Study of phenolic copolymer–acrylic copolymer–non-ionic polymer–transition metal ion interactions and formation of multicomponent complexes

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(Received 16 July 1991; revised 27 October 1991)

Two phenolic copolymers and a methacrylic acid–methacrylamide copolymer have been synthesized and characterized by known methods. The co-ordinating groups of the respective copolymers form complexes through hydrogen bonding and ion–dipole interactions. The unreacted functional groups of the intercopolymer complexes undergo further complex formation with poly(vinylpyrrolidone) and a transition metal ion (e.g. Cu^{2+}). The different stages in the interactions have been studied by several experimental techniques, e.g. viscometry, potentiometry, conductometry and i.r. and u.v. spectrophotometry. Formation of multicomponent complexes with distinct stoichiometries have been predicted, and some schemes have been suggested to explain the mode of interaction between the components.

(Keywords: phenolic copolymer; acrylic copolymer; non-ionic polymer; transition metal ion; multicomponent complex)

INTRODUCTION

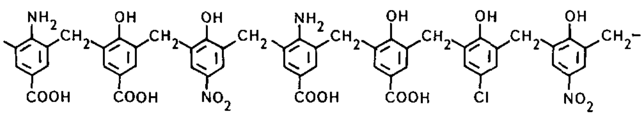
Interaction between two different macromolecular species may lead to the formation of an intermacromolecular complex, which essentially possesses properties entirely different from those of the component polymers. Intermacromolecular complexes have already found wide applications in technology and medicine[1]. Another aspect which has attracted considerable attention is selectivity in intermacromolecular complexation[2]; this is due to the close similarity with substitution reactions in biological systems. Many attempts have been made in recent years to incorporate transition metal ions into an existing polymer chain[3–5]. These metal-containing polymers have potential applications as functional materials particularly in the field of catalysis[6] and as models for biological systems and semiconductors[7]. Though a considerable amount of work has been done on the various aspects of intermacromolecular complex formation between homopolymers or between a copolymer and a homopolymer there seems to be almost no reference in the literature to complex formation between two different copolymers.

Phenolic polymers have unique properties due to the presence of intramolecular hydrogen bonding[8–11]. With this in mind, phenolic copolymers were prepared by condensing formaldehyde (HCHO) with *p*-chlorophenol (PClP), *p*-hydroxybenzoic acid (PHB), *p*-amino benzoic acid (PAB) and *p*-nitrophenol (PNP) in the presence of an acid catalyst. The methacrylic acid–methacrylamide (MA–MAm) copolymer chosen for the present investigation has been synthesized[12] and characterized by known methods[13]. These systems are interesting in view of the fact that the comonomer units of both the copolymers have specific functional groups incorporated in them and the proportion of different comonomer units present in the copolymer are also known. Since phenolic polymers are mostly insoluble in water, a mixture of dimethylformamide (DMF) and methanol (CH_3OH) was used as solvent in the study of interpolymer complex formation. In the present investigation several experimental techniques, such as viscometry, potentiometry, conductometry and i.r. and u.v. spectrophotometry, have been used to study the interaction between polymers and metal ions. Some plausible schemes are proposed to interpret the mode of interactions through the structural characteristics of the copolymers and the nature of the transition metal ion.

EXPERIMENTAL

Materials

PClP–PNP–PHB–PAB–HCHO random copolymers I and II were prepared by refluxing the monomers in definite molecular proportions with 10 N HCl (2 ml) as catalyst for 4 h at 100°C[14].



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The reaction product was poured in ice cold water and washed several times with distilled water to remove unreacted monomers.

MA–MAm copolymer

The MA and MAm monomers were taken in the ratio of 9:1 (w/w) and were polymerized by heating at 70°C for 50 min, using 0.1% $K_2S_2O_8$ as initiator[12]. The random copolymer so obtained was reprecipitated twice with ethyl acetate. The copolymer was characterized by electrometric titration[13], which indicated a composition of 0.8 mol of MA and 0.2 mol of MAm for the copolymer.

0032-3861/92/132868-04

Poly(vinylpyrrolidone) (PVP) was supplied by Fluka (USA). The $\bar{M}_w$ of the polymer was calculated from the viscosity equation[15] and found to be 2.4×10^4.

For all experimental measurements, analytical grade DMF and CH_3OH were used for mixed solvent studies.

Characterization

The conductometric and potentiometric measurements were carried out with a Leeds and Northrup 4959 electrolytic conductance bridge and ECIL digital pH meter (model pH 5651).

The viscosity of the solutions was measured by an Ubbelohde viscometer at $30 \pm 0.05°C$.

The i.r. and u.v. spectra of the complexes were recorded at various stoichiometries in a mixed solvent. For i.r. measurements a Perkin-Elmer model 1710 spectrophotometer and a Shimadzu UV-260 spectrophotometer were used.

RESULTS AND DISCUSSION

The four-component copolymer characterized by electrometric titration techniques was found to contain 0.557 mol ratio of PAB units, 0.093 PHB units, 0.307 PNP units and 0.043 PClP units[14]. The MA-MAm copolymer was found to have 0.8 mol of MA units and 0.2 mol of MAm units. A mixed solvent (e.g. 50% DMF + 50% CH_3OH v/v) was used as the medium in order to obtain a better resolution of the different stages of interaction between the component polymers. *Figure 1* shows the variation of conductance, apparent pH and reduced viscosity of 1 unit mol of phenolic copolymer I solution on adding the components in the following sequence, e.g. MA-MAm (0.696 unit mol), PVP (0.443 unit mol), Cu^{2+} (0.511 mol) and an excess of PVP solution, respectively. The specific quantities of the different components have been added in order to quantitatively complex the respective coordinating groups associated with comonomer units in the phenolic copolymer chain. Since, 1 mol of MA-MAm copolymer has 0.8 mol of MA units and 0.2 mol of MAm units, then 0.696 mol of this copolymer will contain $0.696 \times 0.8 = 0.55$ mol of MA units, which can stoichiometrically interact with $-NH_2$ groups of the PAB units (e.g. 0.55 mol) of the phenolic copolymer. The first break in the apparent pH curve (*Figure 1B*) appeared at 0.225 unit mol ratio (umr), which is equivalent to $0.225 \times 0.2 = 0.045$ mol of MAm units. This break may be assigned to the formation of a 1:2 (MAm: -COOH of PHB) complex. This is in view of the fact that the accessibility of MAm units to -COOH groups of partially complexed PAB units will be less than the -COOH groups of uncomplexed PHB units. One can calculate the total amount of unreacted phenolic -OH groups in the complex which in this case is ($0.043 + 0.307 + 0.093 = 0.443$ mol). Thus, subsequent addition of 0.443 unit mol of PVP, is expected to complex all the phenolic -OH groups by hydrogen bonding[16]. It is also known that the complexation ability of phenolic -OH groups is greater than that of -COOH group with respect to PVP[16]. The unreacted -COOH groups have been complexed subsequently with Cu^{2+} ions. A steep fall in the apparent pH was observed during the addition of Cu^{2+}. This may be attributed to the release of protons[17] as a result of the interaction of unreacted -COOH groups from PAB units with Cu^{2+}. However, the simultaneous fall in conductance may perhaps be due to ion association in a medium of low dielectric constant. The observed breaks at specific unit mole ratios, and the probable stoichiometries of the complexes are summarized in *Table 1*.

In order to probe further into the authenticity of these observations, and also to find the relative complexation ability of unreacted phenolic -OH and -COOH groups of the intercopolymer complex with respect to Cu^{2+} ions, an excess of Cu^{2+} ions, in the presence of sodium acetate was added in small amounts to the stoichiometric complex of phenolic copolymer I with MA-MAm copolymer [e.g. phenolic copolymer (1 unit mol): MA-MAm copolymer (0.696 unit mol)]. As explained earlier, the total amount of unreacted -COOH groups (e.g. from PAB units) is 0.557 mol and a fraction of these -COOH groups will interact with the remaining MAm units (e.g. 0.696 ×

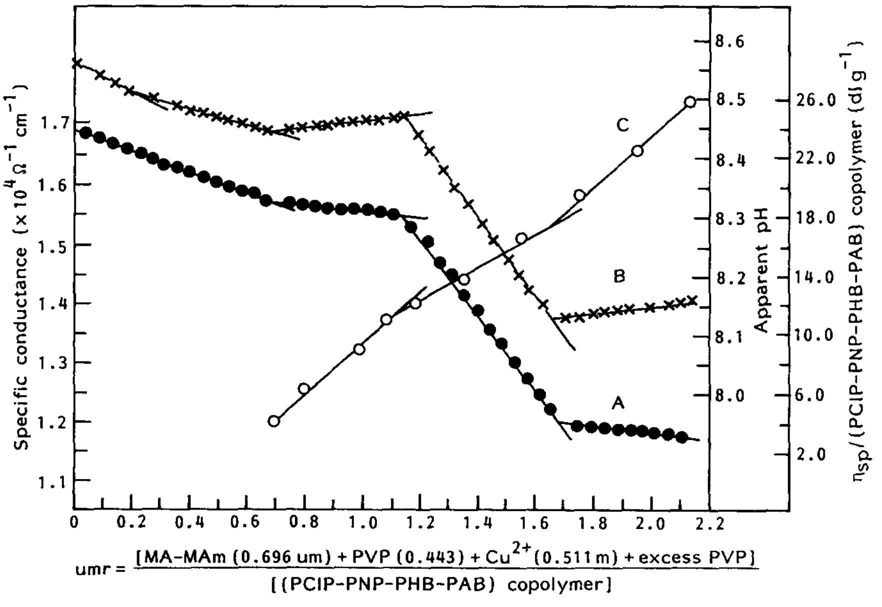


Figure 1 Variation of conductance (A), apparent pH (B) and reduced viscosity (C) with unit mol ratio for the phenolic copolymer I-acrylic copolymer-PVP-Cu^{2+} system

Table 1 Observed stoichiometries in interpolymer complex formation of phenolic copolymer I with MA–MAm, PVP and Cu^{2+}

System	Break observed at umr[a]	Probable stoichiometries
Phenolic copolymer I (1.0 um)[b] + MA–MAm (0.696 um)	0.225	1:2 (MAm: –COOH of PHB)
	0.696	1:1 (MA: $-NH_2$ of PAB)
Phenolic copolymer I (1.0 um) + MA–MAm (0.696 um) + PVP (0.443 um)	1.14	1:1 (PVP: –OH of PClP, PNP and PHB)
Phenolic copolymer I (1.0 um) + MA–MAm (0.696 um) + PVP (0.443 um) + Cu^{2+} (0.511 mol)	1.65	1:1 (Cu^{2+}: –COOH of PAB)

[a] Unit mol ratio
[b] Unit mol

Table 2 Observed stoichiometries in interpolymer complex formation of phenolic copolymer I with MA–MAm and Cu^{2+}

System	Break observed at umr	Probable stoichiometries
Phenolic copolymer I (1.0 um) + MA–MAm (0.696 um)	0.225	1:2 (MAm: –COOH of PHB)
	0.696	1:1 (MA: $-NH_2$ of PAB) 1:1 (MAm: –COOH of PAB)
Phenolic copolymer I (1.0 um) + MA–MAm (0.696 um) + Cu^{2+} (1.5 mol)	1.04	1:1 (Cu^{2+}: –OH of PClP and PNP)
	1.36–1.38	1:2 (Cu^{2+}: –COOH of PAB) 1:1 (Cu^{2+}: –OH of PHB)
	1.65	1:1 (Cu^{2+}: –COOH of PAB)

Table 3 Observed stoichiometries in interpolymer complex formation of phenolic copolymer II with MA–MAm, PVP and Cu^{2+}

System	Break observed at umr	Probable stoichiometries
Phenolic copolymer II (1.0 um) + MA–MAm (0.955 um)	0.954	1:1 (MA: $-NH_2$ of PAB) 1:1 (MAm: –COOH of PHB and PAB)
Phenolic copolymer II (1.0 um) + MA–MAm (0.955 um) + PVP (0.236 um)	1.19	1:1 (PVP: –OH of PClP, PNP and PHB)
Phenolic copolymer II (1.0 um) + MA–MAm (0.955 um) + PVP (0.236 um) + Cu^{2+} (0.684 mol)	1.85	1:1 (Cu^{2+}: –COOH of PAB and PHB)

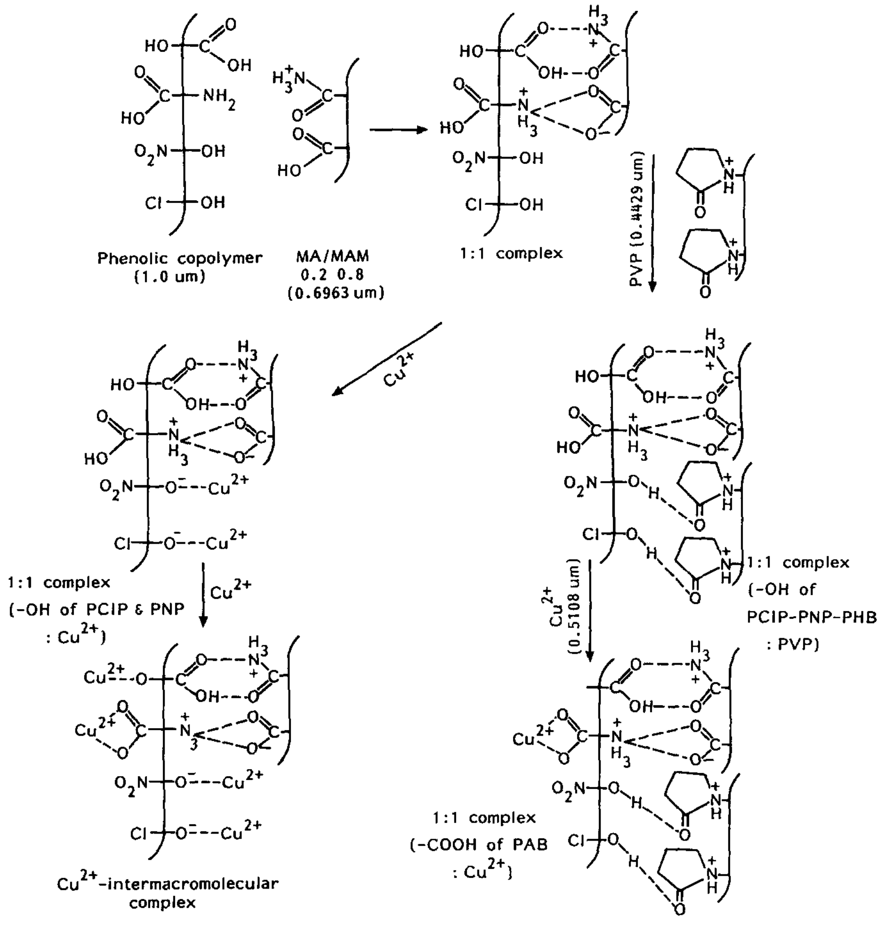
0.2 = 0.139 − 0.045 = 0.094 mol). Thus, the amount of unreacted –COOH groups will be (0.557 − 0.094 = 0.463 mol). In addition to this, the concentration of unreacted phenolic –OH groups, as shown earlier is 0.443 mol. Both these co-ordinating groups (e.g. –COOH and phenolic –OH) are known to form stable chelates[17] with Cu^{2+}. Therefore, it would be interesting to know the sequence of chelation of Cu^{2+} ions with respect to these two co-ordinating groups. The variation of conductance and apparent pH of this intercopolymer complex solution on addition of Cu^{2+} ions in small instalments have been studied. The probable stoichiometries assigned to different metal intercopolymer complexes corresponding to the various breaks observed in the titration curves are summarized in *Table 2.*

These observations indicate that in the intercopolymer complex, unreacted –OH groups of PClP and PNP units have a relatively stronger tendency for complexation compared to –COOH groups with respect to the Cu^{2+} ions. These groups are likely to be more accessible than the remaining unreacted –COOH groups of PAB and PHB units which are partially entangled with MAm units. The break obtained at 1.36 umr may be attributed to the formation of 1:2 and 1:1 complexes (e.g. Cu^{2+} : unreacted –COOH of PAB and Cu^{2+} : –OH of PHB). Finally, at 1.65 umr, a 1:2 complex of Cu^{2+} : –COOH probably changes to a 1:1 complex.

It would be interesting to observe the behaviour of another phenolic copolymer prepared from the same monomers, but with different feed composition. The phenolic copolymer II was found to have a different composition [e.g. PAB (0.764 mol), PHB (0.111 mol), PNP (0.069 mol), PClP (0.055 mol)]. The variation of conductance, apparent pH and reduced viscosity of phenolic copolymer II solution on addition of MA–MAm copolymer (0.955 unit mol), PVP (0.236 unit mol), Cu^{2+} (0.684 mol) and then excess of PVP, in very small amounts has been studied. As mentioned earlier, the specific amounts of the various components have been added in order to complex quantitatively the co-ordinating groups of the phenolic copolymer II. On the basis of the calculations shown earlier, the stoichiometries assigned to the various metal–intercopolymer complexes are given in *Table 3.*

The probable mode of interaction of the component copolymers, the non-ionic polymers and the transition metal ion can possibly be explained on the basis of *Scheme 1.*

On comparing the $\nu_{C=O_{str}}$, $\nu_{N-H_{str}}$, $\nu_{O-H_{str}}$ and $\nu_{C-N_{str}}$ frequencies of the component copolymers with those of the intermacromolecular complexes, distinct shifts were observed, which indicate the involvement of various functional groups during intermacromolecular complex formation.



Scheme 1

The u.v. spectra of the MA–MAm copolymer and phenolic copolymer (I and II) showed λ_{max} at 286.4 nm and 301.2 nm respectively, and λ_{max} shifted to 309.8 nm for the metal–intercopolymer complexes. It seems likely that the new absorption band arises from the formation of a charge transfer complex between the intercopolymer complex and metal ions.

In conclusion, it can be said that phenolic copolymer with specific co-ordinating groups can form multicomponent complexes by incorporating acrylic copolymer, non-ionic polymers and some transition metal ions, in a definite sequence. Such metal-containing intermacromolecular complexes are expected to prove useful for the development of catalysts and membranes with selective permeability[1].

REFERENCES

1 Bekturov, E. A. and Bimendina, L. A. *Adv. Polym. Sci.* 1981, **41**, 99

2 Abe, K., Koida, M. and Tsuchida, E. *Macromolecules* 1977, **10**, 1259

3 Tsuchida, E. and Nishide, H. *Adv. Polym. Sci.* 1977, **24**, 1

4 Nishikawa, H. and Tsuchida, E. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 1557

5 Hagihara, N., Sonogashina, K. and Takahashi, S. *Adv. Polym. Sci.* 1981, **41**, 149

6 Kanoko, M. and Tsuchida, E. *Macromol. Rev.* 1981, **16**, 397

7 Marks, T. J. *Science* 1985, **227**, 881

8 Coggesshall, N. D. *J. Am. Chem. Soc.* 1950, **72**, 2836

9 Sprengling, G. R. *J. Am. Chem. Soc.* 1954, **76**, 1190

10 Cairn, T. and Eglinton, S. G. *J. Chem. Soc.* 1965, 5906

11 Chatterjee, S. K. and Gupta, N. D. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 1261

12 Pinner, S. H. *J. Polym. Sci.* 1953, **10**, 379

13 Chatterjee, S. K., Pandith, R. L. and Pachauri, L. S. *Polymer* 1982, **23**, 1659

14 Chatterjee, S. K., Katyal, A. and Pachauri, L. S. *J. Macromol. Sci. Chem.* 1985, **A22**, 13

15 Levy, G. B. and Frank, H. P. *J. Polym. Sci.* 1955, **17**, 247

16 Chatterjee, S. K., Sethi, K. R. and Yadav, D. *Polymer* 1987, **28**, 519

17 Morcellet, M. *Polym. Bull.* 1984, **12**, 127