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Interpolymer complexes of poly(acrylic acid) with poly(2-hydroxyethyl acrylate) in aqueous solutions

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Abstract Complexes formed from poly(acrylic acid) and poly(2-hydroxyethyl acrylate) were studied in aqueous solutions by viscometric, turbidimetric, FTIR spectroscopic, and thermogravimetric analysis methods. The formation of interpolymer complexes stabilized by hydrogen bonds was observed.
It was found that the compositions of these interpolymer complexes are strongly dependent on the concentration of polymers, the order of mixing the solutions, and the pH.
It was demonstrated that the complexation ability of poly(2-hydroxyethyl acrylate) is relatively low compared to other known nonionic water-soluble polymers. However, it can be significantly increased via hydrophobic modification of the poly(acrylic acid) using cetyl pyridinium bromide.

Keywords Interpolymer complexes · Poly(2-hydroxyethyl acrylate) · Hydrogen bonding · Critical phenomena

Introduction

Complexation between poly(carboxylic acids) and nonionic proton-accepting polymers via hydrogen bonding has attracted considerable attention for more than four decades. Interest in this field has been highly stimulated by potential applications of interpolymer complexes (IPC) to new drug delivery formulations [1, 2, 3], biomaterials [4], novel surfactants [5], emulsifiers [6], thickening reagents [7], and membrane and separation technology [8, 9]. Recently, these complexation phenomena were successfully used for the preparation of polymeric micelles [10, 11, 12], microgels [13], nanoparticles [14], stimuli-responsive hydrogels [15, 16] and thin multi-layered films [17].

The main features of complexation, the properties of polycomplexes, as well as their potential applications have been summarized in a number of comprehensive reviews [18, 19, 20, 21, 22]. At the moment, further development in this field is mostly related to applications and exploration of novel polymers forming IPC.

Water-soluble non-ionic polymers forming complexes with poly(carboxylic acids) can be classified into: polymers containing lactame groups (such as polyvinylpyrrolidone and poly(vinyl caprolactame)); polymers containing etheric groups in the backbone (including poly(ethylene oxide) and poly(propylene oxide)) or as pendants (poly(vinyl methyl ether) for example); acrylic type polymers (polyacrylamide, poly(*N*-isopropylacrylamide), and poly(*N*,*N*-dimethylacrylamide) for instance); polymeric alcohols (such as poly(vinyl alcohol) and poly(vinyl ether of ethyleneglycol)); polysaccharides (examples include methylcellulose and hydroxyethylcellulose); and other synthetic polymers (including polyethyloxazoline and poly(*N*-acetyliminoethylene)) [22].

2-Hydroxyethyl acrylate (HEA) is a hydrophilic monomer of acrylic type that can be used for the preparation of grafted materials, hydrogels, and water-soluble polymers. Various authors have reported on the preparation of various polymers based on HEA. Sawpan and co-workers [23] demonstrated the possibility of grafting HEA onto cellulose via ultraviolet radiation. Safrany [24] reported preparation of hydrogels by radiation-induced copolymerization of HEA and hydroxypropyl acrylate in bulk and in aqueous solutions without any additive. Porous hydrogels were prepared by Monleón Pradas et al [25] via copolymerisation of HEA and ethyleneglycol dimethacrylate (as crosslinking agent) in solution using water or ethanol as solvents. Yu Jin et al [26] prepared blend hydrogels by copolymerization of glycidyl methacrylate-derivatized hyaluronate with HEA in order to study their physicochemical characteristics.

Several reports have been devoted to the preparation of water-soluble copolymers based on HEA. Sun et al [27] reported on the preparation of polymers by copolymerization of HEA with vinyl mercaptoacetate *S*-sulfate sodium salt. The polymers prepared were water-soluble, but upon treatment with an oxidizing agent they were transformed quickly into a water-tolerant material. This again became water-soluble on addition of a reducing agent. The unique solubility alternation was explained by the reversible formation of S–S bond cross-linking in the polymer. Finally, Cowie et al [28] studied the copolymerization reaction between HEA and itaconic acid.

At the moment, however, only limited information is available on the properties of the water-soluble homopolymer of HEA, poly(2-hydroxyethyl acrylate) (PHEA), and to the best of our knowledge the complexation of PHEA with poly(carboxylic acids) has never been reported. In the present study we examined the formation of IPC from PHEA and poly(acrylic acid) (PAA) in aqueous solutions.

Experimental

Materials

HEA and PAA with weight-average molecular weights of 2.5×10^5 Da were purchased from Aldrich Chemical Co. (USA) and used without further purification. Cetyl pyridinium bromide (CPB) was purchased from Vekton (Russia) and used as received.

Synthesis and characterization of PHEA

PHEA was synthesized by radical polymerization of HEA in ethanol solution at 60 °C for 15–20 min. Azoisobutyronitrile was used as an initiator for the radical polymerization (5×10^{-3} M). Before polymerization, the monomer solution was saturated with argon and sealed into glass ampoules. The synthesized polymer was purified by precipitation from ethanol to diethyl ether three times, and then was dried under vacuum until it was a constant weight. The yield of PHEA was about 85%.

The weight-average molecular weight of PHEA determined by gel permeation chromatography combined with laser light scattering was 4.2×10^6 Da, and the polydispersity M_w/M_n was 1.1. The mobile phase consisted of acetate buffer solution with a flow rate of 1.0 mL/min. The refractive index increment d n/d c of PHEA solutions was 0.012 mL/g. The gel permeation chromatograph was calibrated with poly(ethylene glycol) standards.

Preparation of polymer solutions

Aqueous solutions were prepared by direct dissolution of known amounts of PAA and PHEA in distilled water with overnight stirring. Solution pH's were adjusted by addition of small amounts of 0.1 M HCl or 0.1 M NaOH, and measured using a pH-meter (Ion Meter 3345, Jenway Ltd., UK).

Preparation of polycomplex in dry state

The polycomplex in dry state was obtained by mixing 1 g/dL aqueous solutions of PAA and PHEA in stoichiometric proportions, acidification of the solution by adding 0.1 M HCl solution until the pH was less than 2.0, centrifugation of the precipitate, and then by washing it with distilled water and drying under vacuum.

Turbidimetric measurements

The turbidity of the polymer solutions was investigated using a Shimadzu UV/VIS-2401 PC spectrophotometer (Japan) at a wavelength of 400 nm. The temperature of the solutions was maintained constant at 25 ± 0.2 °C with the help of a thermo-electrically temperature-controlled cell positioner (CPS-240A, Shimadzu, Japan).

Viscosity measurements

The viscosities of the solutions were determined with the help of an Ubbelohde viscometer at 25 °C. Viscometers were submerged in a thermostated water bath with a temperature control precision of 0.1 °C. A digital stopwatch provided the flow time, with a resolution of 0.1 s. For each solution, 3–5 viscosity measurements were taken and average values were computed and reported.

Fourier Transform Infrared (FTIR) characterization

The FTIR spectra of the polymers and their IPC were recorded in KBr discs using a Mattson Satellite 3000 FTIR spectrometer (USA).

Thermal behavior

The thermal degradation of the samples were studied using a 951 Thermogravimetric Analyzer (Du Pont Instruments, USA) at a scan rate of 10 degree/min under a dry nitrogen atmosphere. The weight of PAA, PHEA, and IPC samples was 5.51, 5.09 and 5.49 mg, respectively.

The differential scanning calorimetric analysis of the samples was done on a 910 Differential Scanning Calorimeter (DSC) (Du Pont Instruments, USA) at a scan rate of 10 degree/min under a dry nitrogen atmosphere. The weight of PAA and IPC samples was 6.12 and 5.34 mg, respectively. The second scan was taken into consideration.

Results and discussion

Formation of interpolymer complexes in aqueous solutions

PHEA is a water-soluble polymer possessing a hydroxyl group as a pendant in every structural unit. The structure of PHEA allows complex formation with poly(carboxylic acids) via hydrogen bonding. Since the complex formation ability of poly(vinyl alcohol) [29], poly(vinyl ether of ethyleneglycol) [29, 30, 31], and hydroxyethylcellulose [29, 32] (all with similar hydroxyl groups) is relatively low, one can expect that the ability of PHEA to form IPC is also not high. Viscometric and turbidimetric titration showed that the complex formation of PHEA with PAA occurred in aqueous solutions at low pH. Figure 1a,b shows viscometric titration curves for PHEA solutions by PAA (a) and vice versa (b) at different concentrations of polymers at pH 2.6. Mixing of the polymer solutions was accompanied by a decrease in viscosity, indicating the formation of a relatively compact IPC. The extrema on the titration curves indicate the compositions of IPCs, which depend strongly on the concentrations of the polymers. When one of the components of low concentration (0.01 M) was titrated by the other polymer solution with 10 times higher concentration (0.1 M), the composition of IPC was close to 1:1 stoichiometry. At higher concentrations of the titrated polymer, deviation from this stoichiometry was observed. This deviation may be explained by a very high molecular weight of PHEA (M_w), which can hinder the interactions between complementary macromolecules, resulting in low aggregation stability of IPC. It is likely that the high molecular weight of PHEA also causes the precipitation of IPC in more concentrated solutions before achieving a stoichiometric ratio of the components. Even with high molecular weight PHEA, the initial solution viscosity was not high, which can be explained by the significant flexibility of its macromolecules. Indeed, the glass transition temperature of PHEA is relatively low, and in dry state it is a very soft and elastic material.

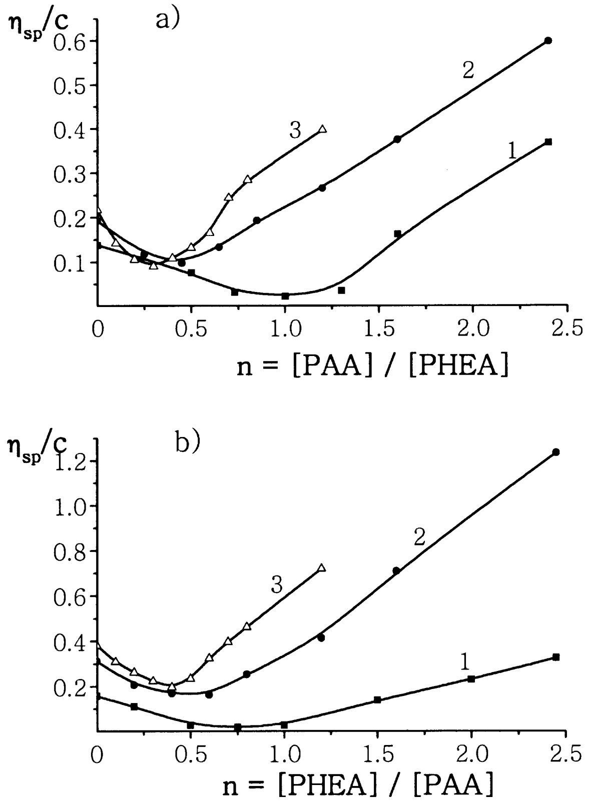


Fig. 1 a Viscometric titrations of PHEA solution by 0.1 M PAA solution: [PHEA] = 0.01 (1); 0.05 (2); 0.1 M (3). **b** Titrations of PAA solution by 0.1 M PHEA solution: [PAA] = 0.01 (1); 0.05 (2); 0.1 M (3). pH = 2.6 in both cases

Complexation of PHEA and PAA in diluted solutions was studied by turbidimetric titration at different pH in the acidic region. Figure 2 shows turbidimetric

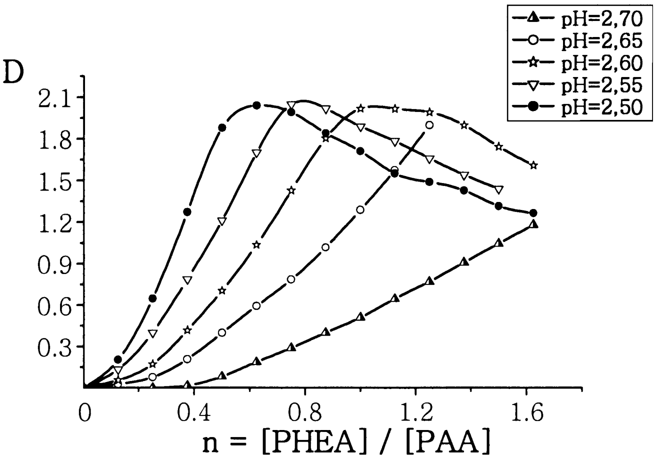


Fig. 2 Turbidimetric titrations of PAA by PHEA solutions at various pH. [PHEA] = [PAA] = 0.02 M

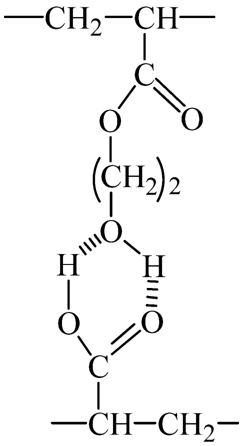


Fig. 3 Interaction scheme for PAA and PHEA

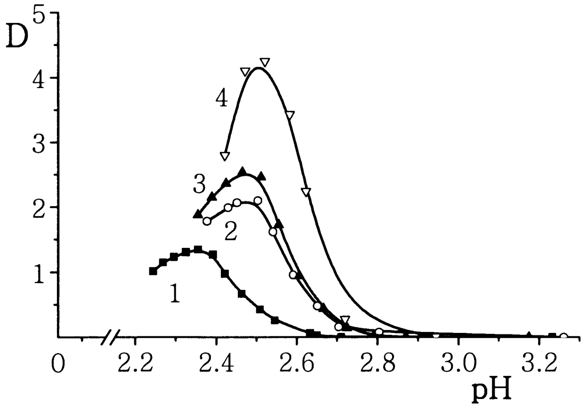


Fig. 4 Dependence of the turbidities of PAA-PHEA aqueous mixtures on pH at various initial polymer concentrations. [PHEA] = [PAA] = 0.005 (1); 0.01 (2); 0.03 (3); 0.05 M (4)

titration curves, which indicate that the composition of IPC depends strongly on pH. Even a slight change in pH results in a significant difference in IPC composition (from $n = 0.5$ at pH 2.50 to $n > 1.6$ at pH 2.70). Such a dependence of IPC composition on pH is likely related to a change in aggregation stability of the polycomplex particles, which depends on the degree of PAA ionization. At relatively low pH values (pH 2.50 and 2.55), the IPC possesses lower aggregation stability because PAA is less ionized. This IPC started to precipitate before the composition of binary mixture achieved the stoichiometric ratio. At higher pH (pH 2.65 and 2.70), the aggregation stability of IPC was increased because the ionization degree of PAA was higher. These IPC were stable to aggregation, even in the presence of an excessive amount of PHEA in comparison with the stoichiometric ratio. In this case, the maxima on the titration curves should probably appear at a greater excess of PHEA, which was outside the range of our titration. Formation of stoichiometric IPC was observed at pH 2.6, which can be justified by the complexation scheme shown in Fig. 3.

In our earlier studies [29, 30, 31, 32, 33, 34] we reported the existence of critical pH values (pH_{crit}) for binary systems involving poly(carboxylic acids) and proton-accepting non-ionic polymers. Below this value, precipitation of IPC was observed. It was shown that pH_{crit} values were specific for every system and depend on their structure, molecular weight, concentration, and the presence of low molecular weight substances in solution. They can be used to evaluate the ability of polymers to form complexes. The high pH_{crit} values correspond to the polymers with high complexation ability.

In the present work, we have determined the pH_{crit} values for the complexation of PAA and PHEA. Figure 4 shows the dependence of the turbidity of PAA-PHEA mixtures on the pH at various concentrations of both polymers. The pH value at which a sharp increase in turbidity (*D*) is observed corresponds to the pH_{crit}. A decrease in absorbance at low pH after passing through pH_{crit} is caused by the aggregation of IPC particles and their partial precipitation. It is clearly seen that pH_{crit} is shifted to a higher pH region upon increasing polymer concentrations, and this indicates an enhancement in complexation ability. It should be noted that the pH_{crit} values obtained for PAA-PHEA are within the 2.6–2.9 range, which confirms our expectations about the low complexation ability of PHEA.

The effect of inorganic salts on the complexation between PAA and various non-ionic polymers is still open to discussion. Opposite effects of inorganic salts on the stability of IPC have been reported by different authors [35, 36, 37, 38]. These effects were discussed in detail in one of our recent publications [29]. It was demonstrated that adding inorganic salts to the solutions of polymers with relatively low ability to form IPC enhances their complexation. Indeed, in the case of PAA-PHEA complexation we can observe a significant shifting of critical pH values to the higher pH region upon the addition of NaCl (Fig. 5). This effect is related to the deterioration of the thermodynamic quality of the solvent with respect to the polymers. It is well known that the ability of a polymeric pair to form IPC depends strongly on the balance between polymer-polymer and polymer-solvent interactions [20, 21]. The formation of IPC is possible only when the polymer-polymer interactions are dominant. Addition of inorganic salts to solutions of polymers results in competition between the macromolecules and low molecular weight ions for the solvation layer of water molecules. It leads to deterioration in the thermodynamic quality of the solvent (water), which actually weakens the polymer-solvent interactions and favors the IPC formation.

Hydrophobic interactions play a significant role in the additional stabilization of IPC. There were a number of reports demonstrating the important contribution of hydrophobic interactions to the complex formation between poly(carboxylic acids) and non-ionic polymers. Tsuchida and co-workers [20] have demonstrated that poly(methacrylic acid) (PMAA) forms stronger polycomplexes with poly(ethylene oxide) (PEO) than PAA does. These results were interpreted in terms of an additional hydrophobic effect from α-methyl groups of PMAA participating in the interaction. Staikos et al [39] have shown higher stability of IPC formed between PAA and poly(*N*-isopropylacrylamide) or poly(vinyl methyl ether) than the polycomplexes of poly(acrylamide) and PEO. The study has shown that hydrophobic interactions only exist in the case of a non-ionic polymer with lower critical solution temperature (LCST).

In our previous works [33, 34] we demonstrated that incorporation of hydrophobic monomeric units of vinyl butyl ether (VBE) into macromolecules of non-ionic poly(vinyl ethers of glycols) resulted in higher stability of IPC with PAA. In the present work, we have attempted to use another approach for the hydrophobic modification of PAA, with the aim of additional stabilization of its IPC with PHEA. It is well known that PAA forms polymer complexes with oppositely-charged surfactants such as cetyl pyridinium bromide (CPB) [40]. Depending on the ratio between the surfactant and PAA, the polycomplexes can form stable, clear solutions, dispersions or precipitates. In our experiments we used negligible amounts of CPB added to PAA in order to ensure that the polycomplex between them is soluble in water. The structure of this polycomplex is shown schematically in Fig. 6. Each PAA is complexed with several molecules of CPB via coulombic forces. The hydrocarbon tails of CPB act as hydrophobic groups attached to PAA. The complexation ability of hydrophobically modified PAA with PHEA was studied by the critical pH method. Figure 7 shows the dependence of absorbance on pH for systems including PHEA and modified (curve 4) and non-modified PAA. It can clearly be seen that the presence of CPB in the system shifted the pH_{crit} values to a higher pH region, confirming the enhancement of complexation ability of PAA by its hydrophobic modification. It should be noted that the effect of the surfactant is more efficient for the enhancement of complexation than the effect of NaCl addition. Curves showing the effects of NaCl are plotted in the same figure for comparison (curves 2 and 3).

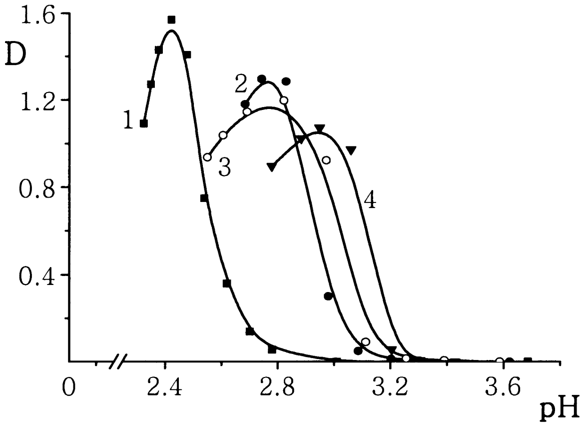


Fig. 5 Dependence of the turbidities of PAA-PHEA aqueous mixtures on pH at various ionic solution strengths. [PHEA] = [PAA] = 0.01 M. [NaCl] = 0 (1); 0.005 (2); 0.01 (3); 0.05 M (4)

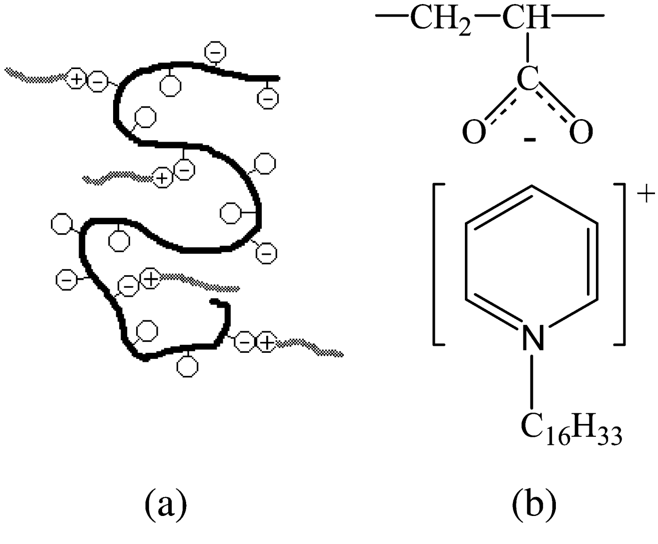


Fig. 6 Interaction scheme for PAA and CPB (**a**) and complexation mechanism (**b**). Open circles show unionised COOH-groups of PAA

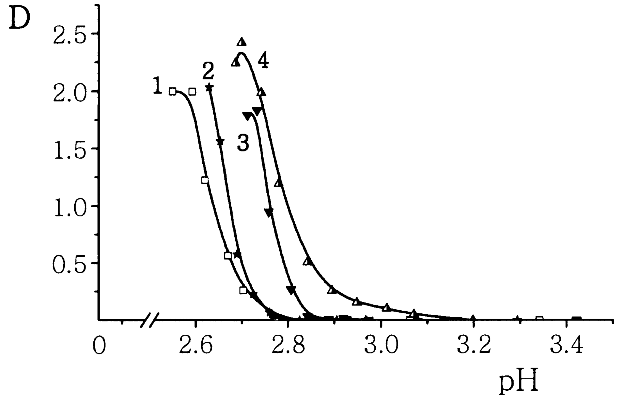


Fig. 7 Dependence of the turbidities of PAA-PHEA aqueous mixtures on pH in the presence of NaCl and CPB additives. [NaCl] = 0 (1); 3.15×10^{-4} (2); 10.0×10^{-4} M (3); [CPB] = 1.5×10^{-4} M (4)

Structure and thermal stability of interpolymer complexes

The structure and properties of IPC formed by PAA and PHEA in the solid state was studied by FTIR spectroscopy and thermal gravimetric analysis (TGA). For this purpose the IPC was obtained as a precipitate, which then was thoroughly washed by distilled water and dried in vacuum. Figure 8 shows FTIR spectra of PAA, PHEA, and their IPC. It can clearly be seen that the spectrum of IPC is characterized by the presence of bands typical of both initial components (shown by arrows). The band at 1700 cm^{-1} typical of carboxylic groups of PAA is shifted slightly to smaller wave numbers, confirming the formation of intermacromolecular hydrogen bonds between the component polymers according to the scheme discussed before. It should be noted that the dry polycomplex could not be redissolved in water at neutral pH, which can be associated with strong intermacromolecular hydrogen bonding or its partial cross-linking via formation of ester bonds. However the FTIR spectra do not give any evidence about the formation of new ester bonds.

Figure 9 presents the results from the thermogravimetric analysis of PAA, PHEA, and their polycomplex. The thermal degradation of PAA proceeds in two steps, which is in agreement with our previous findings [41].

The degradation of PHEA consists of three stages. Recently Demirelli et al [42] published a very detailed study of the thermal degradation of poly(2-hydroxyethyl methacrylate) (PHEMA). Despite the fact that PHEMA differs from PHEA by only a methyl group, their degradation profiles were completely different. The degradation of PHEMA proceeded mainly via a depolymerization mechanism, and yielded the monomer HEMA as a main product.

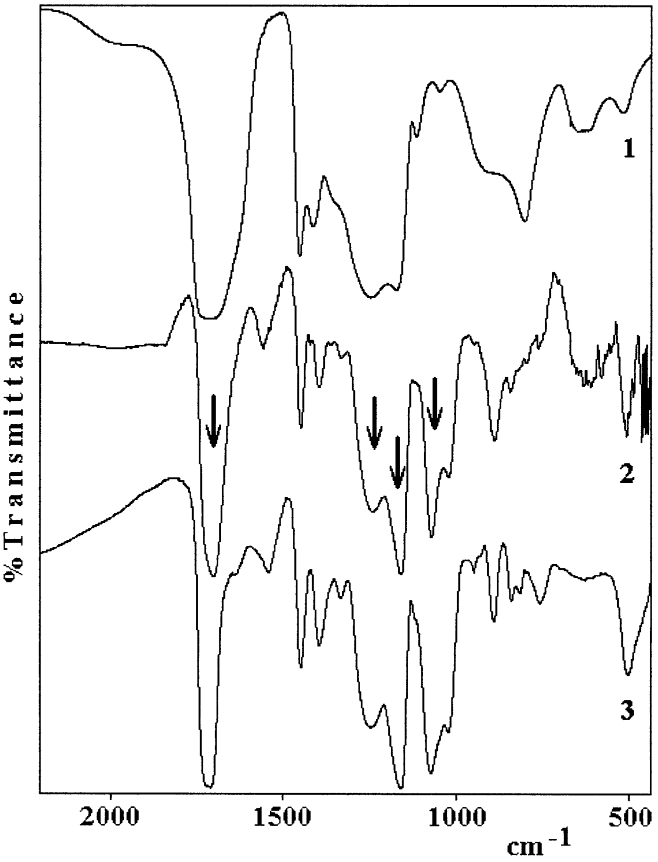


Fig. 8 FTIR-spectra of PAA (1), complex PAA-PHEA (2), PHEA (3)

The thermal stability of the IPC was entirely different from the degradation of its components. The first process occurred at 168–280 °C with a weight loss of about 6–7% and a reaction peak at 238 °C. This change in the thermogram may be related to the formation of ester bonds from carboxylic acid groups of PAA and hydroxyl groups of PHEA. Earlier we reported the formation of similar ester bonds between poly(2-hydroxyethyl vinyl ether) and PAA [43, 44, 45]. The final and full weight loss of IPC up to 80% begins at 361 °C and reaches a maximum at 444 °C, leading to a complete degradation of the polymer complex.

The existence of intermolecular interactions can be confirmed using DSC method (see [46] as an example). Figure 10 shows DSC thermograms of the PAA and PHEA/PAA polycomplex. The glass transition temperature (T_g) of pure PHEA is about 20 °C [47], which unfortunately was out of the range of the calorimeter used in the present work. For pure PAA, the glass transition temperature is observed at 105 °C, which is in a good agreement with the literature [48]. Upon interaction with PHEA, the polycomplex PHEA/PAA showed a single T_g around 60.6 °C, confirming the miscibility of the two components within the IPC. Many polycomplexes of PAA and non-ionic polymers have T_g values higher than that predicted by the linear additivity

Fig. 9 TGA curves of PAA (1), PHEA (2), and their IPC (3)

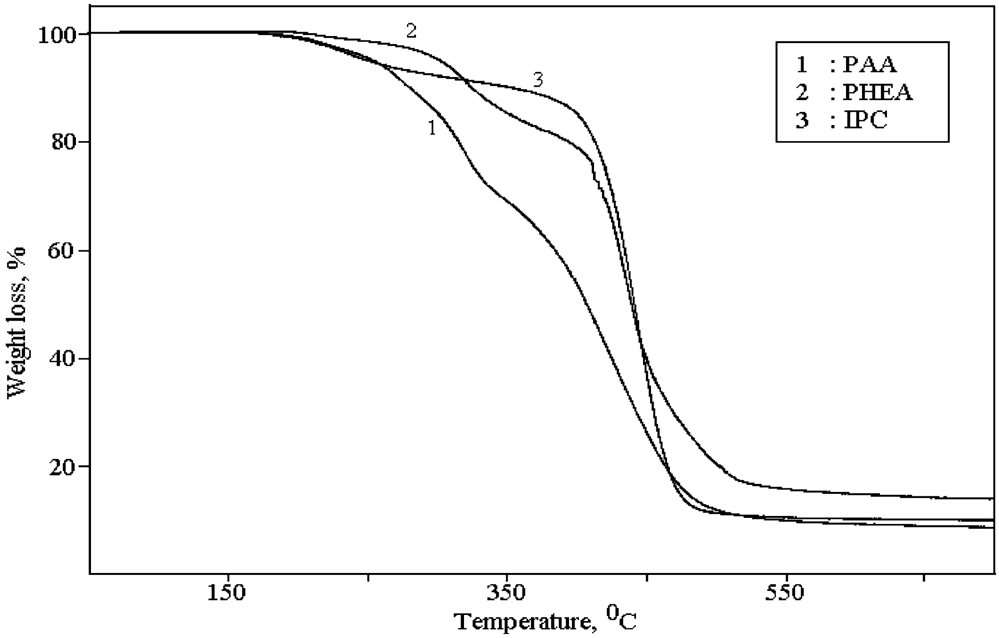
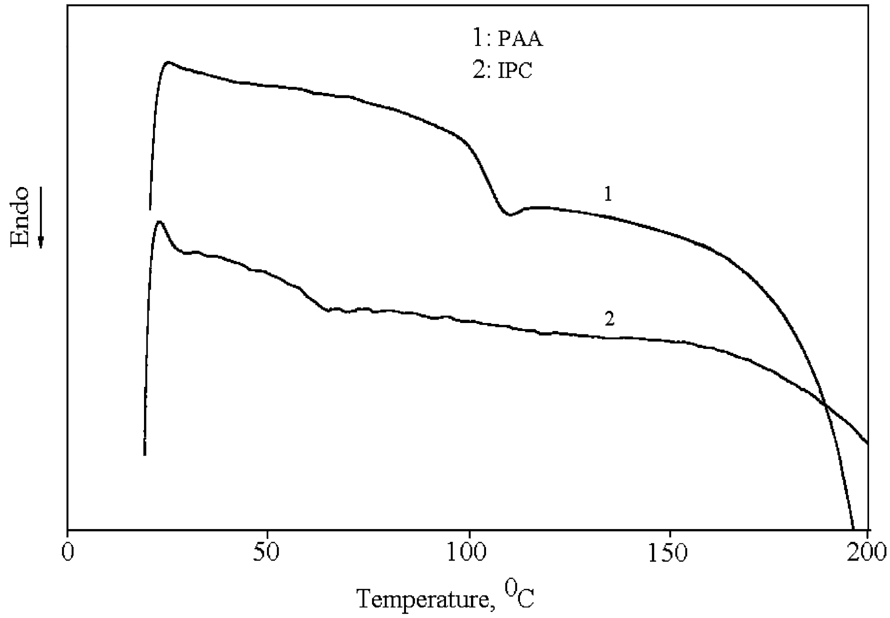


Fig. 10 DSC curves of PAA (1) and IPC (2)



rule using the T_g values of the component polymers [21]. The high T_g has been ascribed to interactions between the component polymers, which act as physical cross-links, reducing segment mobility. So the higher number of physical cross-links, caused by a greater amount of intermacromolecular hydrogen bonds per single macromolecule, results in a higher T_g value, which confirms the stronger complexation between the polymers. The T_g value of the PAA/PHEA complex is higher than T_g of PHEA but lower than T_g of PAA. This can be explained by partial disruption of the self-association of the PAA dimer macromolecules, caused by the interaction with elastomeric PHEA, and it also confirms that the interpolymer interactions are not very strong.

Conclusions

Complex formation between poly(acrylic acid) and poly(2-hydroxyethyl acrylate) has been studied in various aqueous solutions. It was shown that the main force governing the interaction is hydrogen bonding. It was shown that the concentrations of the polymer solutions, as well as their pH, influence the compositions of the polycomplexes formed. Addition of the inorganic salt NaCl to the polymer solutions, as well as the hydrophobic modification of poly(acrylic acid) using cetyl pyridinium bromide, can enhance complex formation. The thermal properties of the interpolymer complex are totally different from the constituent components, confirming the complete miscibility of the components within the polycomplex, and indicating that the interactions between polymers are not very strong.

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