Selective intermacromolecular complex formation between phenolic and nonionic polymers

S. K. Chatterjee and K. R. Sethi
Department of Chemistry, University of Delhi, Delhi-110 007, India
(Received 11 October 1983)

The selective intermacromolecular complex formation between *p*-bromophenol–formaldehyde copolymer (PPF) and poly(vinyl pyrrolidone) (PVP) and poly(ethylene oxide) (PEO) has been investigated. PVP has been found to have greater ability for complex formation compared to PEO with respect to PPF. An open-chain mechanism has been proposed for the substitution reaction between PVP and PPF–PEO complex. The abnormal behaviour of viscosity curves has been interpreted on the basis of probable association between the nonionic polymers.

(Keywords: selective complex formation; phenolic copolymer; poly(ethyleneoxide); poly(vinylpyrrolidone))

INTRODUCTION

Selective intermacromolecular complex formation is of great significance from the biological point of view[1,2]. A macromolecular chain in biological systems may skillfully and effectively select a complementary chain to form an intermacromolecular complex in order to perform specific functions. The nature and cause of such selective intermacromolecular reactions are not fully understood, but some efforts have been made to simulate these reactions with the help of synthetic polymers. Papisov[3], Tsuchida and coworkers[4], have studied selective intermacromolecular complex formation through substitution reactions involving polycarboxylic acids and nonionic polymers. Since interpolymer complex formation is known to be influenced by several factors, such as interaction forces, solvent, ionic strength, temperature, pH etc., therefore, one can expect to realize selective interpolymer complex formation on the basis of these factors[5].

Earlier workers have not used phenolic polymers as one of the components in the study of interpolymer complex formation, but our preliminary work[6,7] definitely indicates distinct complex formation between typical phenolic copolymers and nonionic polymers, such as poly(vinylpyrrolidone) (PVP) and poly(ethyleneoxide) (PEO). This encouraged us to probe into the possible mechanism of selective interpolymer complex formation involving PVP and PEO and some typical phenolic polymers (e.g. *p*-bromophenol–formaldehyde copolymer (PPF))[6]. In the present study, several experimental techniques such as viscosity, potentiometry, conductometry and i.r. spectra have been used and efforts have been made to interpret the nature of interactions through structural characteristics of polymers.

EXPERIMENTAL

Polyvinyl pyrrolidone (PVP)

PVP was supplied by B.D.H. Chemicals Ltd., (Poole, England) and its weight average molecular weight ($\overline{M_w}$) was calculated from viscosity equation[8].

$$[\eta]=6.76\times10^{-2}\cdot M^{0.55}$$

and was found to be 3.75×10^4.

Polyethylene oxide (PEO)

PEO was supplied by Iwai Kagaru Co. Ltd., Japan and its weight average molecular weight ($\overline{M_w}$) was determined to be 1.9×10^4 using a viscosity relation[9].

p-*Bromophenol-formaldehyde (PPF)*

The copolymer was prepared by condensing *p*-bromophenol and formaldehyde in stoichiometric amounts in the presence of acid catalyst (e.g. HCl). The number average *DP* was found to be ~12, by the electrometric titrations in non-aqueous media[10].

Conductometric and potentiometric titrations

The conductometric titrations were carried out with a Leeds Northrup (4959) Electrolytic Conductance Bridge. The limit of error in conductance measurements was ±0.15% of reading at high end of the mho scale increasing to 1% of reading at the low end. The pH of solutions was measured with an ECIL Digital pH meter with a combination electrode. The resolution of the instrument is ±0.01 pH scale.

Infra-red spectra

The i.r. absorption spectra of interpolymer complexes

0032-3861/84/091367-04$03.00

formed at various stages of unit mole ratio were recorded on a Perkin Elmer Grating Infrared Spectrophotometer (Model 621). The resolution of the instrument is 5–10 cm^{-1}.

Solvent

A mixture of 84% acetone + 16% methanol (v/v) has been used in all experimental measurements.

RESULTS AND DISCUSSION

The variation of conductance, pH and reduced viscosity (η_{sp}/c) of mixed solutions of PVP and PEO with the addition of PPF are depicted by the curves A, B and C, respectively of *Figures 1–3*. PVP and PEO have been mixed in the following unit mole ratios i.e. (0.3 PVP + 0.7 PEO), (0.5 PVP + 0.5 PEO) and (0.7 PVP + 0.3 PEO) as indicated in *Figures 1*, *2* and *3* respectively. On the addition of PPF to (0.3 PVP + 0.7 PEO) (umr) mixture, the sharp changes in conductance, pH and reduced viscosity have been observed corresponding to the following stoichiometries PPF/(PVP + PEO) (umr) = 0.3, 0.6, 1.05 and 1.3 (cf. *Figure 1*). Of course only the pH curve (cf. curve B of *Figure 1*) showed all the above stoichiometries and the other curves (e.g. conductance and viscosity curves i.e. curves A and C of *Figure 1*) indicated only some of these stoichiometries. From our experience with the following two component systems e.g. PPF–PVP and PPF–PEO[6], we can attribute the sharp changes in slope in conductance and pH curves and the maxima in the viscosity curve observed at unit mole ratios PPF/(PVP + PEO) = 0.3 and 0.6, to the interpolymer complexes of PPF and PVP of unit mole ratios (PPF/PVP) = 1 : 1 and 2 : 1. Similarly the breaks at 1.05 and 1.3 umr can be correlated with 0.5 : 1 and 1 : 1 stoichiometries of PPF–PEO system. Obviously it indicates that even in a mixture, each component appears to be interacting with PPF independently. However, these observations further substantiate the fact that PVP has a stronger complexing ability compared to PEO with respect to PPF. The sharp increase in conductance and sharp fall in pH (cf. curves A and B of *Figure 1*) could also be accounted for on the basis of the fact that a polyelectrolyte (i.e. PPF) has been added to a mixture of nonionic polymer. The distinct maxima at 0.3 and 0.6 umr in reduced viscosity (cf. curve C of *Figure 1*) may obviously be attributed to 1:1 and 2:1 ([PPF]/[PVP]) complexes. The increase in reduced viscosity particularly at 0.3 and 0.6 umr may probably be interpreted on the basis of polymer–solvent and polymer–polymer interactions. Because of high percentage of acetone, the solvent mixture (i.e. 84% acetone + 16% methanol v/v) is a poor solvent for the nonionic polymers (i.e. PVP and PEO), even though one may expect that these polymers may be having a reasonably extended conformation due to preferential solvation by methanol (a good solvent). The further addition of PPF to the nonionic polymer mixture in the same solvent may cause further extension of the chains due to cooperative bonding between PPF and PEO, which possibly is reflected in the viscosity curve. Other factors which may enhance the reduced viscosity, are the relatively greater rigidity of the complexed molecules as compared to uncomplexed PVP and PEO chains and also due to polyelectrolyte character of PPF.

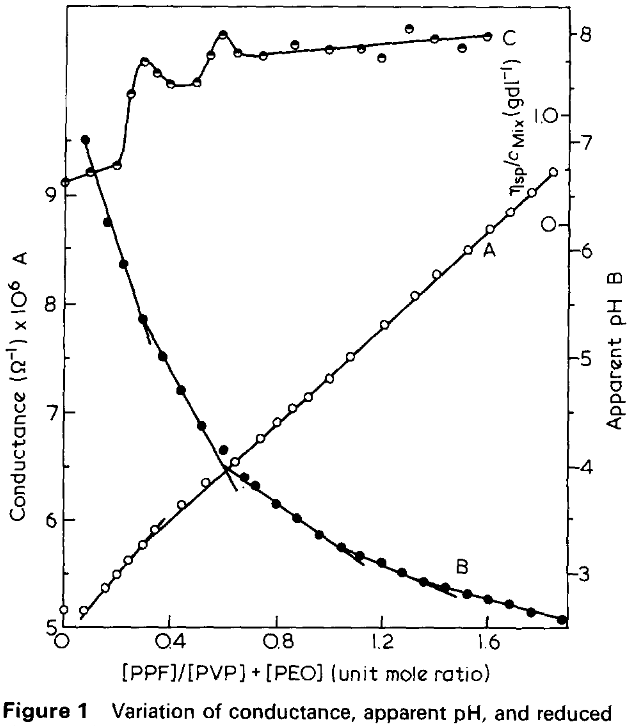


Figure 1 Variation of conductance, apparent pH, and reduced viscosity for (0.3 PVP + 0.7 PEO) (umr) mixture with unit mole ratio [PPF]/[PVP] + [PEO]: (A) conductance (B) apparent pH (C) reduced viscosity ($\eta_{sp}/c_{PVP} + c_{PEO}$)

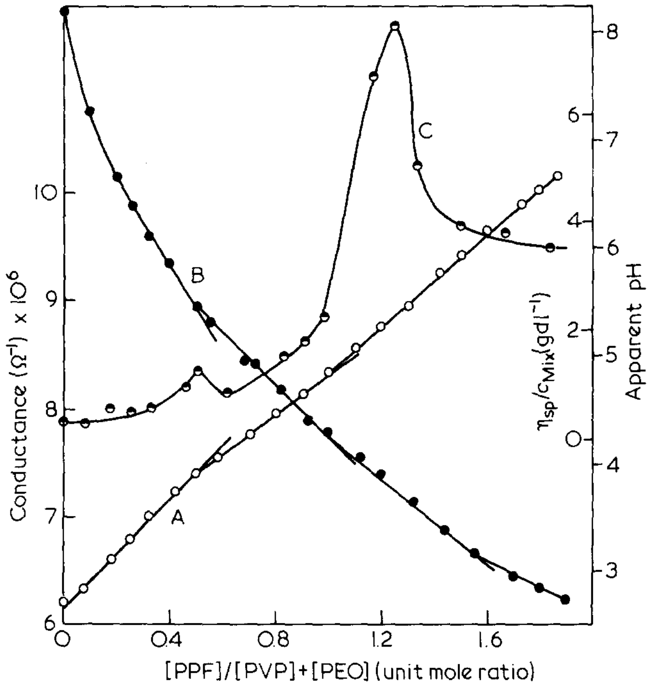


Figure 2 Variation of conductance, apparent pH and reduced viscosity for (0.5 PVP + 0.5 PEO) umr mixture with unit mole ratio [PPF]/[PVP] + [PEO]: (A) conductance (B) apparent pH (C) reduced viscosity ($\eta_{sp}/c_{PVP} + c_{PEO}$)

In order to observe the influence of composition on selective complex formation, two other compositions e.g. (0.5 PVP + 0.5 PEO) and (0.7 PVP + 0.3 PEO) umr have also been studied. The variations of conductance, pH and reduced viscosity on the addition of PPF to these mixtures have been depicted in *Figures 2* and *3* respectively. The nature of the conductance and pH curves was identical, however, a distinct change in the pattern of reduced viscosity curves was observed (cf. curve C of *Figures 2* and *3*). In the case of (0.5 PVP + 0.5 PEO) (umr) mixture, two distinct maxima were observed, in the viscosity curve at [PPF]/[PVP] + [PEO] = 0.5 and 1.25 (umr) (cf. curve C of *Figure 2*). The first maximum corresponds well with 1:1 PVP–PPF interpolymer complex, whereas the second maximum occurring at 1.25 umr is slightly higher than the expected value for the 2:1 PPF–PVP complex. Such an anomaly may probably be due to some sort of association between PVP and PEO at a mole ratio of 1:1. Some evidence for this abnormal behaviour will be presented in the subsequent discussions. The comparison of viscosity curves (i.e. curve C) in *Figures 1* to *3*, shows that the presence of PVP in relatively larger proportion in the nonionic polymer mixture, makes the complex molecule more rigid, which is probably reflected by the steep maxima in their viscosity curves (e.g. curve C of *Figures 2* and *3*). Apart from this, it may also be mentioned that all stoichiometries which have been observed in complex formation between two component systems, e.g. PPF–PVP and PPF–PEO[6], could also be reproduced even when PVP and PEO were present in mixtures of different compositions. The distinct stoichiometries observed through various measurements for the different mixtures of PVP and PEO on addition of PPF, have been summarized in *Table 1*.

We thought that the configurational environment may influence the selective interpolymer complex formation, therefore, we have added the components in the reverse order i.e. to 1 (um) solution of PPF, 0.5 (um) of PEO was added and subsequently, PVP was added up to ([PEO] + [PVP])/[PPF] = 2.0 (umr). The variation of conductance and pH for this system have been depicted in *Figure 4* (curves A and B). Distinct breaks could be seen from this Figure at 0.5 (umr) (which corresponds to the PPF–PEO complex resulting from the interaction of 1.0 (um) of PPF with 0.5 (um) of PEO), and other complex i.e. PPF–PVP at 1.5 (umr), which obviously indicates the substitution of PEO by PVP on PPF chains. However, if PVP is added to PPF first and then followed by PEO, no such substitution reaction takes place (cf. *Figure 4* curve C and D). It can be concluded from this reverse addition of components, that the complex formation ability of PVP is much greater than that of PEO with respect to PPF.

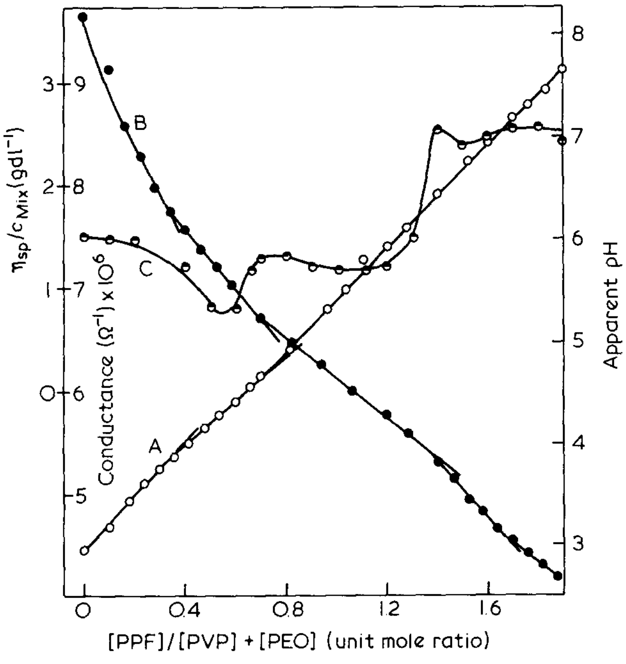


Figure 3 Variation of conductance, apparent pH and reduced viscosity for (0.7 PVP + 0.3 PEO) umr mixture with unit mole ratio [PPF]/[PVP] + [PEO]: (A) conductance (B) apparent pH (C) reduced viscosity ($\eta_{sp}/c_{PVP} + c_{PEO}$)

Table 1 Observed stoichiometries in selective interpolymer complex formation of PVP and PEO with PPF

System	Property	Observed stoichiometry $\frac{[PPF]}{[PVP] + [PEO]}$
(0.3 PVP + 0.7 PEO) *versus* PPF (Fig. 1)	Conductance Apparent pH Reduced viscosity (η_{sp}/c)	0.3 0.3, 0.6, 1.05, 1.3 0.3, 0.6
(0.5 PVP + 0.5 PEO) *versus* PPF (Fig. 2)	Conductance Apparent pH Reduced viscosity (η_{sp}/c)	0.5, 1.0 0.5, 1.0, 1.5 0.5, 1.25
(0.7 PVP + 0.3 PEO) *versus* PPF (Fig. 3)	Conductance Apparent pH Reduced viscosity (η_{sp}/c)	0.35, 0.7 0.35, 0.7, 1.4, 1.7 0.7, 1.4

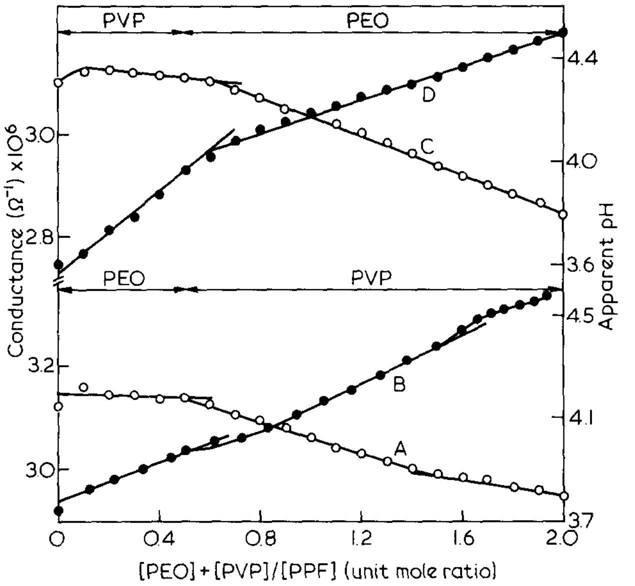


Figure 4 Variation of conductance and apparent pH with different order of addition of PEO and PVP with unit mole ratio [PEO] + [PVP]/[PPF]: (A) conductance (B) apparent pH, when to 1.0 um PPF is added 0.5 um PEO and 1.5 um PVP; (C) conductance (D) apparent pH, when to 1.0 um PPF is added 0.5 um PVP and 1.0 um PEO

Interpolymer complexes were prepared by adding to 1 (um) of PPF the following solutions separately:

(i) 0.5 um of PEO followed by 0.5 um of PVP
(ii) 0.5 um of PEO followed by 1.0 um of PVP
(iii) 0.5 um of PVP followed by 1.0 um of PEO.

The i.r. spectra of the complexes were recorded in KBr and compared with those of the pure components (i.e. PPF, PVP and PEO). Some of the spectral data are given in *Table 2*.

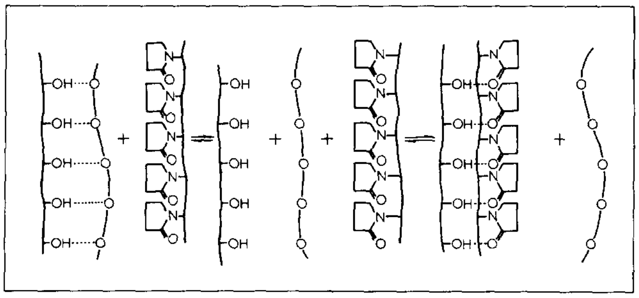
From spectral evidence (cf. *Table 2*), it seems obvious that a ternary complex is probably not formed even when 1.0 um of PPF, 0.5 um of PEO and 0.5 um of PVP are mixed together, as no appreciable shift in the C–O–C stretching frequency is observed in the case of complexes (i), (ii) and (iii) compared to pure PEO. On the other hand

Table 2 I.r. spectra for pure components PEO, PVP, PPF and the interpolymer complexes between them

Component/ interpolymer complex	ν_{C-O-C} stretching in PEO (cm^{-1})	$\nu_{C=O}$ in PVP (cm^{-1})	ν_{C-O} stretching in PPF (cm^{-1})
PEO	1100	–	–
PVP	–	1625	–
PPF	–	–	1225
Complex (i)			
(1 mol PPF + 0.3 mol PEO + 0.5 mol PVP)	1090	1650	1270
Complex (ii)			
(1 mol PPF + 0.5 mol PEO + 1.0 mol PVP)	1100	1650	1290
Complex iii			
(1 mol PPF + 0.5 mol PVP +1 mol PEO)	1095	1650	1280

a distinct shift is observed in C=O frequency of PVP in the case of all the above three complexes.

Thus on the basis of conductance and pH measurements (cf. *Figure 4*) and spectral evidence it may be interpreted that replacement of PEO by PVP on the PPF chains, probably takes place through an open chain mechanism instead of a closed chain mechanism[4]. The following open chain mechanism may probably be suggested for this selective complex formation:



The following argument may also be given in favour of an open chain mechanism for this scheme of complex formation. PPF chains having low DP (i.e. about 12) form complex with PEO (matrix chain) through cooperative bonding. The addition of PVP which has a strong complexing ability compared to PEO with respect to PPF, destabilizes the PPF–PEO complex due to rupture of the system of cooperative bonding, as a result of which some PPF chains get detached from PPF–PEO complex and enter into complex formation with PVP.

In order to explain the abnormal behaviour of viscosity curves in *Figures 2* and *3*, we measured the viscosity of some mixtures of PVP and PEO which are plotted in *Figure 5*. The reduced viscosity (η_{sp}/c) of PVP in mixed solvent (84% acetone + 16% methanol v/v) has been plotted against total concentration c (i.e. PVP + PEO). After a certain stage of addition of PVP i.e. up to 0.7 (um) (cf. curve A of *Figure 5*) and 0.3 (um) (cf. curve B of *Figure 5*), PEO was added in each case. The negative slope of (η_{sp}/c) *versus c* curve suddenly changed to a steep positive slope, probably indicating association of the two nonionic polymers and also probably reflecting the difference in the nature of interaction of the solvent mixture towards the two polymer components. Similarly, the abrupt change in viscosity on adding PVP to PEO solution has been depicted in *Figure 5* (curve C). These observations probably indicate association between the nonionic polymers in the mixed solvent. Thus, the abnormal behaviour of viscosity curves as depicted in *Figures 2* and *3* (curve C) may be attributed to the above mentioned reason i.e. the probable association between the nonionic polymers (e.g. PVP and PEO) in a mixed solvent.

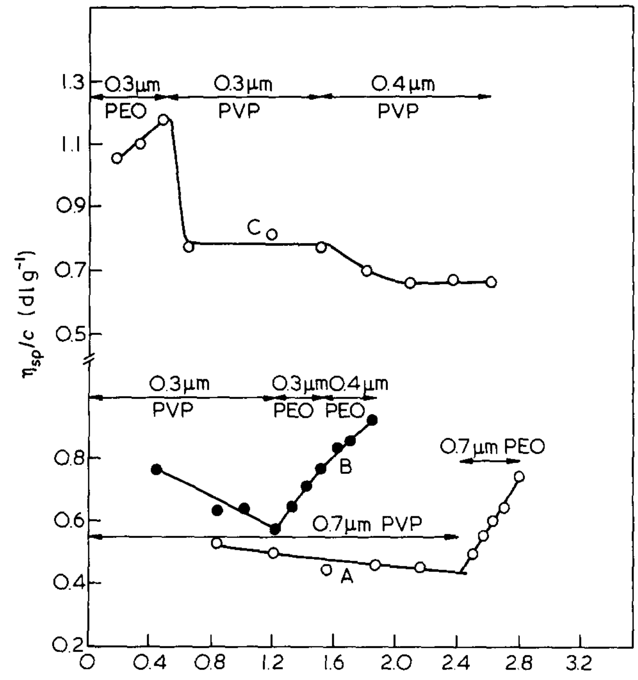


Figure 5 Variation of reduced viscosity η_{sp}/c with C(PVP+PEO)×10^2: (A) To solvent is added 0.7 μm PVP and 0.3 μm PEO; (B) To solvent is added 0.3 μm PVP and 0.7 μm PEO; (C) To solvent is added 0.3 μm PEO and 0.7 μm PVP

In conclusion, it can be said that phenolic polymers enter into distinct complex formation with nonionic polymers, and their relative complexation ability can be compared by studying selective complexation.

REFERENCES

1 Bekturov, E. A. and Bimendina, L. A. *Adv. Polym. Sci.* 1981, **41**, 99
2 Tsuchida, E. and Abe, K. *Adv. Polym. Sci.* 1982, **45**
3 Papisov, I. M., *et al. Vyskomol Soedin* 1973, **A15**, 2003
4 Abe, K., Koida, M. and Tsuchida, E. *Macromolecules* 1977, **10(6)**, 1259
5 Ohno, H., Abe, K. and Tsuchida, E. *Makromol Chem.* 1978, **179**, 755
6 Chatterjee, S. K. and Sethi, K. R. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 1045
7 Chatterjee, S. K. and Sethi, K. R. *Polymer* 1983, **24** (*Commun.*), 253
8 Levy, G. B. and Frank, H. P. *J. Polym. Sci.* 1955, **17**, 247
9 Ring, W., Cantow, J. and Holtrup, H. *Eur. Polym. J.* 1966, **2**, 151
10 Chatterjee, S. K. and Datta Gupta, N. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 1261