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Complexation behaviour of radiation synthesized poly(vinylbenzyltrimethylammonium chloride) and its gel with potassium hexacyanoferrates (II, III) and potassium persulfate in aqueous medium

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Abstract

High energy gamma radiation has been used to synthesize linear poly(vinylbenzyltrimethylammonium chloride) (PVBT) as well as crosslinked PVBT gels. Complexation behaviour of linear and crosslinked PVBT with $K_2S_2O_8$, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ have been studied by viscometry, turbidity and equilibrium swelling measurements. The stoichiometry of the complex formed was found to be a function of charge on the anions of complexing species. Crosslinked poly(vinylbenzyltrimethylammonium chloride) gels were found to desorb some of the embedded water when swollen gels were placed in these salt solutions. Existence of strong ionic interactions between polymer chains and complexing salts was confirmed by changes in equilibrium swelling of complexed crosslinked matrices as well as in the stoichiometry of linear PVBT complexes in presence of strong electrolytes like NaCl.
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1. Introduction

Polymer gels have been suggested as excellent models for studying molecular interactions since a polymer network can be regarded as a single giant molecule. Any phenomena which lead to changes in the conformational size of the linear polymer molecule in homogeneous solution will lead to directly measurable changes in the dimensions i.e. the degree of swelling of the gel consisting of the same monomer units [1,2]. For crosslinked polymer in the gel state, the binding may be directly studied by the equilibrium uptake of low molecular ions by the gel, which act as its own semi-permeable membrane. In many cases, salts can drastically change the physical properties of dissolved macromolecules [3,4]. In gels, salt addition may cause a volume transition [5–8]. These effects are usually explained by changes of the water structure induced by ion hydration [9]. Among the various type of polymers the polyelectrolytes are generally highly sensitive to small changes in pH, ionic strength or temperature because the ionic groups in polymer are considerably influenced by the environment. Usually the changes of environment result in coil-globule transitions for linear polyelectrolytes causing swelling or shrinking of gels [10]. Different types of transitions that occur in linear and crosslinked polyelectrolytes have been extensively studied in aqueous

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media [10,11]. Complex formation due to interaction of polyelectrolytes and low molecular weight ions results in precipitation due to strong electrostatic attraction between oppositely charged polyelectrolytes and ions. This phenomenon is of current interest because of its potential use in chemical sensing, surface modification, device applications, drug-delivery systems, purification technology, selective sorption, ion exclusion resins and ion exchange resins and membranes [12–19]. Poly(vinylbenzyltrimethylammonium chloride) is an amphiphilic polyelectrolyte containing both hydrophobic groups (backbone chain with pendant aromatic ring) and hydrophilic positively charged quaternary ammonium group in every monomer unit, which ionizes to a polycation in aqueous medium. Complexation behaviour of PVBT with other polyanion poly(sodium styrenesulfonate) (PSSS) has been extensively studied using conductometric [20], dielectric [21] and viscosity measurement [22] methods, to probe the complexation kinetics as well as to study the effect of presence of other electrolytes on the extent of their complexation. Swelling behaviour of radiation synthesized PVBT-co-PSSS gels in presence of different ions and solvents has also been reported recently by us [23]. Complexation behaviour as well as solution properties of an another polycation namely poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride (PMADQUAT) have also been documented [24–26]. We recently reported pulse radiolysis and steady state radiation studies on vinylbenzyltrimethylammonium chloride (VBT) [27] and its polymer PVBT [28] in aqueous solution. However very little studies on complexation of low molecular weight ions with PVBT has been reported.

In the present study we have investigated the radiation polymerization behaviour of VBT to its linear and crosslinked polymer in aqueous solution. Further, complex formation reactions between linear and crosslinked PVBT with potassium hexacyanoferrates (II, III) and $K_2S_2O_8$ have been investigated. These salts were chosen since they generate tetra, tri and divalent anions for complexation in aqueous medium and because of their bulkier size can imitate drug molecules. It could be established from the studies that PVBT forms stable complexes with these salts.

2. Experimental

2.1. Material

Vinylbenzyltrimethylammonium chloride (VBT) molecular weight 211.74 in powder form, from Aldrich (purity 99%) was used as received. All other chemicals were of AnalaR grade. Double distilled water (conductivity 1.9 $\mu S\,cm^{-1}$) was used for all experimental purposes. Linear PVBT and crosslinked PVBT were synthesized by irradiating the aqueous monomer solutions at room temperature with gamma rays from a 3×10^{14} Bq Cobalt-60 source at a dose rate of 8 $kGy\,h^{-1}$ as determined by Fricke dosimetry. Lead attenuators of suitable thickness were used to decrease the dose rate to desired levels. Viscosity measurements for molecular weight determination and other studies were carried out using an Ubbelholde viscometer from M/s Scam India having flow time of 86 s for double distilled water at 25 ± 0.5 °C.

The formation of PVBT was determined spectrophotometrically by monitoring the decrease in the absorption peak of monomer VBT at 254 nm (ε_{254} = 20 950 $dm^3\,mol^{-1}\,cm^{-1}$ for VBT). The dissolved PVBT in solution was then precipitated out by pouring solution in excess of acetone. The polymer so obtained was re-dissolved in minimum amount of water and re-precipitated in excess of acetone. Dissolution and precipitation was carried out several times to remove any free monomer. Finally PVBT was vacuum dried at 40 °C. The molecular weight of the polymer was determined by viscosity measurement and dynamic light scattering measurements. The viscosity average molecular weight M_v of PVBT was estimated using Mark–Houwink equation $[\eta]=KM^{\alpha}$, where $[\eta]$ is limiting viscosity number, K and α are constants and M is the molecular weight. The value of $K=5.77\times10^{-3}$ and $\alpha=0.88$ were used in 0.002 N NaCl [29]. For light scattering measurements $D=KM^{a}$ form of Mark–Houwink equation was used where D = diffusion coefficient, K and a are the constant for the polymer-solvent system the molecular weight was determined assuming a value of $K=3.184\times10^{-5}$ and $a=-0.5$, the value reported for DNA in water [30]. PVBT with $M_v=4.5\times10^5$, $M_z=1.4\times10^5$ and $M_w=5.3\times10^5$ as determined by GPC was used for complex formation experiments. PVBT hydrogels were synthesized by irradiating 2 $mol\,dm^{-3}$ solution of VBT with suitable amounts of *N*,*N*′-methylene bisacrylamide (MBA), to a radiation dose of 8 kGy in glass tube under aerated conditions.

Turbidity measurements were carried out using Chemito UV–VIS 2600 spectrophotometer at $\lambda=500$ nm and at room temperature. Millimolar solutions of PVBT and complexing salts were mixed in different ratios and turbidity measured 30 s after mixing. The equilibrium degree of swelling (EDS) of PVBT crosslinked gels were determined gravimetrically using simple relationship

$$\mathrm{EDS}=(W_s-W_d)/W_d \quad (1)$$

where W_s and W_d are the weights of gel in swollen and dry states, respectively. For complex formation studies PVBT hydrogels were cut into thin disc form and placed in the salt until constant weight were achieved.

3. Results and discussion

3.1. Synthesis of linear and crosslinked PVBT

In our recent works we have reported radiolysis of VBT/PVBT in aqueous solution [27,28]. For present studies linear PVBT was synthesized by ^{60}Co gamma irradiation of 1 mol dm^{-3} aqueous deoxygenated VBT solution for a total dose of 1.7 kGy imparted at a dose rate of 4 kGy h^{-1} and the formation of stoichiometric poly-complexes were investigated by viscometric, turbidimetric and swelling studies.

Fig. 1 shows the polymerization yields for different monomer concentrations and Fig. 1 (inset) shows the polymer yields under deoxygenated and aerated conditions. Viscosities of the monomer solutions were seen to change drastically during irradiation. Fig. 2 shows the change in the viscosity of the solutions as a function of radiation dose. Comparatively larger change in the viscosity of deoxygenated solution, and profiles of Fig. 1 (inset) indicated that polymerization of VBT is hindered in the presence of oxygen in the monomer solution. The monomer solution finally gelled to a soft non-flowing mass indicating that polymer formed predominantly undergoes crosslinking on irradiation in aqueous solution. However the gel so formed was very soft and difficult to handle particularly in the swollen state, therefore PVBT gels for complexation studies were prepared by irradiating 2 mol dm^{-3} aqueous solution of monomer in presence of a multifunctional monomer *N*,*N*-methylenebis(acrylamide) (MBA) at different concentrations. The composition of different gels used for complexation studies is indicated in Table 1. Gels were made free of un-reacted residual monomer or MBA by repeated swelling and deswelling. The decrease in equilibrium degree of swelling (EDS) of gels, as observed was expected due to increased crosslink density in presence of higher amounts of MBA. Fig. 3 shows change in the swelling extents of gels when increasing amounts of MBA are incorporated in the gels.

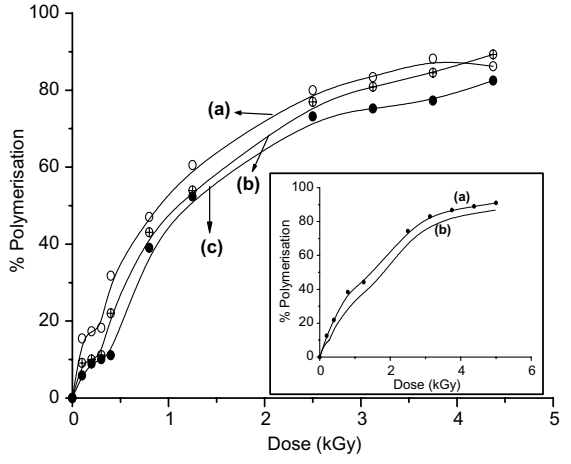

Fig. 1. Effect of monomer concentration on aerated solution: (a) 1 mol dm^{-3}, (b) 0.5 mol dm^{-3} and (c) 0.25 mol dm^{-3}. Inset: Concentration 0.25 mol dm^{-3}—(a) N_2 saturated and (b) aerated, dose rate = 2 kGy h^{-1}.

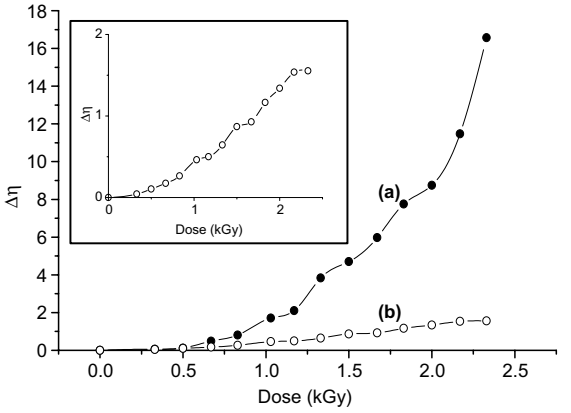

Fig. 2. Effect of irradiation on viscosity of 1 mol dm^{-3} aqueous VBT solution: (a) N_2 purged solution and (b) aerated solution. Inset: Viscosity change at lower doses for aerated solution.

3.2. Viscosity change and turbidity titration of linear PVBT aqueous solution with $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$ and $K_2S_2O_8$

The dilute aqueous solution of PVBT shows relatively high values of reduced viscosity due to polyelectrolyte effect. Fig. 4 shows the decrease in the viscosity of PVBT solution when the solution was diluted with pure DD water and salt solutions of $K_2S_2O_8$, $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$ of same concentration. It can be seen that there is no significant decrease in the reduced viscosity of the polymer solution on addition of water but the salt

Table 1
Composition of PVBT gels used for complexation studies

S. No.	Sample	[VBT] mol dm^{-3}	[MBA]$\times 10^3$ mol dm^{-3}	Dose (kGy)	M_c
1.	Gel#1	2	10	8	2 456 998 ± 400 490
2.	Gel#2	2	20	8	588 581 ± 88 287
3.	Gel#3	2	30	8	298 953 ± 32 884

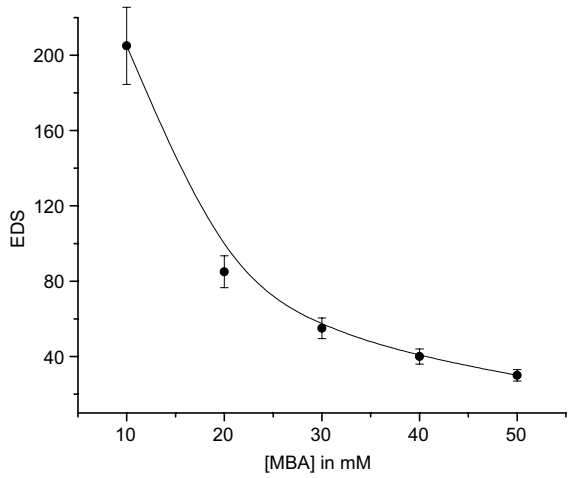

Fig. 3. Effect of crosslinking agent (MBA) on EDS.

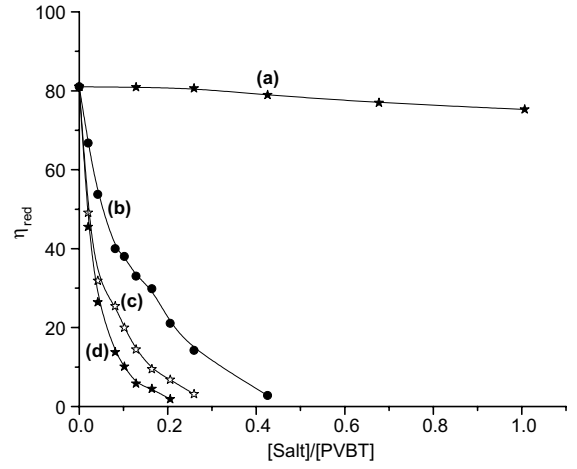

Fig. 4. Viscometric titration of 1×10^{-3} mol dm^{-3} PVBT with 1×10^{-3} mol dm^{-3} of salts: (a) H_2O, (b) $K_2S_2O_8$, (c) $K_3[Fe(CN)_6]$ and (d) $K_4[Fe(CN)_6]$.

solutions decrease the reduced viscosity significantly and to different extents depending on the salts. The decrease in viscosity can be attributed to inter and intra bridging of PVBT chains in presence of salts resulting in formation of insoluble crosslinked polymer-complex aggregates.

The stoichiometry of the complexes, in terms of [Salt]/[PVBT] ratios were estimated at precipitation and the numerical values were found to be in the range estimated to be in the range 0.4–0.45, 0.25–0.3 and 0.2–0.25 for $K_2S_2O_8$, $K_3[Fe(CN)_6]$ or $K_4[Fe(CN)_6]$ respectively. The complexes of PVBT with these ions were quite stable and were not dissociated upon dilution. The experimental data indicates that the interaction of PVBT these salts lead to formation of polymer complexes in which the $S_2O_8^{2-}$ is linked to 2.2–2.5 monomer units, $[Fe(CN)_6]^{3-}$ to 3.3–4.0 monomer units and $[Fe(CN)_6]^{4-}$ to 4–5 monomer units. The association of these negative ions to cationic polyelectrolytes can be expected as a result of electrostatic interaction.

Turbidimetric titration was also carried out to confirm the above observations. The clear dilute aqueous millimolar solution of PVBT turned turbid upon addition of millimolar salt solutions. It has been reported that the turbidity appears due to specific interactions of polyelectrolytes with oppositely charged drugs [31], metallic ions [15,17,19], surfactants [18] and complementary polymers [32–34] that lead to considerable conformation changes of the macromolecules. These interactions are accompanied by the formation of compact poly-complex particles in the solution which leads to decrease in the reduced viscosity and appearance of turbidity in the medium. Fig. 5 shows turbidity changes on addition of equi-molar complex forming salt solutions to polymer solutions. The maxima in the turbidity profiles corresponds to the equi-molar composition of components in the poly-complexes. From the experimental data, the compositions of complexes of PVBT with $S_2O_8^{2-}$, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ were found to be 2.2:1, 3.2:1 and 4.6:1 respectively.

3.3. Interaction of $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$ and $K_2S_2O_8$ with co-valently crosslinked PVBT gel in aqueous solution

Hydrogels of PVBT, when immersed in aqueous complexing salt solution, absorbed these salts from

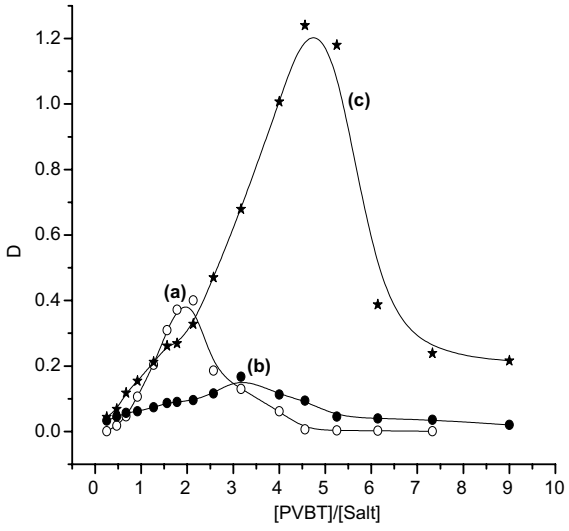

Fig. 5. Turbidimetric titration curves of equi-molar solution of PVBT with (a) 2×10^{-3} mol dm^{-3} $K_2S_2O_8$, (b) 1×10^{-3} mol dm^{-3} $K_3[Fe(CN)_6]$ and (c) 1×10^{-3} mol dm^{-3} $K_4[Fe(CN)_6]$.

solution and underwent contraction. The extent of swelling of hydrogels on the relative concentration of complexing salts are plotted in Figs. 6–8. It can be seen from the figures that even a slight change in salt concentration decreases the swelling degree significantly. At a certain [Salt]/[Gel] ratio the hydrogels are characterised by their completely collapsed state and a further increase in this ratio does not influence the swelling of the hydrogels. The most noticeable aspect in deswelling of PVBT gels was that the value of the ratio [Salt]/[Gel] for complete deswelling in presence of different salts were same as the values at which precipitation occurred for linear PVBT value for these salts. The deswelling curves for PVBT hydrogels with different EDS were different only in their extent of deswelling. The deswelled

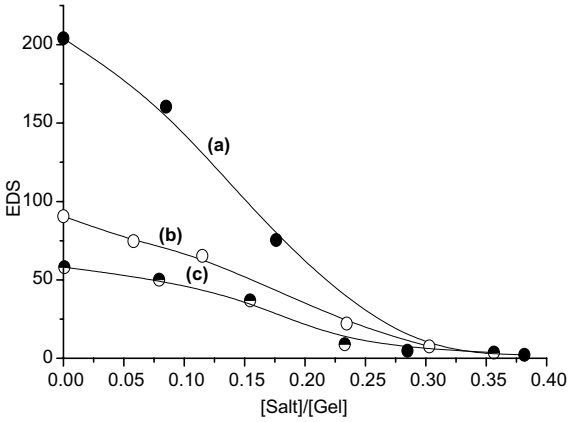

Fig. 6. Equilibrium degree of swelling (EDS) of PVBT hydrogels in aqueous $K_2S_2O_8$ solution: (a) gel # 1, (b) gel # 2 and (c) gel # 3.

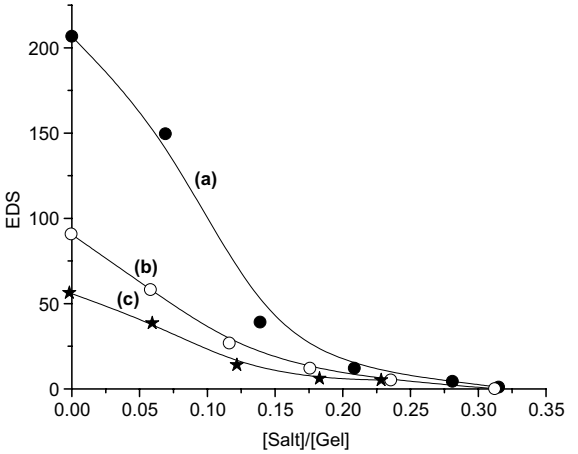

Fig. 7. Equilibrium degree of swelling (EDS) of PVBT hydrogels in aqueous $K_3[Fe(CN)_6]$ solution: (a) gel # 1, (b) gel # 2 and (c) gel # 3.

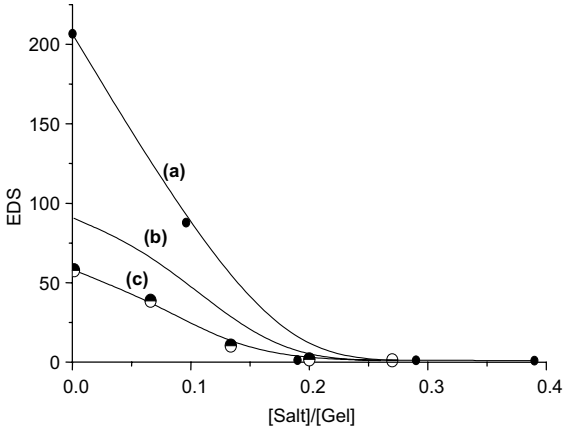

Fig. 8. Equilibrium degree of swelling (EDS) of PVBT hydrogels in aqueous $K_4[Fe(CN)_6]$ solution: (a) gel # 1, (b) gel # 2 and (c) gel # 3.

PVBT gels did not show swelling when they were transferred to pure water indicating stability of the complexes formed. However as polyelectrolytes complex formation is purely electrostatic in nature the complexes were expected to get affected in presence of strong electrolytes like NaCl, therefore the effect of NaCl on stability of these complexes was investigated.

3.4. Effect of NaCl on complexation behaviour of crosslinked PVBT gels

Polyelectrolytes become charged in aqueous environments due to dissociation of ionic groups. Since such systems strive for electro-neutrality there is always distribution of ions to balance the surface charge. The concentration of counter ions fall with increasing distance from the surface and has been well explained and documented by DLVO theory [35,36]. Electrostatic interaction between polyelectrolytes and oppositely charged ions gets perturbed on increasing the ionic strength. The increase in ionic strength effects the complexes by any or all of the three phenomena: (a) reduction of electrostatic interactions due to the screening effect of microsalts, (b) acceleration of dissociation of weak polyelectrolytes owing to the decrease of intramolecular electrostatic repulsion and (c) increase of hydrophobicity caused by the contraction of polyelectrolyte [33]. In order to see the effect of ionic strength on PVBT complexes, the crosslinked gels swelled to equilibrium were first immersed in solutions of complexing salts of different concentrations in order to complex them to different extents. Latter these gels complexed to different extent were immersed in NaCl solution of different concentrations. It was interesting to see that the gels complexed to lower extents further deswelled initially on transferring them to NaCl solution whereas the

gels complexed to greater extent started swelling on transferring to NaCl solution. The initial deswelling may be attributed to contraction of polyelectrolyte due to increased hydrophobicity i.e. better polymer–polymer interaction whereas increased swelling at higher NaCl may be due to its screening effect which screens the attractive interaction between complexing ions and polyelectrolytes and causes the dissociation of complex. The additional crosslinking induced in the co-valently crosslinked PVBT gels due to ionic interactions between complexing salt ions and polyelectrolytes is reduced and it allows the PVBT complex to relax by uptake of water. However it was seen that even on keeping the PVBT gel complexes in NaCl solution for a period of 3 months the gels could not achieve EDS level of prior to complexation indicating that in co-valently crosslinked PVBT gels only a fraction of complex formed are destroyed.

In order to further probe the effect of NaCl the complexation of linear PVBT in NaCl solution was studied. Change in the stoichiometry of these complexes in presence of NaCl was monitored by following the turbidity (OD at $\lambda = 500$ nm) values for polymer–salt solutions containing different ratios of [PVBT]/[Salt] at different NaCl concentrations. Figs. 9–11 show the result of these studies. It was found that the stoichiometry of the poly-complexes varied with the NaCl concentration and finally the complex was dissociated at higher NaCl concentrations, which showed that increasing the ionic strength of the solution could readily dissociate the poly-complex, confirming the electrostatic nature of the interaction. For $K_2S_2O_8$ linear PVBT complexes, it was seen that on introduction of NaCl in the medium,

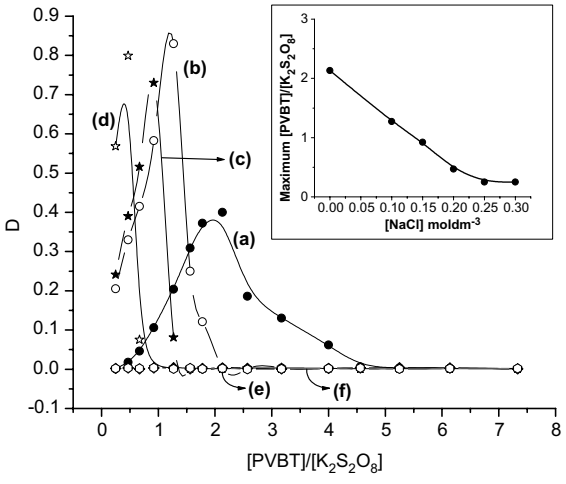

Fig. 9. Turbidimetric titration curves of 2×10^{-3} mol dm^{-3} PVBT by 2×10^{-3} mol dm^{-3} $K_2S_2O_8$ in presence of different concentration of NaCl: (a) no NaCl, (b) 0.1 mol dm^{-3}, (c) 0.15 mol dm^{-3}, (d) 0.2 mol dm^{-3}, (e) 0.25 mol dm^{-3} and (f) 0.3 mol dm^{-3}.

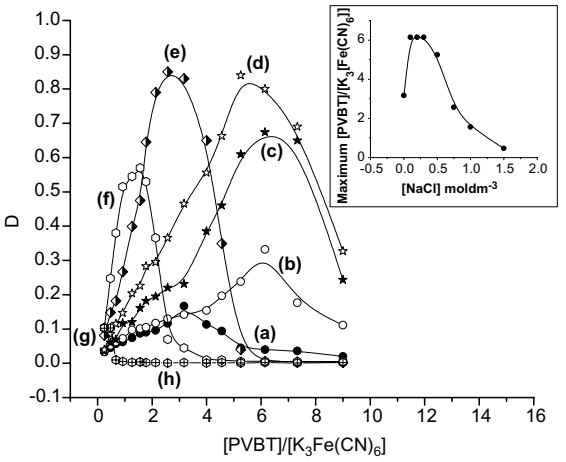

Fig. 10. Turbidimetric titration curves of 1×10^{-3} mol dm^{-3} PVBT by 1×10^{-3} mol dm^{-3} $K_3Fe(CN)_6$ in presence of different concentration of NaCl: (a) no NaCl, (b) 0.1 mol dm^{-3}, (c) 0.2 mol dm^{-3}, (d) 0.3 mol dm^{-3}, (e) 0.5 mol dm^{-3}, (f) 0.75 mol dm^{-3}, (g) 1.0 mol dm^{-3} and (h) 1.5 mol dm^{-3}.

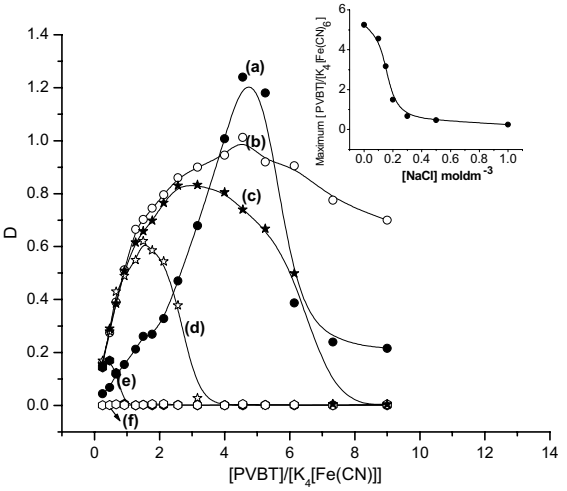

Fig. 11. Turbidimetric titration curves of 1×10^{-3} mol dm^{-3} PVBT with 1×10^{-3} mol dm^{-3} $K_4Fe(CN)_6$ in presence of different concentration of NaCl: (a) no NaCl, (b) 0.1 mol dm^{-3}, (c) 0.2 mol dm^{-3}, (d) 0.3 mol dm^{-3}, (e) 1.0 mol dm^{-3} and (f) 1.5 mol dm^{-3}.

maximum turbidity is observed at lower [PVBT]/[$K_2S_2O_8$] ratio and finally at NaCl concentration ~0.25 mol dm^{-3} complex in the medium is completely dissociated. Fig. 9 inset shows the [PVBT]/[$K_2S_2O_8$] ratio for maximum turbidity as a function of NaCl concentration. It can be seen that the ratio decreases linearly with NaCl concentration. It seems, in the medium of high ionic strength, the electrostatic interaction between polyelectrolytes and complexing ions are screened by

Na^+ and Cl^- ions that ultimately causes the destruction of the poly-complexes. Similar observations were made for PVBT-$K_4[Fe(CN)_6]$ complex system with only difference being that here the complete destruction of complex took place at slightly higher NaCl concentration of $\sim$0.5 mol dm^{-3}. However interesting observations were made on adding NaCl to PVBT-$K_3[Fe(CN)_6]$ complex solution. The value of the ratio [PVBT]/$[K_3Fe(CN)_6]$ for maximum turbidity increased initially. However, at higher NaCl concentration the maximum turbidity was seen at lower [PVBT]/$[K_3Fe(CN)_6]$ ratio and finally the complex was completely dissociated at NaCl concentration $\sim$1.5 mol dm^{-3}. Further experiments are going on to understand this observation.

4. Conclusion

Linear and crosslinked PVBT prepared by irradiation formed stable complexes with potassium hexacyanoferrate (II, III) and $K_2S_2O_8$. The interaction of linear PVBT with these salts resulted in decrease in the hydrodynamic volume of polyelectrolytes and ultimately precipitation of polymer complexes from the solution. The stoichiometry of the complex formed depended on the charge of the anion from the complexing salts. Crosslinked PVBT hydrogels desorb the embedded water when placed in these salt solutions. The complexes of linear and crosslinked PVBT are fairly stable on dilution and get dissociated only when strong electrolytes are introduced in the medium. These studies will be useful for designing drug-delivery systems and nano-particle preparation.

Acknowledgements

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