

## Interpolymer association between random and graft acrylic copolymers with poly(ethylene imine): effects of copolymer structure

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Interpolymer complex formation has been studied between acrylamide–vinyl alcohol graft copolymer, methacrylic acid–acrylamide random copolymer and polyethylene imine. Some blends of binary homopolymer complexes having the same proportion of interacting units as in copolymer complex have also been prepared. Stability constant, degree of linkage and related thermodynamic parameters (e.g.  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) have been compared for the two complexation systems using Osada's methods. The comparative study indicated considerable difference in the values of these parameters, which has been explained on the basis of copolymer structure. © 1997 Elsevier Science Ltd. All rights reserved.

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### Introduction

Study of polymer–polymer interaction and formation of intermacromolecular complexes has assumed considerable importance in the field of polymer science<sup>1–3</sup>. During the last decade, intermacromolecular complex formation involving copolymers with carboxylic acid units and non-ionic homopolymers has been reported<sup>4–9</sup>, but there seems to be almost no mention in the literature regarding the intercopolymer complex formation between two different types of copolymers. Moreover, it may be mentioned that complex formation involving copolymers, is likely to be more complicated in view of the possible presence of non-interacting units, neighbouring group influence and structural characteristics of the copolymers. Keeping this fact in mind, we have studied the interaction of acrylamide–vinyl alcohol graft copolymer (AAM/VA) with methacrylic acid–acrylamide random copolymer (MA/AAM). The resulting intercopolymer complex, which contained some unreacted units (e.g. AAM and VA), could be further complexed with a typical polyelectrolyte e.g. polyethylene imine (PEI). From the known compositions of the two copolymers, one can predict the relative proportions of the different pairs of interacting units, (e.g. AAM–MA, AAM–EI and VA–EI) present in the multicomponent complexes. Since, all these units when present as homopolymers, are known to form binary complexes<sup>10</sup>, therefore it was considered of interest to prepare some blends by mixing stoichiometric proportions of binary homopolymer complexes. These blends have been prepared in such a way that they contained the same proportions of different pairs of interacting units as in intercopolymer–polyelectrolyte complexes. The stability constant ( $K$ ), degree of linkage ( $\theta$ ) and related thermodynamic parameters (e.g.  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) of each of these complexes have been determined by using Osada's method<sup>11–13</sup>. A comparative study of these parameters

indicated considerable difference in the values for copolymer complexes and polymer blend complexes. In this report, an effort has been made to interpret this difference in terms of the non-interacting units present in the copolymers, neighbouring groups and its possible influence on co-operative interactions.

### Experimental

*Poly(methacrylic acid) (PMA)*<sup>14</sup>. Methacrylic acid (distilled twice *in vacuo*) was polymerized with benzoyl peroxide in dioxan–methanol mixture at 65°C for 3 h. Nitrogen gas was constantly bubbled through to maintain inert atmosphere. The reaction mixture was dissolved in methanol and the polymer was obtained by precipitating with ether and then drying *in vacuo*. The average molecular weight ( $\bar{M}_n$ ) was obtained from viscosity data in methanol at 25°C using the following equation<sup>14</sup>:  $[\eta] = 24.2 \times 10^{-4} \bar{M}_n^{0.51}$  and found to be  $2.3 \times 10^5$ .

*Poly(acrylamide) (PAAM)*<sup>15,16</sup>. PAAM was prepared from acrylamide by free radical polymerization using azobisisobutyronitrile (AIBN) as initiator<sup>15</sup>. The polymerization was carried out in acetone medium in nitrogen atmosphere at 50°C for 45 min. The polymer was obtained as a white solid that was removed from the reaction mixture. It was washed thoroughly with acetone and dried *in vacuo*. The number average molecular weight ( $\bar{M}_n$ ) of the polymer was obtained from viscosity measurements in aqueous medium using the following equation<sup>16</sup>:  $[\eta] = 6.8 \times 10^{-4} \bar{M}_n^{0.66}$  and found to be  $1.2 \times 10^5$ .

*Polyethyleneimine (PEI)*. PEI was supplied by BDH Chemicals Limited, Poole, England in the form of 50% viscous water solution. The number average molecular weight ( $\bar{M}_n$ ) of PEI was determined by osmotic pressure measurements by using Polderman's method<sup>17</sup> and found to be  $1.5 \times 10^5$ .

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*Poly(vinyl alcohol) (PVA)*<sup>18</sup>. PVA was obtained from Fluka, USA. The weight average molecular weight was  $\sim 1.5 \times 10^4$ .

*Methacrylic acid-acrylamide (MA/AAm) random co-polymer*<sup>19</sup>. Random copolymer MA/AAm was prepared by free radical polymerization using  $K_2S_2O_8$  as initiator. An aqueous solution of methacrylic acid and acrylamide monomers, taken in 9/1 (w/w) ratio with 0.2%  $K_2S_2O_8$ , was heated in a suitable vessel fitted with a reflux condenser and an inlet for nitrogen gas. Polymerization was carried out in nitrogen atmosphere at 70°C for 50 min. As soon as the product precipitated it was separated, dissolved in acetone and reprecipitated with ether. The process was repeated thrice to remove unreacted monomers. The composition was found to be 0.7/0.3 (i.e. 70% of MA units and 30% of AAm units). The copolymerization reaction was carried out up to a low conversion (i.e. around 10%). At low conversion, the copolymer was easily soluble in aqueous medium, and also heterogeneity in composition is minimum.

*Acrylamide-vinyl alcohol (AAm/VA) graft copolymer*<sup>20</sup>. Poly(vinyl alcohol) and acrylamide monomer were taken in the ratio 1/5 (w/w) in aqueous solution and graft copolymerization was carried out using 0.1 M solution of ceric ammonium nitrate in 1 M  $HNO_3$  as initiator. The mechanism of grafting reaction is that PVA acts as a reducing agent, which reduces  $Ce^{IV}$  to  $Ce^{III}$  and the oxidation is carried out in the presence of vinyl monomer (e.g. AAm). The free radical produced on the polymeric backbone (e.g. PVA), initiates polymerization to produce graft copolymer. This method of grafting yields substantially pure graft copolymer since free radicals are formed exclusively on the backbone<sup>20</sup>. The polymerization was carried out in nitrogen atmosphere at 20°C for 50 min. The reaction mixture was poured in excess of acetone and the graft copolymer was obtained as white solid that was separated and dried. The graft copolymer was purified by repeated fractional precipitation of the gross polymer which showed that no free polyacrylamide was present.

The graft copolymer was characterized by electrometric titrations with PEI and PMA of known concentrations. Specific conductance or pH was plotted at various unit mole ratios of PEI or PMA to AAm/VA graft copolymer  $\{([PEI] \text{ or } [PMA])/[AAm/VA]\}$ . The first break in the curve corresponded to the fraction of AAm units in the copolymer and the second break corresponded to the sum of AAm and VA units. The composition of graft copolymer was found to be 0.55/0.45 (i.e., 55% of AAm units and 45% of VA units).

*Solvent.* For all experimental measurements double distilled water was used as solvent.

*pH measurements.* The pH measurements were carried out with PTA digital pH meter using combination electrode. For thermodynamic studies the solution was taken in a water jacketed cell and the temperature was controlled within  $\pm 0.05^\circ C$  by circulating thermostatically controlled water. The concentration of each polymer solution was  $1 \times 10^{-3} \text{ um l}^{-1}$  (um = unit mole). At these concentrations complexes did not precipitate.

*Conductometric titrations.* Conductometric titrations

were carried out with a Leeds and Northrup (4959) conductivity bridge. The concentration of the copolymer and homopolymer solutions used in both conductance and pH titrations were of the order of  $1 \times 10^{-3} \text{ um l}^{-1}$ .

*Viscosity.* The viscosity of the mixed solution of graft copolymer (AAm/VA) with random copolymer (MA/AAm) and PEI at various unit mole ratios, i.e.  $\{[MA/AAm] + [PEI]/[AAm/VA]\}$  was determined at  $30^\circ \pm 0.05^\circ C$  by an Ubbelohde viscometer for which the kinetic energy correction was negligible. The concentration of graft copolymer was  $5 \times 10^{-4} \text{ um l}^{-1}$  and the concentrations of random copolymer (MA/AAm) and PEI were of the order of  $5 \times 10^{-3} \text{ um l}^{-1}$ .

*Infrared spectra.* The i.r. spectra of interpolymer complex was recorded by Shimadzu Infrared Spectrophotometer IR-435.

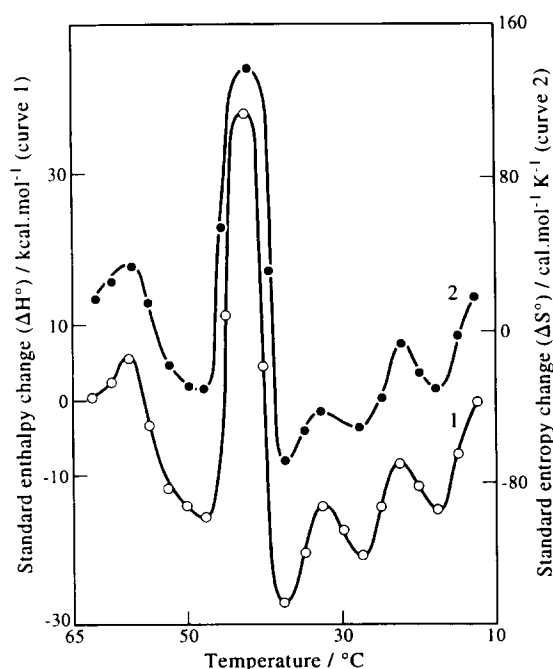
### Results and discussion

A graft copolymer, acrylamide-vinyl alcohol (AAm/VA) and a random copolymer, methacrylic acid-acrylamide (MA/AAm) have been prepared and characterized by known methods<sup>19,20</sup>. The copolymers have been found to have the following compositions: AAm/VA: 0.55 um AAm units and 0.45 um VA units. MA/AAm: 0.7 um MA units and 0.3 um AAm units. MA and AAm units are known to form an interpolymer complex when present as homopolymers<sup>10</sup>. Therefore, the two copolymers were mixed in 1/0.262 (AAm/VA:MA/AAm) unit mole ratio (umr) so as to obtain an intercopolymer complex with unreacted AAm units (0.444 um) and VA units (0.45 um), respectively. The specific stoichiometry has been chosen in order to interact one third of AAm units of graft copolymer with the MA units of random copolymer. The unreacted units (e.g. AAm and VA) of the intercopolymer complex have been further complexed with the stoichiometric amount (e.g. 0.894 um) of a typical polyelectrolyte, [e.g. poly(ethyleneimine) (PEI)]. These units (e.g. AAm and VA) are known to form interpolymer complex with PEI when present in homopolymers<sup>8</sup>. It may be mentioned that unreacted AAm units in the intercopolymer complex are contributed both by graft and random copolymers, whereas unreacted VA units are only from graft copolymer. Since the branched chains of the graft copolymer comprised of only the AAm units, therefore, the reactivity of these units may possibly be different from the same units (e.g. AAm) present in random copolymer due to the neighbouring group influence. We thought that this rather complicated complexation system could be understood better by comparing its thermodynamic and other physical properties with an equivalent blend of binary homopolymer complexes. Such comparison may possibly help in understanding the role of copolymer structure, neighbouring group influence, on the stability of interpolymer complexes.

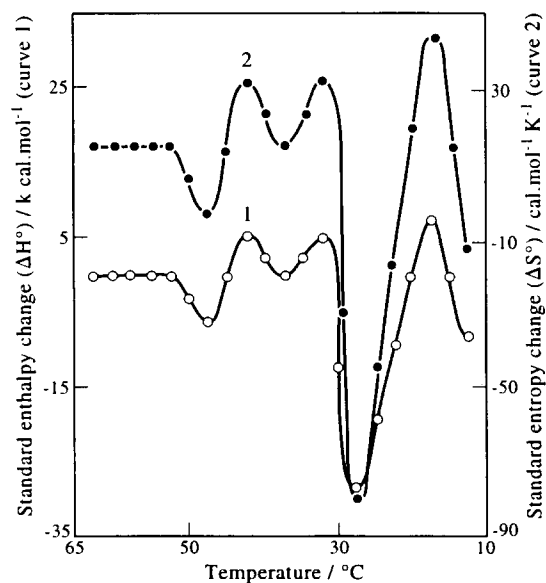
Keeping this object in mind we have determined the stability constant ( $K$ ), degree of linkage ( $\theta$ ), and other related thermodynamic parameters (e.g.  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) for the following complexation systems (I and II) by using Osada's method<sup>11-13</sup>.

**Complex-I:** 1.0 um AAm/VA graft copolymer +  
0.262 um MA/AAm random copolymer +  
0.895 um PEI.

**Complex-II:** (Equivalent blend of binary complexes): (a)



**Figure 1** Temperature dependence of standard enthalpy change,  $\Delta H^\circ$  (Curve 1) and standard entropy change  $\Delta S^\circ$  (Curve 2) for complexation system I



**Figure 2** Temperature dependence of standard enthalpy change,  $\Delta H^\circ$  (Curve 1) and standard entropy change,  $\Delta S^\circ$  (Curve 2) for complexation system II

[0.184  $\mu\text{m}$  PAAm + 0.184  $\mu\text{m}$  PMA] + (b)  
 [0.445  $\mu\text{m}$  PAAm + 0.445  $\mu\text{m}$  PEI] + (c)  
 [0.450  $\mu\text{m}$  PVA + 0.450  $\mu\text{m}$  PEI].

The method involves determination of degree of linkage theta ( $\theta$ ), which is defined as the ratio of binding groups to the total number of potentially interacting groups. The stability constant ( $K$ ) is related to  $\theta$  by

$$\theta = 1 - ([\text{H}^+]/[\text{H}^+]_0)^2$$

$$K = \theta/C_0(1 - \theta)^2$$

where  $C_0$  is the initial concentration of graft copolymer

AAm/VA (unit  $\text{mol l}^{-1}$ ) and  $[\text{H}^+]$  and  $[\text{H}^+]_0$  are the proton concentrations in the copolymer solution in the presence and absence of complementary polymers (e.g. random copolymer MA/AAm and PEI). In the case of complexation system II, the initial concentration  $C_0$  corresponds to stoichiometric mixture of non-ionic homopolymers (e.g. 0.629  $\mu\text{m}$  PAAm + 0.45  $\mu\text{m}$  PVA) and the complementary polymers are PMA (0.184  $\mu\text{m}$ ) and PEI (0.895  $\mu\text{m}$ ).

The thermodynamic parameters (e.g.  $\Delta H^\circ$  and  $\Delta S^\circ$ ) for the interpolymer complexation process can be calculated from the temperature dependence of  $K$ .

$$\Delta G^\circ = -RT \ln K$$

$$d(\ln K)/d(1/T) = -\Delta H^\circ/R$$

$$\Delta S^\circ = -(\Delta G^\circ - \Delta H^\circ)/T$$

where  $\Delta G^\circ$  is the change in standard free energy and  $R$  is the molar gas constant.

The complexation system I involves the following pairs of interacting units, e.g.

|             |                     |                     |                     |
|-------------|---------------------|---------------------|---------------------|
| AAm(graft), | AAm(graft),         | AAm(random),        | VA(graft)           |
|             |                     |                     |                     |
| MA(random)  | EI(polyelectrolyte) | EI(polyelectrolyte) | EI(polyelectrolyte) |
| 1           | 2                   | 3                   | 4                   |

Though the interacting pairs 2 and 3 apparently seem identical, but the reactivities of AAm units present in graft and random copolymer is expected to be different due to neighbouring group influence.

Stability constant ( $K$ ) calculated on the basis of Osada's equation for complexation system, I and II indicated the trend

$$\ln K(\text{cop.-PEI complex}) > \ln K(\text{blend of binary complex}) \text{ (at all temperatures)}$$

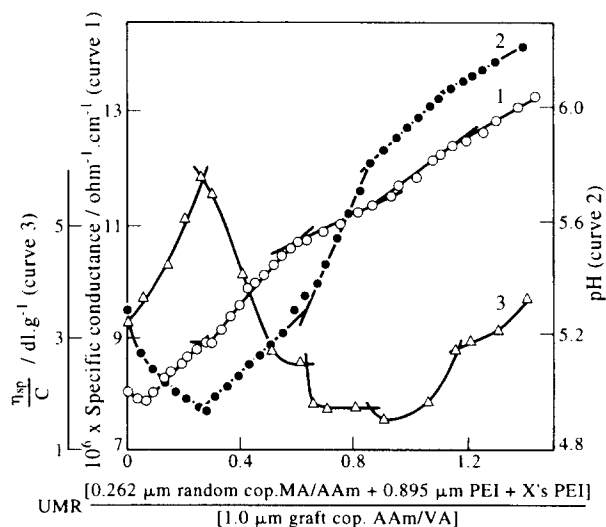
This trend is expected in view of possible entanglement of the random copolymer chains (MA/AAm) and PEI chains within the branched chains (e.g. PAAm) of the graft copolymer (AAm/VA). This will obviously impart more stability to the copolymer complex as compared to simple binary complexes of homopolymers.

The standard enthalpy and entropy change for the complexation systems, I and II, have been calculated at several temperatures on the basis of equations mentioned earlier. The plots of  $\Delta H^\circ$  vs  $T$  and  $\Delta S^\circ$  vs  $T$  for complexes I and II are depicted in Figures 1 and 2 respectively. The complex I showed four distinct maxima in both  $\Delta H^\circ$  vs  $T$  and  $\Delta S^\circ$  vs  $T$  curves (cf. curves 1 and 2 of Figure 1) at 22.5°C, 32.5°C, 42.5°C and 57.5°C, respectively. The four maxima values for complex I are tabulated in Table 1.

As stated earlier, the complex I has four distinct pairs of interacting units. The four maxima observed in  $\Delta H^\circ$  or  $\Delta S^\circ$  vs  $T$  curve, may be assigned to the destabilization of these four pairs of interacting units. The two maxima observed at lower temperatures (i.e. 22.5°C and 32.5°C), may be assigned to the destabilization of VA-EI and AAm(random)-EI interacting pairs respectively. The relatively more stable interacting pairs, e.g. AAm(graft)-EI and AAm(graft)-MA(random) perhaps get destabilized at 42.5°C and 57.5°C respectively. These assignments have been made on the basis of relative strengths of bonds in various interacting pairs<sup>10</sup>. Also the differentiation of interacting pairs 2 and 3 can possibly be made on the basis of reasons mentioned earlier. However,

**Table 1** The maximum values of  $\Delta H^\circ$  and  $\Delta S^\circ$  observed for complexation system I

| Complexation System I   | Maxima observed in $\Delta H^\circ$ (kcal mol <sup>-1</sup> ) |              |              |              | Maxima observed in $\Delta S^\circ$ (cal mol <sup>-1</sup> K <sup>-1</sup> ) |              |              |              |
|---|---|--------------|--------------|--------------|--|--------------|--------------|--------------|
|   | $\Delta H_1$  | $\Delta H_2$ | $\Delta H_3$ | $\Delta H_4$ | $\Delta S_1$   | $\Delta S_2$ | $\Delta S_3$ | $\Delta S_4$ |
| 1.0 $\mu$ m graft cop.<br>AAm/VA + 0.262 $\mu$ m<br>Rand cop. | -7.8  | -14.2        | 38.2         | 6.1          | -8.6   | -44.9        | 136.4        | 33.3         |
| MA/AAm + 0.895<br>$\mu$ m PEI                                 | (22.5°C)  | (32.5°C)     | (42.5°C)     | (57.5°C)     | (22.5°C)   | (32.5°C)     | (42.5°C)     | (57.5°C)     |


**Figure 3** Variation of specific conductance (Curve 1), pH (Curve 2) and  $\eta_{sp}/c$  (Curve 3) with unit mole ratio for complexation system I

one must admit that though these interpretations look reasonable, but still there exists some uncertainty regarding the variation of  $\Delta H^\circ$  or  $\Delta S^\circ$  vs  $T$ . These variations have been found to be much greater than the calculated experimental error in such measurements. Though one cannot say with certainty whether these interpretations will hold good or not, but some unequivocal evidence could possibly be provided from measurements of some independent physical properties during complex formation, which are presented in the subsequent part of this discussion.

In Figure 3 are presented the variation of reduced viscosity ( $\eta_{sp}/c$ ), pH and specific conductance with unit mole ratio (umr) of 1  $\mu$ m of graft copolymer (AAm/VA), with the addition of 0.262  $\mu$ m of random copolymer (MA/AAm) and 1.25  $\mu$ m of PEI (i.e. excess of stoichiometric amount), respectively.

In each of the curves, distinct breaks have been observed at specific unit mole ratios, which could be related to probable stoichiometries of the complex (cf. Table 2). The excellent correlation of different stages of interaction between component polymers, as observed from various physical properties, could provide an unequivocal evidence of the interaction between different units. The correlation refers to the coincidence of breaks observed at different unit mole ratios from various physical properties. It may be mentioned that the third and the fourth maxima in  $\Delta H^\circ$  or  $\Delta S^\circ$  vs  $T$  curves which were assigned to destabilization of AAm (graft)-EI, and AAm (graft)-MA pairs, respectively, could be correlated with the first and second breaks of curves obtained from different physical properties. However, the interaction of VA (graft)-EI, and AAm (random)-EI pairs showed a slightly different behaviour during the variation of physical properties (e.g. specific conductance, pH and viscosity). Unlike in thermodynamic studies (i.e.  $\Delta H^\circ$  /or  $\Delta S^\circ$  vs  $T$  curves), when the four interacting pairs (e.g. 1 to 4), could be differentiated, some merging up and additional stoichiometries have been observed for VA (graft)-EI and AAm (random)-EI pairs during the measurements of the three physical properties. The assignments of stoichiometries have been done by correlating the quantities of various interacting units present in the polymers and the breaks observed (umr) at different stages of interaction.

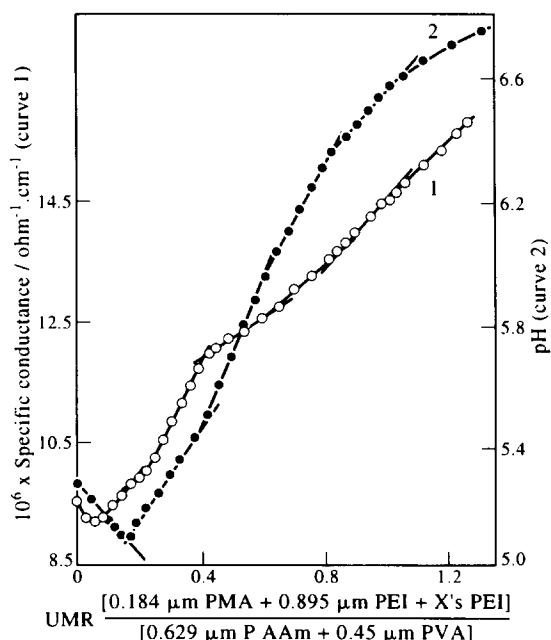
The plot of  $\Delta H^\circ$  or  $\Delta S^\circ$  vs  $T$  for complex II, also indicated four distinct maxima, at 17.5°C, 32.5°C, 42.5°C and 52.5°C, respectively (cf. Figure 2). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  at the respective maxima are summarized in Table 3. However, it may be mentioned that in the blend of binary homopolymer complexes (e.g. complex II) there are only three pairs of interacting units (e.g. AAm-MA, AAm-EI, VA-EI). Obviously on comparing the  $\Delta H^\circ$  or  $\Delta S^\circ$  vs  $T$  curves of complexes I and II, it is

**Table 2** Breaks observed and probable stoichiometry assigned to complex I.

| Complexation system I                  | Breaks observed (unit mole ratios) |                      |           |  | Probable stoichiometries            |
|--|------------------------------------|----------------------|-----------|--|-------------------------------------|
|  | pH                                 | Specific conductance | Viscosity |  |                                     |
| 1.0 $\mu$ m graft cop.                 | 0.26                               | 0.26                 | 0.26      |  | AAm(graft):MA (1/1)                 |
| cop.AAm/VA + 0.262 $\mu$ m random cop. | 0.62                               | 0.62                 | 0.62      |  | AAm(graft):EI (1/1)                 |
| MA/AAm + 0.895 $\mu$ m PEI + X's PEI   | 0.85                               | 0.85                 | 0.85      |  | VA(graft):EI (2/1)                  |
|  | 1.15                               | 1.15                 | 1.15      |  | VA(graft):EI + AAm(random):EI (1/1) |

**Table 3** The maximum values of  $\Delta H^\circ$  and  $\Delta S^\circ$  observed for complexation system II

| Complexation System II  | Maxima observed in $\Delta H^\circ$ (kcal. mol <sup>-1</sup> ) |              |              |              | Maxima observed in (cal. mol <sup>-1</sup> K <sup>-1</sup> ) |              |              |              |
|---|--|--------------|--------------|--------------|--|--------------|--------------|--------------|
|   | $\Delta H_1$   | $\Delta H_2$ | $\Delta H_3$ | $\Delta H_4$ | $\Delta S_1$   | $\Delta S_2$ | $\Delta S_3$ | $\Delta S_4$ |
| [0.184 $\mu$ m PAAm + 0.184 $\mu$ m PMA] + [0.445 $\mu$ m PAAm + 0.445 $\mu$ m PEI] + [0.45 $\mu$ m PVA + 0.45 $\mu$ m PEI] | 8.2  | 5.7          | 5.6          | 0.0          | 44.8   | 33.2         | 32.6         | 14.8         |
|   | (17.5°C)   | (32.5°C)     | (42.5°C)     | (52.5°C)     | (17.5°C)   | (32.5°C)     | (42.5°C)     | (52.5°C)     |


**Figure 4** Variation of specific conductance (Curve 1) and pH (Curve 2) with unit mole ratio for complexation system II

indicated that AAm-EI pair interacts in two distinct stages. However, it may be mentioned that AAm units in complex II are from homopolymer (e.g. PAAm). This was not observed in the case of copolymers containing AAm units. An authentic evidence of the stepwise interaction could be provided by studying the variations of pH and specific conductance of a stoichiometric mixture of PAAm and PVA with the addition of PMA and PEI. The plot of pH and specific conductance against corresponding unit mole ratio (umr) has been depicted in Figure 4. The observed breaks and the probable

stoichiometries assigned to them, have been summarized in Table 4.

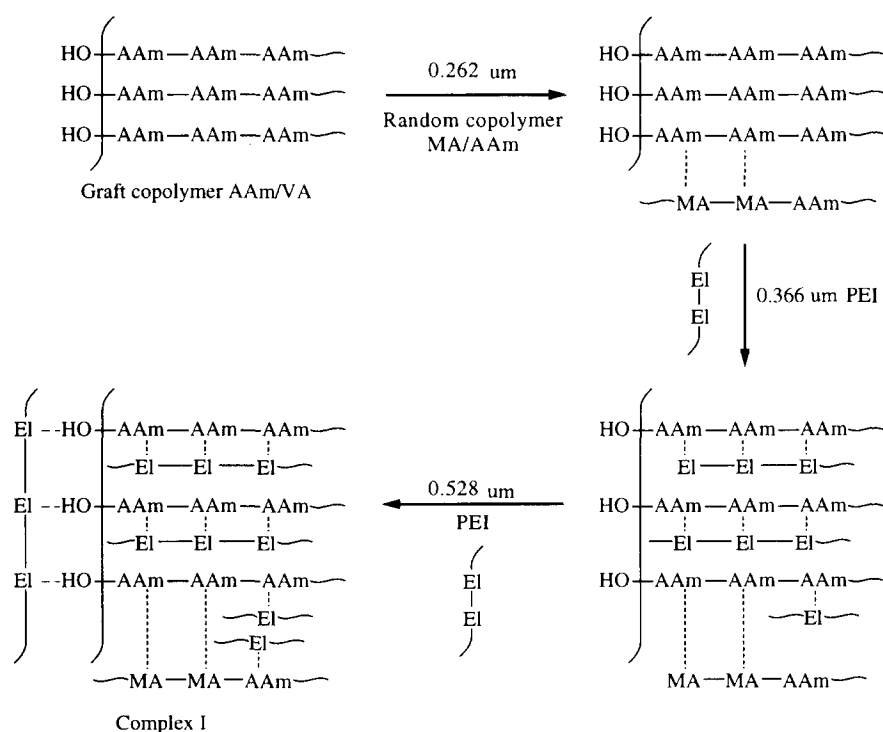
As can be seen from this table that an excellent correlation can be made between  $\Delta H^\circ/\Delta S^\circ$  vs  $T$  curve and pH and specific conductance curves regarding the interaction of AAm and EI in two distinct stages.

It may also be mentioned that the absolute values of  $\Delta H^\circ$  at the various maxima for complexes I and II are different (cf. Tables 1 and 3) even though the different pairs of interacting units are identical. This may be attributed to the structural effect of copolymers as well as neighbouring group influence. The absolute value of  $\Delta H^\circ$  depends on several factors, such as desolvation, complex formation as a result of hydrogen bonding, electrostatic interaction, ion-dipole interaction, etc. and also due to conformational change during complex formation<sup>8</sup>. All these factors are likely to contribute towards the overall value of  $\Delta H^\circ$ . Obviously, the contribution of each of these factors towards complex formation will be different for copolymer complex (i.e. I) and blends of homopolymer complexes (i.e. II).

An additional evidence of the involvement of various functional groups during complex formation could be provided by comparing i.r. spectra of the complex (I) with that of the component polymers (e.g. PEI, AAm/VA graft copolymer, MA/AAm random copolymer). The  $\nu_{N-H}$  frequency for PEI, which was observed at 1580 cm<sup>-1</sup>, shifted to 1550 cm<sup>-1</sup> for complex I. The  $\nu_{C=O(str)}$  frequency of AAm/VA graft copolymer and MA/AAm random copolymer were observed at 1645 cm<sup>-1</sup> and 1700 cm<sup>-1</sup>, respectively. This was observed at 1670 cm<sup>-1</sup> for the complex I. The  $\nu_{O-H(str)}$  frequency of PVA in graft copolymer (AAm/VA) was observed at 3400 cm<sup>-1</sup> and it shifted to 3480 cm<sup>-1</sup> for the complex I. The distinct shift in group frequencies unequivocally indicates the involvement of various functional groups during complex formation.

**Table 4** Breaks observed and stoichiometries assigned to complex II

| Complexation System II  | Breaks observed (unit mole ratios) |                       | Probable stoichiometries |
|---|------------------------------------|-----------------------|--------------------------|
|   | pH                                 | Specific conductances |                          |
| [0.629 $\mu$ m PAAm + 0.45 $\mu$ m PVA] + 0.184 $\mu$ m PMA + 0.895 $\mu$ m PEI + X's PEI | 0.17                               | 0.17                  | AAm:MA (1/1)             |
|   | 0.38                               | 0.38                  | AAm:EI (2/1)             |
|   | 0.58                               | 0.58                  | AAm:EI (1/1)             |
|   | 0.82                               | 0.82                  | VA:EI (2/1)              |
|   | 1.02                               | 1.00                  | VA:EI (1/1)              |



Scheme 1

On the basis of various experimental evidences, *Scheme 1* may be suggested to explain the mode of interaction between the component copolymers and the polyelectrolyte during complex formation.

In conclusion, it can be said that acrylic copolymers form a relatively more stable complex with PEI as compared to an equivalent blend of binary homopolymer complexes. The related thermodynamic parameters (e.g.  $\Delta H^\circ$  and  $\Delta S^\circ$ ) for the two systems have been found to be different. This has been attributed to neighbouring group influence and the specific structural effect of the copolymers.

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