry. As far as the authors are aware, the only reported observations on T_g relate to complexes between P4VP and PSAMPS [24]. As already noted, PAMPS is a very strong acid cf. poly(phosphoric acid). Accordingly, the density of ionic crosslinking is much greater than in the present system. Indeed in the P4VPC–PSAMPS complexes it was not possible to locate a T_g at all by either DSC or NMR relaxation.

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