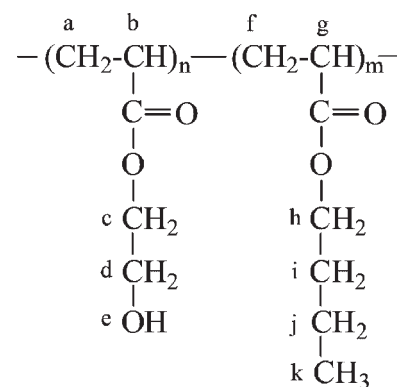


Temperature-Responsive Water-Soluble Copolymers Based on 2-Hydroxyethyl Acrylate and Butyl Acrylate

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Amphiphilic copolymers have been synthesised by free radical copolymerisation of 2-hydroxyethyl acrylate with butyl acrylate, the reactivity ratios of which indicate practically equal reactivity. The copolymers containing less than 30 mol-% of BA were soluble in water and exhibited a LCST in aqueous solutions. It was found that the interaction between these copolymers and poly(acrylic acid) in aqueous solutions resulted in the formation of interpolymer complexes stabilised by hydrogen bonds and hydrophobic interactions. This interaction was significantly affected by solution pH and led to modification of the temperature-responsive behaviour of the copolymers.



Introduction

Stimuli-responsive polymers have attracted significant attention of researchers in the past two decades due to the possibilities of their application in various fields. The ability of these polymers to respond to external stimulation makes them very attractive candidates for development of novel drug delivery systems,^[1–3] selective

membranes,^[4] reagents for enrichment and purification technologies^[5] as well as sensors and actuators.^[6]

A sensitivity of hydrophilic polymers to changes in the temperature of environment can be observed when their macromolecules have a proper hydrophilic-hydrophobic balance and this situation is realised for water-soluble polymers with lower critical solution temperature (LCST). In solutions, these polymers undergo phase separation upon heating and their cross-linked analogues (hydrogels) experience sharp contraction or collapse. Polymers of *N*-isopropylacrylamide (NIPAAm) are a well-known example of such a system with LCST. A number of different reports on temperature-responsive behaviour of NIPAAm homopolymer^[7–9] as well as copolymers with cationic,^[10] anionic^[11,12] and non-ionic monomers^[13] can be found in the literature. The other temperature-sensitive polymers, which are not based on NIPAAm, include poly(vinyl methyl ether), some cellulose ethers, poly(*N*-vinylcaprolactame), poly(2-ethyl-2-oxazoline), etc. In summary, temperature-sensitive polymers can be prepared by homo-

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or copolymerisation of monomers having special structure and hydrophobic-hydrophilic balance.

Another possibility to prepare polymers with LCST is a copolymerisation of some hydrophilic monomers with some hydrophobic ones. The resulting polymers should have a proper hydrophobic-hydrophilic balance and can exhibit temperature-induced phase separation. However, a selection of a suitable pair of monomers is not a simple task. Only a few studies have been reported on the formation of temperature-responsive copolymers via copolymerisation route. Gan et al.^[14] have reported the synthesis of new temperature-sensitive polymers by the copolymerisation of *N*-acryloyl-*N*'-methylpiperazine (AcrNMP) and *N*-acryloyl-*N*'-ethylpiperazine (AcrNEP) with methyl methacrylate by free-radical copolymerisation. The copolymers containing more than 42 mol-% AcrNMP and more than 44 mol-% AcrNEP were soluble in water and exhibited LCST. However, the homopolymers poly(AcrNMP) and poly(AcrNEP) were soluble in water, and no LCST behaviour was observed. New thermosensitive polymers were also synthesised by Mori et al.^[15] by free-radical copolymerisation of *N*-vinylacetamide (NVA) and methyl acrylate, whose homopolymers are soluble and insoluble in water, respectively. The LCST of the obtained copolymers ranged between 59 and 83 °C, and it increased with increasing NVA content.

The monomers with pendant hydroxyl groups have recently been shown to be promising candidates as hydrophilic components in LCST copolymers. Sugihara et al.^[16] have synthesised random thermosensitive copolymers by living cationic copolymerisation. They started the synthesis with copolymerisation of isobutyl vinyl ether (IBVE) and 2-(*tert*-butyldimethylsilyloxy)ethyl vinyl ether. A subsequent desilylation gave a well-defined amphiphilic copolymer of hydrophobic IBVE and hydrophilic 2-hydroxyethyl vinyl ether (HEVE). Upon heating, an aqueous solution of this copolymer underwent phase separation at a critical temperature and this transition was reversible on cooling. Earlier similar random copolymers were synthesised by us using copolymerisation initiated by gamma-radiation.^[17–19] The copolymerisation of hydrophobic vinyl ether with hydrophilic vinyl ether may result in the preparation of thermosensitive system but the synthesis of these copolymers is rather complicated and requires using protection/deprotection chemistry or ionising radiation. From practical point of view this kind of synthesis is quite costly and the possibility to find a new hydrophilic monomer-hydrophobic monomer pair, which exhibits temperature-sensitivity and can be easily copolymerised is rather challenging.

Previously,^[20] we have reported a successful attempt to prepare novel temperature-sensitive polymers by copolymerisation of 2-hydroxyethyl acrylate (HEA) with vinyl butyl ether (VBE). The reactivity of VBE in copolymerisa-

tion was found to be much lower compared to HEA, therefore the copolymers consisted of relatively long sequences of HEA divided by single units of VBE.

In the present work, we have demonstrated that the random copolymers with temperature-sensitive properties can also be prepared by free-radical copolymerisation of two acrylic monomers, namely HEA and butyl acrylate (BA). The first component (HEA) is highly hydrophilic and its presence ensures aqueous solubility of the system and ability to form hydrogen bonds with water and carboxylic groups containing polymers. The second component of this binary system is hydrophobic and it facilitates thermo-precipitation of these copolymers upon heating and favours the stabilisation of self-assembling with complementary macromolecules. Since both monomers are of acrylic nature, the resulting structure of copolymers is completely random.

Experimental Part

Materials

HEA, BA and poly(acrylic acid) (PAA) with weight-average molecular weight of 2, 100, 250, and 750 kDa were purchased from Aldrich Chemical Co. (USA) and used without further purification.

2,2'-azoisobutyronitrile (AIBN, Aldrich Chemical Co., USA) was purified by recrystallisation from ethanol.

Copolymerisation

Synthesis of linear HEA-co-BA was carried out in water-ethanol mixture (20:80 vol.-%) with AIBN as an initiator (0.005 mol · L⁻¹) by free radical copolymerisation. In a typical procedure, dried argon was bubbled through the solution for 10 min prior to polymerisation. After polymerisation at 60 °C for 1.5 h, the mixtures were allowed to cool to room temperature, dissolved in the ten-fold excess of ethanol and reprecipitated in diethyl ether three times to remove unreacted monomers and oligomers. Then the copolymers were collected by filtration, washed with distilled water and dried under vacuum for 3 d. The yield of copolymers after the purification was higher than 70%.

Molecular Weights and Molecular Weight Distributions of the Copolymers

Molecular weight of copolymers and its distribution was determined using a GPC equipped with an Agilent 1100 series RI detector, quaternary pump and Waters Ultrahydrogel columns with pore sizes of 250, 500 and 1 000 Å, respectively. The mobile phase consisted of water-ethanol (50:50 v/v) with a flow rate of 0.6 mL · min⁻¹. The eluent was DMF containing Bu₄NBr (0.1% w/v). The molecular weights were calibrated with poly(ethylene oxide) standards.

Turbidimetric Measurements

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

Preparation of Solutions and Potentiometric Measurements

Aqueous solutions were prepared by direct dissolution of known amounts of PAA and copolymers in distilled water with overnight stirring. The pH of the solutions was adjusted by addition of small amounts of 0.1 M HCl or 0.1 M NaOH and measured with the help of pH-meter Ion Meter 3345 (Jenway Ltd., UK).

Viscometric Measurements

The viscosity of solutions was determined with the help of an Ubbelohde viscometer. Viscometers were placed in a thermostated water bath with a temperature of 25 ± 0.2 °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 the average values were computed and reported.

NMR Spectroscopy

^1H NMR spectra of the (co)polymers were recorded in DMSO- d_6 solutions using NMR spectrometer Bruker ARX300 at 300 MHz. The typical ^1H NMR spectrum with corresponding assignments is

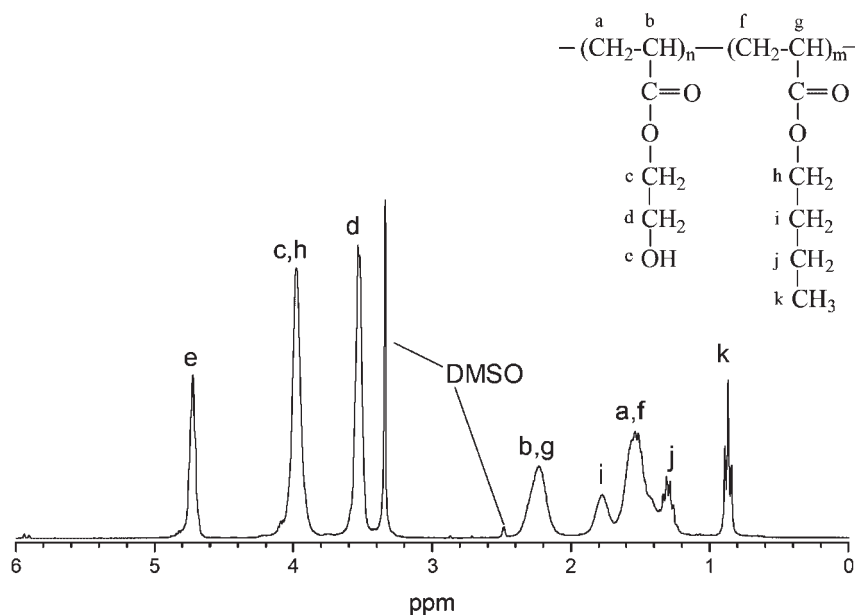


Figure 1. ^1H NMR spectrum of HEA-co-BA 81.2:18.8 mol-%.

Table 1. Composition and molecular-weight characteristics of HEA-co-BA.

Feed composition		Copolymer composition		\overline{M}_n	$\overline{M}_w/\overline{M}_n$
HEA	BA	HEA	BA		
mol-%	mol-%	mol-%	mol-%		
30.0	70.0	29.1	70.9	— ^{a)}	—
40.0	60.0	40.4	59.6	—	—
50.0	50.0	50.6	49.4	—	—
60.0	40.0	60.9	39.1	—	—
70.0	30.0	71.0	29.0	119 900	1.59
80.0	20.0	81.2	18.8	130 260	1.58
90.0	10.0	91.2	8.8	102 970	1.58
93.0	7.0	93.3	6.7	110 200	1.86
95.0	5.0	95.2	4.8	113 370	1.96

^{a)}These copolymers were not analysed because they were not soluble in water.

shown in Figure 1. The composition of the synthesised copolymers was determined by ^1H NMR spectroscopy (Table 1).

Results and Discussion

Copolymerisation

The copolymers were synthesised using the feed mixtures of different compositions. In order to estimate the

reactivity of both monomers the copolymerisation was terminated at the early stages to yield the products with less than 10% conversion. These copolymers were analysed using ^1H NMR spectroscopy and gel permeation chromatography. Table 1 shows the data about the composition of the feed mixtures, composition of copolymers, number-average molecular weights and polydispersity. The copolymers with the content of BA exceeding 30.7 mol-% were insoluble in water, which was of no interest to our research aim; therefore their molecular weights have not been analysed. It can be clearly seen that the resulting copolymers have quite similar molecular weights within 103–130 kDa and polydispersity indexes within 1.58–1.96, which is typical for macromolecules obtained by free radical polymerisation.

The data about the composition of copolymers were used for the estimation of the monomer reactivity ratio using the Mayo-Lewis approach.^[21] Our calculations have shown that the reactivity ratios for both monomers are quite close: $r_1(\text{HEA}) = 0.95$ and $r_2(\text{BA}) = 0.91$, which indicates practically equal reactivity in copolymerisation. It is logical because both monomers are of acrylic nature. It should be noted that Catala et al.^[22] have also reported the reactivity ratios of HEA and BA in copolymerisation. The r_1 value was quite close to our finding ($r_1 = 0.94$) but the r_2 was significantly lower ($r_2 = 0.23$). One of the possible reasons for this difference is the use of different solvent media for copolymerisation (2-ethoxyethanol). Also, the authors^[22] determined the composition of copolymers by analysing the unreacted monomer concentrations in the feed mixture using the vapour phase chromatography. The latter method can give different results because some part of monomers could have been converted into oligomers, which were excluded during the purification procedure via reprecipitation.

Temperature-Responsive Properties of the Synthesised Copolymers

The temperature-responsive behaviour of water-soluble HEA-co-BA copolymers has been studied in aqueous solutions of different concentrations by measuring solution turbidity at different temperatures. Figure 2 shows the dependence of solution turbidity (D) on temperature for HEA-co-BA (93.3:6.7 mol-%) at different concentrations. At relatively low temperatures the solutions remain transparent but heating until certain temperature results in a phase separation and appearance of turbidity, which can be monitored even by the naked eye. The temperature of phase separation is a function of copolymer concentration, and the solutions with higher content of the copolymer exhibit phase separation at lower temperatures. Figure 3 shows the dependence of phase separation

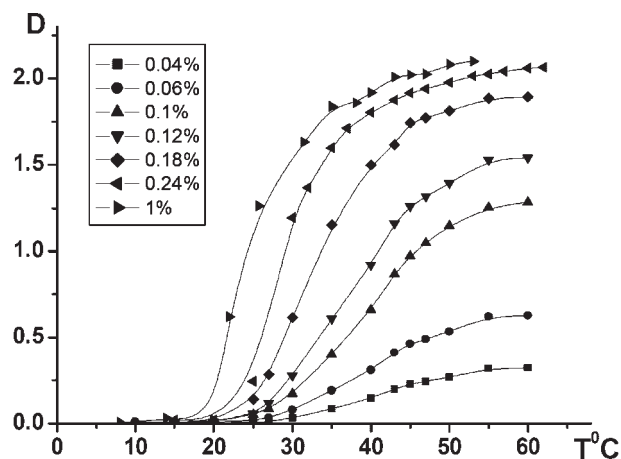


Figure 2. Dependence of turbidity of HEA-co-BA (93.3:6.7 mol-%) aqueous solutions on temperature.

temperature on the concentration for copolymers containing different amounts of BA (4.8, 6.7 and 8.8 mol-%). The copolymers containing more BA undergo phase separation at lower temperatures, which is likely due to a contribution of BA units to hydrophobic interactions. Similar behaviour has been previously reported for copolymers of VBE with HEA^[20] and hydrophilic vinyl ethers.^[17–19]

Complex Formation of the Synthesised Copolymers with PAA

Previously,^[23] we have demonstrated that the homopolymer PHEA forms hydrogen-bonded interpolymer complexes (IPCs) with PAA in aqueous solutions at low pH. However, the stability of these complexes is relatively low and increase in pH results in the dissociation of IPC. An

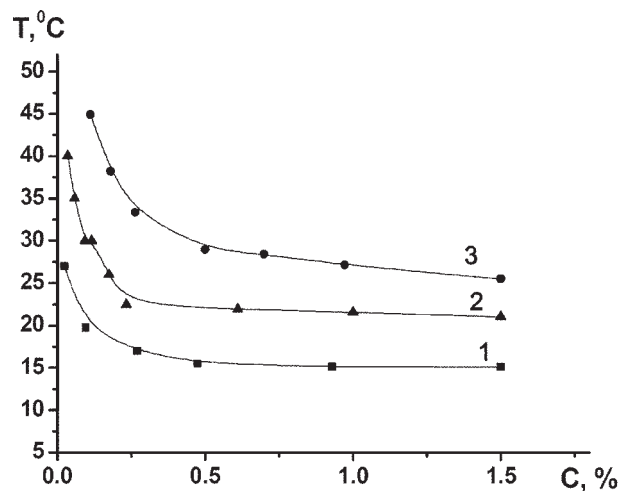


Figure 3. Phase diagrams of HEA-co-BA aqueous solutions. [HEA]:[BA] = 91.2: 8.8 (1), 93.3: 6.7 (2) and 95.2: 4.8 mol-% (3).

introduction of hydrophobic groups of VBE into the structure of PHEA was shown to be a stabilising factor for the formation of hydrogen-bonded IPCs due to the contribution of hydrophobic interactions.^[20] It can be expected that the HEA-co-BA copolymers should also exhibit the ability to form stronger complexes with PAA compared to the homopolymer PHEA.

In the present work, we studied the complexation between HEA-co-BA copolymers and PAA. Figure 4 shows the data of turbidimetric and viscosimetric titration of PAA solutions by HEA-co-BA. The addition of the copolymer solutions to PAA solutions at pH 2.5 is accompanied by a decrease in viscosity and increase in turbidity, which is typical for polymer-polymer complexation. This trend is observed until the [copolymer]:[PAA] ratio reaches the saturation point, which corresponds to the IPC stoichiometry, and then the viscosity goes up and turbidity down. An increase in the viscosity after the polymers ratio reached the saturation is possibly due to the presence of unbound macromolecules in solution.

The complexation between poly(carboxylic acids) and non-ionic polymers in aqueous solutions is significantly affected by a solution pH because only unionised carboxylic groups can form intermolecular hydrogen bonds. Insoluble complexes are formed under acidic conditions, when pH is below the so-called critical pH of complexation (pH_{crit}), which was demonstrated to be a simple criterion for the estimation of the complex formation ability of polymers.^[19,20] The higher pH_{crit} values correspond to a stronger ability of polymers to

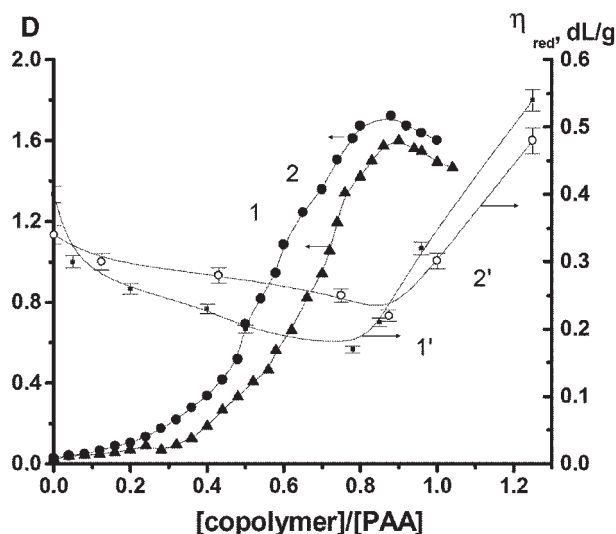


Figure 4. Turbidimetric (1, 2) and viscosimetric (1', 2') titration of PAA solutions by HEA-co-BA copolymer solutions. [HEA]:[BA] = 95:2:4.8 (1,1'), 93:3:6.7 mol-% (2,2'); pH 2.5, \bar{M}_w (PAA) 250 kDa, [HEA-co-BA] = [PAA] = 0.01 mol · L⁻¹.

form complexes. In the present work, we have determined the pH_{crit} values for PAA/copolymer complexes by measuring the solution turbidity at different pH values and compared them with the critical pH for PAA-PHEA [Figure 5(a)]. The introduction of BA units into the structure of PHEA shifts the pH_{crit} to the higher pH region and this shift is slightly more pronounced for copolymers having higher content of BA. It is also important to note that the pH_{crit} depends on the [copolymer]:[PAA] ratio in a solution mixture [Figure 5(b)] and decreases in the presence of excessive PAA. This may indicate the formation of more hydrophilic forms of IPC having more PAA in their structure.

A change in the molecular weight of PAA also significantly affects the complexation [Figure 6(a)]. An increase in PAA molecular weight from 100 to 750 kDa shifts the pH_{crit} to higher pH values region, which means the

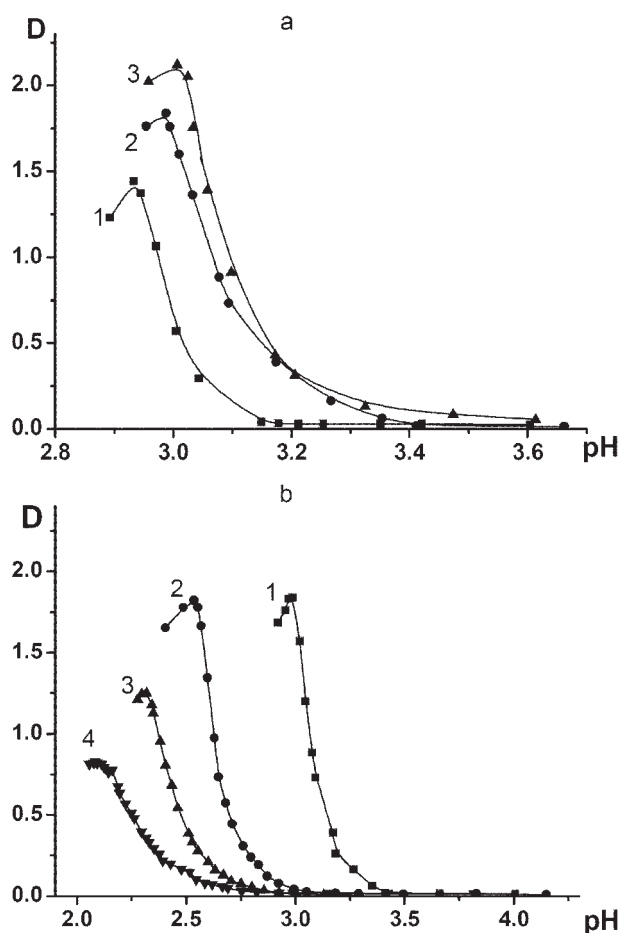


Figure 5. Dependence of turbidity of HEA-co-BA (PHEA)/PAA (250 kDa) aqueous solutions on pH. (a) PHEA (1); [HEA]:[BA] = 95:2:4.8 (2), 93:3:6.7 mol-% (3); [HEA-co-BA] = [PAA] = 0.01 mol · L⁻¹; (b) [HEA]:[BA] = 95:2:4.8 mol %; [HEA-co-BA]:[PAA] = 1:1 (1), 1:2 (2), 1:5 (3), 1:10 (4).

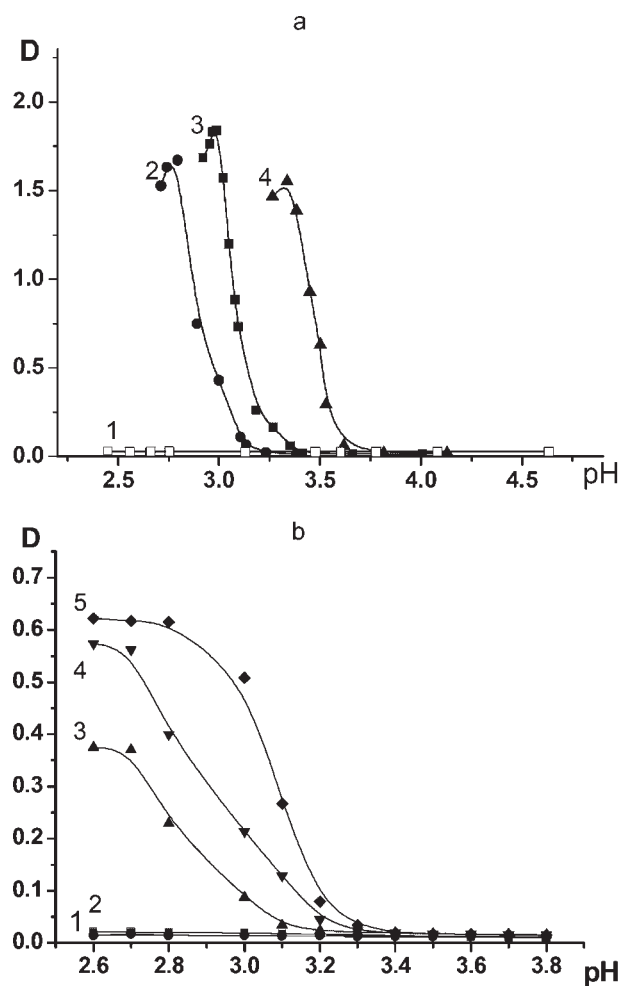


Figure 6. Dependence of turbidity of HEA-co-BA - PAA aqueous solutions on pH at different molecular weights of PAA and polymer concentrations. (a) \bar{M}_w (PAA) 2 (1), 100 (2), 250 (3), 750 kDa (4); [HEA]:[BA] = 95.2:4.8 mol-%, [HEA-co-BA] = [PAA] = 0.01 mol · L⁻¹; (b) [HEA-co-BA] = [PAA] = 0.01(1), 0.05 (2), 0.075 (3), 0.1 (4), 0.2 (5) mol · L⁻¹; \bar{M}_w (PAA) 2 kDa; [HEA]:[BA] = 95.2:4.8 mol-%.

formation of stronger complexes. However, the PAA sample with \bar{M}_w of 2 kDa does not appear to form insoluble complexes even at low pH. Previously, we also studied the complexation of this small molecular weight PAA sample with polyacrylamide,^[24] hydroxyethylcellulose,^[25] hydroxypropylmethylcellulose,^[26] poly(ethylene oxide)^[27] and poly(*N*-vinylpyrrolidone) (PVP)^[28] and found that the IPC are formed only in the case of PAA-PVP. The existence of the polymers critical molecular weight, below which the complexes are not formed, has been suggested as a reason for non-complexation of PAA 2 kDa with most of the non-ionic polymers. This observation was also in agreement with the literature data about the critical phenomena in the complex formation of polymers.^[29] In the present work, we have decided to go a bit further and study the possibility of the complex formation between

PAA (2 kDa) and the copolymers in a broader concentration range. When the concentration of both polymers reaches 0.075 mol · L⁻¹ the sample of low molecular weight PAA starts to form insoluble complexes [Figure 6(b)], which is confirmed by the appearance of turbidity. Based on this data, we can question the existence of the critical molecular weights for the complexation of polymers. It can be hypothesised that when the concentration of polymers in solution is relatively high, the IPC can be formed even by the macromolecules with very low molecular weight. Obviously, for further clarification this effect needs to be checked for complexes of low molecular weight PAA with various non-ionic polymers.

Temperature-Induced Phase Separation of the Synthesised Copolymers in the Presence of PAA

An association of temperature-responsive HEA-co-BA copolymers with pH-responsive PAA via hydrogen bonding is expected to result in materials with dual stimuli sensitivity. Previously, the appearance of this dual sensitivity was reported for complexes of PAA with poly(methyl vinyl ether),^[30] poly(*N,N*-diethylacrylamide)^[31] and some cellulose ethers.^[26] It has also been emphasised that the [PAA]:[temperature-responsive polymer] ratio affects the temperature of phase separation (T_{PS}) of the mixture, significantly. Depending on the polymers ratio a slight increase or significant decrease in T_{PS} has been reported. Also, it was found that the molecular weight of the interacting PAA and the presence of salts in solutions may affect the T_{PS} .^[26]

In the present study, we have explored the effect of the polymers ratio, molecular weight of PAA and solution pH on the solution phase behaviour of PAA/HEA-co-BA mixtures at different temperatures. First, we have studied the effect of polymer ratios on the solution turbidity at various temperatures using the PAA samples with three different molecular weights (100, 250 and 750 kDa). In this series of experiments, we have not adjusted pH in order to make sure that the interaction is relatively weak. It can be seen from Figure 7(a)–7(c), the addition of PAA to HEA-co-BA affects the phase separation temperature, significantly. An increase in PAA content in the mixture shifts the T_{PS} to a higher temperature, which may be due to the formation of more hydrophilic associates having higher charge density. No significant difference has been observed for mixtures with PAA 100 and 250 kDa, however, the mixture with PAA 750 kDa behaved differently. Even at relatively low temperatures (below 20 °C) the solutions were cloudy, which is likely due to the formation of insoluble IPCs. This result is in agreement with our data on the higher complexation ability of PAA 750 kDa discussed above.

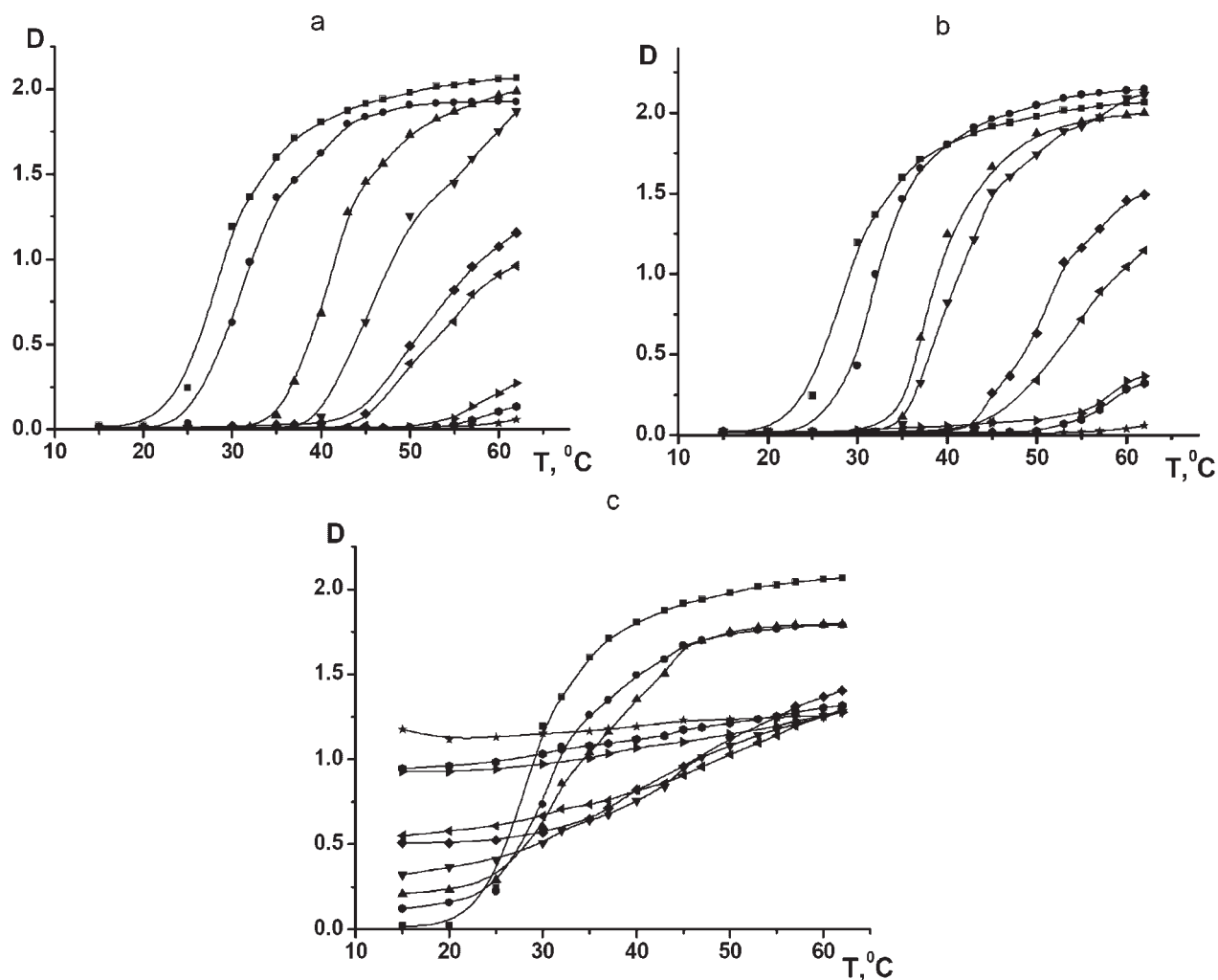


Figure 7. Dependence of turbidity of HEA-co-BA - PAA aqueous solutions on temperature and [PAA]:[copolymer] composition. \bar{M}_w (PAA) 100 (a), 250 (b), 750 kDa (c); [PAA]:[copolymer]: \square , \bullet , \blacktriangle , \blacktriangledown , \blacklozenge , \blacktriangleleft , \blacktriangleright , \bullet , \star ; [HEA]:[BA] = 93.3:6.7 mol-%, [HEA-co-BA] = 0.02 mol · L⁻¹.

In the following series of experiments we have kept the [PAA]:[copolymer] ratio constant but varied the solution pH and temperature [Figure 8(a)–8(d)]. When the pH is 2.2–2.5 the insoluble complexes are formed at any temperature and the solutions remain cloudy. An increase in temperature for these solutions results in a decrease in turbidity, which is likely related to the disruption of intermolecular hydrogen bonding similar to the complexes between weakly complexing polymers such as PAA-hydroxyethylcellulose or PAA-polyacrylamide, reported in our previous publication.^[32] Under these pH conditions the most of the HEA groups are hydrogen-bonded while carboxylic groups of PAA and the temperature-responsive behaviour of HEA-co-BA is disrupted. At pH 3.0, the system is still cloudy at low temperatures (10–20 °C) but the further heating leads to an increase in turbidity, which means that some of the HEA-co-BA fragments are free from hydrogen bonding and can exhibit LCST behaviour

leading to aggregation at higher temperatures. When the solution pH is more than 3.3 the HEA-co-BA/PAA mixtures are transparent at temperatures below 15 °C and undergo phase separation upon further heating. This temperature-responsive behaviour is similar to those of HEA-co-BA alone, but in this case the T_{PS} of the mixture is significantly affected by solution pH. The higher values of solution pH correspond to the higher T_{PS} . It should also be noted that an increase in [PAA]:[copolymer] ratio results in higher T_{PS} values because the interpolymer associates become more changed and hydrophilic.

Conclusion

Copolymerisation of hydrophilic HEA with hydrophobic BA results in water-soluble polymers, when the content of BA does not exceed 30 mol-%. In copolymerisation, both

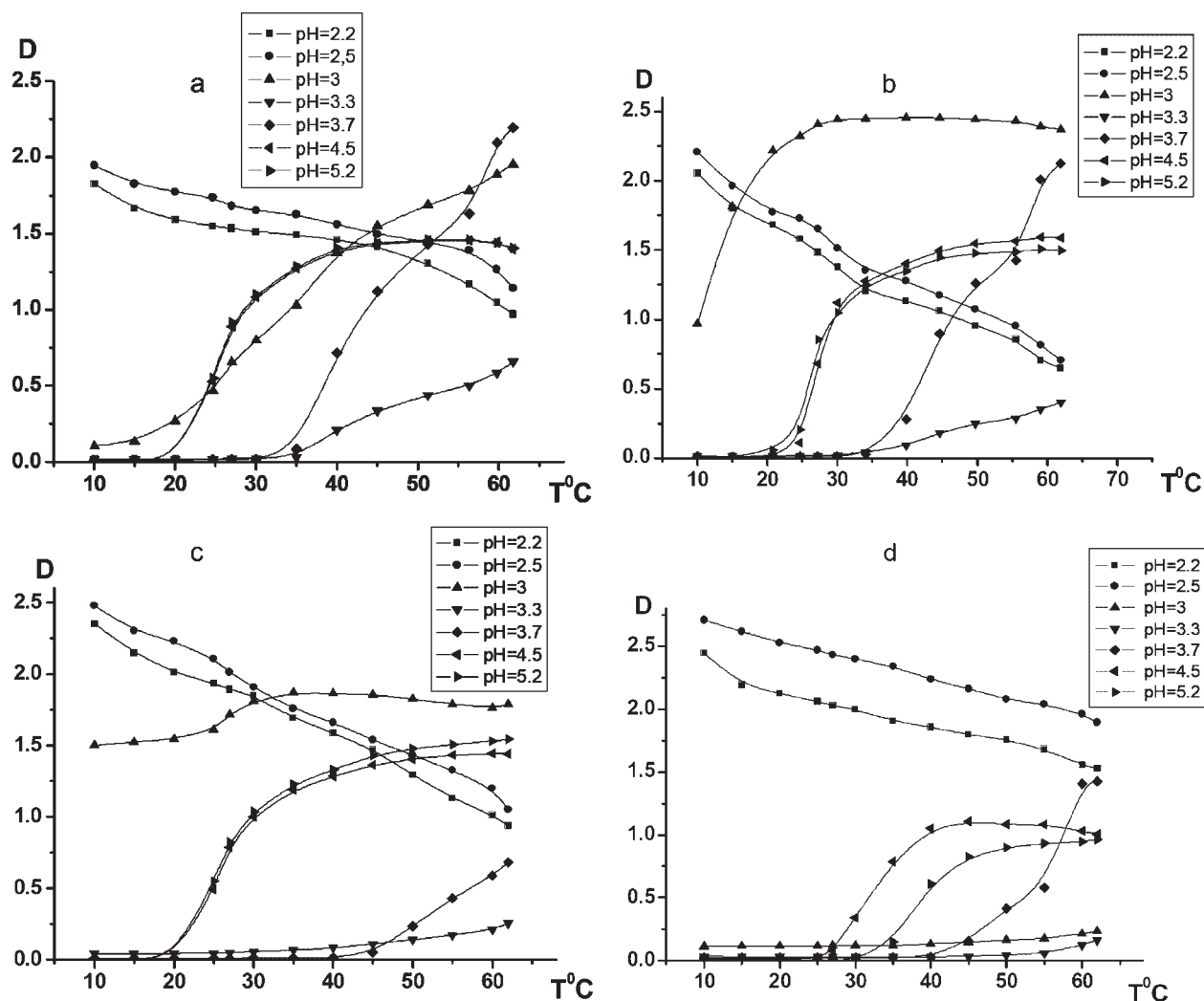


Figure 8. Dependence of turbidity of HEA-co-BA - PAA aqueous solutions on temperature at different pH values and [PAA]/[copolymer] ratios. [PAA]/[copolymer] = 0.08 (a), 0.16 (b), 0.5 (c) and 1 (d); [HEA]:[BA] = 93.3:6.7 mol-%.

monomers were found to have close reaction ability. In aqueous solutions these water-soluble copolymers exhibit LCST, which depends on the hydrophobic monomer content. An association of the copolymers with PAA via hydrogen bonding results in the formation of either hydrophilic or hydrophobic IPCs, which have pH-dependent nature. The formation of IPCs affects the temperature-responsive properties of the copolymers, significantly.

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