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N-Alkylacrylamide copolymers with (meth)acrylamide derivatives of cholic acid: synthesis and thermosensitivity

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Abstract

Copolymers of *N*-alkylacrylamides with acrylamide or methacrylamide derivatives of cholic acid have been prepared to obtain copolymers with desired thermosensitivity and enhanced hydrophilicity. The thermosensitivity of these copolymers depends on their chemical composition as studied by microcalorimetry, differential scanning calorimetry and UV–visible spectroscopy. The lower critical solution temperature and the enthalpy change of the phase separation process of the copolymers in water decreased with increasing content of the bile acid residues in the polymers.

Keywords: *N*-Alkylacrylamide copolymers; Bile acids; Thermosensitive polymers

1. Introduction

Many of the polymers of *N*-substituted acrylamides can undergo a thermally induced reversible transition in aqueous media [1] at a temperature known as the lower critical solution temperature (LCST) or the cloud point. It is believed that the competition of hydrogen bonding and dispersion-force interactions leads to order–disorder transitions at the LCST [2]. The phase separation was attributed to the disruption of hydrogen bonds between water molecules and the polymers [3,4] and the hydrophobic aggregation of the polymer itself.

Thermosensitive polymers can be used to prepare drug release device by attaching hydrophobic monomers to hydrophilic matrices [5] or to control the shrinking properties of gels [6]. They can also be used to remove biologically active agents [7]. Camail et al. showed that some thermosensitive copolymers can have persistent drag reduction activity [8]. Sarkar showed that these polymers could be used in food industry [9]. Cussler et al. reported the size-selective extraction using thermosensitive gels [10] and Winnik reported the thermosensitive permeability of the poly(*N*-isopropylacrylamide) (PIPA) membranes [11].

Biocompatibility is a major concern for polymers used in biomedicine. To improve biocompatibility, natural compounds such as bile acids can be used to prepare new polymers [12–17]. Recently, we have reported the synthesis of thermosensitive copolymers with bile acid derivatives [18,19]. The LCSTs of the *N*-isopropylacrylamide copolymers was decreased significantly even when the content of bile acid derivatives was low (5 mol%) [18]. It has been shown, however, that the LCST of *N*-alkylacrylamide polymers can be varied easily by copolymerization of different *N*-substitued acrylamides [20,21]. Depending on the chemical composition of copolymers one can even predict the change of the LCST [21]. By incorporating *N*-alkylacrylamide monomers that are more hydrophilic, one may obtain copolymers with higher LCSTs. The aim of this work is to modify the thermosensitivity of the copolymers containing bile acid residues with one or more *N*-alkylacrylamides and to study the change of the LCST as a function of the chemical composition. It is also interesting to study the calorimetric parameters of the phase transition process of these copolymers and their phase diagrams.

2. Experimental

2.1. Materials

(Meth)acryloyl chloride, diethylamine, ethylamine,

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sodium dodecyl sulfate (SDS), *N*-isopropylacrylamide (IPA) and sodium chloride were purchased from Aldrich and used as received. 2,2′-Azoisobutyronitrile (AIBN), also purchased from Aldrich, was recrystallized from methanol and stored in a dark bottle in a refrigerator before use. Tetrahydrofuran (THF) was dried with sodium, *N*,*N*-dimethylformamide (DMF) was dried with potassium hydroxide (KOH) before redistillation, and methanol (MeOH) were also redistilled before use. *N*-Ethylacrylamide (EA) and *N*,*N*-diethylacrylamide (DEA) were synthesized as described previously [21,22].

2.2. Preparation of the monomers and copolymers

The (meth)acrylamide monomers from bile acid derivatives and their copolymers with IPA were prepared as described in a previous report [18]. The other copolymers were prepared similarly by free radical polymerization [21]. In the preparation of the copolymers with EA and DEA, the molar ratio of EA to DEA is always fixed as 1:1. Fig. 1 shows the chemical structure of the copolymers. The *N*-alkylacrylamide copolymers with acrylamide derivatives ($R = H$) of cholic acid are denoted as poly(IPA–ACA), poly(EA–ACA) or poly(EA–DEA–ACA) and those with the methacrylamide derivatives ($R = CH_3$) are denoted as poly(IPA–MACA) or poly(EA–MACA) or poly(EA–DEA–MACA). The percentage used in the abbreviation of copolymers indicates the molar percent of the monomers containing the bile acid residue, which can be estimated from the nuclear magnetic resonance (NMR) spectra of the copolymers.

2.3. Polymer characterization

NMR spectra were recorded on a Bruker AMX-300 operating at 300.0 MHz for ^1H and 75.6 MHz for ^{13}C in deuterated chloroform, methanol or dimethyl sulfoxide (DMSO-d_6). The ^{13}C NMR assignments were made by comparison with different bile acids and their derivatives. All chemical shifts are relative to tetramethylsilane (TMS) set at 0 ppm.

A size exclusion chromatography (SEC) system (Waters pump, equipped with a Waters 410 differential refractometer detector, Waters 700 automatic injector and 3 Waters ultrahydrogel columns) was used to determine the average molecular weights of the polymers and copolymers in water solutions (25 mg/10 ml). Poly(ethylene glycol) and poly(ethylene oxide) were used as the calibration standard and the molecular weights were estimated as those of the standards of equivalent elution volume.

The cloud points were measured optically, using a CARY 1 BIO UV–visible spectrophotometer, coupled to a temperature controller. Samples for cloud point and calorimetric measurements were prepared by dissolving appropriate amounts of copolymers in distilled water in an ice-water bath. A 1-cm sample cell, containing approxi-

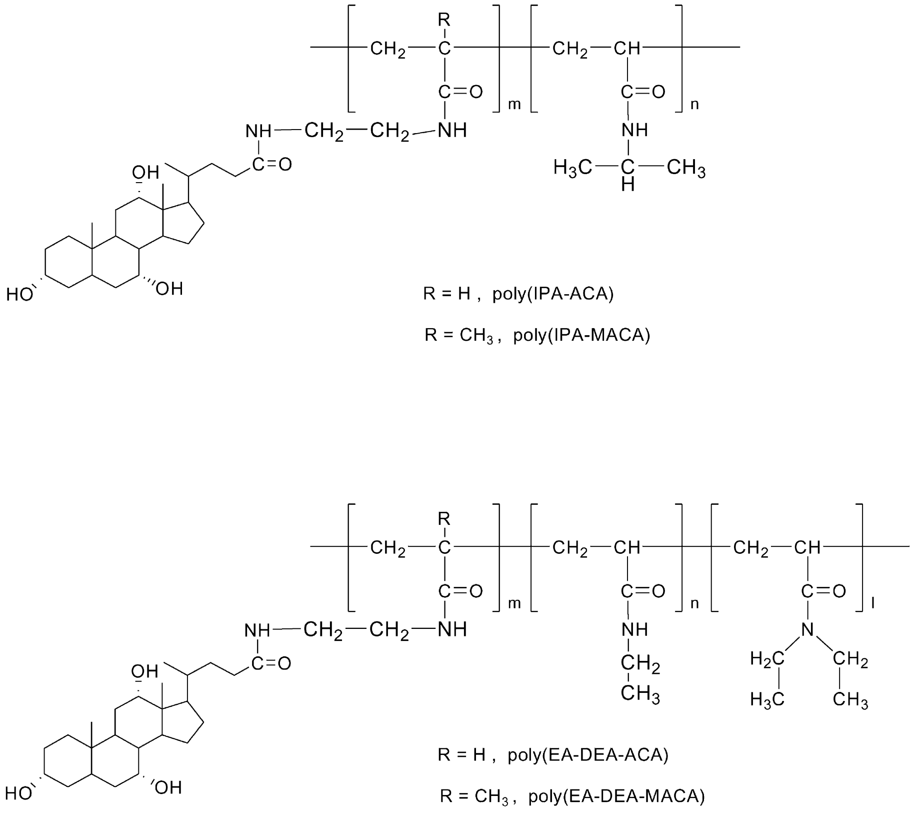

Fig. 1. The chemical structures of *N*-alkylacrylamide copolymers with acrylamide and methacrylamide derivatives of bile acids.

mately 3 ml of copolymer solution, was used against distilled water as reference. The heating rate was fixed at 0.5 °C min^{-1} and the polymer concentrations ranged from 0.1 to 10 wt%. The polymer solutions were heated from 15 to 50 °C. All measurements were taken at a wavelength of 500 nm, unless otherwise specified.

Calorimetric measurements were done on a differential scanning calorimeter (TA Instruments DSC 2910). Solid copolymers were placed and sealed in a DSC cell and were scanned against an empty reference cell from 0 to 200 °C at a heating rate of 10 °C min^{-1} in to determine their glass transition temperature (T_g). For the determination of LCST, polymers solutions were used as samples and the heating rate was set at 5 °C min^{-1}.

Thermogravimetric analysis (TGA) was done with ca. 3 mg of a sample on a Hi-Res TGA 2950 from TA Instruments. Samples were heated from room temperature to 600 °C at a rate of 20 °C min^{-1}.

Microcalorimetric measurements were performed on a Precision Scanning VP-DSC microcalorimeter with a cell volume of 0.5 ml and an excess pressure of 1.5 psi. The heating rate was set at 15 °C h^{-1}.

3. Results and discussion

The chemical composition of the copolymers was determined by ^{1}H NMR spectroscopy. We have reported previously the NMR spectra of the copolymers containing IPA and bile acid derivatives [18]. As shown in Fig. 2 for selected poly(EA–DEA–ACA) copolymers, the peak intensities at 0.56 and 0.79 ppm correspond to the proton signal of the methyl group of the position on C-18 and C-19 of the steroid skeleton of the bile acid, and the peaks at 0.96 and 3.05 ppm correspond to the methyl and methylene proton signals, respectively, of the ethyl groups of EA and DEA in the copolymers.

SEC on ultrahydrogel columns gave a weight-average molecular weight (M_w) of ca. 58,000 and M_w/M_n of 2.0 for poly(EA–DEA–ACAx%) and poly(EA–DEA–MACAx%), where $x = 0$, 1, 3. Both poly(EA–DEA–ACA5%) and poly(EA–DEA–MACA5%) have an M_w of 18,000 and an M_w/M_n of 2.0. The molecular weight (M_w) of IPA copolymers determined by SEC was ca. 100, 000 and the polydispersity was high (2.4–2.9).

3.1. Thermal analyses

The glass transition (T_g) of IPA copolymers were already determined by DSC and it was shown that the T_g of copolymers are much higher than those of PIPA ($T_g = 135$–150 °C) [18]. As we have observed for the copolymers of *N*-isopropylacrylamide and the acrylamide derivatives of cholic acid [18], there is no linear relationship between the T_g changes and the content of bile acid residues in the copolymers. Some examples of the T_g measurements for selected copolymers, i.e. poly(EA–DEA), poly(EA–DEA–ACA1%) and poly(EA–DEA–ACA5%) are shown in Fig. 3. The T_g for EA copolymers ranged from 140 to 155 °C.

The results obtained for poly(EA–ACA) or poly(EA–MACA) and poly(EA–DEA–ACA) or poly(EA–DEA–MACA) are consistent with the results for copolymers of *N*-isopropylacrylamide and bile acid derivatives [15,18,19,23]. The results show that with increasing content in bile acid residue, the copolymers become more rigid. There is only one T_g on the thermogram, indicating that the copolymers are most likely random. In both series of copolymers, the T_g increases with increasing content of bile acid residues in the copolymers, which can be attributed to the rigidity of the steroid backbone. However, the dependence of the T_g on the copolymer composition is not

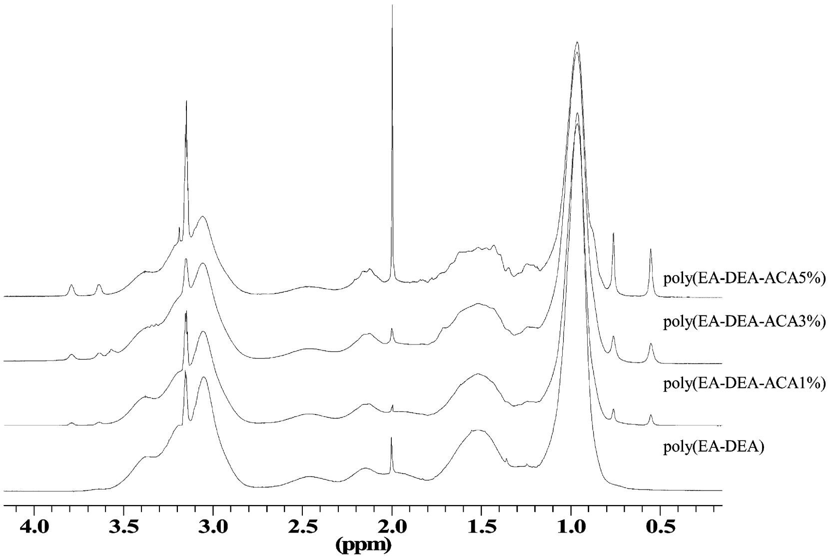

Fig. 2. The NMR spectra of poly(EA–DEA–ACAx%). The peaks at 2.00 and 3.16 ppm are the proton signals of the solvent used (methanol).

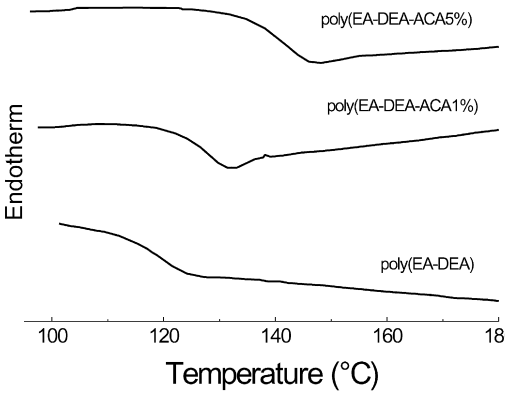

Fig. 3. The glass transition temperatures determined by DSC for EA–DEA–ACA copolymers.

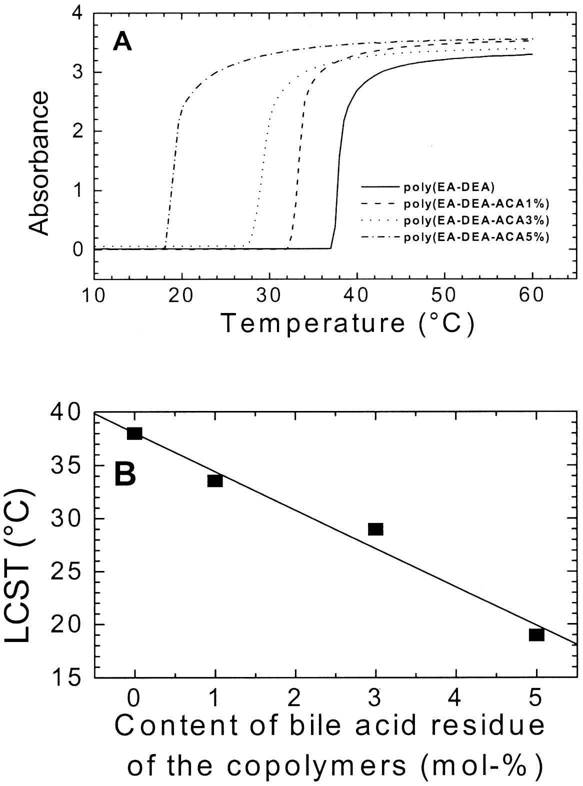

Fig. 4. An example of cloud point measurements of poly(EA–DEA–ACA) (A) and the composition dependence of the LCST determined by turbidimetry (B).

linear. For the copolymers with EA and DEA, the T_g of the copolymers containing the methacrylamide derivatives of bile acids is not significantly different from those containing the acrylamide derivatives.

TGA measurements also show that the temperatures of the 10% decomposition of poly(EA–DEA) are about 40–70 °C lower than those of the copolymers with bile acid residues (350–380 °C). However, for the copolymers with the same amount of bile acid residues, there is practically no difference for the temperature at 10% decomposition between the two series of the copolymers (ACA and MACA). The 10% decomposition temperature also increased with increasing content of bile acid residues, showing improved thermal stability of these monomers.

3.2. Turbidimetry measurements

For the copolymers with IPA, it was shown that even when the content of the cholic acid derivatives was low (1–5 mol%), the LCST of PIPA was decreased significantly because of the hydrophobicity of the bile acid residue [18, 19].

Fig. 4(A) shows an example of cloud point measurements with poly(EA–DEA–ACA). The LCST of the copolymers, determined as the maximum of the derivative of the temperature dependence of the absorbance, decreases with increasing content of bile acid of residue in the copolymers. The absorbance of the copolymers at the same concentration is also slightly higher for the samples containing more bile acid residues. Fig. 4(A) also shows that at the starting point of the phase separation, and the change in absorbance is sharp as in the case of PIPA and PDEA, but these copolymers did not undergo a two-stage aggregation as the copolymers of IPA with bile acid derivatives [18]. Fig. 4(B) shows the composition dependence of copolymers determined by turbidimetry. The higher content of the more hydrophobic bile acid residues made the phase separation easier to occur at a lower temperature. Similar results were also obtained for MACA copolymers.

Fig. 5 shows actually the phase diagrams of poly(EA–DEA–ACAx%)s at relatively low polymer concentrations. The LCST decreases very quickly with increasing concentration of the copolymers (below 2 wt%) and reaches a constant value thereafter at higher polymer concentrations. Similar results were also obtained for the other copolymers. This is similar to the results obtained by Boutris et al. [24] for PIPA and Idziak et al. [25] for PDEA. The results should correspond to a transition from hydrated random coils to hydrophobic globules as described by Fujishige et al. for the aqueous solutions of PIPA [26]. The hydrophobic interactions among polymers reached a maximal effect at a

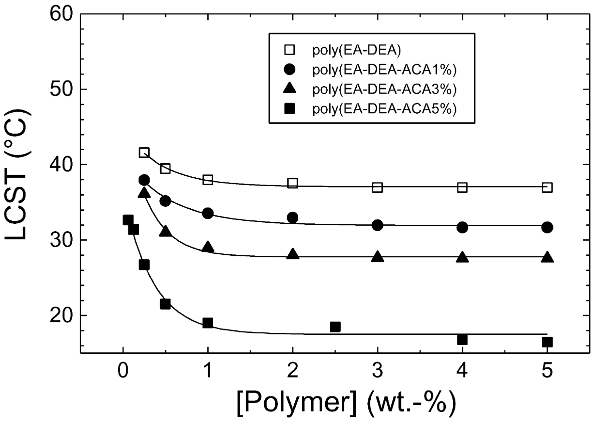

Fig. 5. The concentration dependence of LCST (phase diagrams) determined by turbidimetry for poly(EA–DEA–ACA).

certain polymer concentration and did not increase further at higher concentrations. Fig. 5 also clearly shows that an increase in the content of bile acid residues shifted the phase separation to a lower temperature since the hydrophobic aggregation may be induced by the presence of the steroid skeleton of bile acids.

The UV–visible spectra of copolymer solutions show that below the LCST the absorbance is lower at longer wavelengths, which indicates that the amount of large-sized particles is small, even though the aggregation takes place below the LCST. Above the LCST, the absorbance of all wavelengths in the visible domain is high, indicating the presence of small and large particles.

3.3. Calorimetric measurements

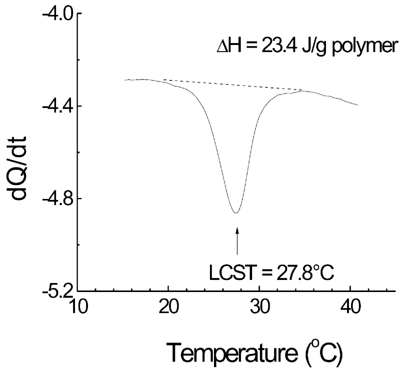

Fig. 6. DSC thermogram of poly(IPA–MACA3%) as an example for the determination of the LCST and the enthalpy change of the phase separation process of the copolymers.

Table 1 lists the LCST, the enthalpy and entropy changes of the phase separation determined by DSC for various compositions of IPA copolymers. An example of DSC thermogram is shown in Fig. 6 for 1 wt% aqueous solution of poly(IPA–MACA3%). The LCST of IPA copolymers is the minimum of the endothermic peak in thermogram. The enthalpy change (ΔH) of the phase separation process is obtained from the integration of the endothermic peak. Clearly, the LCST decreased with increasing amount of bile acid residue. There are no significant differences between the ACA and MACA series of copolymers. The enthalpy change of phase separation decreased from 32.7 to 8.8 J g^{-1} for copolymers containing ACA and for from 34.3 to 3.7 J g^{-1} for those containing MACA. These decreases are significant and clearly indicate the reduced extent of hydrogen bonding with the increasing amount of bile acid residues in the copolymers. It is to be noted that there are no free carboxylic acid groups on the bile acids residues on the monomer units. Furthermore, as expected, the methacrylamide derivative is more hydrophobic than the acrylamide derivative as shown by the greater decrease of the enthalpy change of the phase transition process. Therefore, the difference in the enthalpy change (ΔH) of phase separation between the two series of copolymers became larger at higher contents of the bile acid residues. The ΔH values for poly(IPA–ACA1%) and poly(IPA–MACA1%) solutions are correspondingly lower than the value obtained for PIPA (40.7 J g^{-1})[26]. The entropy change (ΔS) of phase separation can be calculated from the values of ΔH by assuming that the free energy change equals 0 at the LCST. It follows a similar trend as the enthalpy change. For example, the entropy change of the phase separation of methacrylamide copolymers decreased from 0.11 to 0.01 J g^{-1} K^{-1} when the content of bile acid derivatives of the copolymers varied from 1 to 7 mol%. Obviously, there is a smaller loss of entropy when a more hydrophobic polymer aggregates in the solution, which is reasonable and is expected. The entropic change is never favorable to a phase separation process, but the relatively smaller loss of entropy should make the phase separation process less difficult, a contribution of the presence of the hydrophobic moieties on the copolymers. In addition, the hydrophobicity of the cholic acid residues lowered the LCST in both series of the copolymers. The ΔH value also decreased with increasing content of bile acid residues. The copolymers are more hydrophobic with a higher amount of bile acid residues and form fewer hydrogen bonds with water. Therefore, less energy is needed for the disruption of these hydrogen bonds.

Microcalorimetric measurements were carried out to determine the LCST. Fig. 7 shows the endotherms of the aqueous solutions of poly(IPA–ACA) with different amounts of the comonomer containing the cholic acid residue (0–5 mol%). Generally, these endotherms have a Gaussian shape.

The LCST and the enthalpy of phase separation decrease with increasing amount of bile acid residues in the copolymer. For EA and DEA copolymers, the endotherm peaks were broader.

Table 1
The LCST, enthalpy and entropy changes of the phase separation of the aqueous solutions of the copolymers as measured by DSC

Cholic acid content (mol%)	Poly(IPA–ACA)			Poly(IPA–MACA)		
	LCST (°C)	ΔH (J g^{-1})	ΔS (J g^{-1} K^{-1})	LCST (°C)	ΔH (J g^{-1})	ΔS (J g^{-1} K^{-1})
1	31.7	32.7	0.11	30.7	34.3	0.11
3	27.7	30.6	0.10	27.8	23.4	0.08
5	26.8	17.8	0.06	26.1	8.7	0.03
7	24.7	8.8	0.03	24.3	3.7	0.01

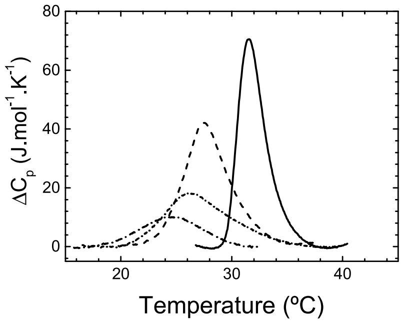

Fig. 7. Microcalorimetric endotherms of the aqueous solutions of poly(IPA–ACA) with different amounts of the comonomer containing 1 (solid), 3 (dash), 5 (dot), and 7 mol% (dash-dot) of cholic acid residues. [Polymer] = 0.1 wt%, heating rate = 0.25 °C min^{-1}. The unit of ΔC_p is J mol^{-1} K^{-1} (mole of monomer units).

Tables 2 and 3 show the dependence of LCST and of the enthalpy change of phase separation on the composition of ACA for IPA and EA–DEA copolymers, respectively. For EA–DEA copolymers, the enthalpy decreased from 55.2 to 7.8 J g^{-1} when the cholic acid content increase from 0 to 5 mol%. These values are correspondingly higher than those of the IPA copolymers because of the increase hydrophilicty of the EA–DEA copolymers. The values of LCST, taken as the maximum of thermograms, are usually above those determined by turbidimetry. The values of LCST by turbidimetry correspond to those of the beginning of abrupt increase of the heat capacity at constant pressure (C_p) in the thermograms. The response in microcalorimetry is slower when there is phase separation. The decrease in the LCST and ΔH with increasing content of bile acid residue can be explained by the increasing hydrophobicity of the copolymers [19].

As reported by Tiktopulo et al. [27], the van't Hoff enthalpy of the transition (ΔH^{eff}) for one mole of cooperative units can be written as

$$\Delta H^{\text{eff}} = 4RT^2 \frac{C_{p,T_0}}{Q_{\text{tr}}} \tag{1}$$

where Q_{tr} is the whole heat of the transition, R the gas constant, T the temperatures at any time of the reaction, C_{p,T_0} the heat capacity of the materials at T_0 (the middle of the transition), respectively.

We can also write

$$\Delta H^{\text{cal}} = MQ_{\text{tr}} \tag{2}$$

where M is the molecular weight and ΔH^{cal} is the enthalpy change associated with the phase separation of one mole of the polymer molecules. If Q_{tr} is known, we can calculate ΔH^{eff} from Eq. (1). The number of cooperative units (N_{units}) is by definition $\Delta H^{\text{cal}}/\Delta H^{\text{eff}}$. Both ΔH^{cal} and ΔH^{eff} can be obtained directly from microcalorimetric measurements. As reported by Tiktopulo et al. [27], ΔH^{eff} is a function of the heating rate. The van't Hoff enthalpy can be obtained from the peak height of the thermogram (C_p) [27]. The results are listed in Tables 2 and 3. One can see that the number of independent units in a single chain of the copolymers decreases with increasing content of bile acid residues. For example, from PIPA to poly(IPA–ACA7%) the number of units decreased from 411 to 35. The reason of this decrease must be due to a decrease in the chain flexibility in the presence of bile acid residues. We have calculated the number of molecules in a cooperative unit for IPA copolymers (Table 2) and EA–DEA copolymers (Table 3). For IPA copolymers, this number increases from 3 to 15 with increasing content of bile acid derivatives residues in the copolymer from 0 to 7 mol%. For EA–DEA copolymers, this number increases from 2 to 11 with increasing content of bile acid derivatives residues in the copolymer form 0 to 5 mol%. This number is smaller than that reported by Tiktopulo et al. [27] for a 700,000 g mol^{-1} PIPA (100). This large difference may be a result of the difference in molecular weights of PIPA. The cooperative unit may contain a much larger number of monomeric repeating units in a polymer of higher molecular weight. Regardless of the size of the cooperative units, however, the energy changes (ΔH^{eff}) associated with the globule-coil transition processes remain comparable, as shown by the results obtained for the two series of copolymers (Tables 2 and 3). This may indicate that the cooperative unit, regardless of its size, behaves as an independent moiety during the transition.

Table 2
The microcalorimetric parameters of the coil-globule transition of *N*-isopropylacrylamide copolymers with acrylamide derivatives of cholic acid (heating rate = 15 °C h^{-1})

Cholic acid content (mol%)	M_w	LCST (°C)	ΔH^{cal}		ΔH^{eff} (kJ mol^{-1})	N_{units}	N_m
			J g^{-1}	kJ mol^{-1}			
0	99,000	33.1	45.2	4474.8	10.9	411	3
1	86,400	29.4	43.3	3741.1	11.2	334	3
3	109,000	26.4	28.8	3139.2	9.8	320	3
5	99,300	25.1	11.5	1142.0	10.9	105	8
7	71,300	25.6	5.2	370.8	10.6	35	15

M_w indicates the weight-average molecular weight of the polymers, N_{units} is the number of cooperative units in a polymer chain, and N_m is the number of monomers in a cooperative unit. For the definitions of ΔH^{cal} and ΔH^{eff}, see Eqs. (1) and (2).

Table 3
The microcalorimetric parameters of the coil-globule transition and the glass transition temperatures (T_g) of copolymers of EA, DEA and the acrylamide derivatives of cholic acid (ACA)

Cholic acid content (mol%)	LCST (°C)	ΔH^{cal}		ΔH^{eff} (kJ mol^{-1})	N_{units}	N_{m}	T_g (°C)
		J g^{-1}	kJ mol^{-1}				
0	41.4	55.2	3201.6	11.6	276	2	120.2
1	37.6	32.1	1861.8	11.0	169	3	131.2
3	35.0	20.5	1189.0	11.0	108	5	141.7
5	30.0	7.8	140.4	10.6	13	11	145.0

N_{units} is the number of cooperative units in a polymer chain, and N_{m} is the number of monomers in a cooperative unit. For the definitions of ΔH^{cal} and ΔH^{eff}, see Eqs. (1) and (2).

4. Conclusions

The use of other *N*-substituted alkylacrylamide than IPA increased the hydophilicity of the copolymers and can raise the LCST of the copolymers to ranges of biological interest. The difference of acrylamide and methacrylamide derivatives of bile acid, however, is quite small for their effects on the thermosensitivity of the copolymers. The phase diagrams of the different copolymers are rather similar; the LCST does not vary significantly at polymer concentrations above 2 wt%. The variation of the enthalpy and entropy changes follows the same pattern as for the variation of the LCST. The aggregation of the *N*-alkylacrylamide polymers is certainly facilitated by the presence of bile acid residues.

Acknowledgements

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