LCST-type thermoresponsive behaviour of interpolymer complexes of well-defined poly(poly(ethylene glycol) methacrylate)s and poly(acrylic acid) synthesized by ATRP

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Abstract

Unexpected tremendous effect of poly(acrylic acid) (PAA) as polydonor on the thermoresponsive behaviour of the comb-like poly(poly(ethylene glycol) methacrylate) (PPEGMA$_{500}$) with short poly(ethylene glycol) (PEG) side chains as H-bond acceptor, both synthesized by atom transfer radical polymerization (ATRP), has been found indicating the formation of a unique class of interpolymer complexes between these well-defined polymers. Dynamic light scattering (DLS) measurements indicate that optimal supramolecular complex formation occurs in the 1-1.3 ethylene glycol / acrylic acid (EG/AA) monomer unit molar ratio, the hydrodynamic diameter of the complexes increases with increasing PPEGMA$_{500}$ molecular weight, and strong pH dependence is found, i.e. large aggregates are formed at low pH and the size of the interpolymer complexes decreases with increasing pH. Strikingly, the

aqueous solutions of the PPEGMA$_{500}$-PAA interpolymer complexes possess LCST-type thermoresponsive behaviour with hysteresis at significantly lower temperatures (~40-50 °C) than that of PPEGMA$_{500}$, which is attributed to the decreased hydrophilicity of the complexes. It is revealed that thermal phase transition temperatures (T_{PT}) of the PPEGMA$_{500}$-PAA interpolymer complexes have a minimum in the 1-1.3 EG/AA ratio, in accordance with the DLS results, and the T_{PT} can be fine tuned by varying the EG/AA ratio, the molecular weight of the PPEGMA$_{500}$ and pH of the solution.

Introduction

Interpolymer complexes and the polymer-polymer interactions in such aggregates are of great scientific and technological importance, ranging from surfactants to nanostructures and life sciences etc. As well-known, the genomes, enzymes and proteins have important roles in the growth and maintenance of life. However, in biological systems, the macromolecular interactions are so complex that modeling is rather difficult and as a consequence additional research with interacting synthetic polymers is desperately needed. Interpolymer complexes of synthetic polymers give easy to handle model systems towards the understanding of the structure-property relations in these macromolecular assemblies. Interpolymer complexes are supramolecular structures formed by association of polymer chains via secondary interactions, e.g. hydrogen bonds. Well-defined polymers obtained by living polymerization techniques provide a promising opportunity to study the different aspects of the behavior of the tailor-made polymer complexes and interpolymer complex formation. Moreover, the application possibilities of H-bonded macromolecular structures have also growing interest [1-4].

One of the most interesting interpolymer complexes is the pair of poly(ethylene oxide) (PEO or PEG) and poly(acrylic acid) (PAA) composed of a non-dissociating (PEG) and a dissociating (PAA) macromolecule [5-8]. The formation of this interpolymer complex has

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been studied mainly by viscometric, potentiometric and fluorescence measurements [9-17]. These investigations with linear PEGs revealed some major characteristics of these systems, e.g. the optimal molar composition for the two kind of monomeric units, i.e. ethylene glycol and acrylic acid, the presence of a critical pH below which phase separation can occur, the important role of hydrophobic interactions and the cooperative nature of the interpolymer complex formation. The recent model of formation of these kinds of interpolymer complexes in water was proposed by Suleimenov et al. [18]. According to this model, the aqueous solution of the polymer mixture has two critical pH values. At the higher critical pH, the formation of soluble interpolymer complexes starts. These complexes can be imagined as extended, partially ionized polyacid coils dynamically coupled with collapsed polyacceptor coils via H-bonds. The lower critical pH value is the formation of insoluble interpolymer complexes possessing only collapsed polymer coils coupled with intermacromolecular H-bonds.

Although the complexes of linear PEO (PEG) with PAA were studied widely, incorporation of comb-like PEG derivatives in interpolymer complex structures is reported only for copolymers of vinyl butyl ether with vinyl ether of di(ethylene glycol) [19]. One type of such kind of derivatives is the family of poly(poly(ethylene glycol) methacrylate)s (PPEGMAs) consisting of a polymethacrylate backbone and PEG side chains. These comb-like polymer structures have been intensively studied in the last decade mainly due to their biocompatibility, thermoresponsive behaviour and antifouling properties [20,21]. Due to the PEG side chains, PPEGMA is expected to have the potential of behaving as a H-bond acceptor in the presence of acidic monomeric units [22,23]. This interaction, i.e. the presence of interpolymer H-bonds was reported as the reason of pH-dependent strengthening of PPEGMA-PAA interpenetrating polymer networks [24]. Moreover, the integration of acrylic acid and PEGMA monomeric units in common macromolecular structures was achieved in a

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variety of cases [25-34]. However, systematic investigations on the interpolymer complex formation between PPEGMA and PAA and their thermoresponsive behaviour in water have not been reported yet to the best of our knowledge. Thus, the aim of this work is the investigation of the formation of interpolymer complexes of poly(poly(ethylene glycol) methacrylate) and poly(acrylic acid) in water solutions, and to reveal the tuning possibilities of the thermoresponsive behaviour of these unique macromolecular systems.

Experimental

Materials

Poly(ethylene glycol) methacrylate macromonomer with 500 g/mol molecular weight (PEGMA$_{500}$), *tert*-butyl acrylate (*t*BuA), L-ascorbic acid, 1,1,4,7,10,10-hexamethyltriethylenetetraamine (HMTETA) and ethyl 2-bromoisobutyrate were purchased form Sigma-Aldrich. PEGMA$_{500}$ was purified by passing through a column filled with basic Al$_2$O$_3$. *t*BuA was vacuum distilled before use. CuCl and CuBr were stirred with acetic acid overnight followed by washing with abs. ethanol and diethyl ether. Toluene and dichloromethane was distilled over sodium/benzofenone and calcium hydride, respectively. Trifluoroacetic acid was purchased from Alpha Aesar and applied without purification.

Synthetic procedures

Polymerization of PEGMA$_{500}$ was carried out under quasiliving atom transfer radical polymerization (ATRP) conditions in a glass vial using ethyl 2-bromoisobutyrate as initiator, HMTETA/CuCl as catalyst (initiator:HMTETA:CuCl molar ratio was 1:1:1) and toluene as solvent under dry N$_2$ atmosphere at 60 ºC for 24 hrs [34-36]. The polymerization of *t*BuA was performed under dry N$_2$ atmosphere at 50 ºC for 72 hrs using ethyl 2-bromoisobutyrate initiator, L-ascorbic acid reducing agent and HMTETA/CuBr catalyst in toluene (initiator:L-

ascorbic acid:HMTETA:CuCl molar ratio was 1:1:1:1). At the end of the reaction, the solutions of the obtained polymers were passed through a column filled with neutral Al_2O_3 to remove catalyst, followed by removing of the solvent and drying the polymer in vacuo until constant weight.

Poly(acrylic acid) (PAA) was synthesized by hydrolysis of the obtained P*t*BuA with trifluoroacetic acid in dichloromethane at room temperature for 24 hrs followed by drying of the precipitated PAA.

The investigated mixed polymer solutions, which were prepared by mixing the solutions of PPEGMA$_{500}$ and PAA homopolymers in deionized water, are summarized in Table 1.

Analysis

Molecular weights of the synthesized PPEGMA$_{500}$ homopolymers were determined by gel permeation chromatography (GPC) equipped by three Styragel HR columns, Waters 515 HPLC pump, Waters 717 Autosampler, Jetstream Column Thermostat and Agilent 1260 Infinity refractive index detector applying tetrahydrofuran as eluent and 1 ml/min flow rate at 35 ºC. Molecular weight distribution (MWD) and average molecular weights were obtained on the basis of calibration made by polystyrene standards with narrow MWD. Transmittance measurements were performed on Jasco V-650 spectrophotometer possessing sample holder with temperature controlling at 488 nm. The applied temperature range was 20-80 ºC, the heating and cooling rate was 0.5 ºC/min and the solutions were stirred with a magnetic stirrer with 60 rpm. Inflection points of the polynomials fitted to the obtained transmittance-temperature curves were plotted as cloud point temperatures. Dynamic light scattering (DLS) measurements were performed on Malvern Zetasizer Nano ZS equipment at 633 nm at 20 ºC. Before the measurements, the solutions were filtered by a 0.45 µm PTFE syringe filter purchased from VWR. In the diagrams the relevant peak positions of the size distributions by

intensity are plotted as the hydrodynamic diameters. ^{1}H NMR measurement was performed on a Varian 500 MHz spectrometer in D_2O at room temperature.

Table 1. The number average molecular weight (M_n) and concentrations of PPEGMA$_{500}$, the ethylene glycol / acrylic acid monomer ratios (EG/AA), the pH and the hydrodynamic diameters (d) based on the intensity size distribution obtained from dynamic light scattering measurements of the combined PPEGMA$_{500}$-PAA polymer solutions (c(PAA) = 0.625 mg/ml).

Sample	M_n(PPEGMA$_{500}$) / (g/mol)	c(PPEGMA$_{500}$) / (mg/ml)	EG/AA molar ratio	pH	d(DLS, int dist) / nm
1	15500	0.250	0.5	n.d.	5.9
2	15500	0.500	1.0	n.d.	6.8
3	15500	0.625	1.3	3.45	6.1
4	15500	0.750	1.6	n.d.	6.0
5	15500	1.000	2.1	n.d.	6.7
6	15500	1.250	2.6	n.d.	6.8
7	3600	0.625	1.3	3.43	5.4
8	9900	0.625	1.3	n.d.	5.4
9	15500	0.625	1.3	3.18*	156.8
10	15500	0.625	1.3	3.89**	7.7
11	3600	0.625	1.3	3.18*	233.5

n.d. = not determined

* the pH was set by adding 1 drop (~30 μl) of 0.1 M HCl solution

**the pH was set by adding 1 drop (~30 μl) of 0.1 M KOH solution

Results and discussion

PPEGMA$_{500}$ (H-acceptor) homopolymers with three different molecular weights were synthesized by atom transfer radical polymerization (Figure 1) [34-36], and the number average molecular weights of the resulting polymers were obtained by gel permeation chromatography (Table 1). According to this analysis, PPEGMA$_{500}$ comb-like polymers with fairly narrow molecular weight distribution having M_w/M_n values of 1.70, 1.18 and 1.15 for

these macromolecules with 3600, 9900 and 15500 g/mol M_n, respectively (see Figures S2-S4 in Supporting Information for the GPC traces).
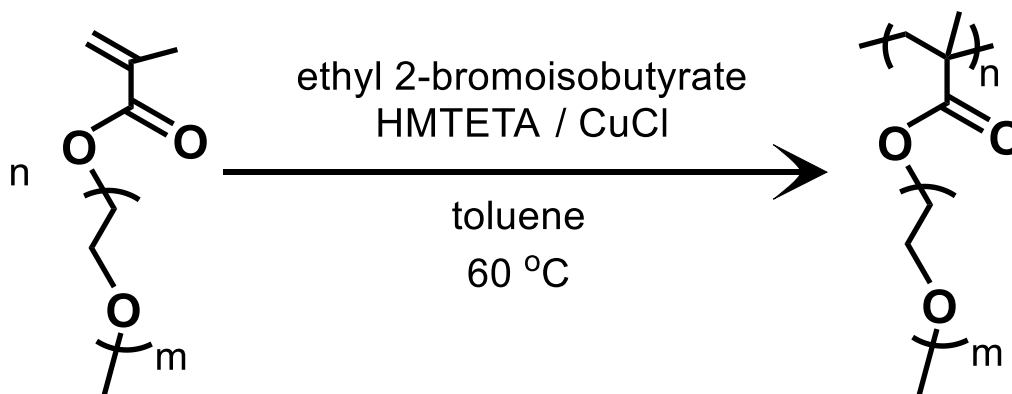

Figure 1. The synthesis of poly(poly(ethylene glycol) methacrylate) (PPEGMA) under ATRP conditions.

PAA (H-donor) was synthesized by atom transfer radical polymerization of *tert*-butyl acrylate followed by hydrolysis of the *tert*-butyl ester groups with trifluoroacetic acid [37]. The hydrolysis was evaluated by ^{1}H NMR spectroscopy (see Figure S1 in Supporting Information). Number average molecular weight of PAA was calculated from the ^{1}H NMR spectrum resulting in M_n of 5700 g/mol.

To investigate the interpolymer complex formation between PAA and PPEGMA$_{500}$ in water, dynamic light scattering (DLS) investigations were performed on PAA and PPEGMA$_{500}$ homopolymer solutions (the concentration for both polymer was 1.25 mg/ml) and on the mixed solution of sample *3* containing PAA and PPEGMA$_{500}$ in 1:1 weight ratio (see Table 1 and Figures S5, S9 and S18 in Supporting Information). In the case of PAA and PPEGMA$_{500}$ homopolymer solutions, the results show the presence of macromolecules with 1 nm and 7 nm hydrodynamic diameters, respectively. These results indicate the compact structure of PAA chains in their homopolymer solution due to intramolecular hydrogen bonds.

However, in the PPEGMA$_{500}$-PAA mixtures (sample *3*) macromolecules with 6 nm hydrodynamic diameter were observed in the DLS measurement. The interpolymer complex formation is generally indicated by the decrease of specific viscosity, i.e. decrease of hydrodynamic volume, of mixed polymer solutions [10] showing that the formation of interpolymer H-bonds results in the collapsing of the macromolecular chains in the given solvent. So the direct evidence of the decrease of the hydrodynamic diameter determined by DLS in the mixed polymer solution of sample *3* related to that measured for the PPEGMA$_{500}$ homopolymer solution proves the intermolecular complex formation between PAA and PPEGMA$_{500}$ polymer chains in water. These measurements also agree with the expectation that the formed complexes have a more compact structure than that characteristic for the PPEGMA$_{500}$ chains in their homopolymer solution. The complex forming process can be imagined as the consequence of turning the intramolecular H-bonds in PAA chains into intermolecular H-bonds between the H-donor carboxylic groups of PAA and the H-acceptor oxygen atoms of PPEGMA$_{500}$ which results in the unfolding of PAA chains and contracting of PPEGMA$_{500}$ chains by the formation of polymer complexes (Figure 2). In the contraction, linking of two non-adjacent PEG side chains of the PPEGMA by a PAA chain may also play a role. The measured hydrodynamic diameter of the interpolymer complex slightly lower than that of the PPEGMA$_{500}$ homopolymer also indicates that a given number of PAA chain forms H-bonds probably only with one PPEGMA chain, and it does not take part in interconnection between two or more PPEGMA chains forming an aggregated complex. However, since PAA chains contain less acrylic acid monomeric units than ethylene glycol monomeric units of PPEGMA, it can be assumed that in the mixed polymer solution of sample *3* the polymer complexes contain more than one PAA chains (the average would be 2.7 PAA chains / complex if all of the PAA and PPEGMA chains were involved in the polymer complex formation).
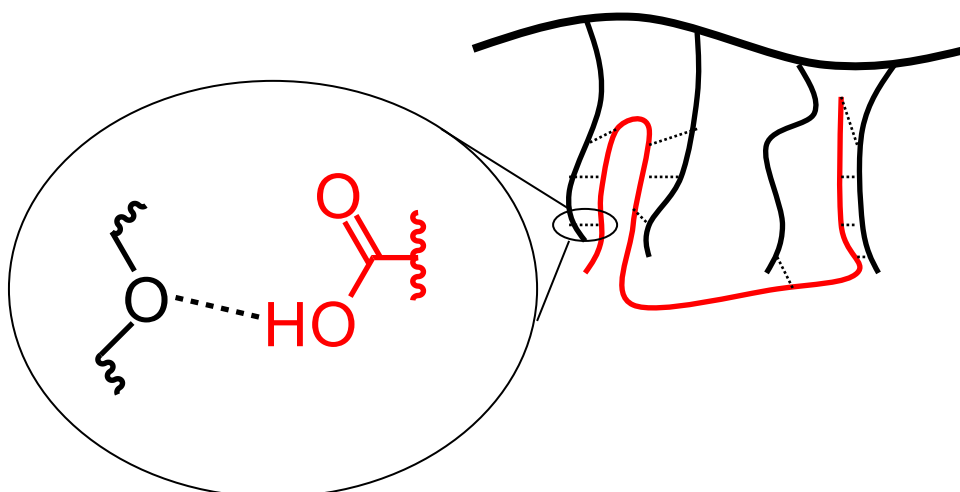
Figure 2. Model of PPEGMA$_{500}$-PAA interpolymer complexes (black chain: PPEGMA, red chain: PAA).

To study the effect of PPEGMA$_{500}$:PAA ratio on the complex formation, mixed polymer solutions with different PPEGMA$_{500}$:PAA ratios (samples *1-6*, see Table 1) were prepared (with constant PAA concentration), and DLS measurements were performed with them. As it can be seen in Figure 3, the change in the PPEGMA$_{500}$:PAA ratio does not result in dramatic change in the peak position of the measured hydrodynamic diameter distribution. This indicates that there is only one polyacceptor chain in a given complex in the whole investigated composition range.
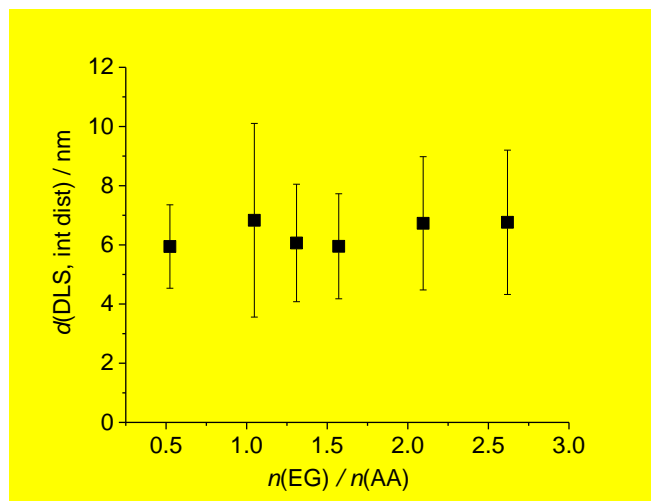
Figure 3. Hydrodynamic diameters (d) of macromolecular structures obtained by DLS in mixed polymer solutions (samples *1-6*, see Table 1) as a function of EG/AA monomeric unit molar ratios at 0.625 mg/ml PAA concentration (see Figure S7-S12 in Supporting Information for the DLS results).
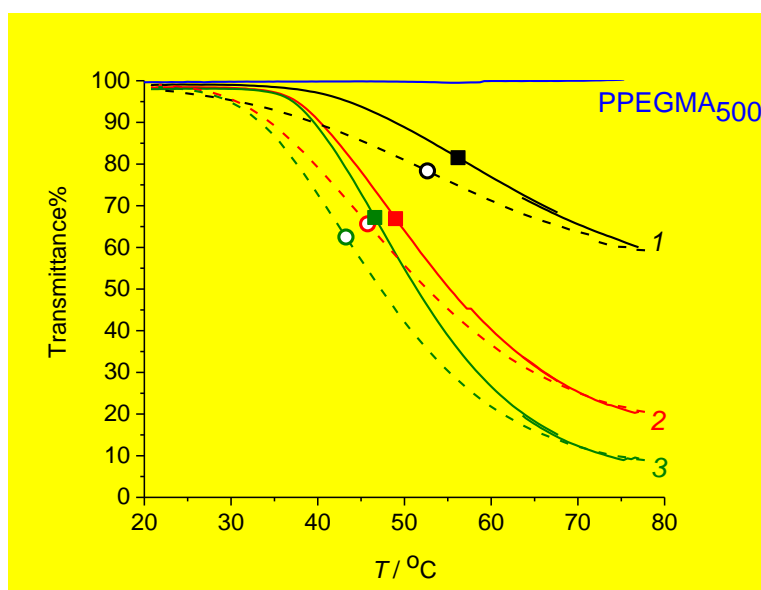
Figure 4. Transmittance-temperature curves of PAA-PPEGMA$_{500}$ mixed polymer solutions (samples *1-3*, see Table 1) and of PPEGMA$_{500}$ (M_n = 15500) homopolymer solution in water (solid lines: heating, dashed lines: cooling, squares: cloud points, circles: clearing points).

The thermal phase transition temperatures of the PAA-PPEGMA$_{500}$ interpolymer complexes were obtained from the transmittance measurements of the mixed polymer

solutions of samples *1-6* (see Table 1) while the temperature was changed with a given rate and the obtained transmittance values were drawn as a function of temperature (Figure 4). Since decrease of transmittance of the corresponding pure PPEGMA$_{500}$ solution occurs at considerably higher temperature in water as shown in Figure 4 (the cloud point temperature is reported as 90-95 ºC) [20], the observed reversible „LCST-type" phase separation indicated by the decrease of transmittance of the mixed polymer solutions of PAA and PPEGMA$_{500}$ at lower temperatures can be ascribed to the thermoresponsive behaviour of the formed PAA-PPEGMA$_{500}$ interpolymer complexes. The decrease of the thermal phase transition temperature (T_{PT}) related to that of the PPEGMA$_{500}$ homopolymer solution indicates the decrease of the hydrophilic character as a consequence of the interpolymer complex formation [10]. Figure 4 shows that hysteresis occurs in the solutions of the PPEGMA$_{500}$-PAA mixtures, i.e. smaller clearing point temperatures are observed in the cooling cycles than the cloud points measured in the heating cycles. The data in Figure 5, in which T_{PT}-s are depicted as a function of the EG:AA monomeric unit molar ratio, show that in accordance with the DLS results (Figure 3) a minimum at 1.3:1 molar ratio of EG units to carboxylic groups is present indicating that the most compact structure of the complexes can be observed at this composition ratio which is near to that reported as optimal composition of the interpolymer complexes of linear PEG and PAA [9]. The minimum can also be observed for the phase transition solution temperatures in both the heating and cooling cycles. The presence of this minimum means that the most compact and less hydrophilic complexes are formed when the EG/AA monomeric unit molar ratio is near to 1.3 in the solution which can be considered as the optimal composition of the PPEGMA$_{500}$-PAA complexes.
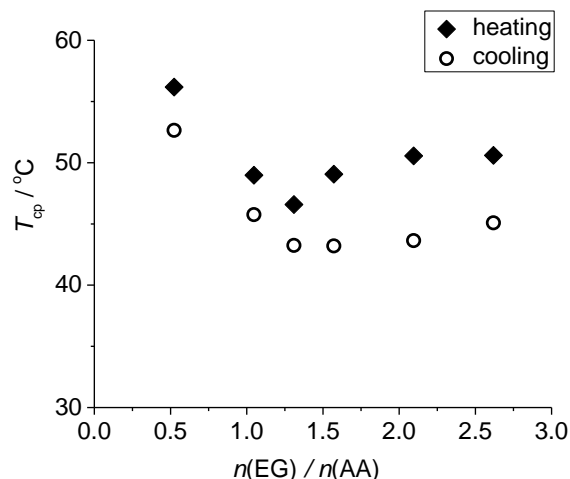
Figure 5. The thermal phase transition temperatures (T_{PT}) of PAA-PPEGMA$_{500}$ mixed polymer solutions as a function of EG/AA monomeric unit molar ratios (samples *1-6*, see Table 1) in water at 0.625 mg/ml PAA concentration.

On the basis of the crucial effect of pH on the interpolymer complex formation of linear PEO (PEG) with PAA [9], the influence of pH on the PAA-PPEGMA$_{500}$ complexes was also investigated by us. Samples *3*, *9* and *10* (Table 1) have the same polymer content, but the initial pH = 3.45 was left unchanged for sample *3*, lowered with one drop (~30 μl) of 0.1 M HCl solution for sample *9* and highered with one drop (~30 μl) of 0.1 M KOH solution for sample *10*. The DLS measurements (Figure 6) show that at pH 3.18 the size of the polymer complex increases dramatically (from 6 nm to 157 nm) indicating strong aggregation even at room temperature, which means that phase separation occurs. This is in accordance also with the transmittance-temperature curve since the transmittance of such system is quite low at the whole temperature range of the measurement, i.e. the solution is milky (Figure 7). This means that part of the carboxylic groups are dissociated in the associations in sample *3* (at pH = 3.45), i.e. these become protonated by adding an acid. The resulted decrease in the degree of dissociation of PAA chains decreases the hydrophilicity of the complexes and results in the formation of additional interpolymer H-bonds leading to the appearing of separated

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interpolymer complex phases. However, in the opposite case, i.e. when the pH was increased from 3.45 to 3.89, the phase transition temperature increased over to 80 ºC (Figure 7) while the average size of the complexes does not changed considerably (Figure 6, see also Figure S9, S15 and S16 in Supporting Information).
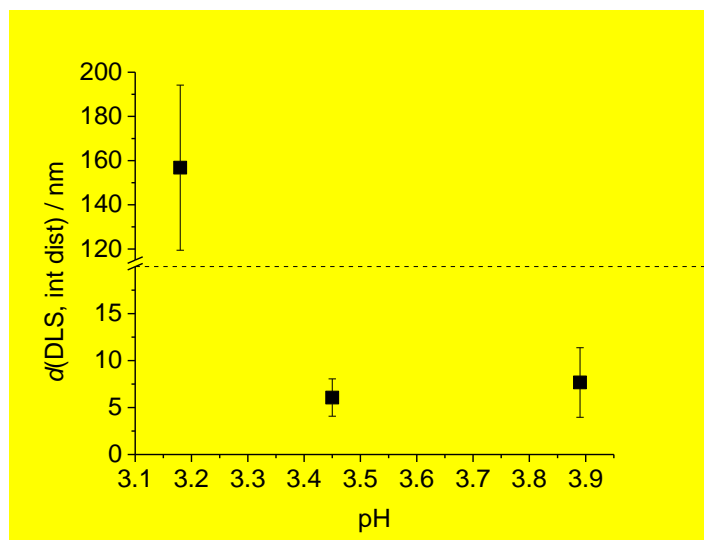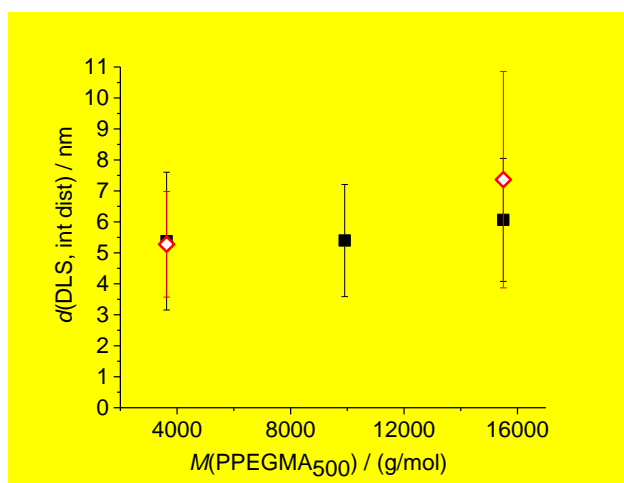

Figure 6. Hydrodynamic diameters (d) of macromolecular structures obtained by DLS in mixed polymer solutions (samples *3*, *9* and *10*, see Table 1) with different pH at 0.625 mg/ml PAA and PPEGMA$_{500}$ concentration.
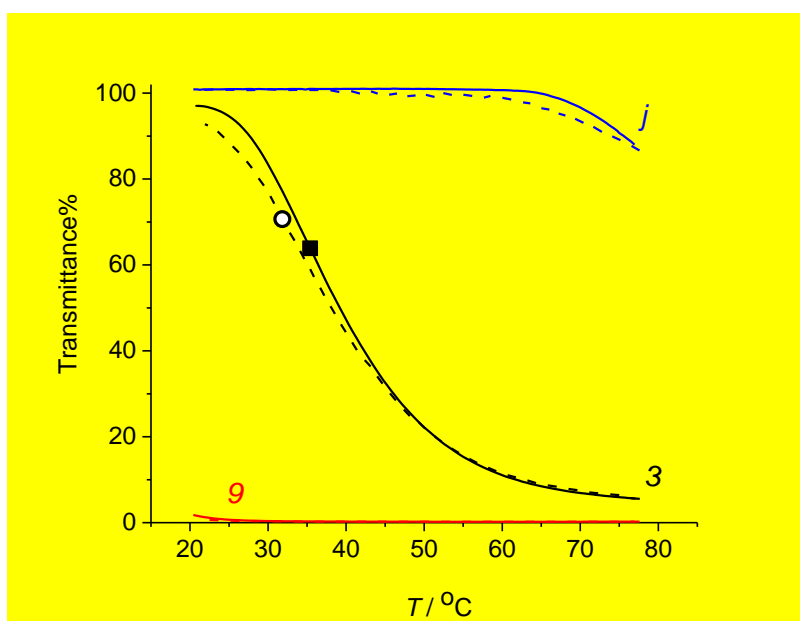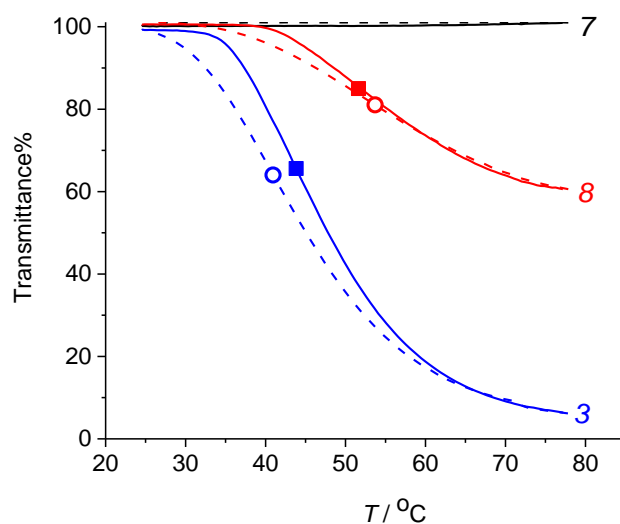

Figure 7. Transmittance-temperature curves of PAA-PPEGMA$_{500}$ mixed polymer solutions of different pH (samples *3*, *9* and *10*, see Table 1) at 0.625 mg/ml PAA and PPEGMA$_{500}$

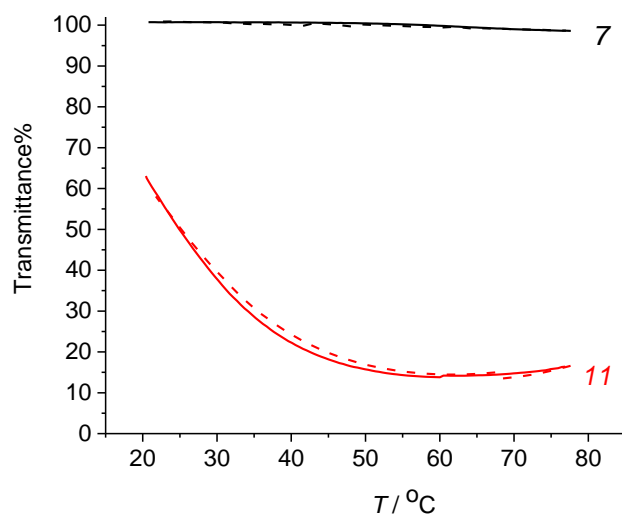concentration (solid lines: heating, dashed lines: cooling, square: cloud point, circle: clearing point).

Figure 8. Hydrodynamic diameters (*d*) of macromolecular structures obtained by DLS in mixed polymer solutions (samples *3*, *7* and *8*, see Table 1) with different PPEGMA$_{500}$ molecular weight at 0.625 mg/ml PAA and PPEGMA$_{500}$ concentration (black squares) and in PPEGMA$_{500}$ homopolymer solutions at 1.25 mg/ml concentration (rhombs with red edges) (see also Figures S5, S6, S9, S13 and S14 in Supporting Information).

Figure 9. Transmittance-temperature curves of PAA-PPEGMA$_{500}$ mixed polymer solutions with different PPEGMA$_{500}$ molecular weight (samples *3*, *7* and *8*, see Table 1) (solid lines: heating, dashed lines: cooling, squares: cloud points, circles: clearing points).

The molecular weight of PPEGMA$_{500}$ was also varied (samples *3*, *7* and *8*, see Table 1). The DLS measurements indicate a slight increase in the hydrodynamic diameter of macromolecular complexes with increasing PPEGMA$_{500}$ molecular weight (Figure 8). However, the thermal phase transition temperatures of the PAA-PPEGMA$_{500}$ mixed solutions show dramatic decrease with increasing PPEGMA$_{500}$ molecular weight at the same mass ratio of the two kinds of polymers, PAA and PPEGMA$_{500}$ (Figure 9), i.e. at the same molar ratio of EG and acrylic acid monomeric units. The explanation of the increased hydrophilicity of the polymer complex in sample *8* related to that in sample *3* is that in the case of shorter PPEGMA$_{500}$ chains the number of interpolymer H-bonds for a PAA chain is expected to be lower since the entropy of PAA chains decreases in higher extent due to an additional H-bond formation in the case of shorter acceptor chains. To study the interpolymer complex formation in the mixed polymer solution containing short (M_n = 3600 g/mol) PPEGMA$_{500}$ chains investigations at lowered pH = 3.18 (sample *11*, see Table 1) were performed when a thermal phase transition temperature appears below room temperature (Figure 10). The hydrodynamic diameter of these macromolecular structures also increases dramatically at lowered pH of 3.18 at room temperature (Figure S19 in Supporting Information) compared to that of at pH = 3.43, i.e. formation of aggregated polymer complexes occurs at decreased degree of ionization of PAA chains. These observations indicate that interpolymer complexes are present in the case of 3600 g/mol PPEGMA$_{500}$ molecular weight with PAA and the complex formation can be enhanced by protonation of the dissociated carboxylic groups. Since the lowest critical molecular weight of linear PEG which forms interpolymer complexes with PAA was determined in near to 6000 g/mol [10], it can be concluded that the presence of the hydrophobic polymethacrylate main chain and/or the special comb-like structure promotes the association between PEG and PAA. Moreover, these results also show the formed complex,

i.e. sample *11* with PPEGMA$_{500}$ having M_n of 3600 g/mol has thermoresponsive nature at pH = 3.18 in contrast to Sample *9* with PPEGMA$_{500}$ of 15500 g/mol molecular weight in the applied temperature range (Figure 7).

Figure 10. Transmittance-temperature curves of PAA-PPEGMA$_{500}$ mixed polymer solutions with different pH (samples *7* and *11*, see Table 1) at 0.625 mg/ml PAA and PPEGMA$_{500}$ (3600 g/mol) concentration (solid lines: heating, dashed lines: cooling).

Conclusions

On the basis of our results, we can conclude that comb-like PPEGMA$_{500}$ polymers can form interpolymer complexes with PAA in water, and these complexes show LCST-type thermoresponsive behaviour, also with quite low number average molecular weight as 3600 g/mol in contrast to linear PEO (PEG). Thermal phase transition temperature and DLS measurements show that the „optimal" condition of complex formation is in the near of 1.3 molar ratio of EG and acrylic acid monomeric units. Moreover, our results prove that the thermal phase transition temperature of these complexes can be fine tuned by varying the PPEGMA$_{500}$ molecular weight or pH of the solution.

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Acknowledgements

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