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Copolymers of *N*-alkylacrylamides and styrene as new thermosensitive materials

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Abstract

New thermosensitive copolymers were obtained by copolymerization of styrene with *N*-methylacrylamide, *N*-ethylacrylamide or *N*,*N*-dimethylacrylamide. The turbidity measurements showed that these polymers can undergo a thermally induced phase transition at various temperatures, depending on their chemical composition, molecular weight and concentration in water. Fluorescence measurements indicated the occurrence of aggregation through hydrophobic interactions even below the lower critical solution temperature. The enthalpy and cooperativity of phase transition determined by microcalorimetry were strongly dependent on the chemical structure of the *N*-alkylacrylamide comonomer.

Keywords: *N*-alkylacrylamide; Styrene copolymers; Aggregation

1. Introduction

Reversible phase separation or precipitation can occur for amphiphilic polymers with an appropriate balance between hydrophilic and hydrophobic moieties. The temperature at which the phase separation occurs is called the lower critical solution temperature (LCST) or the cloud point (CP) [1,2]. Below LCST the water is bound to the hydrophilic moieties through hydrogen bonds, and the presence of hydration water prevents the interaction between hydrophobic moieties so that the polymer exists as an extended coil. Above LCST, the hydrogen bonds are disrupted, and water is expelled from the polymer coils, which start to collapse due to the interactions between hydrophobic moieties. This process results in the formation of compact globules which further aggregate into larger particles and phase separate from the solution [1,3,4]. This behavior is similar to that of proteins and can serve as synthetic models for the reversible cold denaturation of proteins. The thermosensitive polymers present also great potential in application as drug delivery systems [5–8], human gene vectors [9], biocatalysts [10,11], superabsorbents [12], in separation and purification of metal ions [13,14] and biomolecules [15].

The most known example of thermosensitive polymer is poly(*N*-isopropylacrylamide) (PNIPAM) in which a hydrophilic–hydrophobic balance is established inside the repeating units, providing a sharp phase transition at 32 °C. Polymerization of NIPAM with hydrophilic or hydrophobic monomers results in a shift of LCST to higher or lower values, respectively [16–21]. Actually, it was stated that a polymer soluble in water at all temperatures might be made thermosensitive by incorporating hydrophobic moieties [2]. This can be achieved for instance by copolymerization of a hydrophilic monomer with a hydrophobic one. The approach has been already used for the copolymerization of acrylamide with diacetone acrylamide [2] or *N*,*N*-diethylacrylamide [21], and for the copolymerization of *N*,*N*-dimethylacrylamide with *N*-alkylacrylamides [22], *N*-phenyl acrylamide [23], alkylacrylates [24] or 3-(acrylamido) phenyl boronic acid [25]. Besides acrylamides, other monomers such as vinyl lactams with different hydrophilicity were copolymerized in order to obtain thermosensitive polymers [26].

We have used a similar approach for the synthesis of new thermosensitive polymers, by copolymerizing styrene with several hydrophilic acrylamides N-substituted with methyl

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and ethyl groups. Except for *N*-ethylacrylamide, the other monomers give either water-soluble or water-insoluble homopolymers in the temperature range of 0–100 °C. The objective of this study is to synthesize copolymers, which can cover a large range of phase transition temperatures. Turbidity measurements were correlated with steady-state fluorescence and microcalorimetric analysis, in the attempt to obtain insight into the mechanism of the thermally induced phase transition process.

2. Experimental

2.1. Materials and instruments

Acryloyl chloride (96%), *N*,*N*-dimethylacrylamide (DMA, 99%), ethylamine (70 wt% in water), methylamine (40 wt% in water), styrene (St, 99%), 2,2′-azobisisobutyronitrile (AIBN, 98%) and *N*-phenyl-1-naphthylamine (NPN, 98%) were from Aldrich and all the solvents were of ACS grade. The materials were used as received, except for those mentioned below. DMA and St were purified by distillation under vacuum before use. AIBN was recrystallized from methanol and dried under vacuum. Methanol was dried by refluxing on CaO followed by distillation.

2.2. Instruments and methods

^{1}H NMR *spectra* of the monomers and the polymers were recorded on Bruker ARX-300 and ARX-400 NMR spectrometers operating at 300.0 and 400.0 MHz, respectively. $CDCl_3$ and CD_3OD were used as solvents and served also as internal references.

Size exclusion chromatography (SEC) was performed on a system equipped with a Waters 600 pump, a Waters 410 differential refractometer and a Waters 740 autosampler. We used either 3 Waters Styragel columns eluted with THF or $CHCl_3$ at 1 ml/min flow rate, or 2 Waters Ultrahydrogel columns eluted with Millipore water at a flow rate of 0.6 ml/min. The columns were thermostatted at 33 °C. The concentration of the injected polymer solutions was in the range of 0.1–0.3 wt%. The average molecular weight and molecular weight distribution were determined relative to polystyrene standards (in organic solvents) or poly(ethylene oxide) standards (in water).

Turbidimetry measurements were performed with a Cary 300 Bio UV–Visible spectrophotometer coupled with a temperature controller. The polymer solutions were prepared using Millipore water and the variation of the absorbance with the temperature was measured at 500 nm and at a heating rate of 0.5 °C/min. Millipore water was used as a reference. The CP was determined as the temperature corresponding to a loss of 10% of the initial transmittance of the solution [27].

Microcalorimetric traces were recorded with a VP-DSC microcalorimeter (MicroCal, LLC, Northhompton, MA) at a heating rate of 15 °C/h and a pressure of 23–24 psi in the range of 2–120 °C. Millipore water was used as a reference. The best fitting for experimental endotherms was obtained with a model which allowed the calculation of both calorimetric and van't Hoff enthalpy.

Differential scanning calorimetry (DSC) on a DSC 2910 calorimeter (TA Instruments) was used for the determination of the glass transition temperature of the polymers at a heating rate of 10 °C/min.

Steady-state fluorescence studies were performed at 15 °C on a Spex Fluorolog-2 spectrophotometer with an L-conformation and a 450 W Xe lamp, equipped with a temperature controller. The excitation and emission slits were set at 1.5 and 0.5 nm, respectively. Millipore water containing 10^{-6} M NPN has been used for the preparation of polymer solutions. The excitation wavelength was fixed to 340 nm and the NPN emission spectra were recorded between 350 and 700 nm.

2.3. Monomer synthesis

N-Ethylacrylamide (EA) was synthesized from acryloyl chloride and ethylamine, using a procedure previously described [28]. After distillation under vacuum (60 °C, 0.5 mm Hg), EA was obtained in a 60% yield. ^{1}H NMR ($CDCl_3$), δ in ppm: 6.90 (bs, 1H, N*H*); 6.17 (m, 2H, =CH_2); 5.54 (m, 1H, =C*H*); 3.3 (m, 2H, N–CH_2–CH_3); 1.11 (t, 3H, N–CH_2–CH_3).

N-Methylacrylamide (MA) was synthesized from acryloyl chloride and methylamine according to the procedure described by Shea et al. [29]. After vacuum distillation (58 °C, 0.3 mm Hg), MA was obtained in a 60% yield. ^{1}H NMR ($CDCl_3$), δ in ppm: 6.85 (bs, 1H, N*H*); 6.23 (m, 2H,=CH_2), 5.55 (dd, 1H,=C*H*), 2.83 (d, 3H, N–CH_3).

2.4. Copolymer synthesis

All copolymerizations were performed in methanol, in the presence of AIBN as initiator, for 24 h at 67 ± 1 °C. The amount of the initiator was 0.5–3 mol% related to the monomers, and monomer concentration in the polymerization solution was 10–30 wt%. The synthesis of a poly(DMA-*co*-St) is given below as a typical example: 0.189 g St (1.81 mmol), 2.81 g DMA (2.84 mmol) and 0.15 g AIBN were dissolved in 15 ml of dry methanol and the solution was purged for 15 min with dry nitrogen, and then heated to 67 °C for 24 h. Methanol was removed from the polymer solution by evaporation, and the solid residue was re-dissolved in a mixture of THF/methanol (10/1, v/v), then purified by precipitation in a 1/1 mixture of petroleum ether/diethyl ether. The precipitate was filtered, rinsed on the filter with diethyl ether, and finally dried under vacuum and 30 °C. The yield was 95 wt%. ^{1}H NMR (CD_3OD), δ in ppm: 7.30 (bm, 5H, phenyl); 2.60–3.10 (bm, 6H, N(CH_3)$_2$); 1.32–1.63 (2 bm, 3 H, –C*H*–CH_2–). The content in styrene,

as calculated from NMR analysis, was 5.7 mol% and the polymer was abbreviated as poly(DMA-*co*-St-6).

The EA and MA copolymers with St were purified by the same procedure, but the redissolution was done in $CHCl_3$/methanol (10/1) and THF/methanol (3/2), respectively.

3. Results and discussion

3.1. Copolymer synthesis and characterization

The copolymerization of DMA with St was previously studied to determine the reactivity of DMA [30,31]. It was found that the copolymerization ratios were $r_{DMA} = 0.42$ and $r_{St} = 1.30$ in ethanol [31], indicating that styrene has a higher reactivity than DMA, and the values were not significantly influenced by the dielectric constant of the solvent. The product $r_{DMA} \cdot r_{St}$ is less than 1, showing that the copolymers should be mainly random.

The copolymerizations of *N*-alkylacrylamides with styrene were carried out in methanol, which is a good solvent for all the monomers and the corresponding copolymers. The copolymer compositions were determined from the analysis of their ^{1}H NMR spectra. Using the integration of aromatic proton signals (7.0–7.5 ppm) and the aliphatic protons of the polymer backbone (1.0–2.2 ppm) the monomer ratios in the copolymers could be calculated. The results shown in Table 1 indicate that the content of styrene in copolymers is close to that used in the copolymerization mixture. All the copolymers displayed a single glass-transition temperature (T_g) between the T_g values of the corresponding homopolymers, an indication of the formation of random copolymers. The T_g values of the copolymers decreased with the increase in the styrene content, and this effect is more pronounced for the most rigid MA copolymers.

Table 1
Characteristics of the copolymers of *N*-alkylacrylamides and styrene

Polymer[a]	Styrene content (mol%)		M_w[b]	M_w/M_n	T_g (°C)
	In feed	In copolymer			
PolyDMA	–	–	156,000	3.4	125.7
Poly(DMA-*co*-St-5)	5	4.95	57,000	2.4	125.6
Poly(DMA-*co*-St-6)	6	5.70	52,000	2.2	125.6
Poly(DMA-*co*-St-7)	7	6.85	49,000	2.2	124.8
PolyEA	–	–	204,000	3.3	138.6
Poly(EA-*co*-St-3)	3	2.70	55,000	2.6	133.8
Poly(EA-*co*-St-4)	4	3.74	53,000	2.5	134.7
Poly(EA-*co*-St-5)	5	5.00	50,500	2.2	134.5
PolyMA	–	–	185,000	3.6	178.5
Poly(MA-*co*-St-5)	5	4.70	72,000	2.4	172.6
Poly(MA-*co*-St-6)	6	6.60	67,000	2.4	171.5
Poly(MA-*co*-St-7)	7	7.40	65,000	2.2	171.0

[a] Polymerization conditions: monomer concentration: 20 wt%, 3 mol% AIBN.
[b] Weight-average molecular weight determined in water, relative to poly(ethylene oxide) standards.

Except for poly(DMA-*co*-St), the other copolymers are insoluble or sparingly soluble in non-polar solvents such as THF or $CHCl_3$. In order to find a suitable solvent for all the copolymers under study, comparative GPC experiments were performed with poly(DMA-*co*-St) in different solvents. In all cases, only one elution peak was obtained, and the results in Table 2 show no significant difference among the molecular weights measured for these copolymers, in both non-polar solvents and water, or at different concentrations of the injected water solutions. The results indicate that no stable aggregates are formed in the aqueous solutions used for the SEC experiments. Consequently, the molecular weights for all copolymers were determined in water, for the sake of comparison, and the results are shown in Table 1. The values indicate a decrease of M_w and polydispersity index with increasing St content. The polymer samples were used in the subsequent experiments without fractionation.

3.2. Thermosensitivity of the copolymers

The variation of transmittance with temperature is shown in Fig. 1 for the poly(EA-*co*-St), at different St contents, and indicates that these copolymers undergo a phase transition at a temperature depending on the chemical composition of the copolymers. The process of phase transition was reversible (data not shown). The transition is rather broad, what can be attributed to the chemical heterogeneity of the copolymers. It is known that copolymers obtained by radical polymerization at high conversion rates (>90%) contain chains with different ratios of monomer units [32,33]. These chains will behave differently during the phase transition. Therefore, such chemically heterogeneous copolymers will undergo a stepwise transition, which is not as sharp as in the case of chemically homogeneous polymer like PNIPAM.

The values of the CPs obtained from the variation of

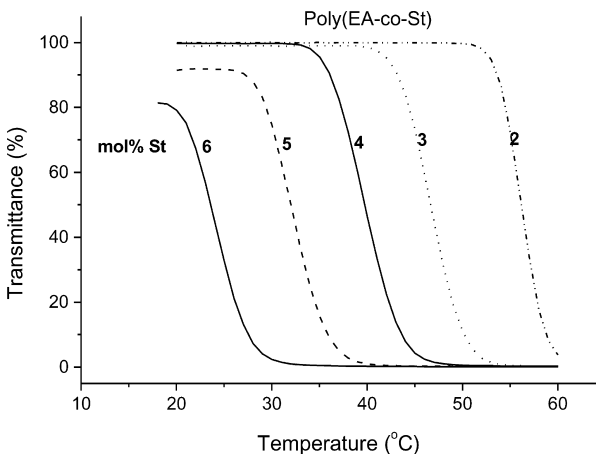

Fig. 1. Variation of light transmittance with temperature for copolymers of *N*-ethylacrylamide (EA) with various content in styrene (St). [Polymer] = 1 wt%.

Table 2
Weight-average molecular weights (M_w) and polydispersity indices (M_w/M_n) for copolymers of DMA with St, obtained by SEC using different eluents

Polymer	Solvent used as eluent							
	THF[a]		$CHCl_3$[a]		Water,[b] polymer concentration[c]			
	M_w	M_w/M_n	M_w	M_w/M_n	3 mg/ml		1 mg/ml	
					M_w	M_w/M_n	M_w	M_w/M_n
Poly(DMA-*co*-St-6)[d]	86,200	1.5	80,400	2.0	104,600	2.8	89,600	2.9
Poly(DMA-*co*-St-7)[d]	77,000	1.6	61,500	2.7	70,700	2.5	70,000	2.7
Poly(DMA-*co*-St-6)[e]	53,000	1.8	47,000	2.5	52,000	2.2	47,300	2.2

[a] Polystyrene used as standards, polymer concentration in injected solution: 3 mg/ml.
[b] Poly(ethylene oxide)s used as standards.
[c] Polymer concentration in injected solutions.
[d] AIBN concentration: 1 mol%.
[e] AIBN concentration: 3 mol%.

transmittance with temperature showed that the temperature of the phase transition in water solutions of the synthesized copolymers depends on their chemical composition, molecular weight and concentration.

3.2.1. Chemical composition

The effect of the chemical composition of the copolymers on their CPs in water solutions of 1 wt% concentration is shown in Fig. 2. An increase in the St content of the copolymers from 0.5 to 8 mol% induced a decrease in the CP from 100 to 0 °C, indicating a change from a completely water soluble to a water insoluble polymer. At St contents higher than 9 mol% the polymers are not water-soluble, even at concentrations as low as 0.1–0.5 wt%. In a recent report, Chee et al. synthesized and studied copolymers of NIPAM and St with a St content as high as 17 mol% [34], but the authors performed all their experiments with water solutions containing 0.01 wt% copolymers, and no information about the solubility of their copolymers at higher concentration was given. In our case, at a given styrene content, the CP increases with increasing hydrophilicity of the acrylamide comonomer, i.e. in the order: EA < DMA < MA.

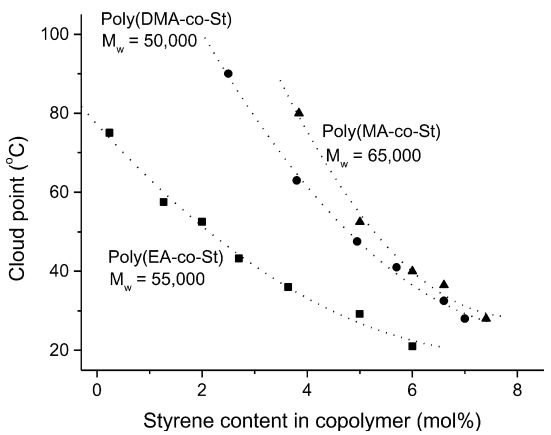

Fig. 2. The cloud points for aqueous solutions containing 1 wt% copolymers of *N*-alkylacrylamides and styrene as a function of styrene contents in copolymers.

3.2.2. Molecular weight

The dependence of phase transition temperature of the thermosensitive polymers on their molecular weight is a matter of dispute. Fujishige et al. [35] found that CP of PNIPAM is independent of molecular weight, and argued that the coil–globule transition takes place only through intramolecular interactions and the chain length has no influence on the process, at least at concentrations lower than 1 wt%. However, a certain influence of the polymer chain length on the phase transition temperature of PNIPAM at concentrations as low as 0.01–0.04 wt% was found by other authors [36,37]. At higher concentration, where the coil–globule transition is followed by globule aggregation through intermolecular interactions, molecular weight should have an important influence on CP, as the overlapping concentration is dependent on the chain length. The decrease in the CP with increasing molecular weight was established for PNIPAM and other thermosensitive polymers such as poly(*N*,*N*-diethylacrylamide) [38,39].

The influence of the molecular weight on the CPs of our copolymers in water solution of 1 wt% concentration was more significant at higher St contents, as exemplified in Fig. 3. In the case of poly(DMA-*co*-St), the decrease in CP values (Fig. 3) seems to reach a plateau above $M_w = 70,000$. However, when the difference in M_w is much higher, as in the case of the poly(EA-*co*-St) presented in Fig. 3, the decrease in CPs with increasing M_w is very pronounced at high St contents. This trend is similar to what was found for PDEA [39].

3.2.3. Polymer concentration

Literature data on the variation of the CP of the thermosensitive polymers with solution concentration are not consistent. The only complete phase diagram for PNIPAM was reported by Heskins et al. [1] who found a concave curve with a minimum between 15 and 30 wt%.

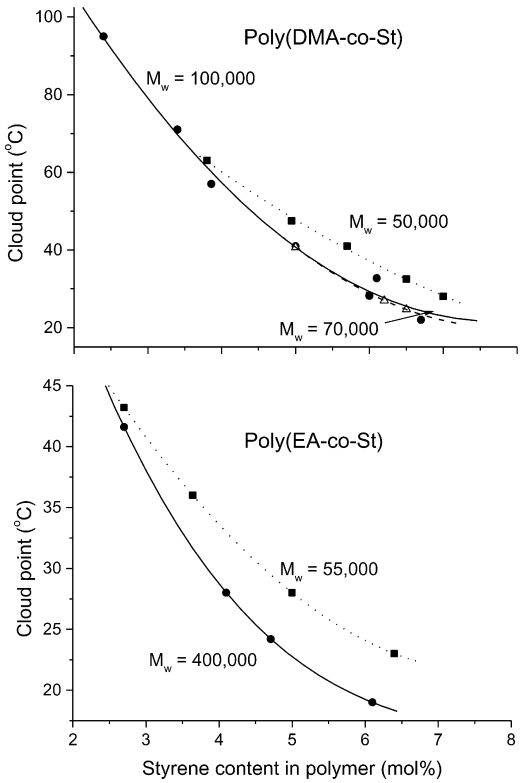

Fig. 3. The cloud points for aqueous solutions containing 1 wt% copolymers of *N*-alkylacrylamides and styrene as a function of styrene contents in copolymers of different molecular weights.

Later, there have been conflicting reports showing no influence of the polymer concentration on their CP [2,28], or a sharp decrease of the CP upto a concentration of 5 wt%, after which a plateau was reached [27]. The differences were attributed to the polydispersity of the different polymer samples used by different authors [3].

Partial phase diagrams have been established for our copolymers (Figs. 4 and 5). In the case of the poly(EA-*co*-St) the shape of the phase diagram is similar to that reported

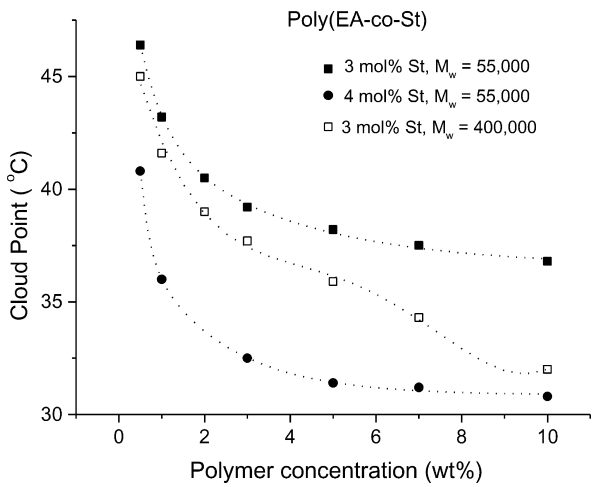

Fig. 4. Variation of cloud points of aqueous solutions of copolymers of *N*-ethylacrylamaide and styrene as a function of polymer concentration.

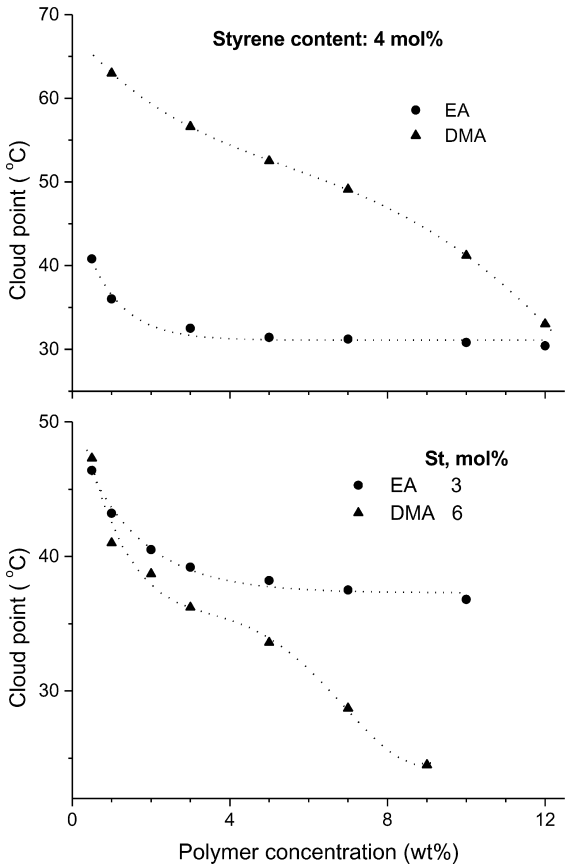

Fig. 5. Variation of cloud points of aqueous solutions of copolymers of *N*-ethylacrylamaide or *N*,*N*-dimethylacrylamides with styrene as a function of polymer concentration.

by Boutris et al. [27] for PNIPAM, with a significant decrease in CP upto 5 wt%, and a plateau between 5 and 10 wt% (Fig. 4). However, when the M_w of poly(EA-*co*-St) is high (about 400,000), a small deviation from this behavior was found at higher St contents (Fig. 4).

A different behavior was observed for poly(DMA-*co*-St), as shown in Fig. 5 in comparison with poly(EA-*co*-St) having the same molecular weight and the same St content (Fig. 5(a)), or the same molecular weight and the same CP at 0.5 wt% (Fig. 5(b)). The decrease in the CP for poly(DMA-*co*-St) is sharp and continuous upto a polymer concentration of 10–12 wt%, but no plateau was established. This phenomenon might be related to the larger difference in hydrophilicity/hydrophobicity between the comonomers styrene and DMA.

3.3. Aggregation of copolymers below LCST

In order to demonstrate the occurrence of hydrophobic interactions before the thermally-induced phase transition, we have performed some steady-state fluorescence measurements, using NPN as a fluorescent probe. The maximum intensity of NPN fluorescence emission spectra was plotted as a function of polymer concentration and inflection points were noticed (Fig. 6(a)). From these

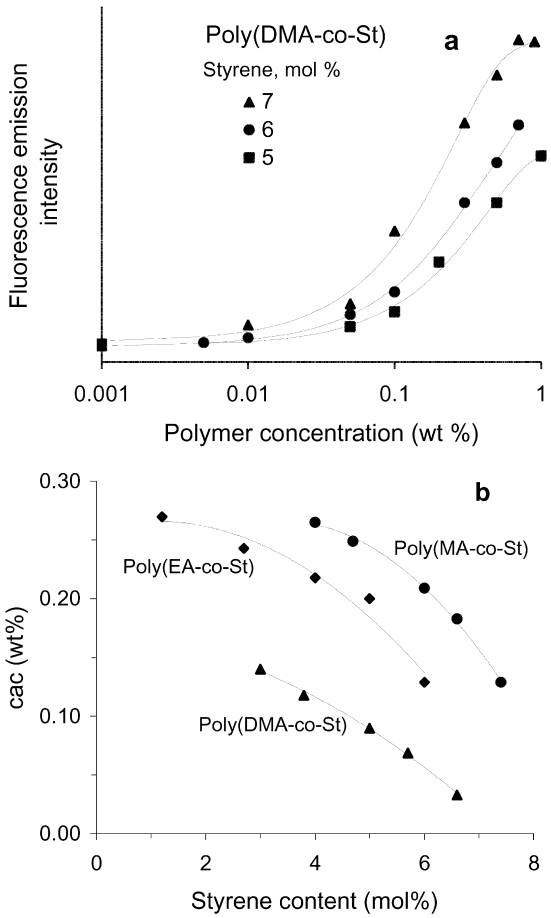

Fig. 6. Variation of fluorescence emission intensity of NPN (10^{-6} M) with the concentration of copolymers of *N*,*N*-dimethylacrylamide and styrene with different contents of styrene (a); and variation of critical aggregation concentration (*cac*) of copolymers of *N*-alkylacrylamides with styrene as a function of styrene content in copolymers (b). All measurements were performed at 15 °C.

inflection points critical aggregation concentrations (*cac*) of the polymers could be calculated [40,41]. As expected, the *cac* values decrease with the increasing content of St in all copolymers and depend on the hydrophobicity of *N*-alkylacrylamide comonomer (Fig. 6(b)). At the same St content, the *cac* values increase in the order: DMA < EA < MA, and DMA copolymers have *cac* values 2–3 times lower than those obtained for EA copolymers. It is apparent that the polymers start to aggregate due to hydrophobic intra- and/or intermolecular interactions, even before the temperature-induced aggregation, and the phenomenon seems to be more pronounced for poly(DMA-*co*-St). Using several fluorescence techniques, Chee et al. [34] proved that the poly(NIPAM-*co*-St) can also aggregate below LCST. This finding can partially explain the dependence of CP on polymer concentration, but does not explain the different shapes of the phase diagrams for DMA and EA copolymers. This aspect should be further verified by other methods, for instance by light scattering.

3.4. Thermodynamic parameters

In order to obtain a better insight in the process of phase transition, microcalorimetric measurements have been performed with 3 selected copolymers which have similar values for the CP determined by turbidity measurements. Microcalorimetry provides thermodynamic parameters, which can describe better the factors responsible for the phase transition. Experiments performed at heating rates in the range of 2–30 °C/min showed no significant difference in the shape, height and position of the endothermic peaks. Therefore, all the experiments were carried out at a heating rate of 15 °C/min. The endotherms obtained for the selected copolymers are shown in Fig. 7. The height of the endotherms differs very much for the different copolymers, but all endotherms are very broad. From the characteristics of the endotherms, some thermodynamic parameters could be calculated (Table 3). The polymer concentration used for microcalorimetric experiments was about 1 wt%, therefore the calculated parameters describe the whole process of phase transition, including coil-to-globule change and inter-chain aggregation. Nevertheless, the calculated data can give a rough idea about the behavior of these new thermosensitive polymers and offer a useful comparison among them.

According to the data presented in Table 3 the maxima of the endotherms were recorded at higher temperatures than the corresponding CPs. This difference has been noticed before for hydroxypropylcelulose [36], and was explained by the fact that the two experimental methods detect different physical phenomena. Microcalorimetry detects the hydrogen bond disruption phenomenon, whereas the turbidity detects the macroscopic phase separation phenomenon, i.e. the formation of polymer aggregates. The difference between CP and T_{max} indicates, as fluorescence measurements have already shown, that the aggregation occurs before the disruption of hydrogen bonds.

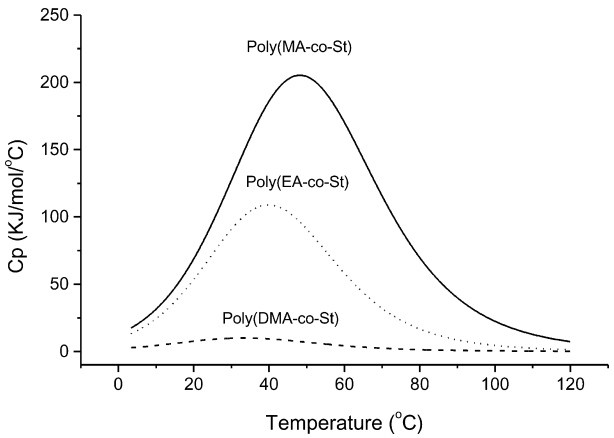

Fig. 7. Variation of partial specific heat capacity with temperature for copolymers of *N*-alkylacrylamides with styrene. The curves are obtained from the best polynomial fits for the endothermic traces. [Polymer] = 1 wt%.

Table 3
Thermodynamic parameters calculated from microcalorimetric endotherms (Polymer concentration: 1 wt%. $M_w = 50,000-65,000$)

Polymer	CP[a] (°C)	T_{max}[b] (°C)	ΔH_c[c] (kJ/mol)	ΔH_v[d] (kJ/mol)	$\Delta T_{1/2}$[e] (°C)	N_c[f]
Poly(MA-*co*-St-7)	36.5	48.2	10.2	68.2	44.2	100
Poly(EA-*co*-St-4)	36.0	40.1	4.7	75.7	38.5	35
Poly(DMA-*co*-St-7)	32.5	36.4	0.5	73.2	41.2	4

[a] Cloud point determined by turbidimetry.
[b] Temperature corresponding to the endothermic peak maximum.
[c] Calorimetric enthalpy in kJ/mol of structural units. The molecular weight of the structural unit of the copolymers was taken as that of the corresponding *N*-alkylacrylamide, as the content in styrene is very low in all cases.
[d] van't Hoff enthalpy in kJ/mol of cooperative segment.
[e] Width of the endotherm at its half-height.
[f] Number of cooperative segments per macromolecular chain.

The model used for the calculation of the thermodynamic data allowed the determination of both enthalpy change of phase transition (ΔH_c) and van't Hoff enthalpy (ΔH_v). ΔH_c is the enthalpy change of the phase transition per mole of structural unit and is given by the area under the endotherm. ΔH_v is the enthalpy change of phase transition of the chain segment which participates independently in the transition (cooperative segment), and is related to $\Delta T_{1/2}$, the width of the endotherm at its half-height [36,37]. From these data one can calculate the enthalpy of the phase transition of the whole macromolecule, ΔH, and the number of cooperative segments in a macromolecular chain, according to the following equations [36,42]:

$$\Delta H = \mathrm{DP}\cdot\Delta H_c \quad (1)$$

$$N_c = \Delta H/\Delta H_v \quad (2)$$

where DP is the degree of polymerization of the polymer and N_c is the number of cooperative segments in a polymer molecule.

The ΔH_c values are very different for the three types of copolymers (Table 3). The lowest ΔH_c value was obtained for poly(DMA-*co*-St) and is about 418 J/mol of structural units or 4.2 J/g polymer. This value is close to the value of 8–12 J/g reported before for the thermally induced phase transition of the copolymers of DMA with *N*-phenylacrylamide [23]. ΔH_c is considered as the measure of the energy needed for the disruption of hydrogen bonds and was found to be about 5.5–7.5 kJ/mol of structural units for PNIPAM [27,35–37], a value close to that required for the disruption of one hydrogen bond per structural unit. The very low ΔH_c obtained for DMA copolymers can arise from the lack of a hydrogen atom of the amide group, which minimizes its ability to form a hydrogen bond with water, and perhaps the carbonyl groups alone form very weak hydrogen bonds.

ΔH_c of poly(EA-*co*-St) is 4.7 kJ/mol of structural units, a value close to that reported for PNIPAM. This indicates that the phase transition takes place after the disruption of one hydrogen bond per structural unit of acrylamide comonomer.

The much higher value of ΔH_c for poly(MA-*co*-St) indicates that in this case the phase transition takes place after the disruption of more than one hydrogen bond, what can be assigned to the higher hydrophilicity of MA, in comparison with EA, NIPAM or DMA.

The ΔH_v values listed in the Table 3 are very similar for the three copolymers, as was expected from the similar width of the endothermic peaks (similar $\Delta T_{1/2}$). The width of the endothermic peaks is also an indication of a broad phase transition process, also observed in the turbidity measurements. The number of cooperative segments calculated with Eq. (2) is very different for copolymers containing different *N*-alkylacrylamides. Thus, the lowest N_c was found for poly(DMA-*co*-St), the highest for poly(MA-*co*-St). In all cases, $N_c > 1$, meaning that several chain segments participate independently in the phase transition (cooperative transition), and not the macromolecular chain as a whole ('all-but-none' transition specific to small proteins). The cooperative transition of several independent chain segments was reported before for the PNIPAM with molecular weight higher than 20,000 [37,42].

4. Conclusion

New thermosensitive polymers have been synthesized by copolymerization of hydrophilic and hydrophobic monomers which do not form thermosensitive homopolymers. *N*-alkylacrylamides and styrene were used as comonomers. We have thus demonstrated that any N-substituted acrylamide (except acrylamide itself) can be made thermosensitive by using a very common hydrophobic comonomer such as styrene. The thermosensitivity could be tuned to cover a wide range of temperatures by varying the chemical composition of the copolymers, molecular weight and copolymer concentration.

The phase transition process studied by turbidimetry, steady state fluorescence and microcalorimetry proved to be broad, due to the chemical heterogeneity of the copolymers, and hydrophobic interactions may occur below the temperature-induced disruption of the hydrogen bonds. The new synthesized copolymers have interesting properties and might be used in a wide range of applications, as we will show in a forthcoming paper.

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