

Effect of Temperature on Aggregation/Dissociation Behavior of Interpolymer Complexes Stabilized by Hydrogen Bonds

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ABSTRACT: The effect of temperature on the aggregation/dissociation behavior of interpolymer complexes based on poly(acrylic acid) and various nonionic polymers—poly(vinyl pyrrolidone), poly(ethylene oxide), poly(acrylamide), hydroxypropylcellulose, hydroxyethylcellulose, poly(vinyl methyl ether), poly(vinyl ether of ethyleneglycol), and vinyl ether of ethyleneglycol-co-vinyl butyl ether—has been studied in aqueous solutions. It was shown that nonionic polymers could be classified into two groups according to the stability of their polycomplexes with respect to temperature. The first group of nonionic polymers forms interpolymer

complexes, which are stable and undergo further aggregation upon increase in temperature. The second group forms polycomplexes, which dissociate at higher temperatures. The nature of forces stabilizing different interpolymer complexes in aqueous solutions is discussed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1946–1950, 2004

Key words: interpolymer complexes; hydrogen bonding; water-soluble polymers; stimuli-responsive polymers; phase separation

INTRODUCTION

Interpolymer complexes (IPC) of poly(carboxylic acids) with nonionic polymers have been intensively studied during the past decades. Regularities of their formation in aqueous and organic solutions, their structure, composition, and stability were thoroughly studied by various physicochemical methods and reported in a huge number of research articles and several reviews.^{1–5} It is well known that IPC of poly(carboxylic acids) with nonionic polymers are formed via cooperative system of hydrogen bonds and in aqueous solutions are additionally stabilized by hydrophobic interactions.

One of the most important factors governing interpolymer complexation is environmental temperature. Hydrogen bonds are mainly formed at a relatively low temperature and weaken upon an increase in temperature. However, the hydrophobic interactions are strengthened at higher temperatures. Hence, the stability of IPC greatly depends on a delicate balance

between the contributions of hydrogen bonding and hydrophobic interactions.

Several authors studied the effect of temperature on stability of IPC using a viscometric technique. Staikos and coworkers⁶ reported the effect of temperature on viscometric behavior of complexes between poly(acrylic acid) (PAA) and poly(acrylamide) (PAAM) as well as PAA with poly(*N*-isopropylacrylamide) (PNIPAAm) in aqueous solutions. They found that solution viscosity of PAA-PNIPAAm polycomplexes is decreased upon increase of temperature and an opposite trend is observed for complexes of PAA with PAAM.

Manolova et al.⁷ have studied the stability of polycomplexes formed from poly(methacrylic acid) (PMAA) and new copolymers of 5-chloro-8-quinolinyl acrylate with *N*-vinyl-2-pyrrolidone at different temperatures by viscometric technique. They found the absence of temperature dependence of IPC solution viscosity in the broad temperature range 20–80°C and concluded that the complexes are stable in these conditions.

Katime and coworkers⁸ studied the effect of temperature on the phase behavior of polycomplexes composed of poly(mono *n*-alkyl itaconates) and tertiary polyamides in aqueous and organic solvents of different nature. It was found that the stability of IPC with

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TABLE I
Characteristics of Polymers Used in the Present Study

Polymer	Abbreviation	Characteristics	Source
Poly(acrylic acid)	PAA	$M_w = 4.5 \times 10^5$	Aldrich (Milwaukee, WI)
Poly(vinyl pyrrolidone)	PVP	$M_w = 2.4 \times 10^4$	Aldrich
Poly(acrylamide)	PAAM	$M_w = 6 \times 10^6$	Aldrich
Poly(ethylene glycol)	PEG	$M_n = 2 \times 10^4$	Sigma (UK)
Poly(vinyl methyl ether)	PVME	$M_w = 6 \times 10^4$	BASF (Germany)
Hydroxypropylcellulose	HPC	$M_w = 1 \times 10^5$, substitution degree 66–70 %	Fluka (Buchs, Switzerland)
Hydroxyethylcellulose	HEC	Substitution degree 1.54–1.57	Fluka
Poly(vinyl ether of ethyleneglycol)	PVEEG	$M_w = 4 \times 10^4$	Synthesized, purified, and characterized as described in experimental part
Copolymer of vinyl ether of ethyleneglycol- <i>c</i> -vinyl butyl ether (78: 22 mol %)	VEEG-VBE	$M_w = 2.4 \times 10^4$	Synthesized, purified, and characterized as described in experimental part

respect to temperature greatly depends on the nature of the solvent and structure of the polymer.

In the present work we attempted to study the effect of temperature on the aggregation behavior of IPC composed of PAA and various nonionic polymers—PAAM, poly(vinyl pyrrolidone) (PVP), poly(ethylene oxide) (PEO), poly(vinyl methyl ether) (PVME), hydroxypropylcellulose (HPC), hydroxyethylcellulose (HEC), poly(vinyl ether of ethyleneglycol) (PVEEG), and vinyl ether of ethyleneglycol-*co*-vinyl butyl ether (VEEG-VBE).

EXPERIMENTAL

The polymers used in this study, their characteristics, and sources are listed in Table I. They were used without further purification.

PVEEG and copolymer VEEG-VBE were synthesized by γ -irradiation homopolymerization of vinyl ether of ethyleneglycol and copolymerization of vinyl ether of ethyleneglycol with vinyl butyl ether with the initial feed mixture 70 : 30 mol %, respectively. The synthesis of the polymers was performed in bulk at high degrees of conversion (more than 40%) with absorbed dose 15 kGy using ^{60}Co "MRX- γ -25M" radiation facility at an irradiation dose rate 1 Gy/s as described in cited references.^{9,10} The synthesized polymers were purified by a three-fold precipitation from ethanol to diethyl ether and dried in a vacuum dessicator at 30°C until constant weight. The molecular weight of PVEEG was determined viscometrically in water using the following relationship¹¹:

$$[\eta] = 8.8 \cdot 10^{-4} \times M^{0.50}$$

The composition of VEEG-VBE was determined by ^{13}C -NMR spectroscopy in dimethylsulfoxide solutions. The spectra were recorded using a Bruker Avance 250 DPX spectrometer (Darmstadt, Germany).

The composition of the copolymer was calculated through the intensity ratio of the chemical shifts $[\text{CH}]/[\text{CH}_3]$. The weight-average molecular weight of VEEG-VBE was determined by gel permeation chromatography using Millipore Waters GPC Instrument.

IPC were prepared by mixing 0.01M solutions of starting components in required ratio and adjusting the pH of solution by addition of small amounts of 0.1N HCl or NaOH. pH of solutions was determined using a digital ionmeter Jenway-3345 (Essex, UK).

Turbidity of IPC solutions was measured with UV-2401 PC spectrophotometer (Shimadzu, Japan) at the wavelength 400 nm. The temperature of IPC solutions was regulated with the help of thermoelectrically temperature-controlled cell positioner CPS-240A (Shimadzu, Japan).

RESULTS AND DISCUSSION

According to Maunu and coworkers¹² the complexation of poly(carboxylic acids) with nonionic polymers occurs instantaneously after mixing the solutions and this process is very fast. However, the fast complexation is followed by aggregation of complexes, which leads to appearance of solution turbidity. We have used the solution turbidity as a simple and convenient tool to monitor the changes that occurred with IPC upon heating.

Earlier^{5,13} we demonstrated that different polymeric pairs form IPC below critical pH values (pH_{crit}), which depend on the structure of the polymers, their concentration in solution, and other factors. Taking into account the values of pH_{crit} determined in our previous work¹³ for complexes of PAA with different nonionic polymers we prepared the polycomplexes at required pH values (Table II). In fact, these pH values reflect the complex formation ability of polymers. Different poly-

TABLE II
Polycomplexes of PAA with Different Non-Ionic
Polymers. Polymer Concentration Is 0.01 base-mol/L.

Non-ionic polymer	[Non-ionic polymer]/ [PAA]	pH
PVME	1 : 1	4.82
PVP	1 : 1	4.75
VEEG-VBE	1 : 1	3.76
HPC	1 : 1	3.71
PEO	1 : 1	3.00
PAAM	1 : 1	2.94
HEC	1 : 1	2.75
PVEEG	1 : 1	2.72

complexes could not be compared at the same pH because the weakly complexing polymers like PAAM, HEC, PVEEG, and PEO can form IPC dispersions in strongly acidic medium only but stronger complexing polymers like PVME and PVP form polycomplexes that precipitate in these conditions. In this connection we used different pH values for preparation of each IPC to ensure the formation of relatively stable dispersions. Studying the dependence of turbidity of IPC on temperature, we found that IPC composed of different nonionic polymers show two different modes.

The first mode is an increase or at least insignificant change in turbidity of IPC solutions in response to an increase in temperature. This behavior was observed for complexes of PVME, HPC, and VEEG-VBE (Fig. 1) This phenomenon indicates that the particles of polycomplexes continue to aggregate and form larger structures at higher temperatures. It should be noted that aqueous solutions of PVME,¹⁴ HPC¹⁵, and VEEG-VBE¹⁰ are characterized by lower critical solution temperature (LCST). The aqueous solutions of these polymers undergo phase separation upon heating above LCST. The transitions between clear solution and turbid system are quite sharp and occur within insignificant change in temperature.^{16,17} However, in our case the polymers have already formed IPC with PAA and

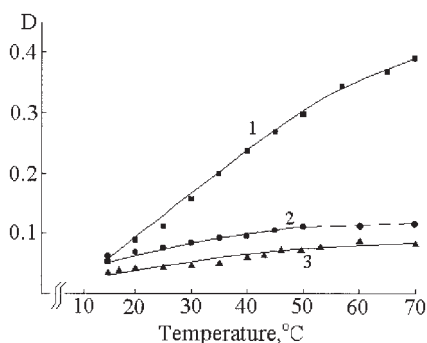


Figure 1 Effect of temperature on turbidity of PAA complexes with HPC (1), PVME (2), and VEEG-VBE (3).

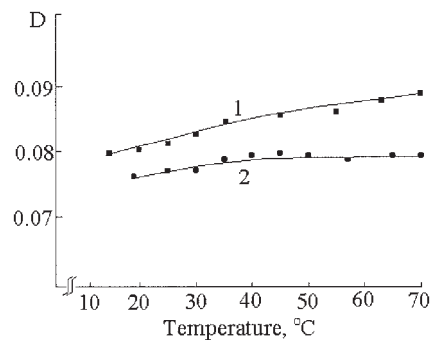


Figure 2 Effect of temperature on turbidity of PAA complexes with PVP (1) and PEO (2).

their aggregation with further increase in temperature is gradual without any extreme points. Karayanni and Staikos,¹⁷ as well as Bian and Liu,¹⁸ reported recently about the phase behavior of IPC formed by PAA with PVME and poly(*N,N*-diethylacrylamide) (PDEA), respectively. They studied the dependence of solution absorbance on temperature for polymer mixtures with different ratios. It was found that at low [PAA]/[PVME] or [PAA]/[PDEA] ratios (below stoichiometric 1 : 1 ratio), the mixtures of polymers exhibit specific sharp transition from clear solution to cloud system. At the polymer ratios higher than 1 : 1 the solutions remained turbid irrespective of temperature and the absorbance values were practically constant. In our experiments we studied the behavior of IPC in more broad temperature range and observed an increase of turbidity upon heating. The most significant increase in turbidity is observed for PAA-HPC system. Kousathana and coworkers¹⁹ and we earlier^{20,21} showed that the polymers with LCST form stronger complexes because of more efficient stabilization of IPC by hydrophobic interactions. The results obtained in the present work indicate that the complexes of LCST polymers form stable IPC and their stability is increased at higher temperatures instead of weakening the hydrogen bonds. It is likely that the contribution of hydrophobic interactions into stabilization of these IPC is significant.

The less significant changes are observed for complexes of PAA with PVP and PEO. It can be seen from Figure 2 that the turbidity of IPC solutions changes slightly in the temperature range 20–70°C. Earlier, Osada and Sato²² as well as Tsuchida, Osada, and Ohno²³ studied the temperature dependence of the degree of linkage and stability constants for IPC composed of PAA (PMAA) with PEO and PVP. They found that for complexes of PAA with PEO of molecular weight 2000 Da the degree of linkage (θ) passes through a maximum upon increase of temperature. At 10°C the complexes were not formed ($\theta = 0$) but at 20, 30, and 40°C $\theta = 0.05, 0.04,$ and $0.02,$ respectively. The

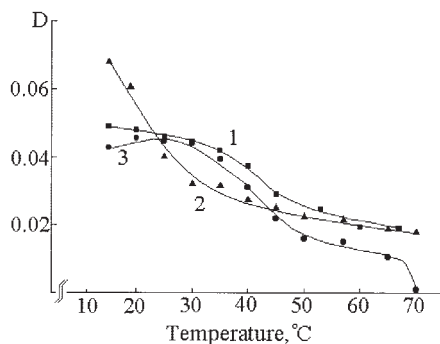


Figure 3 Effect of temperature on turbidity of PAA complexes with PVEEG (1), PAAM (2), and HEC (3).

same trend was observed for stability constants. In our case the complexes of PAA with PEO were slightly more stable because we used PEO of 10 times higher molecular weight and kept the solution pH at constant acidic level (pH = 3.0). Nevertheless the turbidity behavior of PAA-PEO complexes upon increase of temperature resembles the data reported by the authors.^{22,23} An increase of temperature from 15 to 45°C leads to a slight increase in turbidity and then it remains practically constant. It is likely that these complexes are characterized by relatively strong hydrogen bonding and in addition hydrophobic interactions play a significant role in their stabilization.

Quite different mode is observed for complexes of PAA with PAAM, PVEEG, and HEC. It can be seen from Figure 3 that an increase in temperature decreases the turbidity of IPC solutions significantly until complete dissociation of polycomplexes occurs. This is evident from the low turbidity values typical for true solutions. It should be noted that PAAM,²⁴ PVEEG^{5,25,26}, and HEC²⁷ form relatively weak IPC. In our previous studies it was shown that PAAM, PVEEG, and HEC have low values of critical pH, below which the complexation is observed. Thus in the present work these IPC were obtained at low pH values (Table II). Low values of critical pH are an indication of weak complexing ability of these polymers in respect to PAA. Dissociation of IPC at higher temperatures shows that the main force playing a significant role in their stabilization is hydrogen bonding, which is weakened at higher temperatures. The contribution of hydrophobic interactions into stabilization of these complexes is insignificant. The results obtained for complexes of PAA with PAAM are in good agreement with the data reported by Staikos et al.⁶

The fundamental information about stability of different IPC at higher temperatures obtained in the present work may be useful for design of intelligent materials, which undergo temperature induced phase

transitions. Ilmain and coworkers,²⁸ for instance, demonstrated the possibility of volume transitions in a gel driven by hydrogen bonding. They prepared an interpenetrating network based on PAAM and PAA and found that the samples swell sharply upon increase in temperature from 20 to 30°C, which is related to dissociation of interpolymer hydrogen bonds. A decrease in temperature leads to a collapse of the network, which is caused by formation of interpolymer hydrogen bonds again. Thus, the results reported by the authors for crosslinked PAA-PAAM system are in good agreement with our data for IPC in solutions.

CONCLUSION

Interpolymer complexes of poly(acrylic acid) with nonionic polymers in aqueous solutions can be classified into two groups by their response to an increase in temperature. The first group includes the nonionic polymers, which have high complex formation ability and some of them are characterized by lower critical solution temperature. These complexes are quite stable and continue to aggregate to form larger structures at higher temperatures due to strengthening of hydrophobic interactions, which have an important role in IPC stabilization. The second group of IPC undergoes destruction at higher temperatures because the contribution of hydrophobic interactions into their stabilization is minimal and hydrogen bonds are weakened.

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