Selectivity in interpolymer complexation involving non-ionic polymers, polycarboxylic acid and phenolic polymer

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Selectivity in interpolymer complex formation involving polymethacrylic acid (PMAA), *p*-bromophenol–formaldehyde copolymer (PPF) and non-ionic polymers, e.g. poly(vinyl pyrrolidone) (PVP) and poly(ethylene oxide) (PEO), has been studied in an acetone–methanol solvent mixture by several experimental techniques, e.g. viscometry, potentiometry, conductometry, turbidimetry, and infra-red spectroscopy. Complexation ability of PPF has been found to be greater than PMAA with respect to PVP. However, this trend in the interactions is reversed with respect to PEO. These substitution reactions have been interpreted in terms of a closed chain mechanism.

(Keywords: selectivity in complex formation; non-ionic polymers; poly(methacrylic acid); *p*-bromophenol–formaldehyde copolymer)

INTRODUCTION

Selective reactions in macromolecular substitution are of great interest from a biological point of view[1,2], particularly for genetic engineering[2]. Biological systems can skilfully perform specific functions as a result of such substitution reactions. Not much information seems to be available in the literature regarding the ability of a synthetic polymer to select a complementary chain as in biological systems. However, Bekturov[1] and Tsuchida *et al.*[3] have studied some substitution and exclusion reactions involving synthetic polymers. Since interpolymer complex formation is influenced by several factors, such as specific type of interaction force, temperature, pH, etc., selective and substitution reactions in intermacromolecular complex formation may therefore be realized under suitable conditions[3,4].

Our preliminary work conclusively established the formation of intermacromolecular complexes between phenolic polymers and non-ionic polymers, such as poly(vinyl pyrrolidone) (PVP), poly(ethylene oxide) (PEO), etc.[5,6] Selectivity in complexation in such systems and the probable mode of interaction between the component polymers were also discussed in a subsequent paper[7]. The present investigation involves selective and substitution reactions between a typical phenolic polymer, a polycarboxylic acid and a non-ionic polymer, such as PVP and PEO. Efforts have been made to interpret the mode of interaction through the structural characteristics of the component polymers.

EXPERIMENTAL

Poly(methacrylic acid) (PMAA)

Methacrylic acid (from BDH) was distilled twice at 12 mmHg (b.p. 63°C) and polymerized with $K_2S_2O_8$ as initiator in an aqueous medium. The monomer concentration was $\sim 0.2\,\mathrm{mol\,l^{-1}}$. The polymerization was carried out for 5 h in a nitrogen atmosphere at 50°C. The reaction mixture was evaporated, dissolved in methanol and reprecipitated twice with ethyl acetate. The molecular weight ($\bar{M}_w$) of the polymer was calculated from viscosity measurements in methanol at 25°C by using the equation[8]:

$$[\eta] = 24.2 \times 10^{-4} \bar{M}_w^{0.51}$$

and found to be 4.2×10^4.

Poly(vinyl pyrrolidone) (PVP)

The weight average molecular weight ($\bar{M}_w$) of the PVP sample (also from BDH) was determined by the equation[9]:

$$[\eta] = 6.76 \times 10^{-2} \bar{M}_w^{0.55}$$

(in aqueous solution at 25°C) and was found to be 3.75×10^4.

Poly(ethylene oxide) (PEO)

The molecular weight ($\bar{M}_w$) of the PEO sample (from Iwai Kagaru Co. Ltd, Japan) was found to be 1.9×10^4 as calculated by a viscosity relation[10].

p-Bromophenol–formaldehyde copolymer (PPF)

PPF was prepared and characterized by known methods[11] and its average degree of polymerization (*DP*) was found to be approximately 12.

Solvent

An acetone–methanol mixture in the volume ratio of 84:16 (v/v) was used as solvent in all experimental techniques.

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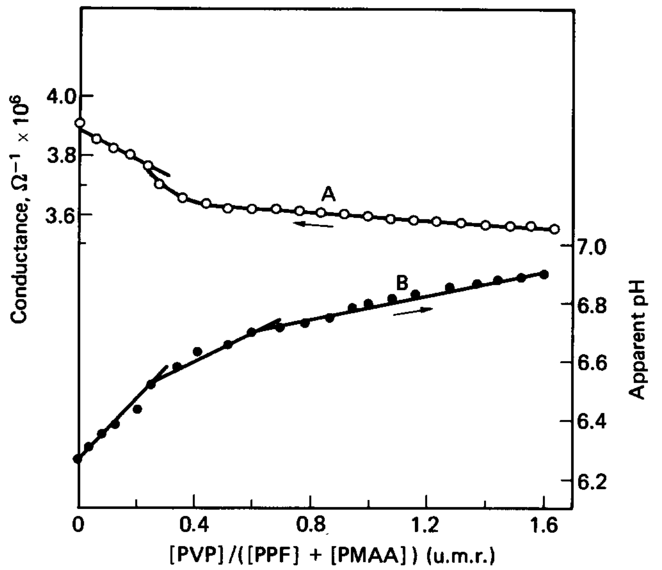


Figure 1 Variation of conductance (curve A) and apparent pH (curve B) for 0.25 PPF+0.75 PMAA (u.m.r.) mixture with unit mole ratio [PVP]/([PPF]+[PMAA])

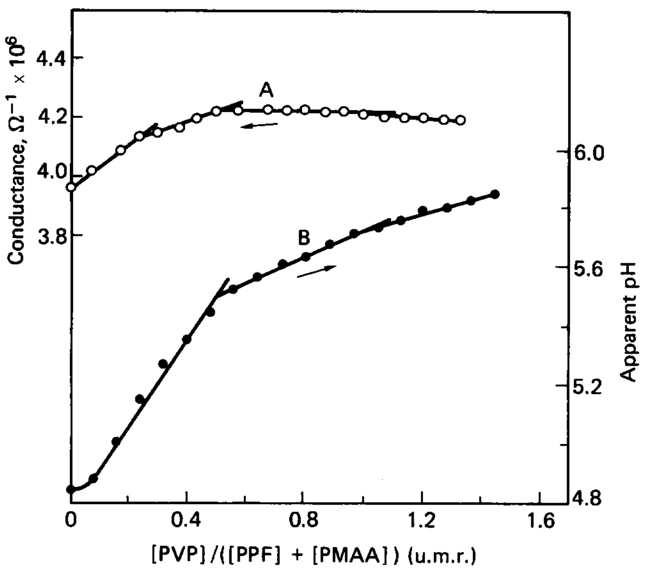


Figure 2 Variation of conductance (curve A) and apparent pH (curve B) for 0.5 PPF+0.5 PMAA (u.m.r.) mixture with unit mole ratio [PVP]/([PPF]+[PMAA])

Conductometric and potentiometric titrations

The conductometric titrations were carried out with a Leeds Northrup (model 4959) electrolytic conductance bridge. The limit of error in conductance measurements was ±0.15% of the reading at the high end of the mho scale, increasing to 1% of the 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 unit.

Infra-red spectra

The infra-red (i.r.) absorption spectra of interpolymer complexes were recorded by a Perkin–Elmer grating infra-red spectrophotometer (model 621). The resolution of the instrument is 5–10 cm^{-1}.

Viscosity

The viscosity measurements at various unit molar ratios were performed at 30±0.05°C by an Ubbelohde viscometer for which the kinetic energy correction was negligible.

Turbidity measurement

The percentage transmittance in mixed solutions of component polymers was measured 5 min after mixing by a Perkin–Elmer spectrophotometer (model 554). The sensitivity of the instrument was within ±0.1% in terms of percentage transmittance.

RESULTS AND DISCUSSION

The selectivity of a particular polymer in interpolymer complex formation is attributed to a small difference in the interaction energy between complementary polymers. It is known that PMAA interacts more strongly with PVP than with PEO[3] in an aqueous medium and the authors have established that PPF forms a more stable complex with PVP than with PEO in a non-aqueous medium[7]. Therefore, it could be of interest to study the relative complexation abilities of PMAA and PPF *vis-à-vis* PVP and PEO respectively. Since, PPF is completely insoluble in water and soluble in acetone, whereas PMAA, PVP and PEO are insoluble in acetone and soluble in methanol, an acetone–methanol mixture (84:16 v/v) was therefore used for dissolving the component polymers.

PPF and PMAA were mixed in several unit molar ratios (u.m.r.) and to each mixture PVP was added in several stages. The variation of conductance and apparent pH for some representative mixtures at various stages of addition of PVP are shown in *Figures 1* to *3*. The compositions of all the mixtures and the stoichiometries of the corresponding complexes, indicated by various breaks in the titration curves, are summarized in *Table 1*.

The general trend of the potentiometric curves for all the mixtures (e.g. curve B of *Figures 1* to *3*) is identical, whereas the corresponding conductometric curves (e.g. curve A of *Figures 1* to *3*) showed a gradual change in nature. A distinct fall in conductance was observed in

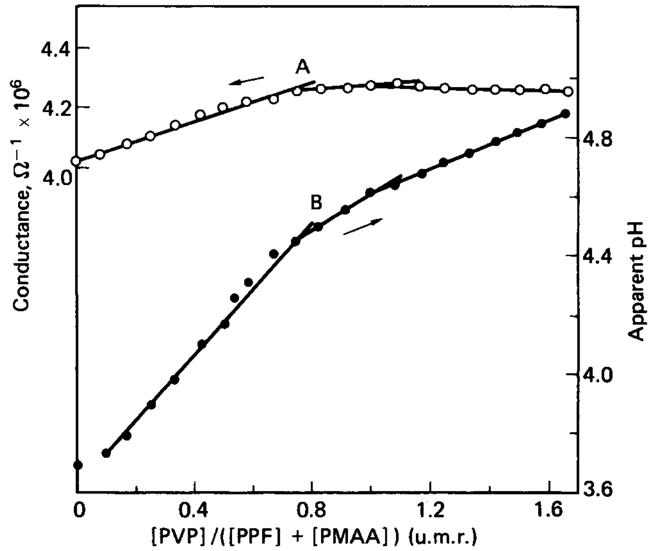


Figure 3 Variation of conductance (curve A) and apparent pH (curve B) for 0.75 PPF+0.25 PMAA (u.m.r.) mixture with unit mole ratio [PVP]/([PPF]+[PMAA])

Table 1 Observed stoichiometries in selective interpolymer complexation of (PPF + PMAA) vs. PVP

Composition of mixtures	Property	Observed stoichiometry ([PVP])/([PPF] + [PMAA]) (u.m.r.)
0.25 PPF + 0.75 PMAA	Cond.	0.25
(*Figure 1*)	App. pH	0.25, 0.62
0.3 PPF + 0.7 PMAA	Cond.	0.3, 0.65
	App. pH	0.3, 1.0
0.5 PPF + 0.5 PMAA	Cond.	0.25, 0.5, 1.0
(*Figure 2*)	pH	0.5, 1.0
0.7 PPF + 0.3 PMAA	Cond.	0.7
	App. pH	0.7
0.75 PPF + 0.25 PMAA	Cond.	0.75, 1.0
(*Figure 3*)	App. pH	0.75, 1.0

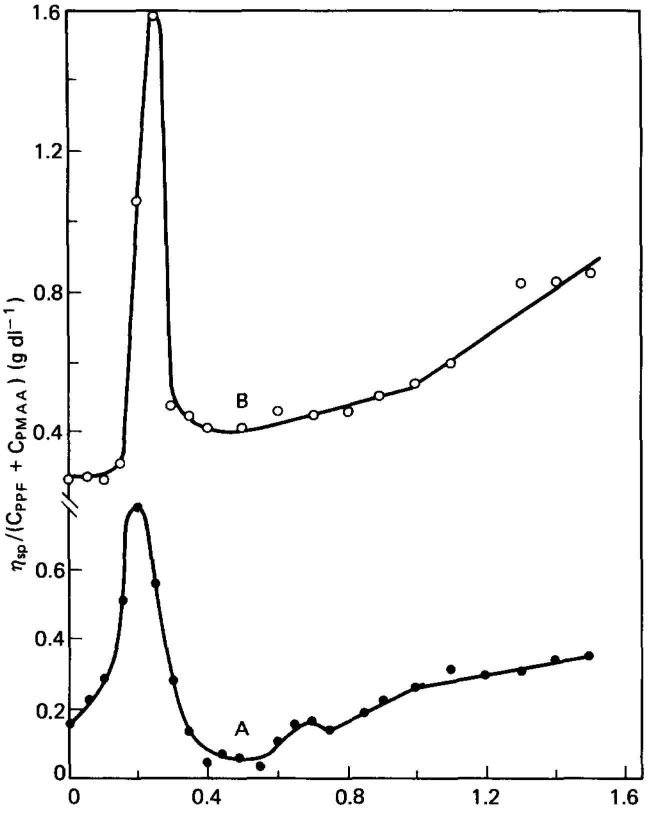


Figure 4 Variation of reduced viscosity $\eta_{sp}/(C_{PPF} + C_{PMAA})$ with unit mole ratio [PVP]/([PPF] + [PMAA]) for two different mixtures: curve A, 0.7 PPF + 0.3 PMAA (u.m.r.); curve B, 0.3 PPF + 0.7 PMAA (u.m.r.)

mixtures having less than 0.5 unit mole (u.m.) of PPF (cf. curve A of *Figure 1*) and as the proportion of PPF in the mixture was increased to 0.5 (u.m.) and beyond, the conductometric curves (e.g. curve A of *Figures 2* and *3*) showed an increase during PPF–PVP complex formation.

The corresponding viscosity curves (cf. curves A and B of *Figure 4*) showed a steep maximum. The gradual change in nature of the conductometric curves as well as the maxima in the viscosity curves may be attributed to some sort of association that may possibly exist between PMAA and PPF. The associated PMAA–PPF chains, on further interaction with PVP, perhaps form a bulky complex structure, which may account for the increase in reduced viscosity. When the proportion of PPF is small in the mixture (e.g. in *Figure 1*), most of it is probably in an associated state. Thus the decrease in conductance may be due to the replacement of a more conducting species by a less conducting one. But when the proportion of PPF is high enough, a substantial proportion of it may be in an unassociated state. Thus the relative mobility of the PPF–PVP complex may be greater than the PPF–PMAA–PVP complex, obviously due to the very high molecular weight of PMAA compared to PPF.

Table 2 Selective interpolymer complexation of PMAA–PVP–PPF systems

System	Property	Stoichiometry [PPF]/[PVP] (u.m.r.)
PMAA–PVP (1:1 + x PVP) ↑ Addition of PPF	Cond. (curve B)	0.5, 1.0
(*Figure 5*)	App. pH (curve C)	0.5, 2.0

The steady increase in apparent pH on addition of PVP (cf. curve B of *Figures 1* to *3*) is probably due to involvement of the protons of the component polymer in the interpolymer complex, resulting in increase in pH. Such behaviour during interpolymer complex formation has been reported by several authors[4,8,12].

Surprisingly enough, these studies indicate that PPF has a stronger complexation ability than PMAA with respect to PVP. This is particularly interesting, in view of the fact that PMAA and PVP are known to form stable complexes as a result of hydrogen bonding, ion–dipole and hydrophobic interactions[8]. The stronger complexation ability of PPF may be attributed to its structural characteristics, particularly intramolecular hydrogen bonding between its neighbouring OH groups[13,14].

Perhaps the most authentic proof in support of the above arguments could be provided by adding PPF to a stoichiometric mixture of PMAA and PVP (*Table 2*). The observed changes in pH and conductance at various stages of addition are shown in *Figure 5*. PMAA and PVP are known to form a 1:1 (u.m.r.) complex (cf. curve A of *Figure 5*)[8], whereas all the stoichiometries which have been observed earlier for the PVP–PPF system[5] could be reproduced in these substitution reactions (cf. curves B and C of *Figure 5*).

In order to probe further into these substitution reactions, some specific interpolymer complexes were prepared by adding separately to 1 unit mole (u.m.) solution of PVP the following solutions:

(i) 0.5 u.m. of PMAA followed by 0.5 u.m. of PPF,
(ii) 1.0 u.m. of PMAA followed by 1.0 u.m. of PPF,
(iii) 1.0 u.m. of PMAA followed by 2.0 u.m. of PPF.

These complexes have been separated by centrifugation and washed several times with the solvent mixture to remove unreacted polymer components. The complexes were finally dried in vacuum and their i.r. spectra were recorded in KBr pellets, and compared with those of the component polymers. From the spectral evidence (cf. *Table 3*), it seems obvious that (i) and (ii) are complexes involving the three components, PPF, PVP and PMAA, as the shifts in $\bar{\nu}_{C=O}$(PMAA), $\bar{\nu}_{C=O}$(PVP) and $\bar{\nu}_{C-O}$(PPF) are quite appreciable when compared with pure components. Broad bands between 1600 and 1700 cm^{-1}, and the appreciable shifts of $\bar{\nu}_{C-O}$ band from 1225 to 1270 cm^{-1}, probably indicate simultaneous involvement of carboxylic groups of PMAA, carbonyl groups of PVP and phenolic –OH groups of PPF, to form complexes of three components. The presence of a relatively narrow band at 1610 to 1660 cm^{-1} in complex (iii) perhaps indicates the absence of carboxyl group (of PMAA) in the complex, possibly showing the formation of a binary complex between PPF and PVP.

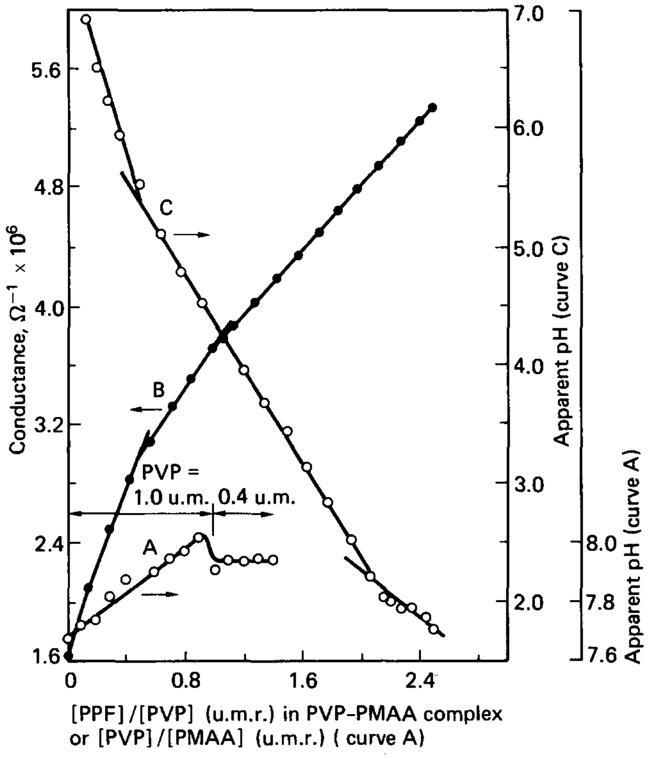
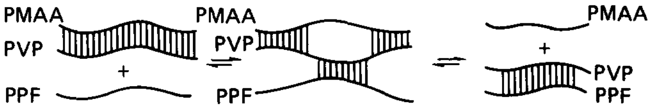


Figure 5 Variation of apparent pH with unit mole ratio [PVP]/[PMAA] (curve A). Variation of conductance and apparent pH with unit mole ratio [PPF]/[PVP] in a 1:1 PVP:PMAA complex (curves B and C respectively)

On the basis of the foregoing evidence, it seems reasonable to suggest the following closed chain mechanism[4] for the substitution reaction:



The following arguments may be given in favour of a closed chain mechanism for this scheme of complex formation. PMAA chains have a very high *DP* (i.e. about 500) and form a fairly stable complex with PVP through cooperative hydrogen bonding. In this medium, PPF, which has a very strong complexing ability compared to PMAA with respect to PVP, but which has a very small *DP* ~ 12, gradually replaces PMAA from PMAA–PVP complex, thus resulting in an intermediate stage which may be associated with all three components.

In order to find out whether this abnormal behaviour of PPF is specific for PVP or not, the studies on selective complexation of PPF–PMAA system were carried out with another non-ionic polymer, PEO. Though interpolymer complex formation between PEO and PMAA has been reported in an aqueous medium by several authors[2,4,12], we considered it necessary to study the behaviour of these components in this particular solvent mixture (i.e. acetone–methanol (84:16 v/v). *Figure 6* shows that interpolymer complexes of the following stoichiometries are formed:

Table 3 I.r. spectra of pure components PMAA, PVP, PPF, PEO and the interpolymer complexes between them

Component/interpolymer complex	$\nu_{C=O}$ stretching in PMAA (cm^{-1})	$\nu_{C=O}$ stretching in PVP (cm^{-1})	ν_{C-O} stretching in PPF (cm^{-1})	ν_{C-O-C} (cm^{-1})
PMAA	1690	–	–	
PVP	–	1625	–	
PPF	–	–	1225	
PEO	–	–	–	1100
Complex (i)				
1 mol PVP + 0.5 mol PMAA + 0.5 mol PPF	1600–1700 (broad band)		1270	
Complex (ii)				
1 mol PVP + 1 mol PMAA + 1 mol PPF)	1600–1700 (broad band)		1275	
Complex (iii)				
1 mol PVP + 1 mol PMAA + 2 mol PPF	1610–1660		1270	
Complex (iv)				
1 mol PEO + 0.5 mol PPF + 0.5 mol PMAA	1720–1640		1260	1090
Complex (v)				
1 mol PEO + 0.5 mol PPF + 1 mol PMAA	1720–1640		–	1090

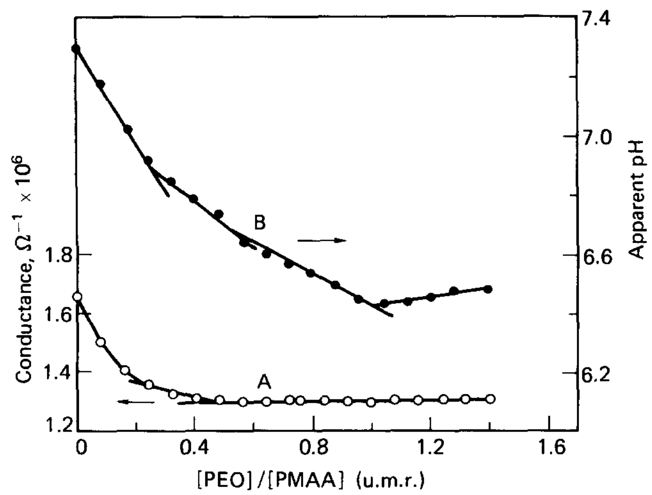


Figure 6 Variation of conductance (curve A) and apparent pH (curve B) with unit mole ratio [PEO]/[PMAA]

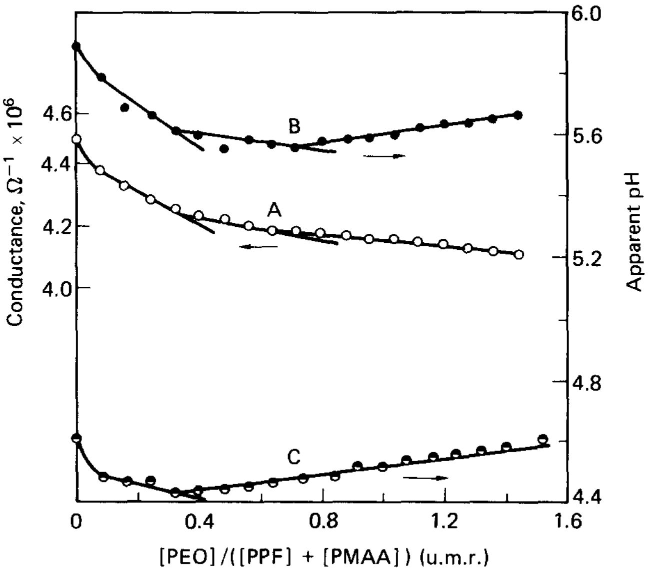


Figure 7 Variation of conductance and apparent pH with unit mole ratio [PEO]/([PPF]+[PMAA]). Curve A, conductance, and curve B, apparent pH, for a mixture of 0.3 PPF+0.7 PMAA (u.m.r.); curve C, apparent pH for a mixture of 0.7 PPF+0.3 PMAA (u.m.r.)

[PMAA]/[PEO] (u.m.r.)=0.25, 0.5 and 1.0

The variation of conductance and apparent pH, on addition of increasing amounts of PEO to mixtures of two extreme compositions of PPF and PMAA, are depicted in *Figure 7*.

It is obvious from these results that the complexation ability of PMAA is greater than that of PPF with respect to PEO. This difference in behaviour of PVP and PEO regarding their complexation ability with respect to PPF and PMAA can be interpreted in terms of the nature of the interaction forces. In the case of PEO, the mode of interaction is confined only to hydrogen bonding, whereas, apart from hydrogen bonding, ion–dipole and solvophobic interactions may also be involved in interpolymer complex formation between PVP and other component polymers (e.g. PMAA and PPF). Additional experimental evidence of this observation is provided by transmittance measurements at various stages of addition of PEO to the mixed solutions of different compositions (e.g. 0.3 PMAA+0.7 PPF, and 0.7 PMAA+0.3 PPF) as shown in *Figure 8*. The substitution of PPF from PPF–PEO complex by PMAA is once again indicated by an independent measurement (cf. *Figure 9*).

However, the most unequivocal proof of the stronger complexation ability of PMAA compared to PPF with respect to PEO is provided by the i.r. spectra of the interpolymer complexes formed by adding separately to 1 u.m. of PEO, the following solutions:

(iv) 0.5 u.m. of PPF followed by 0.5 u.m. of PMAA,
(v) 0.5 u.m. of PPF followed by 1.0 u.m. of PMAA.

As mentioned earlier these complexes were isolated and freed from unreacted components. The i.r. spectra of these complexes were compared with those of the component polymers (i.e. PEO, PPF and PMAA). It is evident from the spectral data (cf. *Table 3*) that complex (iv) is perhaps a three-component complex because of the simultaneous involvement of PEO, PPF and PMAA, as indicated by shifts in corresponding group frequencies, whereas complex (v) is a binary complex between PEO and PMAA, indicated by the absence of $\bar{\nu}_{C-O}$ band of PPF. However, a very slight shift in $\bar{\nu}_{C-O-C}$ for PEO was also observed (cf. *Table 3*). On the basis of these observations, the substitution of PPF by PMAA may perhaps also take place by a closed chain mechanism as suggested earlier.

Thus, it may be concluded that the relative complexation ability of phenolic polymers is greater than that of poly(carboxylic acids) with respect to PVP. However, the poly(carboxylic acids) form a more stable complex with PEO as compared to phenolic polymers. A

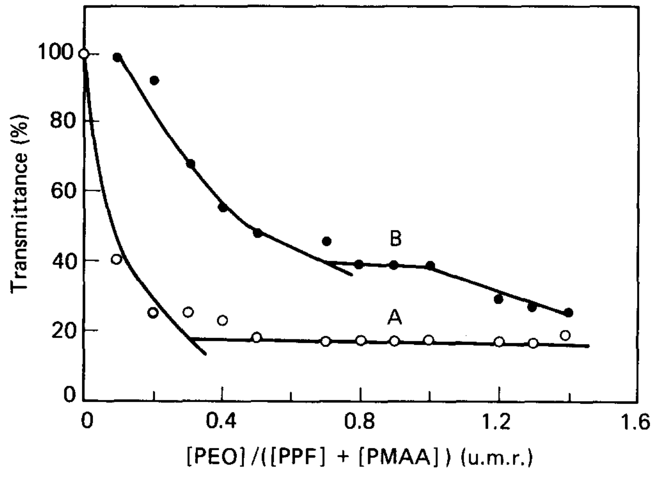


Figure 8 Variation of percentage transmittance with unit mole ratio [PEO]/([PPF]+[PMAA]) for two different mixtures: curve A, 0.3 PPF+0.7 PMAA; curve B, 0.7 PPF+0.3 PMAA (u.m.r.)

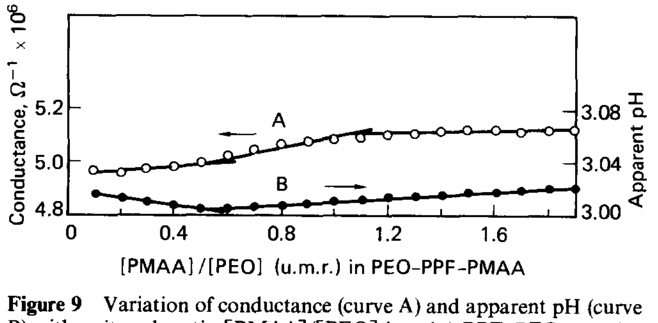


Figure 9 Variation of conductance (curve A) and apparent pH (curve B) with unit mole ratio [PMAA]/[PEO] in a 1:1 PPF–PEO complex

closed chain mechanism may possibly explain the substitution reactions of poly(carboxylic acids) and phenolic polymers with respect to non-ionic polymers.

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